The structure of water; from ambient to deeply supercooled

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A B S T R A C T

Here we discuss the structure of water in terms of a temperature-dependent balance between two classes of hydrogen-bonded structures. At high and down to mildly supercooled temperatures most molecules favor a closer packing than tetrahedral, with strongly distorted hydrogen bonds. This allows the quantized librational modes to be excited and contribute to the entropy while the loss of enthalpy due to breaking hydrogen bonds is compensated by enhanced van der Waals interactions. Tetrahedral hydrogen bonding is of lower enthalpy resulting in tetrahedrally bonded water patches appearing, but only as fluctuations with size and life-time increasing at lower temperatures. Measurements of the structure at deeply supercooled conditions show a continuous increase in tetrahedrality which becomes accelerated below the temperature of homogeneous ice nucleation. The two local structures are connected to the liquid–liquid critical point (LLCP) hypothesis in supercooled water and correspond to high density liquid (HDL) and low density liquid (LDL). We propose that both HDL and LDL behave as normal liquids and that the anomalous properties of water result from the transition between them, which occurs over a wide temperature range at ambient pressure. The key issue is the competition between incompatible conditions for maximizing the entropy, favored in HDL, and minimizing the enthalpy, favored in LDL, which leads to the instability in the liquid and is the fundamental origin of the proposed LLCP.

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1. The inhomogeneous structure hypothesis

Understanding the structure and dynamics of the hydrogen-bonding (H-bonding) network in water is essential for many problems in chemistry, physics, biology and geoscience. The ability to form up to four H-bonds in addition to the interactions in normal liquids leads to many quite unusual properties such as increased density upon melting, decreased viscosity under pressure, density maximum at 4 °C, high surface tension and many more [1]. Water properties are also affected by various solutes and are fundamental to biological activity [2,3].

In the low-temperature regime, below the freezing point, these properties deviate particularly strongly from those of a normal liquid. Although the anomalies are extreme in the supercooled region they are also present at ambient conditions where most of water’s physical, chemical and biological processes occur. Here we will focus on thermodynamic response functions that depend on fluctuations in various properties [4]. One example (Fig. 1a) is the isothermal compressibility, κ T , related to volume, or equivalently density, fluctuations in the liquid. κ T decreases upon cooling as for a normal liquid, but only down to 319 K (46 °C). At this temperature κ T exhibits a shallow minimum and upon further cooling starts to increase again, indicating that density fluctuations in

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mostly driven by the directional strong H-bonding while the HDL structure is more due to the isotropic van der Waals interaction [15] that leads to a collapse of the tetrahedral structure and implies a local structure more towards a hexagonal arrangement [16].

Fig. 2 shows a hypothetical variation of the density of water from hot temperatures down deep into the supercooled region. This curve is consistent with measured data of water ranging from hot temperatures and down to roughly 240 K showing the density maximum and the initial part of the decline of the density with decreasing temperature [17] whereas the full curve has been obtained in simulations using the TIP4P/2005 model [18] and experimentally for water in nanoliter [19]. We distinguish three different regions where water in both the hot and extremely cold regions corresponds to a normal liquid with the anomalous region in between. The deviation of the thermodynamic response functions as shown in Fig. 1 corresponds to entering into the anomalous region. This corresponds to temperatures where the density starts to deviate from a linear relationship and where the isothermal compressibility and the heat capacity pass through a minimum and instead rise upon further cooling, as seen in Fig. 1. This should be around 315 K [20] meaning that water at the important ambient temperature is already in the anomalous region.

The normal liquid regions at high and low temperatures are dominated by structures resembling either HDL or LDL. They have a normal behavior of increasing density with decreasing temperature as expected for any liquid. The HDL-like structure, with thermally excited librational modes, dominates at high temperature and is continuously changing with temperature to become less disordered upon cooling as these modes become less excited. Similarly, at low temperatures the LDL-like structure dominates characterized by strong tetrahedral bonds which make thermal excitation of librational modes unfavorable. In comparison to the HDL structure the LDL patches show less variability with temperature in terms of local structure since disorder due to librational excitations is largely absent. The anomalous region is where the liquid structure is transforming from a HDL to a LDL dominated structure. This is a continuous transition which at ambient pressure occurs over a large temperature range. In this transition, coming from higher temperatures, spatially separated patches of the LDL-like structure form on temperature-dependent length and time scales as illustrated in the inset in Fig. 2. This occurs through collective fluctuations as H-bonding becomes more important at lower temperatures [11–13,18,20–27]; note that in a recent study the similarity of thermodynamic properties of water at slightly elevated temperatures and argon-like liquids was pointed out [28]. These patches have a size of the order of around 1 nm at ambient temperature and grow in size upon cooling [11]. Similarly, when at low temperatures LDL dominates, there will instead be fluctuations into HDL-like patches which decrease in size and persistence as the liquid is cooled further.

The presence of a density maximum and minimum seen in Fig. 2 becomes obvious with the transition from one type of normal liquid with higher density to one with lower density when also each normal liquid changes density with temperature. In particular, in the supercooled region such fluctuations increase anomalously which explains the enhancements of the thermodynamic response functions shown in Fig. 1. These observations are consistent with the proposed liquid–liquid critical-point (LLCP) [29,30] terminating the coexistence curve separating two macroscopic states of the liquid, HDL and LDL, in deeply supercooled and pressurized water. However, it is not yet entirely clear where the critical point would lie in terms of pressure [31,32]. There are also theoretical investigations indicating that the liquid is not in a metastable equilibrium under deeply supercooled conditions, but instead ice would form on a timescale faster than the liquid can be equilibrated [33,34]. In contrast, several recent simulation studies do find both LDL and HDL as equilibrated metastable liquids [35–39].

In this contribution we will go through various arguments for the inhomogeneous model based on the temperature dependence of the thermodynamic response functions. We will present X-ray and neutron scattering experiments together with simulations leading to a deeper interpretation of the data. Evidence from X-ray and vibrational spectroscopies has been reviewed recently [3,12,13,40,41] and will not be discussed in detail here.

2. Molecular dynamics simulations and the inherent structure

Many molecular dynamics (MD) models of water do indeed obtain HDL- and LDL-related structures, but only in the supercooled regime
instead applied to the low values (HDL-like) and extending to high values (LDL-like). When the stability of the minimum at 0.13 Å² at all temperatures. The same minimum is seen at various pressures as well and pressures is quite remarkable and a strong indication of a clear distinction between the two classes of local environments in the inherent structure. This implies that the 3N-dimensional potential energy surface (PES) on which the simulation evolves contains two qualitatively different types of local projections relating to local configurations of molecules in agreement with X-ray absorption spectroscopy (XAS) [3,14, 51] and X-ray emission spectroscopy (XES) [23,52] experimental data. There are sharp changes in the relative amplitude of the high-LSI and low-LSI peaks at deeply supercooled temperatures, while at higher temperatures the simulations sample very similar regions of the PES since only weak temperature-dependence is seen. A very clear connection to thermodynamic behavior is established in Fig. 5 where we show the populations in each class as a function of temperature using the minimum around 0.13 Å² as classification.

In the LLCP scenario the two liquid phases, HDL and LDL, are assumed separated at elevated pressure and supercooled temperatures by a coexistence line terminating at a critical point where thermodynamic structure. This implies that the inherent structure in simulations at ambient and elevated pressures, shown as a function of temperature. A temperature and pressure invariant isosbestic point is seen around 0.13–0.14 Å².

Figure adapted from Ref. [24].
response functions diverge. In the one-phase region, thermodynamic response functions show maxima in the $P-T$ plane defining the so-called Widom line as an extension of the coexistence line into the one-phase region beyond the critical point [53]. The Widom line divides the one-phase region into regions dominated by properties characteristic of either phase, but the distinction and magnitude of the maxima, diminish with increasing distance to the critical point [54]. Earlier studies [55] have located the LLCP and the Widom line of the TIP4P/2005 model where the LLCP was found close to $P_c = 1350$ bar and $T_c = 193$ K with the Widom line at $-230$ K at 1 bar pressure. Fig. 5 shows that the Widom line coincides closely with the temperature where a 1:1 ratio between low-LSI and high-LSI populations is seen [24,56], which is consistent with a maximum in fluctuations between the two and consequently in fluctuations of density, entropy and their cross-correlations.

We relate the observed two populations of low-LSI and high-LSI species in the inherent structure of simulated water to experimental observations of real water, in particular the temperature dependence of the XES spectra of D$_2$O [23]. The spectrscopically assigned tetrahedral component is related to the high-LSI species and the distorted component to the low-LSI species. In particular we note that the populations at ambient conditions, $-25\%$ high-LSI (LDL-like) and $75\%$ low-LSI (HDL-like), coincide closely to experimental estimates [11,23,57] of the two components in the XES and XAS/XRS [14,51]. Furthermore, the XES data also show quite weak temperature dependence in the ambient regime of the relative intensities of the two components, fully consistent with the temperature dependence of the two LSI components in Fig. 5.

There is another important observation that can be made from Fig. 4 in the ambient to hot regime where the peak position of the low-LSI component shifts to lower values with increasing temperature whereas the position of the maximum of the high-LSI component remains constant; the latter shifts first in the deeply supercooled regime. This has a direct correspondence in the XES [23,52] and XRS [3] spectra where the tetrahedral peak remains at constant energy within the probed ambient temperature regime, which is fully consistent with the temperature dependence of the high-LSI component. On the other hand, the distorted component, which would correspond to low-LSI, continuously shifts to higher emission energies and lower absorption energies towards the gas phase value indicating larger distortions and further weakened H-bonding similar to the shift to lower values of the low-LSI component with increasing temperature.

We thus have a direct correspondence between the two LSI components and the spectroscopic observations. However, this is only seen in the inherent structure in the simulation when the effects of thermal motion and disorder are eliminated. The simulation thus seems to contain the prerequisites for generating a bimodal spectroscopic signal in that the underlying potential energy surface on which the simulation evolves does contain two minima consistent with the interpretation of the spectra. However, seemingly the minima are too shallow such that, when a finite temperature is included, the simulation is not constrained by the minima and an average structure is obtained. In this picture the two minima would thus need to be deeper to constrain the simulation more closely to either minimum.

In simulations using classical force-fields there are several effects missing that could deepen the minima. In Fig. 6 we illustrate these effects in a qualitative picture of the balance between HDL and LDL at ambient conditions. The picture is in terms of two separated free-energy wells with separation and depth dependent on which interactions are included in a sequence of stepwise improved simulations. In this illustration the relative populations of HDL and LDL are illustrated as a probability dependent on the position along the LDL to HDL scale which could be given, e.g., by the LSI parameter similar to Fig. 4. At the top (Fig. 6a) we show the qualitative behavior in a classical force-field simulation where the minima are present but not deep enough to constrain the simulation to either of the two wells. One effect which is missing in classical force-fields is electronic structure cooperativity in H-bond formation which strengthens individual H-bonds if a more extended tetrahedral network is created [58,59]. This effect is included in ab initio MD simulations using density functional theory (DFT) at the generalized gradient level and, indeed, the minimum corresponding to tetrahedral or LDL-like structures becomes strongly enhanced as indicated in Fig. 6b. This is underlined by the melting temperature of ice simulated using the PBE or BLYP functionals, which is found to be around 420 K [60]. The balance has thus shifted strongly towards tetrahedral H-bonding and LDL.

The effect of adding the van der Waals interaction is illustrated in Fig. 6c. HDL is a more close-packed structure, where close-packing generally is given by non-directional interactions. Non-local correlation, or van der Waals interactions, could thus enhance the other, HDL-like, minimum in the simulations. Indeed, including dispersion corrections to the BLYP functional lowers the melting point to 360 K [61]. For the liquid, recent MD simulations using new functionals containing non-local correlation fully ab initio [15,62,63] find a dramatic structure
change from a very LDL-like O–O pair-correlation function (PCF) with the PBE functional to a very HDL-like PCF with the vdw-DF2 non-local correlation functional [15].

The size of the simulation box is also of importance for the LDL component as illustrated in Fig. 6d. It should be noted that in a recent benchmark study [64] shell structure was resolved for ambient water out to the sixth nearest neighbor at around 14 Å in the O–O pair-correlation function. If one assumes that this structure is mainly associated with fluctuations into tetrahedral patches, and remembers that the PCF describes the radial distribution, then significantly larger simulation boxes than the standard 64 or 128 molecules would be required to allow fluctuations into tetrahedral patches to fully develop, if they are favorable. Ideally, the simulations should also be run in the NpT ensemble to allow the density in the simulation box to fluctuate.

Fig. 6e illustrates, finally, that quantum effects are also important where it has recently been found that strong H-bonds are further strengthened through more efficient delocalization along the H-bond while weak H-bonds are further weakened due to delocalization in the librational motion [65]. In fact, nuclear quantum effects are proposed to discriminate between LDL and HDL since it is only when the librational motion is fully quantized that these modes become thermally inaccessible for tetrahedrally H-bonded molecules and the contribution to the entropy from these modes is lost while the less restricted motion in the HDL environment with broken H-bonds leads to a softer librational potential and quantized energy levels that are thermally excited already at ambient temperatures.

3. Density fluctuations

The isothermal compressibility $\kappa_T$ is a response function that is directly related to volume or density fluctuations. If we look at Fig. 1 we see that for a typical normal liquid $\kappa_T$ decreases with decreasing temperature. This is quite expected since the amplitude of the thermal motion of the liquid decreases with decreasing temperature. It is therefore very surprising that for water this is true at high temperatures but then suddenly, when the temperature approaches the ambient regime, $\kappa_T$ flattens out and then instead increases with decreasing temperature and seemingly diverges towards a difficult to access temperature of 228 K [7,66].

In the supercooled regime this anomalous behavior is commonly viewed as due to fluctuations between HDL and LDL [4,30] but it is debated whether the two types of liquid exist as unique phases in some part of the phase diagram although in very recent simulations of ST2 water unambiguous evidence of two separate liquids has been obtained [39]. However, the anomalous behavior sets in already under ambient conditions where spectroscopic data using XAS/XRS and XES together with small-angle X-ray scattering (SAXS) indicate two specific local species in the liquid with instantaneous local patches of tetrahedral structures appearing that have a rather different density and that persist on some time-scale before collapsing back into the background normal-like liquid [11,57]; this picture thus extrapolates the behavior from deeply supercooled conditions into the ambient regime. The more open network of the tetrahedral structures generates local regions with lower density which results in the density maximum at 277 K (4 °C) as the density decrease due to fluctuations into LDL-like tetrahedral patches overcomes the increased density with cooling of the HDL-like background normal liquid (Fig. 2): this is also the origin behind the change in sign of the thermal expansivity $\alpha_T$ in Fig. 1c. When fluctuations open up to create the tetrahedral structures we have another contribution to $\kappa_T$ that has the same sign as the thermally induced random fluctuations. However, the temperature dependence is the opposite. The anomalous contribution leads instead to an increase in the compressibility upon cooling since we expect that the patches of more compressible tetrahedral structures are formed with higher probability, can survive longer and grow in size when the temperature decreases and H-bonding becomes more important.

3.1. Normal and anomalous contributions to $\kappa_T$

There is no strict division based on thermodynamic grounds between normal and anomalous contributions to $\kappa_T$. However, both Conde et al. [67] and Kanno and Angell [8] have made such a division by observing the influence of small impurities of molecular compounds in water and then extrapolating to infinite dilution. The normal component follows an expected normal liquid behavior. Fig. 7 shows the division of $\kappa_T$ into two components for the two different extrapolations [8, 67]. First we note that the normal component dominates at high temperatures and the anomalous component at low temperatures. The two contributions to $\kappa_T$ become equal at 279 K (6 °C) and 273 K (0 °C) for the two decompositions. Note that, since HDL and LDL can be expected to differ strongly in their inherent compressibility, the fact that their contributions to the resulting $\kappa_T$ are equal does not imply equal populations of the two types of local structures. However, it does demonstrate that there is an appreciable amount of anomalous contribution to the density fluctuations already in the ambient regime.

It is therefore essential to realize that fluctuations into tetrahedral patches, or LDL-like local structures, are significant well above the supercooled region and contribute to water properties and dynamics in the otherwise HDL dominated liquid. Upon heating, the tetrahedral patches might eventually become so small that the anomalous contribution becomes negligible. It has recently been proposed that this occurs just above the isothermal compressibility minimum [20].

Based on Fig. 1 we also note that the magnitude of the normal component is much smaller than what is expected for a normal liquid. However, what is interesting is that the normal component becomes quite similar to the full $\kappa_T$ for water under pressure [67]. In this case the larger volume tetrahedral patches, or LDL structures, will be converted to the
smaller volume HDL structures. Clearly the HDL structures are much less compressible than a normal liquid.

3.2. Compressibility in MD models

In order for a water model to realistically describe both the structure and the dynamics of the fluctuations that occur in water at ambient conditions it is essential that such a large anomalous contribution to $\kappa_T$ is well reproduced. Fig. 8 shows computed $\kappa_T$ from a number of MD models [68]. In the left part of the figure the TIP5P, TIP4P and SPC/E models are shown. First we note that all three models resemble more the normal liquid behavior in Fig. 1 than real water, with a strong over-estimation of $\kappa_T$ at high temperatures and an underestimation at low temperatures. A real well-defined minimum in $\kappa_T$ is also lacking in the studied temperature range. This means that there is only a negligible anomalous contribution to $\kappa_T$ and instead the random thermal fluctuations clearly dominate. We should not expect to observe any major tetrahedral patches or local LDL structures to evolve in the ambient regime for these MD models, as was indeed not the case in the large-scale simulations of Ref. [70]. We assume that a much larger anomalous contribution will appear deeper down into the supercooled regime since a LLCP with HDL and LDL local structures has been seen for these models [71]. This has indeed been shown to be the case for the TIP4P/2005 model where a significantly larger enhancement is seen at the Widom line (230 K) of the model [18], but, as is evident from Fig. 8, at ambient pressure the model still severely underestimates structural fluctuations under supercooled conditions.

There is another important aspect that we can observe in a comparison between Figs. 7 and 8 regarding the absolute value of the normal contribution to the experimental $\kappa_T$ and the normal-liquid behavior of the MD models at high temperatures. The MD models are much more compressible than the normal component of the real $\kappa_T$. This means that, although the MD models behave more like a normal liquid, they are still far from a HDL-like liquid, which should have much lower compressibility. We can infer that in the MD models there must also be random fluctuations involving some sort of tetrahedralicity which enhance the volume fluctuations. It seems that the MD models have stochastic fluctuations leading to a smeared out structure without generating spatially separated local regions of HDL and LDL structures. The amplitude of the stochastic fluctuations simply decreases with decreasing temperature. On the contrary the fluctuations in real water, that give rise to the anomalous contribution, are strongly correlated and lead to organized tetrahedral patches associated with larger volume and consequently lower density [11].

It is interesting to note that the SPC/E potential gives rise to a bimodal distribution in the inherent structure also in the ambient regime similar to what was presented in the previous section [47]. Clearly the thermal random motion smears this out giving only the normal liquid behavior of $\kappa_T$. As discussed above, we propose that the local potential energy minima related to HDL and LDL structures are not deep enough to give rise to the normal and anomalous parts of $\kappa_T$ in the MD models. We would not expect to observe any major density inhomogeneities in the ambient regime for any of the models. We will discuss this further in the next section.

Before proceeding to discuss the structural implications of the anomalous contribution we should inspect the right part of Fig. 8 that shows the temperature dependence of $\kappa_T$ for the TIP4P/2005 model at two different pressures [68]. Here indeed we observe a minimum in $\kappa_T$ that is not too far from the experiment. This is the reason why we have chosen to use this particular MD model for our simulations in the ambient and deeply supercooled regimes [18,22,72]. However, in this context it is important to note that this model is not perfect. There is still an overestimation at high temperatures and an underestimation at lower temperatures although with respect to $\kappa_T$ it is superior to the other models. It would be interesting to find an MD model that would underestimate $\kappa_T$ at higher temperatures and overestimate at lower temperatures and investigate if in this case indeed local structures similar to what is observed in the inherent structure would also be seen in the real structure.

One such way would be to use the model at another thermodynamic state point to represent this aspect of ambient water. We note in Fig. 8 that going to 1000 bar shifts the compressibility to lower values and that the simulation then is closer to the experiment at that pressure. This means that the model represents the fluctuations of HDL water with a low compressibility quite well. However, we note that the rise in $\kappa_T$ at lower temperatures beyond the minimum is more rapid than for 1 bar. We could expect that the TIP4P/2005 model could have an even better representation of the balance between the normal and anomalous contributions to $\kappa_T$ at 500–1000 bar higher pressure and 25–40 K lower temperature, which would be closer to the critical point in the model. This is also the case in terms of the phase diagram involving the various ices and liquid water for this model where such a shift would give a perfect agreement with the experiment [50].

We note that Overduin and Patey [73] recently questioned the existence of an LLCP in TIP4P/2005 water based on investigations around the suggested LLCP from Abascal and Vega (193 K and 1.35 kbar) [55]. However, in parallel work Sumi and Sekino [74] reported an LLCP at 182 K in TIP4P/2005 water in the vicinity of which Yagasaki et al. [75]
later found maximal fluctuations between HDL and LDL which led them to support an LLCP close to 185 K. Although the situation around an LLCP in TIP4P/2005 water is still unclear we note that fluctuations between HDL and LDL can occur in the model and that the equilibration time of the two liquids is significantly shorter than nucleation of ice [74]. This has also been demonstrated for the well-studied ST2 model where two separate equilibrated liquid free-energy minima have very recently been unambiguously demonstrated [39].

Although we truly believe that the TIP4P/2005 model qualitatively captures both the anomalous and normal contributions to density fluctuations we know that the local nearest neighbor interaction is somewhat too strong. This gives rise to a too high and sharp first peak in the O-O pair-correlation function [50, 76, 77]. We can anticipate that this is part of the origin of the smearing of the two structures in the real structure. This will be further discussed below.

4. Density inhomogeneities and small-angle X-ray scattering

Let us now turn to the structural inhomogeneities that the anomalous part of the fluctuations gives rise to. These have been interpreted as fluctuations involving local LDL patches that become more extended with decreasing temperature [11, 12, 78, 79]. In a more rigorous statistical mechanical language these increased fluctuations into LDL patches have been called concentration fluctuations between different local structural environments [25]. This seems simply a different terminology for the original interpretation of Huang et al. [11] in terms of density inhomogeneities due to fluctuations into tetrahedral patches.

4.1. Small-angle X-ray scattering (SAXS)

Small angle X-ray scattering (SAXS) is the most direct probe of density variations or fluctuations on different length scales in a liquid. Through an enhancement of the structure factor in the region of low momentum transfer Q it can reliably identify small deviations from the average electron density due to instantaneous aggregation structures. Fig. 9 depicts the scattering structure factor, S(Q), at different temperatures for H2O, with the experimental structure factor S(Q), derived from SAXS of H2O, bottom to top at high Q: (left) 280, 284, 293, 298, 302, 311, 320, 329 and 347 K [11] and (right, top to bottom at low Q) 252, 254, 258, 263, 268, 273, 278 and 284 K [21]. The extrapolations of scattering intensity to zero-scattering angle using a 2nd order polynomial fit at low Q are represented by dashed lines in the left panel.

Fig. 9. Experimental structure factor, S(Q), derived from SAXS of H2O, bottom to top at high Q: (left) 280, 284, 293, 298, 302, 311, 320, 329 and 347 K [11] and (right, top to bottom at low Q) 252, 254, 258, 263, 268, 273, 278 and 284 K [21]. The extrapolations of scattering intensity to zero-scattering angle using a 2nd order polynomial fit at low Q are represented by dashed lines in the left panel.

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Fig. 10. Isothermal compressibility determined from either macroscopic thermodynamic measurements (dashed line) [81] or extracted from the SAXS data (circles and squares) [11, 21].
temperatures varying from 347 K to 280 K [11] and from 284 K down to 252 K [21]. The experimental data show an enhanced scattering as Q approaches zero, indicating large density fluctuations in the system, which increase at low temperatures.

There is a thermodynamic relationship that relates $\kappa_T$ to the structure factor at $Q = 0$ as $S(0) = k_B T n \kappa_T$, where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $n$ is the molecular number density [80]. Fig. 10 compares the isothermal compressibility determined from macroscopic thermodynamic measurements and as obtained from the SANS data [11,21] which demonstrates an excellent agreement. This shows that the anomaly of the minimum and then rise of $\kappa_T$ towards cooler temperatures are directly related to the enhancement observed in the SANS data and thus to the density inhomogeneity arising due to structural fluctuations [57]. Clearly this can be interpreted in terms of structural components giving the anomalous contribution to $\kappa_T$.

We now inspect the low-$Q$ structure factor for a simple or normal liquid and how it varies with temperature. Fig. 11a shows the temperature-dependent SANS intensities of ethanol from 273 K to 328 K measured under similar conditions as in Ref. [11]. First of all we observe no significant enhancement at low $Q$ and secondly the shape of the curves is constant with only a vertical offset as a function of temperature. This is clearly very different from the water scattering data in Fig. 9 which show a similar offset at intermediate $Q$ as ethanol with increasing temperature, but rather different behavior at low $Q$ where the slope of the curve changes from positive to increasingly negative with higher intercept with decreasing temperatures.

In Fig. 11b we show the simulated temperature-dependent SANS signal for SPC/E water using a simulation box containing 45,000 molecules and sampled over 300–440 ps to reduce artificial oscillations. Due to the reciprocal correlation between $r$ and $Q$ space a large box size is needed to reach low $Q$; the mathematical properties of the Fourier transform from $r$ space to $Q$ space still prohibit observation of the behavior below $Q = 0.13 \text{ Å}^{-1}$ for the used box size ~106 Å (note that a weight function has been applied in the Fourier transform to reduce truncation errors beyond the reciprocal box size [11,18,82]). The most important scattering enhancement observed at small $Q$ in the experiment on real water (Fig. 9) is completely missing from the SPC/E water data even down to $Q = 0.13 \text{ Å}^{-1}$. The SPC/E simulated $S(Q)$ instead shows similarity with the experimental data for normal liquids such as ethanol (Fig. 11a) and CCl$_4$ [11,13]. This is also what must be expected from the normal liquid behavior of SPC/E water in terms of the isothermal compressibility (see Fig. 8).

4.2. Qualitative understanding of SAXS data

Let us now discuss what we would expect from a comparison between simulated and measured $S(Q)$ for different models. If a model such as those shown in the left part of Fig. 8 would be used, we would not expect a rise in the low-$Q$ region since the anomalous contribution to $\kappa_T$ is too small. We can easily understand why there is no real enhancement at low $Q$, i.e. that there is no increase with a lowering of the temperature. The curves with positive slope at $Q$-values above 0.5 Å$^{-1}$ are related to the first diffraction peak in water, which, at higher temperatures, is broadened due to thermal disorder enhancing $S(Q)$ also at lower $Q$-values. The amplitude in the intermediate region before the first peak goes down with decreasing temperature simply because disorder is decreasing and the first peak gets sharper. This is seen for both the experimental and SPC/E simulated $S(Q)$. If we now look at the low-$Q$ region we observe for the $S(Q)$ from the SPC/E simulation only a similar displacement with temperature as for the high-$Q$ region causing the curves to become parallel. This is not surprising since we have the relationship between $S(Q)$ at $Q = 0$ and $\kappa_T$. If $\kappa_T$ decreases with decreasing temperature it is expected that also the low-$Q$ region will be lowered similar to the high-$Q$ region.

However, for a model that indeed has a minimum in $\kappa_T$, followed by a rise at lower temperatures we would expect the reverse. Now instead the low-$Q$ region would increase upon cooling whereas the high-$Q$ region would still decrease. This should give rise to a change of sign in $S(Q)$ to negative slope for low $Q$ for models that have a large anomalous contribution. Maybe this is what we should expect for the TIP4P/2005 model, which fulfills this requirement.

Fig. 12 shows the temperature-dependent $S(Q)$ for this model simulated at ambient pressure and indeed a change of sign is observed at low
Q [18] for the 253 K simulation. This enhancement becomes much larger in the more deeply supercooled regime exhibiting a maximum between 240 and 230 K. This corresponds to crossing the Widom line in the model where the HDL:LDL ratio is close to 1:1 and the fluctuations show a maximum [18,24] (see Figs. 5 and 12 (right)). At even lower temperatures (220 and 210 K) the simulated liquid becomes increasingly dominated by LDL-like structures which reduces the structural fluctuations and as a consequence the low-Q enhancement; in this region fluctuations are instead related to collapse of tetrahedral structures into more HDL-like in the LDL-dominated liquid. This demonstrates the connection between temperature dependence of \( \kappa_T \) and the enhancement at low Q. It is therefore clearly very important to develop water models that describe the anomalous or HDL-LDL fluctuations correctly.

This is further underlined by studying the isothermal compressibility of model water (TIP4P/2005 and SPC/E) down to deeply supercooled conditions and comparing with real water down to the lowest temperatures at which \( \kappa_T \) has been determined (Fig. 13a). The fluctuation formula was used to determine \( \kappa_T \), which requires rather long simulations to converge. The simulations were thus run with 512 molecules for 1 µs for temperatures 230 K and lower and for the higher temperatures for 500 ns. We note for both TIP4P/2005 water and for SPC/E water a maximum in the isothermal compressibility as the Widom line in the respective model is crossed. We also note the significantly lower amplitude of the maximum for SPC/E water than for TIP4P/2005 water, which can be related to the distance to the liquid–liquid critical point in the respective models; fluctuations associated with a critical point decrease with increasing distance in the phase diagram from the critical point [54] and TIP4P/2005 water has its LLCP at \( P_c = 1.35 \) kbar and \( T_c = 193 \) K [55] or 182–185 K [74,75] while for SPC/E water an LLCP has been reported at \( P_c = 2.90 \) kbar and \( T_c = 130 \) K [83]. The significantly smaller rise for TIP4P/2005 water compared to real water then indicates that real water at ambient conditions should be significantly closer to its critical point than the TIP4P/2005 model. Indeed experimental and theoretical estimates of the location of the proposed LLCP of real water have placed it at a modest pressure of less than 500 bar [31,84].

In Fig. 13b we compare the computed SAXS signal from TIP4P/2005 water with the measured SAXS signal of real water. At the highest temperature shown (278 K) we note an excellent agreement between experiment and simulation, albeit with a small shift of the simulated signal. However, going into the supercooled region we find it increasingly difficult to reproduce the experimental signal and an increasing offset, both in temperature and in magnitude, is required for best fit to the experiment [18]. We note here that, even at the Widom line (230 K) of the TIP4P/2005 model where fluctuations reach a maximum, the anomalous enhancement is still smaller than experiment at 253 K [18] emphasizing that real water at ambient pressure is closer to a possible critical point, real or virtual, than is the case of the simulation.

4.3. The relation between correlation length and spatial extent

In order to obtain more information on spatial extent of fluctuations giving rise to the anomalous enhancement at low Q-transfer we consider Ornstein–Zernike (OZ) theory in which the total correlation, \( h(r) = g(r) - 1 \), between two particles is expressed as the sum of their direct correlation and the indirect correlations propagated via all other particles in the system [85,86]; this is a widely applied framework for describing critical phenomena where the correlation length, \( \xi \), tends towards infinity in the vicinity of a critical point, i.e. fluctuations become correlated at all length-scales. OZ theory is, however, quite general and can also be applied to, e.g., describe the dynamical correlation between electrons in a molecule [87]; this is not at all related to critical phenomena, but simply a way to describe how one pair-wise interaction can affect a second since that partner is part of another pair and so on ad infinitum. OZ theory simply describes in real space through the correlation length \( \xi \) how such indirect interactions decay.

In order to extract the correlation length from the data we fit the OZ expression for the structure factor, valid for small Q,
S(Q) \propto \frac{1}{Q^2 + \xi^{-2}}

to the anomalous contribution to the structure factor \[11,13,21\]. The form of the function is a Lorentzian where the inverse correlation length, $\xi^{-1}$, is simply the half-width-at-half-maximum (HWHM). The extracted correlation lengths for supercooled water were obtained in Ref.\[21\] and are shown in Fig. 14 for different subtractions of the normal component. It is clear that the extracted correlation lengths are small, 2–3 Å, so how can this be understood and related to the real-space correlation? Is such a small correlation length, comparable to molecular dimensions, even relevant?

The Lorentzian above is the asymptotic expression valid for small Q and in order to relate to the real-space correlation function we must take the Fourier transform to obtain the asymptotic contribution to $h(r)$ \[86\], representing the main contribution for large $r$. This becomes $\exp(-r/\xi)$ showing that, in real space, the OZ correlation length simply has the role of a damping factor in the asymptotic decay of the total correlation. It is thus not a specific distance in the measured system and effects on the real-space correlation extend well beyond the OZ correlation length. To illustrate this point further we consider simulations

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Fig. 13. a) Temperature dependence of the isothermal compressibility for TIP4P/2005 water and SPC/E water compared with that of real water \[81\]. The compressibility of the water models was obtained from the fluctuation expression based on trajectories of length 1 μs ($T \leq 230$ K) or 500 ns ($T > 230$ K) with 512 molecules. b–e) Computed SAXS for TIP4P/2005 water compared to real water at temperatures (TIP4P/2005, real): b) (278 K, 278 K), c) (253 K, 263 K), d) (240 K, 258 K), and e) (230 K, 252 K), i.e. an increasing offset in temperature and absolute value for TIP4P/2005 water is required for best comparison with real water. At the Widom line (230 K) at ambient pressure for TIP4P/2005 water the SAXS signal is maximal but still underestimates the SAXS signal of real water at 252 K.

Figure adapted from Ref.\[18\].
close to the liquid–gas critical point (LGCP) of TIP4P/2005 water where the effects are significantly larger \[18\].

The simulations were performed in the NVT ensemble at the reported liquid–gas critical temperature and density \[88\] of the TIP4P/2005 forcefield \[50\] using 45,000 molecules in a box with ~163 Å sides \[18\]. The SAXS signal, S(Q), was computed showing a very strong enhancement in magnitude at low Q due to the strong density contrast, but the extracted correlation length, or inverse HWHM, remained rather small, 5.9 Å, similar to earlier simulation results \[89\]. That this actually gives a good description of the asymptotic decay of the correlation function is seen in Fig. 15 where we show the O–O g(r) of the simulation near the LGCP together with the asymptotic function \(1 + A \exp(-r/\xi)/r\) verifying that it describes the O–O g(r) accurately beyond 6 Å (the factor A = 1.4 was fitted by hand) and that the enhancement clearly remains well beyond 10 Å (the curve remains above the statistical mean of 1). Similarly OZ correlation lengths of ~2–3 Å for ambient and supercooled water, as determined in Refs. \[11,21\], will imply real-space correlations extending well beyond 2–3 Å.

To further illustrate the lack of a direct real-space correspondence between the correlation length and extent of actual spatial inhomogeneities in the simulation we show a snap-shot of the LGCP simulation in Fig. 16 including a ruler showing the \(\xi = 5.9\) Å correlation length as obtained from the simulation. In order to allow a visualization of the system we have cut a 10 Å thick slab from the ~163 Å side simulation box. The granularity in the system is very visible and it is also clear that the granularity has a spatial extent which is significantly larger than the derived correlation length.

The same anomalous component in the SAXS data can, however, be analyzed in different ways depending on the expected character of the system. In terms of critical behavior the OZ fit is the established approach, but when dealing with, e.g., macromolecules or colloids with fixed structure, the same curve shape would rather be analyzed in terms of a Guinier analysis \[90\] with the low-Q shape described by the scattering expression \(\exp(-1/R_G Q^2)\) with \(R_G\) the Guinier radius, which, in contrast to the OZ correlation length, in its interpretation is more directly related to real-space physical dimensions.

The X-ray photon interaction time with the probed electron density is of the order attoseconds, which implies that the SAXS experiment samples molecules frozen in time. It can thus be justified to consider analyzing the LGCP simulation in terms of a Guinier analysis to obtain a better estimate of the real-space extent of the scattering density inhomogeneities. From the scattering expression one finds \(R_G = \xi \sqrt{3}\) and, assuming a spherical shape, the diameter becomes \(D = 2\sqrt{3/5}R_G\) which with \(\xi = 5.9\) Å gives \(D = 26\) Å. This is indicated in Fig. 16 with the longer bars which clearly provide a better estimate of the actual size of the scattering inhomogeneities. However, we have to be aware that there will

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**Fig. 14.** Dependence of correlation length \(\xi\) upon the temperature \(T\) for \(H_2O\) with a best-fit power law \[21\] with different subtraction of the normal component using either the Percus–Yevick approximation (circles) or the method used in Ref. \[11\] with an assumption of the cut-off \(Q_{\max} = 0.9\) Å\(^{-1}\) (diamonds) and 0.8 Å\(^{-1}\) (squares).

**Fig. 15.** a) Small-angle structure factor S(Q) from an NVT simulation at the reported liquid–gas critical point (LGCP) 540 K and \(\rho = 310\) kg/m\(^3\) \[88\] for the TIP4P/2005 model of water with 45,000 molecules \[18\]. b) The obtained g(r) together with the asymptotic OZ correlation function \(1 + A \exp(-r/\xi)/r\) (dashed) which gives real-space correlations \(g(r)\) even beyond 10 Å in spite of a correlation length \(\xi\) of 5.9 Å \[18\]. Reproduced with permission from Elsevier Ref. \[13\].

**Fig. 16.** Snap-shot from a TIP4P/2005 water simulation near the liquid–gas critical point including ruler showing the 5.9 Å correlation length on the same scale as the simulation box as well as measures (longer white lines) showing the Guinier estimate \(D = 26\) Å of the spatial extent (see text).
be many sizes, as is evident from Fig. 16, and the derived value of $D$ only gives a rough estimation of the mean value of the distribution.

4.4. Anticorrelation between tetrahedrality and density

Let us return to the TIP4P/2005 water model that indeed shows an anomalous behavior in the ambient regime both in $n_T$ and in the SAXS enhancement. Fig. 17 shows colored regions in a simulation box at 253 K and 340 K of TIP4P/2005 water where two different selection criteria have been used of either high tetrahedrality (blue) corresponding to LDL or high density (yellow) as HDL and indeed we observe a spatial separation [18]. We clearly see the inhomogeneous structure where the regions of LDL and HDL occupy different parts in the real space. It is also remarkable to see that the inhomogeneous structure is maintained even at the high temperature of 340 K although the tetrahedral regions have become smaller. It should be noted here that high tetrahedrality and high density are strongly anticorrelated [18]. The pictured inhomogeneity is thus not the result of clipping a single Gaussian field [91] although it is clear that varying the thresholds for tetrahedrality respectively density affects the appearance of a single snapshot. However, the comparison between snapshots at different temperatures using fixed thresholds is not affected by the specific choice of threshold (Fig. 17). We have also observed that low- and high-LSI species, as defined in the inherent structure, form regions in the real structure [24]; here the strict bimodality given by the LSI index in the inherent structure gives an unambiguous decomposition. Although the strict bimodality in local structure is washed out by the thermal motion the clustering together is maintained.

5. Wide-angle scattering and pair-correlation functions $g_{OO}(r)$

The $O-O$, $O-H$ and $H-H$ pair-correlation functions (PCFs) provide a much used test of the performance of models of water in MD simulations in terms of structure. It should be noted, however, that X-ray and neutron diffraction are rather insensitive to H-bonding and caution must be exercised when drawing conclusions on the reliability of MD simulation results based on diffraction data; reproducing the experimental structure factor $S(Q)$ and the derived PCFs. A difficulty for simulators has been to select which PCF to compare to, where in particular the range of published $O-O$ PCFs has been problematic. In order to remedy this situation we have recently published a detailed analysis of four recent data sets going up to high Q-transfer and derived a converged benchmark $O-O$ PCF [64]. We have furthermore, as one of these data sets, measured temperature-dependent X-ray diffraction of water with a unique set-up where we experimentally separate the elastic contribution from the Compton scattering using an X-ray spectrometer [22]. The water sample was a liquid jet eliminating potential beam damage effects. A higher Q-range furthermore allowed us to obtain more details in the pair-correlation function and their dependence on temperature. In the following we will discuss different aspects of the $O-O$ PCF starting with intermediate range correlations and their dependence on temperature which reveals interesting aspects of structural transformations in the liquid.

5.1. Correlations at intermediate range (6–15 Å)

An issue of debate is the interpretation of SAXS data in terms of density heterogeneities and their size [11,12,18,24,57,70,93–95] where MD simulations have been shown to result in the expected unimodal Gaussian density distribution. However, it has also been shown that the LSI index determined in the inherent structure of TIP4P/2005 water divides the distribution into a sum of two superposed, shifted Gaussian distributions which behave with temperature similar to what is expected for HDL respectively LDL-like components [24]. In Section 4 above we discussed the correlation length and how it is connected to the real structure only through the asymptotic decay of the pair-correlation function. We showed that the Guinier analysis gives a better estimate of the size of density fluctuations in water simulated close to the liquid–gas critical point of TIP4P/2005 water. This provides support for using the Guinier analysis also for experimental SAXS curves of ambient water which has led to an estimated average size of density heterogeneities ~1 nm [11], still assuming fluctuations between distributions of structures, but on a time-scale significantly longer than the attosecond experimental probe. We have recently confirmed the 1 nm characteristic average length scale by considering the $O-O$ pair-correlation function at longer distances [22,64]. Here we focus on the correlations at
longer distances that are relevant in connection to the discussion of the SAXS data.

The pair-correlation function (PCF) at intermediate distances is magnified by plotting in Fig. 18a the scaled difference in the radial distribution function (dRDF) defined as \(4\pi r^2 \rho_0 (g(r) - 1)\) [22]. We observe structural correlations up to \(r \sim 12\) Å, indicating the presence of a medium-range order in the liquid. In particular, the 4th PCF peak at \(r \sim 9\) Å and the 5th peak at \(r \sim 11\) Å are resolved while after the 5th shell, the correlations are gradually washed out within the noise level of the experiment. A 5th PCF peak, similar to the present data, has been observed in supercooled water in two previous independent X-ray studies [96,97].

Yokoyama et al. [96] studied both supercooled and ambient water, but the signal-to-noise level made it difficult to draw firm conclusions on intermediate-range correlations at 25 °C. However, in a very recent X-ray diffraction study of ambient water using 115 keV photons giving high-quality data out to 26 Å\(^{-1}\) [98,99] also a 6th coordination shell (Fig. 19b) was observed at \(r \sim 13\) Å in ambient water [64].

5.2. Temperature dependence of intermediate-range correlations

There are interesting differences in the temperature dependence of the different O–O PCF peaks as shown in Fig. 18a: the 1st and 4th
peaks exhibit less temperature sensitivity compared to the 2nd, 3rd and 5th peaks whose magnitudes strongly increase as temperature decreases from 340 K to 280 K. It directly indicates that there are temperature-dependent structural changes in liquid water in addition to the effects of disorder induced by normal thermal motion.

In order to extract further information we compare to the dRDF from the TIP4P/2005 model as shown in Fig. 18b. The simulation clearly contains the experimentally observed intermediate-range correlations giving the 4th and 5th PCF peaks in the correct positions. In terms of the temperature dependence, an excellent agreement between the MD simulation and experimental data is found: the 5th peak at \( r - 11 \text{ Å} \) is observed to significantly increase in amplitude with decreasing temperature both in the XRD data and in the TIP4P/2005 simulation while the amplitude of the 4th peak exhibits less dependence on temperature. Moreover, the position of the 4th peaks is seen to shift to larger distances at higher temperatures as indicated by the vertical line in Fig. 18b; this is consistent with the shift observed between 280 and 340 K in the experimental data shown in Fig. 18a.

To investigate the structural origin of these peaks at intermediate distances we characterize the molecules in the simulation according to the LSI parameter (discussed in Section 2), \( I(i) \), and thus define subensembles of water molecules in either disordered or structured environments. Since at the highest temperature, 340 K, rather few molecules are LDL-like according to the strict bimodal criterion of an LDL local structure.

This is fully consistent with respect to the proposed regions of HDL and LDL local structures.

The close similarity between simulated and experimental intermolecular PDFs on the intermediate length scale suggests that the 4th and 5th correlation peaks, and in particular the latter, are attributable to the existence of fluctuations into highly ordered (LDL-like) structural environments in ambient water. The loss of intensity in the 5th peak with increasing temperature can then be regarded as a sign of conversion of LDL-like to HDL-like species upon heating alongside the increased thermal disorder, as reflected also in simulations by the diminishing contribution from high-LSI species at higher temperatures seen in Fig. 18c. That we observe correlations of local LDL structures out to 11 Å [22] or even 13 Å [64] (Fig. 19b) fully supports the interpretation of the SAXS data in terms of fluctuations on some time-scale resulting in local patches of tetrahedrally H-bonded molecules with characteristic size around 1 nm [11, 57]; the length-scale of these fluctuations (patches) increases further upon supercooling the liquid [21].

It is interesting to compare the observed medium-range order in water with that of a simple liquid. For example, a Lennard-Jones (LJ) liquid also exhibits long-range ordered structure, as shown in Fig. 19a, solely governed by the effect of packing in the liquid. The fundamental difference between the dRDF functions of the LJ liquid and water, however, lies in the fact that the correlation peaks in dRDF decay smoothly in the case of the LJ liquid (Fig. 19a) while water shows a nonmonotonically decaying envelope function that is strongly \( r \)-dependent and where furthermore the peaks exhibit a more complicated dependence on temperature (Figs. 18a, 19b). It implies that a single packing structure, such as for the LJ liquid, is not enough to explain the structure of liquid water. Using a simplified core-softened model, Perera explained the abrupt drop of the amplitude of the correlation peaks in the dRDF beyond the 3rd coordination shell as a consequence of destructive cooperation between H-bonding and packing correlations at large distances [100]. This is fully consistent with respect to the proposed regions of HDL and LDL local structures.

5.3. The first O–O peak

Even though TIP4P/2005 water reproduces the peaks at intermediate range in the O–O PCF together with their temperature dependence the first peak is significantly too high and sharp with a height above 3
In comparison with the PCFs derived in 2000 by Hura et al. [101] based on an X-ray diffraction data set going out to only 10.8 Å\(^{-1}\) and by Soper [102] based on an EPSR analysis of neutron diffraction data, the peak height was too high, but the discrepancy was not too alarming. However, both these PCFs show a significantly too high first O–O correlation, but for different reasons. Due to the small Q-range measured by Hura et al. a Fourier transform of \(S(Q)\) to real space could not be performed and instead the data in terms of the total scattering \(I(Q)\) was fitted based mainly on PCFs from MD simulations under the assumption that the MD PCFs provided a sufficient range of possible PCFs. However, the total \(I(Q)\) is dominated by the molecular structure factor masking the weaker intermolecular scattering such that small, but significant, deviations were not taken into account [77]. Similarly, the EPSR fit applied by Soper uses an initial MD force-field which is modified iterative-ly to give structures that reproduce the experimental scattering data. However, neutrons are more sensitive to O–H and H–H correlations than to the O–O correlation such that the initial overstructuring in the first O–O peak from the MD force-field was not fully corrected by the data. Since the two investigations, using very different techniques and appearing closely in time, arrived at similar results for the first O–O peak this was taken as evidence of a correctly derived O–O PCF and this was for long the standard comparison for developers of MD force-fields.

However, when actually fitting the Hura et al. data set using either RMC [76,77] or EPSR [103] together with neutron diffraction data with large Q-range the peak height came down to a low 2.3. This then initiated efforts to establish experimentally with low uncertainty the shape, position of the O–O peak this was taken as evidence of a correctly derived O–O PCF and this was for long the standard comparison for developers of MD force-fields.

For the data set going to highest Q (26 Å\(^{-1}\)) [98,99] a series of Fourier transforms was performed truncating the data at the different zeros in the structure factor to establish the minimum \(Q_{\text{max}}\) necessary for a converged O–O PCF [Fig. 20] [64]. It is clear that a high \(Q_{\text{max}}\), greater than 18 Å\(^{-1}\), is necessary to converge the first peak in terms of position, height and shape; lower \(Q_{\text{max}}\) values lead to a lower height of the first peak. Indeed, when fitting the Hura et al. [101] data with \(Q_{\text{max}}\) 10.8 Å\(^{-1}\) using either empirical potential structure refinement (EPSR) [103] or RMC [76,77] a low peak height of 2.3 was obtained in agreement with Fig. 20b, but in contrast to the original analysis where a peak height of 2.8 was estimated. Note that also O–H correlations contribute to the X-ray scattering and must be removed to derive the O–O correlation from Fourier transformed experimental data as discussed in Ref. [64]; in RMC and EPSR fitting this is taken into account as part of the procedure.

6. Deep supercooling

We have recently used X-ray scattering to probe the structure of water over a wide range of temperatures from close to boiling and deep down into the supercooled regime. In particular, by using micrometer-sized water droplets that were evaporatively cooled in vacuum it was even possible to probe water structure at temperatures in the “no-man’s land” of water [107]. The name derives from the fact that below the temperature, \(T_{\text{f}}\), of homogeneous ice nucleation at 232 K [108] and above about 160 K [109] at ambient pressure, ice nucleates so rapidly that measurements on the liquid in this region have been impossible. However, by exploiting the 50 fs, fully coherent X-ray pulses from the free-electron X-ray laser Linac Coherent Light Source (LCLS) Selberg et al. [107] were able to obtain structure information down to 227 K, i.e. 5 degrees below \(T_{\text{f}}\) and below the 228 K towards which the thermodynamic response functions in Fig. 1 seem to diverge.

Each individual droplet diffraction pattern was analyzed for the presence of ice indicated by characteristic Bragg peaks superposed on the diffuse rings due to diffraction from liquid water. The onset of ice nucleation was found between 232 and 229 K, but even at 227 K a fraction of the droplets remained liquid on a millisecond timescale [107]. In Fig. 21 we show the split first peak in the structure factor, \(S(Q)\), the position of the first O–O peak maximum (\(r_1\)), and the peak height (\(g_1\)) are plotted as a function of \(Q_{\text{max}}\) in c) and d) respectively. Both peak position, \(r_1\), and height, \(g_1\), are found to be sensitive to the value of \(Q_{\text{max}}\) for values smaller than 20 Å\(^{-1}\). Reproduced from Ref. [64].
and LCLS data as well as through MD simulations of evaporatively cooling droplets [107].

The split of the first peak in $S(Q)$ is related to the first two peaks in the pair-correlation function $g_{OO}(r)$ which gives two characteristic distances 2.8 and 4.5 Å where the latter corresponds to the distance between waters tetrahedrally coordinated to the studied molecule. Clearly, there is a continuous structural transformation towards a tetrahedral liquid as indicated by the increasing split between the two peaks; the continuous transformation was highlighted in a commentary by Soper [110]. In order to determine the degree of tetrahedrality the structure factor was calculated from MD simulations using the TIP4P/2005 model [50] at a range of temperatures and a correlation between the split, $\Delta q$, and the height, $g_2$, of the second peak in $g_{OO}(r)$ was established. With this correlation an experimental $g_2$ value could be extracted based on the measured $\Delta q$. This is shown in Fig. 22a for droplets of four different sizes and compared with MD simulations using TIP4P/2005 and SPC/E.

One observes a continuous increase in the tetrahedrality (as indicated by $g_2$) which, however, becomes strongly accelerated in the deeply supercooled regime. As discussed previously, the MD simulations underestimate the enhanced rate and the highest experimental $g_2$ value at 227 K corresponds to the value for TIP4P/2005 at 220 K, i.e. the simulation needs to go to lower temperature to achieve the same tetrahedrality. In Fig. 22b we compare the PCF from TIP4P/2005 at 220 K with that of low-density amorphous ice (LDA) showing strong similarity. However, water at ambient conditions shows a much less structured PCF in accordance with the picture that at ambient conditions water is strongly dominated by HDL-like environments.

Since the main structural feature in the LDL species is high tetrahedrality we can compare the temperature-dependence of $g_2$ to that of the high-LSI population in Fig. 5 and note that the curves are very similar for the TIP4P/2005 model. We therefore expect that the Widom line as discussed in Section 4 is also seen at 230 K. However, we notice that in real water the growth of $g_2$ is faster than in the simulation and we infer from this that also the increase in LDL population, as seen in Fig. 5, should be faster in real water. We have thereby experimentally confirmed the rapid change of HDL to LDL deep down in the supercooled regime.
7. Concluding remarks

We have here presented a picture of water that connects many ideas discussed in the supercooled regime with recent results obtained from various X-ray spectroscopic and scattering experiments and molecular dynamics simulations at ambient conditions. Here we summarize our findings in a simple picture related to the cartoon shown in Fig. 2. At temperatures close to the boiling point, water behaves as a simple liquid where most interactions are isotropic and dominated by van der Waals interactions. This is a local structure where most molecules are in strongly disordered environments with no well-defined separation between the 1st and 2nd shell. This type of non-directional bonding gives high flexibility for various vibrational motions and thereby high entropy.

As the liquid cools down the water molecules start to stick to each other through directional H-bonds. This will appear in two classes of configurations, tetrahedral and asymmetric, with fluctuations between them on some time-scale. When participating in a fluctuation into a tetrahedral structure each molecule is involved in four strong hydrogen bonds which minimizes the enthalpy, i.e. a locally favored structure [112,113]. Since cooperativity effects make the bonds stronger if water is bonded to other waters that are also in a tetrahedral structure, a fluctuation into a tetrahedral structure expands into a small local region. Since the molecules are directionally bonded with four bonds the librational motion becomes restricted and thereby contributes only weakly to the entropy.

In the other class of structures that is formed the local coordination is asymmetric with fewer, but paired, donor–acceptor H-bonds. Here the energy per H-bond is higher than in the tetrahedral structures, but since there are fewer directional H-bonds there is less enthalpic stabilization. With less directional H-bonds there is more flexibility for librational and translational motions and thereby a higher entropy. The OH groups that are involved in either a strong or a weak H-bond can switch on a very fast time scale [114]. In this structure isotropic molecular van der Waals interactions are important causing interstitial molecules to come in from a collapsed 2nd shell combined with distortions around the 1st shell. Since there are more water molecules in the first coordination shell (defined out to 3.5 Å rather than to the minimum in $r^2g_{\text{OC}}(r)$ at 3.30 Å) than in the tetrahedral structures we call these high density liquid (HDL) structures. Another way of viewing such species is that we start not with hexagonal ice but with high density amorphous (HDA) or very high density amorphous (VHDA) ices where we have a large collapse of the second shell. In these ices we also have a local tetrahedral bonding but with other angles towards the second shell (often called interstitials). With increasing temperature, we induce asymmetric distortions around these tetrahedrally bonded molecules in the first shell while keeping the interstitials.

There are fluctuations between the tetrahedral structures and asymmetric or high density structures. As we cool the liquid down the molecules in the asymmetric structures fluctuate more and more frequently into tetrahedral structures which grow in size since the balance between enthalpy and entropy in the free energy shifts more and more to favor enthalpy with decreasing temperature. The timescales for the fluctuations between these two classes should furthermore slow down. There is also a continuous change in the asymmetric/high density with temperature. The switching time of OH-groups between strong and weak/broken H-bonding is expected to slow down with decreasing temperature and thereby also the amplitude in the motion. We will be approaching more and more a local arrangement with four strong H-bonds. However, not as in hexagonal ice, but more towards high density ices with still many interstitials. That the density decreases below 4 °C is simply due to that we are at the same time converting many molecules into tetrahedral, LDL-like, structures more similar to hexagonal ice but disordered towards low density amorphous ice with the second shell at the tetrahedral angle causing an open network with low density. In this picture we have to consider both these two classes of fluctuations (between tetrahedral and asymmetric) separately but most likely there should also be some coupling.

All of the experimental information presented here is consistent with the above hypothesis but we need to complement these with results from simulations. We have shown that the local structure index (LSI) [45,46] distribution based on the inherent structure in simulations with the TIP4P/2005 model is strictly bimodal in the distribution between HDL- and LDL-like local structures [24] and the ratio between the two adheres closely to estimates from XAS [14] and XES [11,23]. In addition, the changes with temperature of the distribution in the inherent structure mimic closely what is observed in XAS, XES as well as in OH stretch vibrational Raman spectroscopy of liquid water where in all cases the features corresponding to tetrahedral, LDL-like structures are seen to vary in intensity with temperature, but stay at fixed position. The features due to the HDL-like structure, on the other hand, are seen to shift in position with temperature in addition to the variation in intensity due to conversion between LDL- and HDL-like species. This holds true also for SPC/E water [47,48] and we speculate that this should be a general property of the inherent structure of force-fields and ab initio techniques that give a reasonable representation of water. However, when the simulations are run at finite temperature the bimodality is largely washed out, except in the deeply supercooled region where there are reports of fluctuations between HDL and LDL liquid [35,39,43]. However, in the important ambient regime, where most processes relevant to life, chemistry and geochemistry occur, the bimodality observed experimentally is not reproduced by simulations. It seems that the underlying potential energy surface on which the simulations move is not sufficiently corrugated and more of an average structure is obtained.

We have discussed effects that are necessary to include in a simulation that realistically mimics real water in terms of structure and fluctuations and deduced lower bounds on simulation size based on experimental observations. These include the important electronic structure cooperativity effects which lead to a strengthening of H-bonds if they form part of a chain or network with balanced contributions from donors and acceptors, i.e. for each molecule an equal number of acceptors and donors; this will enhance the growth of tetrahedral regions as evidenced by DFT simulations that neglect dispersion or van der Waals effects giving a very LDL-like liquid [15]. Note that, although polarizable force-fields introduce more flexibility and can give improvements, the charge redistributions in a molecule upon H-bond formation go against expectation from electrostatics; the accepting lone-pair polarizes away from the donating proton in order to minimize Pauli repulsion which allows a closer approach and enhanced electrostatic interaction [59]. Introducing the more isotropic van der Waals interaction through non-local correlation functionals in DFT simulations balances the directional H-bonding and leads to a softer structure and even to a collapse into strongly LDL-like structure [15,62] demonstrating that the HDL-like minimum has been too strongly enhanced. However, there are two additional effects to consider where one is the common protocol to run simulations in the NVT ensemble at the experimental density and also the size of the simulation box; assuming the HDL type structures dominate at ambient conditions the density is mainly determined by this component and fluctuations into larger LDL-like environments will be prevented by the effective pressure from the fixed simulation box. For a large enough box this pressure penalty can be small, but the experimental observation of shell-structure out to ~14 Å from X-ray diffraction [64] in accordance with estimates from SAXS [11] would imply that significantly larger simulation boxes than commonly used in ab initio MD simulations should be used and preferably in the NpT ensemble to allow the entire box to convert; note that at ambient conditions a simulation box of 64 molecules corresponds to a box side of 12.44 Å. The other effect to include is the effects of the quantum nature of hydrogen which manifests as significant differences in macroscopic properties of H2O and D2O water. In terms of
References
