Specific properties of supercooled water in light of water anomalies

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ABSTRACT

We review the effect of water anomalies on the properties of low-temperature water. When supercooled, liquids dynamical properties change drastically. Supercooled liquids undergo an at least exponential decrease of their diffusion coefficient when temperature decreases while their structure merely does not change. We discuss how that still unexplained change of dynamical properties at low temperatures affects water differently from other liquids and what can be deduced from it.

1. Introduction

While of quite simple structure and composition, water is a strange liquid [1], displaying a number of anomalies [1,2]. Water is also very important as the liquid where biological processes take place. The large number of anomalies relates to the presence of hydrogen bonding that lead to the formation of a network-organised liquid, and to various possible structures. Merely, a hundred anomalies have been reported for water; however, the most striking anomalies are probably the existence of a maximum on the density and on the viscosity versus temperature. In other words, unlike in most other liquids, the density and viscosity of water do not evolve monotonously with temperature. Three decades ago, to explain these behaviours, Poole et al. [3] postulated the existence of two different liquid states of water, a low-density liquid (LDL) and a high-density liquid (HDL), with a critical point located at low temperature in the supercooled region [3–12].

Below the homogeneous nucleation temperature \( T_H = 232 \text{ K} \), water crystallises rapidly [13–17]. Thus, it is very difficult to access experimentally with bulk liquid water the region of temperature below \( T_H \) and above the glass transition \( T_g = 136 \text{ K} \). Due to that difficulty, that region of temperature has been called the ‘no man’s land’. As the putative liquid–liquid transition between HDL and LDL is located inside the ‘no man’s land’, it is difficult to observe experimentally and the metastability of these two liquid states is still the subject of controversy [18,19]. We will nonetheless in this paper use that picture of coexisting different structures (polyamorphism) to understand how it fits or not the properties that we observe at low temperatures.

When cooled rapidly enough, liquids can remain in the liquid state below their melting temperature [20]. Usually, the more complex the molecule, the easier the crystallisation can be avoided leading to that supercooled ‘state’. As discussed above, for water the crystallisation always occurs when the temperature decreases below a limit temperature \( T_H = 232 \text{ K} \), leading to the so-called no-man’s land region of temperature that thus cannot be accessed experimentally for bulk supercooled water. If the temperature can be further decreased, the viscosity of the liquid \( \nu \) increases exponentially for Arrhenius (or strong) liquids like silica or even more rapidly for super-Arrhenius (or fragile) liquids like most molecular liquids and water. The viscosity \( \nu \) and diffusion coefficient \( D \) follow laws of the form:

\[
\nu = \nu_0 \exp(\frac{E_a}{kT})
\]

(1)

and

\[
D = D_0 \exp(-\frac{E_d}{kT})
\]

(2)

with activation energies \( E_a(T) \) and \( E_d(T) \) that are approximately constant for strong liquids and increase for fragile liquids when temperature drops. Note that around the melting temperature \( E_a(T) \approx E_d(T) \) then they differ at lower temperature due to the breaking of the Stokes–Einstein law. However as the trend of the variations of both quantities is relatively similar (if one is inverted) as shown in Equations (1) and (2), we will use in this work sometimes the term viscosity and sometimes the diffusion coefficient, but only scarcely both, to avoid repetitions. Eventually, at low enough temperature the medium becomes so viscous that it behaves as a solid and is called a glass. The reason for that increase in viscosity that occurs without structural change is however still unknown [21] and the object of active researches. In the supercooled state, spontaneous transient cooperative motions, called dynamic heterogeneities, appear in the liquid and increase when the temperature drops. The appearance of cooperative motions [22] that is also still not explained is however expected as a signature of the approach of a phase transition [23].

2. Models

A variety of intermolecular potentials exist to model water [24–30]. The comparison of the properties of water obtained using different potentials has been the subject of various works, see for example [24,27,31]. We list here the most important potentials for supercooled water simulations. One of the simplest and most often used water potentials [24,25]
is the SPC(E) potential. Due to its simplicity, it is very efficient for simulations as it takes only three beads into account to model the three atom molecule. Unfortunately, the diffusion is too large with that potential in comparison with experiments. The TIP5P(E) potential [26–28] is a little more complex and less efficient as it models water with five beads instead of three, but it leads to a better dynamics [31], a better structure and can induce crystallisation. Coarse graining [32,33] is often used in simulations to increase drastically the efficiency of the calculations. In biological systems, a very large number of water molecules has to be used due to the large size of the biopolymers they surround. Thus coarse graining of water is of large interest, but rather difficult to model due to the hydrogen bondings, polyamorphism and electrostatic interaction. Several coarse grained potential have however been proposed for water. The Molinero’s coarse grained potential [30] that model water as an intermediate element between carbon and silicon is very efficient and has been used extensively for low-temperature simulations.

Long-range electrostatic interactions, while screened [34,35] by the presence of the surrounding molecules, have to be handled with some care. While a few models use a simple cutoff for interactions at distances larger than R cutoff, the most common ways of dealing with electrostatic interactions are the Ewald method and the Reaction field method. The Ewald method uses the infinite number of replica of the simulation box (Born–Von Karman periodic conditions) to calculate the global interactions on each atom. To solve the infinite-range calculation, the long-range part of the global potential is transformed into Fourier space where the calculation is short ranged. The reaction field method approximates the long-range interactions (defined as the interactions for distances larger than a chosen cutoff Rc) between each atoms, by the interaction with a continuous medium with a dielectric constant ε.

The two methods are included in most simulation codes. However for scientists using their own simulation programmes, the reaction field is much easier to implement and leads to faster simulations. For the physics of the system, we expect the Ewald method to somehow increase the tendency for crystallisation, while the reaction field will not affect that tendency. Notice that it is important in the reaction field method to apply the reaction field cutoff on the whole molecule (i.e. on the centre of masses) to avoid charge fluctuations. Note also that at low temperatures, finite size effects [36,37] appear in supercooled liquids and modify their dynamics. Thus, the simulation box has to be large enough to prevent from these effects to happen, and the lower the temperature, the larger the box must be chosen to avoid finite size artefacts.

In this paper, we model the water molecular interactions with the TIP5P-E potential [28] and the long-range electrostatic interaction with the reaction field method using a cutoff radius Rc = 9Å and an infinite dielectric constant for the continuous medium. The water molecule is modelled as a rigid body and we will focus our attention on the centre of masses behaviour (that is also approximately the oxygen atoms behaviour as the differences in the position of the centre of masses and of the oxygen atom is quite small in water). Our simulation box contains 2000 water molecules in a cubic box with usual periodic conditions and is aged at the temperature of study during 10 ns (for $T \geq 250 \text{ K}$) or 20 ns (for $T \leq 240 \text{ K}$) before any recorded run.

3. Results and discussion

We will show a few results from simulations of supercooled water before discussing them, together with previous works with the perspective of a connection with the water anomalies. It is possible to rationalise most of the anomalous properties of water from its two most important particularities: the presence of hydrogen bounding leading to a network structure and the polyamorphism or equivalently the existence of several metastable structures. We will now discuss the properties of supercooled water in relation to these two important particularities of water.

3.1. Large super-Arrhenius behaviour

Water is a fragile liquid in Angell’s classification, as its viscosity increases (diffusion decreases) more than exponentially when the temperature drops below its melting temperature. Most molecular liquids are fragile; however, water is a very fragile liquid and the super-Arrhenius evolution of the viscosity with temperature is larger in water than in most liquids. Fragility is usually related to the extent of cooperative motions as one explains the increase of the activation energy $E_a(T)$ by the need for an increasing number of molecules to cross energy barriers cooperatively for diffusion to take place. Consequently, the large super-Arrhenius behaviour of water suggests that cooperative motions are particularly large for water.

We will now illustrate the evolution of the diffusion with temperature in supercooled water from the calculation of the mean square displacements and diffusion coefficients of oxygen atoms. Figures 1 and 2 show the mean square displacement $\left\langle r^2(t) \right\rangle$ evolution with temperature of supercooled water, respectively, at the density of room temperature liquid water and slightly above the density of ice (at atmospheric pressure). Below the melting temperature $T_m = 273 \text{ K}$ that corresponds approximately to the third curve from the top, the mean square displacements display the three characteristic time regimes of supercooled liquids, namely the ballistic time regime at short time scales (below 0.3 ps), the plateau regime for intermediate time scales and the diffusive time regime for large time scales. While the temperature decreases, the plateau time regime increases showing that the molecules need more time to escape the cages of their neighbours, leading to a slowing down of the dynamics and a decrease of the diffusion coefficient. If we compare Figures 1 and 2 that correspond to the densities $\rho = 1 \text{ g/cm}^3$ and $\rho = 0.92 \text{ g/cm}^3$ respectively, we see that the plateaus are larger for the same temperatures in Figure 2. The diffusion is smaller (or viscosity larger) for the smallest density. That counterintuitive property is one of the water anomalies that the presence of several possible structures explains.

Figure 3 shows the diffusion coefficient as a function of temperature for the two densities considered in our simulations. The triangles correspond to the recent experimental data [38] at ambient pressure. The diffusion coefficient $D$ is
here calculated from the relation:

$$\lim_{t \to \infty} \langle r^2(t) \rangle = 6Dt$$

(3)

We see from the figure that the diffusion coefficient departs rapidly from the Arrhenius pure exponential law materialised by the green dashed line. This evolution shows that water is a very fragile liquid in that temperature range. The activation energy $E_a(T)$ increases significantly when the temperature drops, suggesting the presence of large cooperative motions. Understanding the activation energy as the energy that is necessary to overcome, to be able to move inside the environment, an increase of the activation energy means that several molecules have to overcome the one-molecule activation energy for the motion to be possible. As a result, the increase of the activation energy when the temperature drops reflects the average number of molecules involved in cooperative clusters at different temperatures.

### 3.2. Effect of density or pressure

Increasing the pressure or the density leads to a decrease of the super-Arrhenius behaviour [39–41] in water. This effect has been observed experimentally and with molecular dynamics simulations using various potentials. We observe that effect in the diffusion coefficients of Figure 3, and by comparison of the mean square displacements of Figures 1 and 2 for the two different densities studied. As the density is made smaller in Figure 3, the diffusion departs more from the Arrhenius law displayed with a green line and consequently water becomes more fragile.

As the fragility is connected with the cooperative motions, we deduce that increasing the pressure (or the density) decreases the cooperative motions and accelerates the dynamics (i.e. decreases the viscosity) in supercooled water. We interpret this effect from the pressure-induced structural modifications in the liquid. Increasing the pressure promotes the high-density structure and as a result decreases the structural fluctuations that are responsible for the large cooperative motions in water.

### 3.3. Large cooperative motions

We will now use a more direct measure of the clusters of cooperative motions inside the liquid. For that purpose, we define the Non-Gaussian parameter (NGP) $\alpha_2(t)$ as:

$$\alpha_2(t) = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1$$

(4)

When the temperature drops, the self part of the Van Hove correlation function [42] that represents the probability at time $t$ to
find a molecule a distance $r$ apart its previous position at time zero, changes. A tail develops for large $r$ values, that is the signature of cooperative motions that are larger than the average motions. As a result, the Van Hove is no longer a Gaussian. The Non-Gaussian parameter is a measure of that departure from a Gaussian shape and consequently quantifies the cooperative motions. Figures 4 and 5 show the NGP evolution when the temperature drops for the two densities of our study. The Non-Gaussian parameter is small at high temperature and progressively increases when the temperature drops. Simultaneously, the curves are shifted to larger time scales due to the decrease of the probability for a molecule to escape the cage of its neighbors. The maximum of the curves corresponds to the plateau ending time regime for the mean square displacement. For that time, some molecules are escaping the cages while over are still trapped. In what follows we will call $t^*$ that characteristic time for which the NGP is maximum. This time has been shown in numerous works [22,36–48] to be a universal characteristic of cooperative motions in supercooled liquids. It was found to correspond to the characteristic time of string-like motions that is the typical time for a molecule to replace another in a string of mobile molecules [22,44,45,47,48].

Figure 6 shows the evolution of the maximum value of the NGP $\alpha_2(t^*)$. As discussed above, the NGP measures the intensity of cooperative motions in the liquid. We see from the figure the rapid increase of the NGP (i.e. cooperative motions) when the temperature drops. The figure also shows that the cooperative motions are larger and increase faster at low density.

To resume that first part, supercooled water [41, 47, 49, 50] displays large cooperative motions in comparison to other liquids [36,48,51,52]. We observe here that behaviour from the large fragility of water (Figure 3) and from the NGPs (Figure 6).

How does these particularly large cooperative motions relate to the high-temperature particularities of water (the hydrogen bonding and the possible liquid–liquid transition in the no man’s land)? A first possible explanation is that the existence of polyamorphism favours structural fluctuations in the supercooled liquid that result in large dynamic heterogeneity. If that picture is correct, we expect the cooperative motions to sharply increase near the liquid–liquid transition between LDL and HDL, as well as in mixtures [50]. Actually the cooperative motions increase in low-temperature water when we decrease the density from $\rho_0 = 1$ to $\rho_1 = 0.92 \text{g/cm}^3$ to promote the LDL phase. During that density decrease however the viscosity increases, a particular behaviour of water, and the increase of cooperative motions could be attributed to that increase of the viscosity. A second possible origin of these large cooperative motions is that the network structure organises the liquid increasing the probability of string like motions. In favour of that second explanation we observe also relatively large cooperative motions in silica [36,48]. Also the string-like cooperative motions follow the pre-existing structure leading to curved string motions for water. Note that the two explanations do not exclude each other.

### 3.4. Structure-related dynamic heterogeneities

Most scientists expect cooperative motions in supercooled liquids to be related to some structural defects. The underlying
idea being that if the cage surrounding a molecule is too tight, the molecule is less likely to move. Similarly, if the cage is loose the molecule will move more likely than the average. This leads to the hypothesis of structural fluctuations known as hard zones and soft zones that result to the least mobile and most mobile molecule aggregation. However, if there is some structure-related effect indirectly observed from the propensity [53,54], the structural modification leading to these effects is elusive in most liquids.

Contrary to other liquids, in supercooled water we find a clear relation between the local structure and the cooperative motions [47]. As discussed above, we actually find for water that the local structure around moving molecules is less organised than around non-moving molecules. We observe this behaviour in Figure 1(b) of Ref. [47] from a comparison between the radial distribution functions around mobile, non-mobile, and average molecules. Why is that structural modification visible in water and not in other liquids?

Here, again polymorphism induced by the existence of different minima in the potential energy, will increase the structural fluctuations, leading to a more visible correlation between structure and dynamics.

3.5. Confinement inside nanopores

Confinement of liquid water inside nanopores permits to avoid crystallisation at $T_{Tt}$, and thus gives experimental access to the no man’s land. For that reason among others, the effects of confinement of supercooled water have been the subject of a large number of works [55–61]. However, the fact that confined supercooled water is or not significantly different from bulk supercooled water is still a matter of debate. In supercooled water, confinement increase or decrease the viscosity depending on the wall hydrophilic or hydrophobic nature. Confinement is also expected to cutoff the cooperative motions as they cannot propagate inside the wall. The diameter of the pore thus appears as a maximum cooperative length for two dimensions of the system. Simulations however show that nature is more complex. Actually, for an hydrophilic wall, the cooperative motions do not decrease but instead increase when supercooled water is confined [49].

4. Conclusion

Water is a complex liquid due to its polymorphism (i.e. the possibility to have different structures) and hydrogen bonding that leads to a network structure. These characteristics lead to various anomalies that extend to the supercooled region. Inside that category, we have the density and viscosity anomalous behaviours. Moreover, some new types of anomalies appear at low temperatures, that are mainly amplified behaviours of supercooled liquids. In that second category, we have the large cooperative motions and a visible connection between dynamic heterogeneities and the underlying structure of the liquid.

Disclosure statement

No potential conflict of interest was reported by the authors.

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