

X-ray and neutron scattering studies of the structure of hyperquenched glassy water

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X-ray and neutron diffraction measurements were performed on glassy water prepared by rapid cooling of water droplets on a cryoplate. Structure factors and radial distribution functions were found to be nearly identical to those obtained from amorphous ice formed either by vapor deposition onto substrates cooled at 77 K or after heating the high-density amorphous ice.

I. INTRODUCTION

Due to its unique properties, water is the most intensively studied of all liquids. Since the first x-ray diffraction patterns obtained in the 1930's, various experiments related to its structure have been performed by x-ray diffraction,¹ by neutron scattering,² and additionally, by electron diffraction.³ Moreover, the studies were not limited to liquid water under normal conditions; experiments were also performed in the superheated⁴ state, in the supercooled regime,⁵ and under high pressure.⁶

Some models can predict many of the anomalous properties of water by taking into account the hydrogen bonding behavior whose role is enhanced at low temperature. This explains the tendency to study the physical properties of supercooled water⁷ and glassy (or vitreous) water. However, for a long time, any attempt to obtain glassy water by cooling bulk water invariably led to the formation of hexagonal ice I_h . Therefore, for many years, only one technique for preparing noncrystalline ice was known. It consists of depositing water vapor in vacuo onto substrates cooled at low temperature. The structure of the amorphous solid so-prepared has been studied either by x-ray diffraction⁸ or neutron⁹ scattering. It has been shown that the basic structure is similar to that found in deeply supercooled water¹⁰ but, in view of older works^{8,11} and some recent experiments,¹² it seems that both structure and thermal properties of this amorphous form are strongly dependent on the mode of preparation or are influenced by the presence of occluded gases.

Another way to prepare amorphous ice has been discovered recently. When compressed at 77 K, hexagonal ice

I_h (Ref. 13) or cubic ice I_c (Ref. 14) transforms to a high-density amorphous phase. The transition is irreversible and the amorphous ice can be recovered at atmospheric pressure. On heating, a transition to a low-density amorphous ice occurs. Both x-ray¹⁵ and neutron¹⁶ scattering studies show that the low- and high-density amorphous forms of water exhibit significant differences at the level of the second- and third-nearest neighbors, whereas the structure of the low-density form is very similar to that of the noncrystalline solid obtained by vapor deposition.

When confined in a hydrogel whose pores are smaller than 50 Å, water vitrifies for relatively slow cooling rates¹⁷ and the x-ray diffraction measurements reveal a distortion of the local environment, which is attributed to a bending of the H bonds.¹⁸

In view of these observations concerning similarities or differences between the various kinds of noncrystalline forms of water, it seemed desirable to study the structure of glassy water. However, to vitrify water, very high cooling rates are required. This was recently achieved using special techniques of rapid cooling or "hyperquenching." Among the various techniques developed for vitrifying pure liquid water, hyperquenching of aerosol droplets on a cryoplate¹⁹ was chosen because it yields vitrified water samples without contamination by a liquid cryomedium. In this work, we describe the structure of hyperquenched glassy water using both x-ray diffraction and neutron scattering from H_2O and D_2O samples, respectively. The two techniques are complementary since x-ray data give information about the O-O correlations, whereas neutron measurements give information about the D-D and O-D correlations.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

The detailed procedure to obtain vitrified water by hyperquenching, of aqueous aerosol droplets and the thermal properties of the resulting samples are described elsewhere.¹⁹ Briefly, droplets of H₂O or D₂O water were made by means of an ultrasonic nebulizer and suspended as an aerosol in gaseous nitrogen and were subsequently allowed to enter a high-vacuum cryostat through a 300 μm aperture. Once inside, the droplets moved at supersonic speeds and deposited on a copper substrate held at 77 K. After 1 h of deposition, a 2–3 mm thick disc-shaped sample of glassy water was obtained. The samples so-prepared were maintained under liquid nitrogen before loading, at 77 K, the sample holders suitable for diffraction studies.

B. X-ray diffraction study

The x-ray diffraction measurements were carried out on a standard Θ -2 Θ diffractometer operating in the transmission mode. $\text{MoK}\alpha$ radiation ($\lambda = 0.7093 \text{ \AA}$) monochromated by a bent asymmetric quartz crystal was used. Scattered intensities were measured in steps of 0.1° (2 Θ) in the 1° – 40° (2 Θ) range and steps of 0.25° at higher angles. The corresponding momentum transfer, $q = 4\pi \sin\Theta/\lambda$, extended from 0.3 to 15 \AA^{-1} .

The sample holder was made by means of a copper framework (5 mm thick, $20 \times 25 \text{ mm}^2$ hollow) equipped with two beryllium windows. After filling under liquid nitrogen with the glassy ice pieces detached from the copper target, the sample holder was attached within a previously cooled cryostat. Throughout the study, the sample was maintained under vacuum. The x-ray absorption of the two samples studied in this work was determined experimentally. The scattered intensity from the empty cell was also measured.

C. Neutron scattering study

The measurements were performed at the reactor Orphée of the Laboratoire Léon Brillouin (Saclay) on the 7C2 spectrometer, which is equipped with a BF₃ position sensitive detector with 640 cells. The wavelength used ($\lambda = 0.704 \text{ \AA}$) allows experiments to be performed in the q range 0.3 – 16 \AA^{-1} .

The sample container was a vanadium cylinder with a diameter of 8 mm and a 0.1 mm wall thickness. It was filled in the same manner as for the x-ray measurements with the sample under liquid nitrogen. It was then transferred inside a cryostat cooled at 77 K. Independent measurements of the empty cell, of the background and of a vanadium rod were performed and used in the data treatment.

III. DATA ANALYSIS

A. X-ray diffraction

It is well-known that the coherent scattered intensity from water can be expressed either as the sum of atomic or

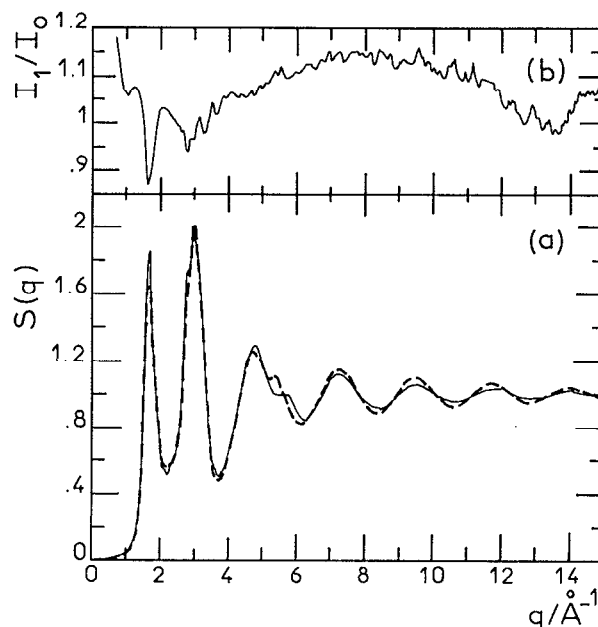


FIG. 1. (a) Structure factor of glassy water at 77 K (solid line) as determined by x-ray scattering; the structure factor of low-density amorphous ice, Ref. 15, is given for comparison (dotted line). (b) Ratio vs q of the scattered intensities measured after and before annealing glassy water at 130 K.

molecular intensities. We have chosen the latter because it takes advantage of the fact that the electron density is almost spherical.²⁰ Thus, the pair-correlation function yields information about the molecular centers, which are, in fact, not very different from the positions of the oxygen atoms.

The measured intensities were corrected using the usual procedure, but because the measurements were performed on samples with an unknown packing, we refined the effective irradiated volume contribution by minimizing the oscillations of the pair-correlation function, $g(r)$, for intermolecular distances lower than 2.0 \AA , that is, within a region where it is known that $g(r)$ is featureless.

The two samples studied give quite similar results. The continuous line in Fig. 1(a) shows the structure factor $S(q)$ of glassy water as obtained by averaging the two sets of data. Clearly, the samples exhibit the characteristic features of noncrystalline solids; nevertheless, they contain, as expected,²¹ about 5% of cubic ice. In Fig. 1(a) we have also drawn (dotted line) the structure factor related to the low-density amorphous ice and the similarity of the two curves is evident. Since we have already demonstrated¹⁵ that the structure of low-density ice is identical to that of the amorphous ice obtained by vapor deposition, we conclude, within our experimental error, that all of these noncrystalline solids have the same structure independent of the mode of preparation.

We have noticed increased damping of the oscillations of $S(q)$ at high q values in glassy water when compared to that for the low-density form [Fig. 1(a)]. This may reflect the fact that the former is more disordered. We attempted

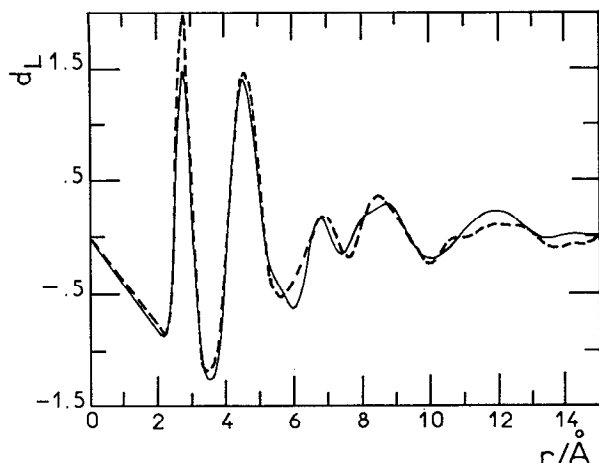


FIG. 2. Weighted molecular pair-correlation function of glassy water at 77 K determined by x-ray diffraction (solid line) and that of low-density amorphous ice (dotted line).

to relax the structure by heating the samples. During annealing up to 146 K, the first sample crystallized to ice I_c . The second sample was annealed for 30 min at 130 K and then studied at 77 K. We chose 130 K because differential scanning calorimetry²² has shown a relaxation of hyperquenched glassy water to a structural state of lower enthalpy (and free energy) at this temperature. In Fig. 1(b) we have drawn the ratio, i.e., $I_1(q)/I_0(q)$, of the raw scattered intensities measured after and before annealing. The curve shows that the structure is not significantly modified by the heat treatment. Only a small relaxation effect is seen at the level of the two first maxima of $S(q)$ as shown by the slight decrease of these oscillations; however, no significant variation can be seen in $g(r)$. Otherwise, a slight departure from 1 of the ratio I_1/I_0 versus q in Fig. 1(b) is due to a variation of the packing of the powder on heating.

Figure 2 (solid line) displays the weighted function $d_L = 4\pi\rho [g(r) - 1]$ obtained by Fourier inversion of $S(q)$. Termination effects in the calculation of $g(r)$ were avoided by using a modification function, $[1 + \cos(\Pi q/q_m)]/2$, where q_m was the upper limit of q . In the radial distribution function, first- and second-nearest neighbors are clearly separated. The corresponding first-nearest-neighbor distance is 2.80 Å. The coordination number, inferred from the radial distribution function $4\pi r^2 \rho g(r)$, is equal to 4.2 when the density ρ is kept equal to 0.031 mol Å⁻³. The second-nearest-neighbor distance, approximately 4.6 Å, is consistent with a local tetrahedral configuration of the molecules around a central one. All these results confirm the analogy of the structure of glassy water and that measured for low-density amorphous ice whose pair-correlation function is represented by the dotted line in Fig. 2.

B. Neutron scattering

The initial pattern of the vitrified D₂O sample was found to be contaminated by 15% of cubic ice. This is significantly more than in the H₂O samples. This addi-

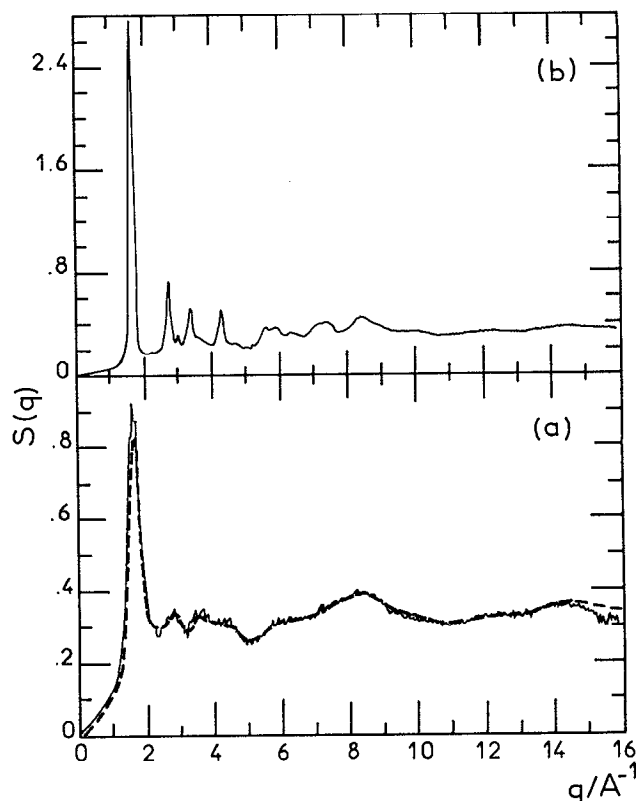


FIG. 3. (a) Structure factor of glassy water (solid line) as determined by neutron scattering compared with that of low-density amorphous ice, Ref. 16 (dotted line). (b) The structure factor of the sample after annealing at 130 K and crystallization into cubic ice.

tional amount of ice was probably produced either during the container filling or during the transfer to the cryostat. The removal of these spurious Bragg peaks has been readily done by using the pattern of the cubic ice phase obtained at 150 K after the crystallization of the whole sample.

We deduced the total differential scattering cross section after the usual correction procedure. To correct the inelastic scattering, we used an empirical method.²³ The resulting structure factor $S(q)$ of glassy water at 77 K is shown in Fig. 3(a) by the continuous line. The corresponding curve for low-density amorphous ice¹⁶ is given by the dotted line. Clearly, vitreous ice produced by hyperquenching and amorphous ice obtained after pressure amorphizing exhibit great similarities. A recent neutron investigation²⁴ of the structure of glassy water compared to the amorphous form produced by vapor deposition led to the same conclusion.

To detect an eventual relaxation effect in the vitreous state, as was done in the x-ray measurements, we measured the diffracted intensity by heating the sample at various temperatures. However, during annealing, crystallization occurred and the sample appeared to be all crystallized into cubic ice before 137 K. Figure 3(b) shows the $S(q)$ curve obtained subsequently after cooling to 77 K.

Returning to the results concerning the vitreous state,

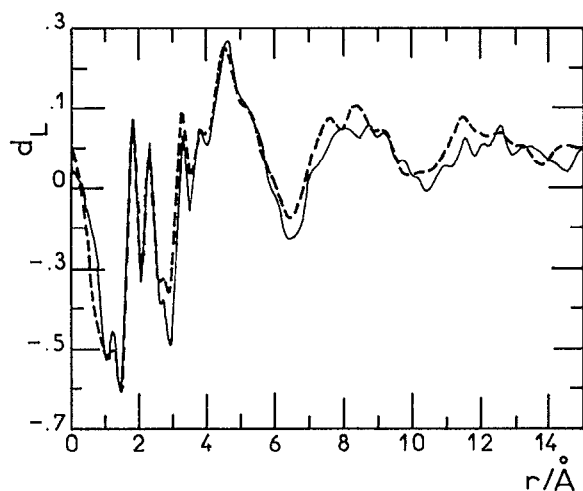


FIG. 4. Weighted intermolecular pair-correlation function of glassy water (solid line) as determined by neutron scattering and compared with that of low-density amorphous ice (dotted line).

that is, before annealing, we have split the structure factor $S(q)$ into two parts:

$$S(q) = f_1(q) + D_m(q),$$

where $f_1(q)$ is the molecular form factor and $D_m(q)$ the function containing only the intermolecular contributions. Using the procedure given in Ref. 23 to adjust the flexible parameters in $f_1(q)$, one can determine the geometrical factors of a water molecule in the glassy state. We found that the O–D distance is equal to 0.98 Å with $\langle u^2 \rangle / 2 = 3.8 \times 10^{-3}$ Å², where $\langle u^2 \rangle$ is the mean-square amplitude of displacement from equilibrium position. The D–D distance was determined to be 1.55 Å, with $\langle u^2 \rangle / 2 = 3.7 \times 10^{-3}$ Å² and this indicates a D–O–D angle of about 105°.

By subtracting the molecular form factor $f_1(q)$ from $S(q)$, one obtains $D_m(q)$, which may be Fourier transformed to obtain the pair-correlation function for the intermolecular terms only:

$$d_L = 2/\pi \int q D_m(q) \sin(qr) dq.$$

The weighted function d_L is characterized by structural peaks (see Fig. 4), which are well identified at least for the nearest neighbors. For comparison, the function d_L of low-density amorphous ice is also represented in Fig. 4 (dotted line). The hydrogen bond distance O–D is close to 1.80 Å and the O–O distance appears as a hump located near 2.8 Å. This O–O distance is consistent with the 2.80 Å value determined by x-ray diffraction. All the other interatomic distances are very close to those found for an ideal tetrahedral symmetry and can be well described by the continuous random network of tetrahedrally coordinated H bonds.²⁵

IV. CONCLUDING REMARKS

In a comparative study of glass transition behavior of the amorphous water using calorimetric²⁶ or optical²⁷ mea-

surements, some differences were observed between the amorphous forms of water made by pressure-amorphizing ice on the one hand, and by quenching the vapor or the liquid on the other hand. For instance, spectral differences in the infrared peak positions of the decoupled O–D stretching transitions between the amorphous forms made from the vapor and the liquid have been related to small differences in structure between these two amorphous solids. Nevertheless, we have presented in this work a structural study of glassy water using x-ray diffraction and neutron scattering, which show that the local environment is similar to that of low-density amorphous ice obtained by vapor deposition onto cold substrates or by heating high-density amorphous ice. It appears that either the calorimetric and optical techniques are more sensitive to small structural differences between the various noncrystalline forms than in scattering measurements performed in our experimental conditions or the quoted differences are not attainable by means of radial distribution functions, which are an averaged representation of the structure.

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