

Structures of High-Density and Low-Density Water

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The three site-site partial structure factors for water have been measured as a function of pressure, using neutron diffraction, at a temperature of 268 K. It is found that the measured structure functions imply a continuous transformation with increasing pressure from a low-density form of water ($\rho_L \sim 0.0295$ molecules/Å³), with an open, hydrogen-bonded tetrahedral structure, to a high-density form of water ($\rho_H \sim 0.0402$ molecules/Å³), with nontetrahedral O-O-O angles and a collapsed second coordination shell, which implies broken hydrogen bonds between the first and second coordination shells.

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Three different conjectures have been proposed over the last decade to account for the phase behavior of metastable water at low temperature. These are the retracing spinodal [1,2], the second critical point [3–7], and the singularity free scenarios [8,9]. Another recent model shows that both the second critical point and singularity free scenarios can be reproduced by a change in the strength of the hydrogen bonding interaction in the model [10]. The first conjecture implies anomalous increases of the response functions in the proximity of the spinodal curve, the second assumes the existence of a first order transition between two different forms of liquid water, terminating at a metastable critical point (distinct from the usual liquid-vapor critical point), while in the singularity free scenario the response functions remain finite, although they do exhibit extrema. In particular, both the second critical point conjecture and the singularity free scenario suggest that two forms of water exist in the supercooled regime [3,9]: these are expected to have different densities and microscopic structures and are referred to in the literature as low-density water (LDW) and high-density water (HDW). Roberts *et al.* [11] demonstrated that under certain circumstances a simple waterlike model could exhibit liquid-liquid immiscibility. Above the temperature corresponding to the conjectured second critical point, and under all thermodynamic conditions in the singularity free scenario, the two forms of water will transform into each other continuously along an isotherm. Indeed, some experimental evidence already suggests that ambient and supercooled water undergo a structural transition when compressed [12–14], and the similarity of that transition to the one that takes place at lower temperatures between ice Ih and ice II [15] has been noted [16]. The structural details of this transition in the liquid have so far not been elucidated.

The aim of the present work therefore was to verify the previous diffraction work that indicates a phase transfor-

mation in liquid water, and to uncover the local molecular arrangements that occur in these two forms of water. Neutron diffraction experiments on compressed water, using isotope substitution on the water hydrogens, were performed in a temperature regime where the anomalous properties of water are most visible [17,18], namely close to the ice I/ice III triple point ($T = 251$ K, $P = 209$ MPa), since this is the lowest temperature at which water is a stable liquid. The temperature chosen was slightly above this, 268 K, so that the structural trend as a function pressure (26, 209, and 400 MPa, corresponding to molecular number densities of 0.0338, 0.0362, and 0.0381 molecules/Å³, respectively [19]) could be observed. The experiments followed the same procedures as previous neutron diffraction work on water under pressure [20]. The pressure cell was mounted on a closed cycle refrigerator, which, combined with heaters inserted into the body of the pressure cell, was used to control the temperature to within 0.1 K. Diffraction data were recorded for heavy water, light water, and an equimolar mixture of these on the small angle neutron diffractometer for amorphous and liquid samples [21] at the ISIS pulsed neutron source. The pressures and temperatures for the heavy water and mixture samples were increased slightly above those for the H₂O sample to take account of the slightly higher temperature and pressure of this triple point for heavy water.

From this diffraction data it is possible to extract the OO, OH, and HH partial structure factors [22], $S_{\alpha\beta}(Q) = 4\pi\rho \int_0^\infty r^2 dr [g_{\alpha\beta}(r) - 1] \frac{\sin(Qr)}{Qr}$, where $g_{\alpha\beta}(r)$ is the site-site radial distribution function between distinct atoms α and β . Figure 1 illustrates the OO partial structure factors obtained in this experiment. It can be seen that the principal changes occur in the region $Q = 2-3$ Å⁻¹, with the first peak near 2.0 Å⁻¹ growing steadily in amplitude with increasing density, and the second peak near 2.9 Å⁻¹ decreasing in amplitude. Some movement of

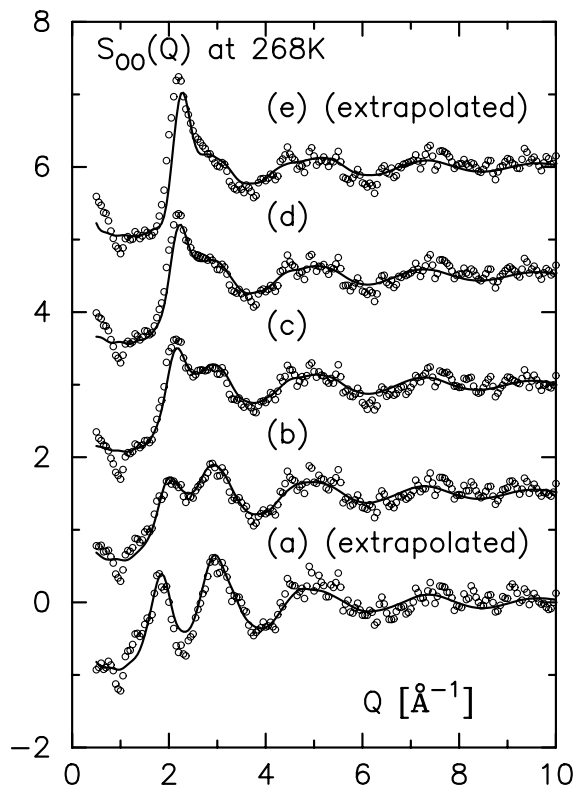


FIG. 1. Values of the measured OO partial structure factors of water at 268 K and pressures of 26 MPa ($\alpha = 0.4$) (b), 209 MPa ($\alpha = 0.63$) (c), and 400 MPa ($\alpha = 0.8$) (d) for several Q values. The remaining curves (a) and (e) correspond to the linear extrapolation of these data to $\alpha = 0.0$ and $\alpha = 1.0$, respectively, corresponding to number densities 0.0295 and 0.0402 molecules/ \AA^3 , respectively. The circles show the measured or extrapolated data as appropriate, while the lines show EPSR fits to these data.

the first peak to larger Q values is also seen. Similar, but smaller changes were seen in the OH and HH functions. The changes seen here in the OO structure factor parallel closely those seen in the earlier x-ray work on water at higher temperature [12].

In order to interpret these changes, and to investigate what might happen to these structure factors at densities appropriate to HDW and LDW, an extrapolation procedure is invoked. Earlier work [13,16] made the assumption that the structure of water can be represented as a linear combination of the structures of the end points, namely the structures of HDW and LDW. In the spirit of this approximation it is assumed here that

$$\rho(T, P) = \alpha(T, P)\rho_H(T) + [1 - \alpha(T, P)]\rho_L(T), \quad (1)$$

where $\alpha(T, P)$ represents the volume fraction of high density structure in the liquid, and $\rho_H(T)$, $\rho_L(T)$ are the molecular number densities of HDW and LDW, respectively. Once $\rho_H(T)$ and $\rho_L(T)$ are defined $\alpha(T, P)$ can be calculated for any intermediate density. Corresponding to this density the site-site radial distribution functions and structure factors are themselves assumed to be

linear combinations of their low-density and high-density counterparts,

$$\rho g_{\alpha\beta}(r) = \alpha(T, P)\rho_H(T)g_{\alpha\beta}^{(H)}(r) + [1 - \alpha(T, P)]\rho_L(T)g_{\alpha\beta}^{(L)}(r), \quad (2)$$

$$S_{\alpha\beta}(Q) = \alpha(T, P)S_{\alpha\beta}^{(H)}(Q) + [1 - \alpha(T, P)]S_{\alpha\beta}^{(L)}(Q). \quad (3)$$

We reverse the procedure of [13] and exploit the observed variation of the site-site structure factors with density to estimate, by least squares analysis using Eq. (3) at each measured Q value, the equivalent site-site structure factors at high and low density. This approach circumvents the difficulty of trying to make reliable measurements of the partial structure factors of water in the metastable region of the phase diagram, although the assumption of a linear dependence on density may lead to some uncertainty in the structure functions obtained. The extrapolated forms will in any case at least indicate the likely structural trend with density. It remains only to assign values for ρ_H and ρ_L , for which there are no *a priori* choices.

Limiting values of ρ_H and ρ_L can be obtained from the requirement that any extrapolated structure factors and radial distribution functions must satisfy the limits $g_{\alpha\beta}^{(H)}(r)$, $g_{\alpha\beta}^{(L)}(r) \geq 0$, and $S_{\text{OO}}^{(H)}(Q)$, $S_{\text{OO}}^{(L)}(Q) \geq -1$, for all r and Q values, respectively: the former constraint ensures that the density in real space is never less than zero, while the latter constraint ensures that the density of points in reciprocal space for the molecular centers distribution is also non-negative.

In order to refine the values further a second requirement on the extrapolated structure factors and radial distribution functions is that they must be derivable as close as possible from model distributions of molecules. The trial high- and low-density site-site structure factors (OO, OH, and HH) were subjected to empirical potential structure refinement (EPSR) simulations [23,24]. In this process a computer simulation of the liquid is performed at the density and temperature of the system in question, using a literature reference potential [25] as the starting interatomic potential energy function. By introducing perturbations to this potential derived from the difference between measured and simulated structure factors, the simulated distributions are constrained to reproduce the measured structure factors as closely as possible. Once this has been achieved, the simulation can be used to accumulate ensemble averaged values for the site-site distributions and other structural quantities. The advantage of this process for water is that it means that all measured data are fit simultaneously, instead of the traditional approach of direct Fourier inversion of individual site-site structure factors.

A number of trial values of ρ_L and ρ_H were attempted until the simulation was able to produce good fits to both the predicted high- and low-density structure

factors. The results were $\rho_H = 0.0402$ molecules/ \AA^3 (equivalent to a macroscopic density of 1.20 g/cm 3) and $\rho_L = 0.0295$ molecules/ \AA^3 (equivalent to 0.88 g/cm 3). It will be recognized that although approximate these values are quite close to the reported densities of high-density and low-density amorphous ice [26]. With these choices of ρ_L and ρ_H we obtain $\alpha(26$ MPa) = 0.40 , $\alpha(209$ MPa) = 0.63 , and $\alpha(400$ MPa) = 0.80 . The extrapolated OO structure factors for high- and low-density water are shown in Fig. 1, and it should be noted that they show considerable resemblance to the x-ray diffraction data from high-density and low-density amorphous ices [27], even though they have been obtained by a quite separate procedure.

The high- and low-density radial distribution functions estimated by the EPSR procedure are shown in Fig. 2. The principal feature to emerge is that, while the first peak in $g_{OO}(r)$ is barely altered in position between the two densities, the second peak moves from ~ 4.5 \AA in LDW to ~ 3.4 \AA in HDW, with corresponding shifts occurring in the third and subsequent coordination spheres. At the same time the first intermolecular peak in the OH distribution near 1.81 \AA in LDW actually moves *inwards* to 1.77 \AA for HDW, which implies, if anything, a more linear hydrogen bond in HDW compared to LDW. Therefore the collapse of the second shell cannot be accounted for as

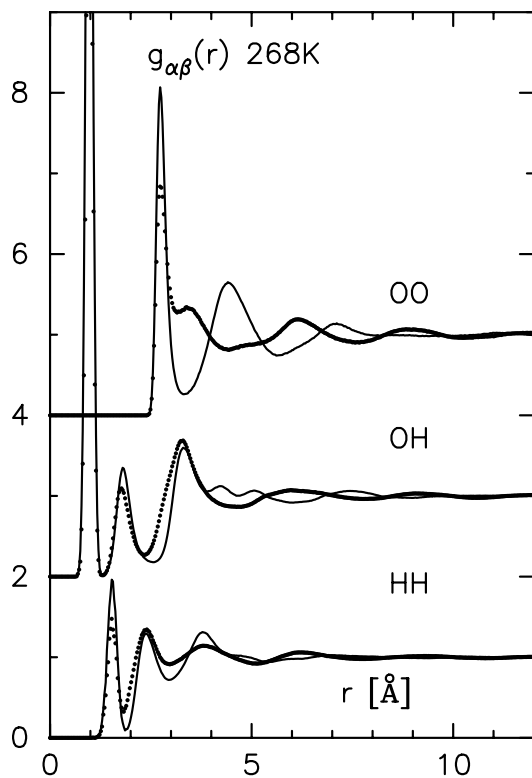
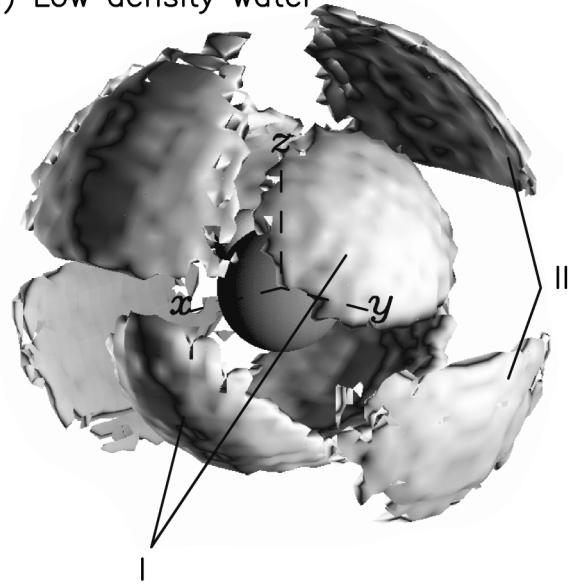


FIG. 2. Site-site radial distribution functions for low density (lines) and high density (circles) water as obtained by EPSR simulation of the corresponding structure factors, curves (a) and (e), respectively, of Fig. 1.

(a) Low density water



(b) High density water

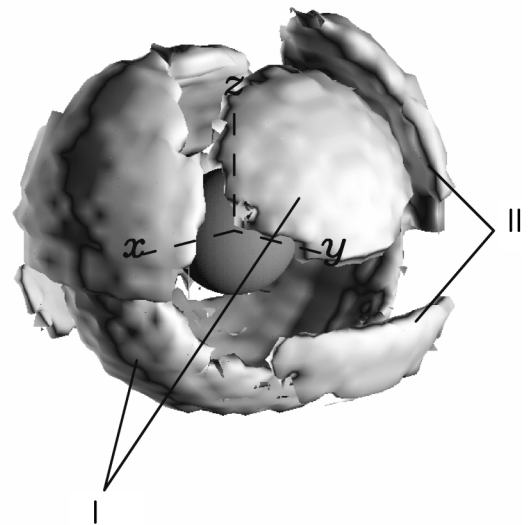


FIG. 3. Spatial density function (SDF) for water as determined from the EPSR simulation of low (a) and high (b) density water. Each map is plotted in a 10 $\text{\AA} \times 10$ \AA window. A central water molecule lies in the z - y plane of the coordinate system. The lobes of density outside are a three-dimensional rendering of contours of the SDF at a level 1.9 times the average density of the liquid in each case. Pronounced lobes (I) are observed opposite each OH vector on the central molecule and in a broad band of density at right angles to these underneath the central molecule, corresponding to the first shell of (approximately) tetrahedrally bonded water molecules. A second shell is seen (labeled II) which is in antiphase with the first shell. Note how this shell collapses in going from LDW to HDW, and in the x - z plane merges with the first shell near the x axis. This collapse is the primary signature of the structural transformation that occurs as water density is increased.

a simple bending of the hydrogen bond: on the contrary the evidence here is that hydrogen bonds from the first to the second shell are broken in HDW compared to LDW, allowing hydrogen bonds between the central molecule and the first shell to become more linear.

To identify the structural differences between the two phases further the simulated molecular distributions were used to estimate the spatial density functions of water [28] in each phase (Fig. 3). Here we discover that the first coordination shell is tetrahedral in shape for *both* high- and low-density forms of water. The coordination number of this shell is about four water molecules in each case. The second shell retains its overall orientational symmetry between the two forms, but for LDW it sits at approximately the tetrahedral distance ($\sim\sqrt{8/3}$ times the near neighbor distance), while for HDW it has substantially collapsed, to a point where it is almost coincident with the first shell. This also implies that the distribution of the O-O-O angle between three neighboring molecules is almost flat in HDW, while it is peaked at $\sim 70^\circ$ in LDW (data not shown). The evidence here supports therefore the notion that water can exist in two distinct structural forms, depending on the density. The primary distinction between these forms is the distance of the second shell away from the first, and the breaking of the hydrogen bonds between the two shells which occurs in HDW.

It is important to be quite clear that the approximate validity of equations such as (1)–(3) to describe the structure of water *cannot* be used to infer that ambient water can be described as a mixture of two liquids, HDW and LDW, the so-called “two state” model. Such a scenario would require the presence of concentration fluctuations between the two liquids which in turn would give rise to enhanced scattering (over and above the compressibility limit) in the diffraction pattern at low Q . Such enhanced scattering has never been observed either in the present measurements, or in previous x-ray or neutron diffraction measurements on the stable liquid. Instead, these equations simply reflect the empirical trend of the structure factors and radial distribution functions of water with increased density.

It is also worth emphasizing that the present conclusions can be drawn only because the structure factors, OO, OH, and HH, were determined separately for cold water as a function of pressure. All three structure factors are needed to construct unambiguously the distribution of molecular centers, the spatial dependence of this distribution, and the relative orientations of neighboring molecules. The behavior of water structure as a function of density that emerges from this analysis indicates that it is the *second* shell of water which is where the main structural changes occur: the primary effect of increased pressure is to *break* the hydrogen bonds between the first and second neighbor water shells.

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