RESEARCH ARTICLE

More accurate X-ray scattering data of deeply supercooled bulk liquid water

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Deeply supercooled water droplets held containerless in an acoustic levitator are investigated with high-energy X-ray scattering. The temperature dependence of the X-ray structure function is found to be nonlinear. Comparison with two popular computer models reveals that structural changes are predicted too abrupt by the TIP5P-E model, while the rate of change predicted by TIP4P-Ew is in much better agreement with experiment. The abrupt structural changes, predicted by the TIP5P-E model to occur in the temperature range between 260 and 240 K as water approaches the homogeneous nucleation limit, are unrealistic. Both models underestimate the distance between neighbouring oxygen atoms and overestimate the sharpness of the OO distance distribution.

Keywords: supercooled water; acoustic levitation; X-ray scattering

Introduction

The peculiar thermodynamic behaviour of liquid water and in particular its density maximum has fascinated scientists for centuries. W.C. Roentgen in his article proposing what is known as the iceberg theory of liquid water concedes [1]:

Die hier gegebene Erklärung des Dichtemaximums ist nun keineswegs neu; wir finden dieselbe, wenn auch manchmal in etwas anderer Form, an vielen Stellen der Litteratur. Wer sie zuerst gefunden hat, ist mir nicht bekannt geworden.

(Translated) The explanation for the density maximum given here is not at all new. We find the same, however sometimes in slight modifications, at many instances in the literature. I haven’t found out who came up with it first.

Most observers agree that there is some truth to the picture evoked by the iceberg theory: Liquid water has two energetically close types of intermolecular arrangements, an open, low density structure exhibiting a relatively ordered tetrahedral network, and a higher density more disordered structure in which local tetrahedra are distorted. Even if we take that much as a consensus (compare however Refs. [2–4]), we are left with four [5] scenarios for how the phase behaviour of bulk liquid water would unfold at low temperatures: In no particular order they are the stability limit, second critical point, singularity free and critical point free scenarios.

The phase behaviour of these four scenarios is markedly distinguishable in the so-called ‘no man’s land’ [6], the temperature range above the crystalization temperature of glassy water and below the homogeneous nucleation temperature of supercooled liquid water. Attempts to navigate the waters of ‘no man’s land’ have perhaps been more numerous then failed attempts to find the North-West passage. Experimental approaches include the extrapolation of the behaviour of aqueous solutions to zero concentration [7], water in thin films [8], nanoconfined water [9] and residual water included in ice [10]. Yet all experimental approaches look at ‘no man’s land’ from somewhat afar. That is in principle not much different for computer simulations, as the potential models have to be verified outside ‘no man’s land’. The strategy we will follow in the present paper is to determine the X-ray scattering of bulk supercooled water down to temperatures as low as possible. Since synchrotrons allow measuring the structure function of liquid water in seconds, we can follow the structural changes in bulk water in situ as it is supercooled. It is thus the structural trends that we are most interested in and it seems intuitive – if we choose to use computer simulations to extrapolate the structure of bulk water into ‘no man’s land’ – that then preference should be given to those models that predict the correct structural trends in the accessible temperature range.
It was shown decades ago [11,12] that the use of high-energy (∼100 keV) X-rays is advantageous to obtain high-precision scattering data from amorphous substances. At the time the virtual absence of absorption and the accessibility of high momentum transfers \((Q)\) were most important. With the advent of large area detectors, the concentration of the useful signal in the forward direction enables the orientation of the area detector normal to the incoming beam while maintaining high \(Q\) accessibility in a single shot experiment. This significantly simplifies data correction (see Appendix) and ultimately leads to higher precision data.

**Experiment and data analysis**

A schematic view of the experimental setup is shown in Figure 1. Droplets of either D\(_2\)O or deuterium depleted H\(_2\)O (Cambridge Isotopes) were held in an acoustic levitator [13]. Gravity is counteracted by an acoustic wave field and therefore allows maintaining the water droplets in the X-ray beam without contact with a container. The droplets are loaded at a temperature at which the liquid is stable and then brought into contact with a laminar flow of cooled dry N\(_2\) from a Cryostream Plus (Oxford Cryosystems, Inc., Devens, MA). The Cryostream allows ramping the temperature of N\(_2\) gas down at a maximum rate of 0.1 K s\(^{-1}\). In some experiments a secondary gas jet heater was used to reheat the gas from the Cryostream. When the secondary heater was turned off, the gas stream temperature decreased at a rate of approximately 5 K s\(^{-1}\). In this way the liquid could be rapidly supercooled and X-ray measurements made before the liquid crystallised. Instantaneous (on the timescale of the experiment) crystallisation did occur however in a narrow temperature window around \(-20^\circ\text{C}\) under these experimental conditions. The surface temperature of the levitated droplet was measured with an Inframetrix 760 Infrared camera. It was observed that at higher temperatures around room temperature the water droplets were several degrees cooler than the surrounding gas due to evaporative cooling. All measurements were carried out at the high-energy X-ray beamline 11 ID-C at the Advanced Photon Source at Argonne National Laboratory. The intensity of the scattered 115 keV X-rays was measured using a Perkin-Elmer amorphous silicon flat plate area detector placed centred and normal to the incident beam. The system was calibrated using a cerium dioxide coated Styrofoam\textsuperscript{\textregistered} sphere levitated at the same position as the water drops. The scattered X-rays were collected in 20 s sets [13]. The area detector was arranged approximately 40 cm from the sample position to provide a data collection \(Q\)-range of \(\sim 36\,\text{Å}^{-1}\). Details of the simple data correction and normalisation procedure are given in the appendix.

![Figure 1. Schematic setup. A, sample; B, transducer (two); C, tungsten X-ray beam stop; D, Perkin-Elmer X-ray area detector; E, thermocouple; F, modified Cryostream plus with additional gas heater; G, infrared thermal imaging camera (insert: typical image); H, video camera; I, base plate mounted on a precision motor-driven \(X-Y-Z\) translation stage.](image)
The corrected scattered intensity is proportional to the differential cross section per molecule, which in turn can be subdivided into the interference scattering containing the structure information, coherent self scattering and Compton scattering.

\[
\left(\frac{d\sigma}{d\Omega}\right) = \sum_{\text{uc}} f_i f_j 4\pi \rho \int r(g_{ij} - 1) \sin(Qr)dr + \sum_{\text{uc}} f_i^2 + F_{KN} \sum_{\text{uc}} C_i, \tag{1}
\]

where the sum extends over the unit of composition uc, \(f_i\) are the X-ray form factors, and \(C_i\) the atomic Compton intensities. The differential cross section is in units of the Thomson cross section and is to be understood per molecule, \(\rho\) is the molecular density, and \(F_{KN} = (1 + \hbar^2 Q^2 / 8\pi^2 m_e c)^{-2}\) takes into account that the Klein–Nishina cross section for Compton scattering differs from the Thomson cross section.

To facilitate comparison with literature data we define the coherent cross section:

\[
\left(\frac{d\sigma}{d\Omega}\right)_{coh} = \left(\frac{d\sigma}{d\Omega}\right) - F_{KN} \sum_{\text{uc}} C_i. \tag{4}
\]

Furthermore, the definition of a reduced intensity is useful:

\[
i(Q) = \left(\frac{d\sigma}{d\Omega}\right) - \frac{\sum_{\text{uc}} f_i^2}{\sum_{\text{uc}} f_i^2} F_{KN} \sum_{\text{uc}} C_i = \sum w_{ij}(s_{ij} - 1). \tag{5}
\]

It is noted that in this definition the weighting factors \(w_{ij}\) of the partial structure factors \(s_{ij}\) are normalised \(\sum w_{ij} = 1\) and \(s_{ij} \geq 0\). The X-ray weighted pair distribution function is obtained by Fourier–Bessel transform:

\[
x^g = 1 + \frac{1}{2\pi^2 \rho} \int Q i(Q) \sin(Qr) dQ. \tag{6}
\]

### Results

A set of coherent differential cross sections obtained during an in-situ cool-down is shown in Figure 2(a). The height of the main peak at 1.9 Å\(^{-1}\) is consistent with water data at 4°C [19]. It is noticeable that the low-Q intensity increases with temperature. That increase is consistent with the increasing compressibility of supercooled liquid water [20] and the data extrapolate correctly to the \(Q \rightarrow 0\) compressibility limit (Figure 2(b)). A minimum in the intensity at \(Q = 0.4\) Å\(^{-1}\) has recently been observed in small-angle X-ray data (observed prior in supercooled water by Xie et al. [21]) and interpreted as a sign of an inhomogeneous structure of water at ambient conditions [22]; that interpretation has been challenged by Soper et al. [23]. Even though our experiment was not designed to detect a small-angle signal, we note that within our window of momentum transfer (\(\geq 0.4\) Å\(^{-1}\)) we see no sign of a minimum moving to higher \(Q\) at low temperatures. Furthermore, the intensity at 0.4 Å\(^{-1}\) is already very close to the \(Q \rightarrow 0\) compressibility limit which leaves little room for the intensity to increase at lower values of \(Q\).

The change of the differential cross section at some values of \(Q\) is shown in Figure 2(c) and it is immediately evident that the change is nonlinear and the rate of change becomes larger with decreasing temperature. A polynomial of degree 2 is sufficient to describe the temperature dependence at a particular \(Q\)-value and represents the first three terms of a Taylor expansion:

\[
\left(\frac{d\sigma}{d\Omega}\right)(Q, T) = \left(\frac{d\sigma}{d\Omega}\right)_{T=T_0} + T \frac{d^2(d\sigma/d\Omega)}{dT^2} \bigg|_{T=T_0} dT + \frac{T^2}{2} \frac{d^2(d\sigma/d\Omega)}{dT^2} dT^2 + \cdots. \tag{7}
\]
We arbitrarily choose \( T_0 = 268.15 \, \text{K} \) since all temperature scans included that temperature and thus no extrapolation is required. All three terms of the expansion are shown in Figures 3(a)–(c).

The first term of Equation (7) is the differential cross section at \( T = T_0 \). The X-ray weighted pair distribution function calculated from \( (d\sigma/d\Omega)_{T=T_0} \) via Equations (3) and (4) is shown in Figures 4(a) and (b) for all four temperature scans showing the degree of reproducibility achieved with this approach. It is noteworthy that the low-\( r \) region looks very comparable to the function \( G(r) \) in Figure 1 of Ref. [19] except...
for $r < 0.5\,\text{Å}$ where $G(r)$ has been set to zero in Ref. [19]. The width of the first neighbour OO peak is not resolution limited as $i(Q)$ is essentially decayed to zero at the maximum $Q$ value used for the Fourier transform ($18.3\,\text{Å}^{-1}$). It is furthermore noted that there is a maximum in $\chi g$ at $10.8\,\text{Å}$ in agreement with observations by Yokohama et al. [24].

Figure 5 compares the X-ray weighted pair distribution function with simulation results by one of the present authors (DP) for TIP5P-E [25] and TIP4P-Ew [26] water. Beyond the first neighbour shell the agreement is better for the TIP4P-Ew than for the TIP5P-E model. Both models however overestimate the height (underestimate the width) of the OO next neighbour peak. We will quantify that observation later. It is our view that the deviations at $r < 1.5$ reflect the fact that the electron distribution in real water is different from the simplistic model that went into the calculation of $\chi g(r)$ for the simulation models, namely the placement of a charged atom form factor at the site of the nucleus [17] (see also the Appendix). This is unrelated – because it is at low $r$ – to the molecular arrangement. For a meaningful comparison in $Q$ space we transform the deviation at low $r$ into $Q$ space and add it to the simulation $(d\sigma/d\Omega)_{\text{coh}}$ calculated via Equation (2).

Figure 6 compares the prediction via the TIP4P-Ew and TIP5P-E models of the temperature dependence in $(d\sigma/d\Omega)_{\text{coh}}$ across ‘no man’s land’ with the experimental result in the range of temperatures.
accessible to this study. It is very clear that the structure changes too abruptly in the TIP5P-E model. These abrupt structural changes predicted by the TIP5P-E model in the temperature range from 260 to 240 K in the vicinity of the homogeneous nucleation limit do not occur in real bulk water. Figure 7 shows a comparison with experiment of the linear and quadratic component of Equation (7) after Fourier transform into $r$-space. Especially beyond the first neighbour shell the agreement of the linear component of the TIP4P-Ew model with experiment is excellent, with the TIP5P-E model changing structure too quickly. The same observation is true for the second derivative. The second derivative is in anti-phase with the linear component, indicating that the rate of change increases over the entire range of $r$.

![Figure 6. Temperature dependence at specific values of $Q$ of the coherent differential cross section; comparison between the experiment (H$_2$O, symbols) and predictions of the TIP4P-Ew (a) and TIP5P-E (b) potentials. In order to better visualise the difference in the trends the absolute difference between the differential cross section calculated for the model (thin line) and the experiment has been subtracted (thick line). It can be seen that the abruptness of the structural changes predicted by TIP5P-E in the temperature range between 260 and 240 K as the system approaches 'no man's land' is not realistic. This is demonstrated for all values of $Q$ in (c), which shows the linear Taylor coefficient from Figure 3(b) compared with both models.](image)

![Figure 7. (a) Linear component of the change in $g(r)$ as a function of $T$, derived from the linear component in Figure 3(b). Again the changes predicted by the TIP5P-E potential are too abrupt. (b) Second derivative of the pair distribution function with respect to temperature derived from the quadratic component in Figure 3(c). The second derivative is in antiphase with the first derivative, indicating that the rate of change increases with decreasing temperature. The lines are Fourier transforms with $Q_{\text{max}} = 18.3\,\text{Å}^{-1}$ (a), $Q_{\text{max}} = 9\,\text{Å}^{-1}$ (high-$r$ side experimental curve in (a)) and $Q_{\text{max}} = 5.3\,\text{Å}^{-1}$ (b).](image)
Finally, we take a look at the metrics of the first OO neighbour shell peak. This is not a well-separated peak and at high \( r \) it likely has contributions from non-hydrogen-bonded water molecules. To obtain consistent values for the peak position and peak width we assume that the underlying distribution is Gaussian and corresponds to a coordination number of four. We Fourier-transform into \( Q \) space, multiply by the appropriate form factors and transform back into real space (i.e. we convolute with the electron distribution) and \( \chi^2 \)-minimise the Gaussian distribution with respect to the X-ray weighted pair distribution function. This procedure is done in the same way as for the experimental and simulation results, i.e. we do not take advantage of the fact that, for the simulations, we know the underlying OO partial pair distribution function. However, the simulation results allow us to estimate the contribution of the OH and HH partial to the peak at 2.8 Å, which is small, as the OH contribution has a minimum at 2.5 Å and the weighting of the HH partial is down by a factor of \( 4^*(Z_H-q_H)^2/(Z_O-q_O)^2 = 0.009 \). An example for the fit quality that can be achieved with this simplistic model is shown in Figure 8(a). The agreement is fair, however it is noted that the experimental distribution is asymmetric enough that the maximum deviates visibly from the maximum of a Gaussian. Obviously that fit quality could be improved by increasing the number of fit parameters. This is not needed here to investigate the trends and to make a quantitative comparison between simulation and experiment. We obtain, however, a result in agreement with Ref. [27] if we follow a similar approach in which two additional parameters are used to approximate a high-\( r \) ‘background’ and one free parameter for the coordination number. The Gaussian position and width parameter of this procedure is shown in Figures 8(b) and (c). Equally in agreement with Ref. [26] we find that the changes of position and width with temperature are largely linear (as opposed to the nonlinear changes in the overall structure). As we concluded before, both models underestimate the OO bond distance and overestimate the sharpness of the peak. The rate of change is again better represented by the TIP4P-Ew model. The OO distance in \( D_2O \) is found to be slightly longer and sharper than in \( H_2O \), as expected, however the difference between \( H_2O \) and \( D_2O \) is considerably smaller than the difference between experiment and the better of the two models. Because the changes in the Gaussian parameters are essentially linear, it is convenient to characterise it by the OO distance at 0°C and the rate of change, which are summarized in Table 1.

![Figure 8](image)

**Figure 8.** Example of the fit (a), position (b) and width (c) of the first neighbour OO peak (compare text) as a function of temperature. The OO is slightly shorter and the distribution broader in \( H_2O \) compared with \( D_2O \). The predictions by both potential models deviate from experiment: The distance and the width of the distribution are estimated too small. The rate of change in both parameters is closely approximated by the TIP4P-Ew model.

**Conclusion**

We conclude that the TIP4P-Ew model is found to be more successful in describing the X-ray diffraction data of supercooled water presented here on multiple counts. In particular, the rate of change both of the
OO first neighbour distance and the intermediate range order with temperature is much more in line with experiment. Even if the agreement is not quantitative, in particular with respect to the OO first neighbour peak, this model should be preferred when extrapolating into the ‘no man’s land’. This observation is true for the TIP4P and TIP5P models as currently parameterized, however it seems unlikely that a better parameterization with respect to the X-ray structure can be achieved without altering the thermodynamic behaviour of the models.

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References


Appendix A

After angular integration and polarisation correction, an example for the scattered intensity from a water droplet compared with the empty diffractometer is shown in Figure A1. At Q < 0.4 Å⁻¹ the detector is shielded by a beamstop, and at Q > 36 Å⁻¹ we reach the outside edge of the detector. The sample intensities I_sample are corrected for polarization by a factor P(Q,η), the varying sample-to-detector distances by a factor G(Q) and the background intensity I_background is subtracted, so that the total correction procedure can be summarised by

\[ I_{\text{corr}} = P(Q)G(Q)[I_{\text{sample}} - I_{\text{background}}]. \]  

(A1)

The polarisation correction depends on the scattering angle θ and the azimuthal angle η and is therefore applied before
linearly with the background scattering, which would make the experiment performed here rather intractable. In this case it can be seen that at \( Q < 0.4 \text{ Å}^{-1} \) the signal is perturbed by the beam-stop.

Angular integration:

\[
P(Q) = \frac{1}{(\cos \eta^2 + \sin \eta^2 \cos \theta^2)}
\]

and

\[
G(Q) = \frac{1}{\cos(2\theta)^2}.
\]

No attenuation or multiple scattering corrections are applied as these are small at 100 keV and partially mutually compensating.

The corrected intensity is proportional to the differential cross section and the proportionality constant needs to be determined. It is useful for that purpose to plot the ratio \( R(Q) \) between the scattered intensity \( I(Q) \) and the sum of coherent and incoherent self-scattering shown in Figure A2:

\[
R(Q) = \frac{I(Q)}{\sum_c f_i^2 + F_{KN} \sum_c c_i}.
\]

Ideally, \( R(Q) \) would oscillate around a constant value, the normalisation constant. In experimental setups with a well-collimated single point solid state detector, that can indeed be achieved. Unfortunately, that mode of data acquisition takes approximately four orders of magnitude longer counting times, which would make the experiment performed here rather intractable. In this case it can be seen that \( R(Q) \) varies linearly with \( Q^2 \) for \( Q < \sim 25 \text{ Å}^{-1} \). Therefore, we use a \( Q \)-dependent normalization that varies about 3\% over the entire \( Q \) range used for Fourier transform (<18.3 \text{ Å}^{-1}). The \( Q \)-dependence of the absorption and multiple scattering corrections are considerably smaller. As shown in Figure A2, variation of the fit range within reasonable limits changes the absolute value of the normalization factor by less than 0.2\%.

To assess the effect of the omitted absorption and multiple scattering procedures we estimate them by assuming that the sample is a perfect sphere of 2 mm diameter completely immersed in a uniform beam. Furthermore, all background scattering is assumed to pass through the sample and therefore is attenuated by it. Finally, only multiple scattering within the sample is assumed to be relevant, but not multiple scattering with ancillary equipment. At 115 keV the mass attenuation coefficient of water is 0.1646 cm\(^2\)g\(^{-1}\) [28]. Attenuation in the forward direction is thus 2.2\%. Multiple scattering is assumed to be a constant in \( Qk_{MS} \). Equation (A1) then becomes

\[
I_{corr} = P(Q)G(Q)[I_{sample}f_{abs} - I_{background} - K_{MS}].
\]

Figure A2 also shows \( R(Q) \) (Equation (A4)) for the absorption and multiple scattering corrected intensity.
We are still left with a $Q^2$-dependent normalisation factor and the $Q$ dependence has actually become slightly larger. In summary, absorption and multiple scattering corrections are small and not the cause of the main remaining uncertainty.

The experimental pair distribution function shown in Figure 5(a) deviates at small distances from what is expected within the charged atom model for the intramolecular electron distribution. This is not completely surprising since we approximate the electron distribution by placing charged spherical atoms at the position of the nuclei – nonetheless an improvement compared with the independent atom model where those atoms would have been neutral. We take the deviation at low $r$ and transform it back into $Q$ space to improve our model of the atomic self-scattering. The result is shown in Figure A3. The correction is of the order of 3–5 electron units at low $Q$ and disappears, as required, at high $Q$. 