# Reports

## Amorphous Solid Water: A Neutron Diffraction Study

Abstract. *The structure factor of amorphous solid $D_2O$ deposited from the vapor at 10°K has been obtained by measuring the neutron diffraction spectrum in the wave vector transfer from 0.8 to 12.3 reciprocal angstroms. The results indicate that the phase investigated is amorphous and has a liquid-like structure factor. The Fourier-transformed structure factor yields a real space pair distribution function consistent with local tetrahedral coordination and hydrogen bonding, as in other condensed phases of water. The intramolecular OD separation is 1.00 angstrom; the lack of data for very large wave vector transfer and the expected near equality of the intramolecular DD separation and intermolecular O . . . D separation make it impossible to determine the intramolecular DOD angle with precision. The neutron scattering data presented are complementary to the x-ray diffraction studies of Venkatesh, Rice, and Narten.*

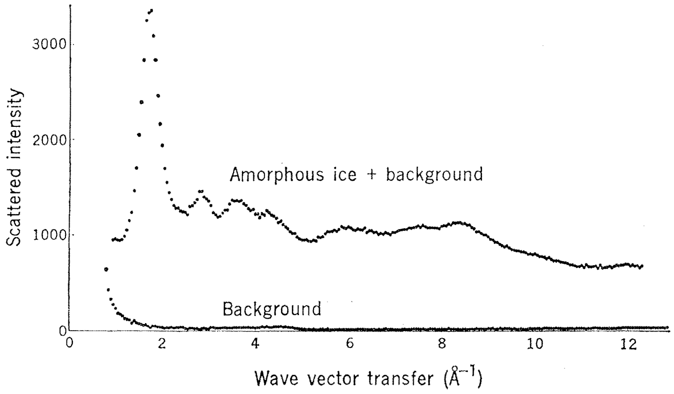
Olander and Rice (*1*) have suggested that amorphous solid water may be a useful model of the liquid. The report of Venkatesh *et al.*, which concerns an x-ray diffraction study of this material, shows the strong resemblance between the oxygen-oxygen distribution in the amorphous solid and that in the liquid (*2*). This report is concerned with neutron diffraction from amorphous solid $D_2O$ prepared at 10°K.

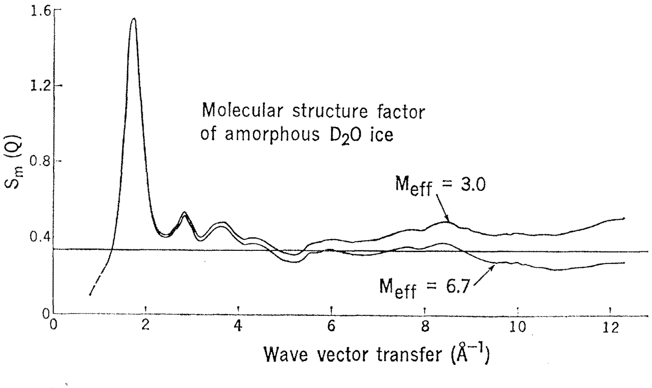
The cryostat used for sample preparation by vapor deposition is similar to that employed by Olander and Rice (*1*) except for the following changes: (i) The substrate temperature was held below 10°K. (ii) The delivery tube was modified by the insertion of a copper liner which was thermally anchored outside the cryostat. This ensured that no water vapor froze in the delivery tube so that deposition could be continued for an extended period. Since only a fraction of the vapor was deposited on the substrate, 1 week was necessary to obtain a sample approximately 2 mm thick with a deposition rate of 20 mg/hour.

The substrate used was a cadmium plate (10 by 30 mm). With masks for the incident and scattered beams (15 by 40 mm), the sample was completely bathed in neutrons for all scattering angles. The beam size was such that extraneous parts of the cryostat did not intrude into the scattering volume.

The scattered neutron intensity was measured with a standard double-axis neutron spectrometer at the DR-3 reactor at Risø; 0.8616-Å neutrons were selected by means of a Be(110) monochromator reflection, and the collimation was chosen to produce 0.10-$Å^{-1}$ full width at half maximum resolution near the first peak in the structure factor $S_m(Q)$ [here $Q$ (wave vector transfer) $= 4\pi \sin \theta/\lambda$, where $2\theta$ is the scattering angle and $\lambda$ is the wavelength]. The incident beam was monitored with a thin $^3He$ counter, and scattered neutrons were detected with an enriched $BF_3$ counter.

The experiment was carried out in several steps. First, the cryostat background at 6°K was determined. Second, with the cryostat on the spectrometer water was degassed by several freeze-thaw cycles and a deposit of amorphous solid water was made. The temperature of the substrate rose nearly 4°K during the deposition. Third, scans were taken at constant $\Delta(2\theta) = 0.20°$ over the





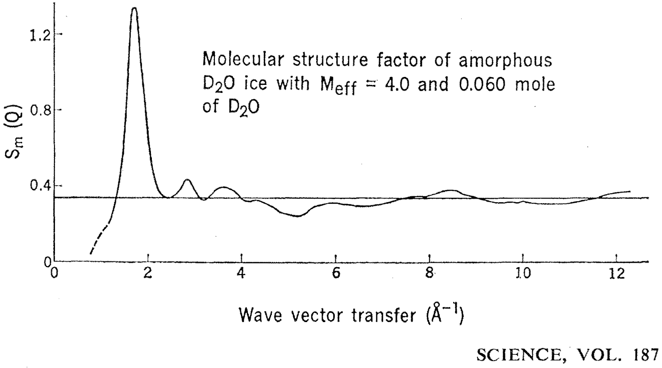


Fig. 1 (left). Uncorrected intensity of scattered neutrons as a function of wave vector transfer for amorphous solid $D_2O$ at 10°K. Fig. 2 (top right). Effect of $M_{eff}$ (Placzek correction) on the intensity of scattered neutrons as a function of wave vector transfer for amorphous solid $D_2O$ at 10°K. Fig. 3 (bottom right). Adopted corrected ($M_{eff} = 4.0$ amu) intensity of scattered neutrons as a function of wave vector transfer for amorphous solid $D_2O$ at 10°K.

angular range $6° \leqslant 2\theta \leqslant 115°$ with the cryostat being half-angled in reflection geometry. One month was required to collect $10^4$ counts at each angular position. Finally, the cryostat was warmed up, a thin vanadium strip (10 by 30 mm) was inserted in place of the amorphous solid water sample, and the neutron scattering by the foil was measured at 77°K.

In a preliminary experiment the cryostat with sample was quickly warmed up and disassembled after a desposition was completed. The sample collected was found to be of the same isotopic purity (99.8 percent) as the starting material.

The data obtained, after averaging a number of runs and interpolating to intervals of $\Delta Q = 0.05$ Å$^{-1}$, are shown in Fig. 1. The reduction of these data to a differential coherent scattering cross section requires corrections for background, multiple scattering, absorption, and Placzek (recoil) effects (*3*). These corrections were made separately for amorphous solid water and vanadium. Then the amorphous solid water intensities were normalized to those of vanadium, which is an isotropic scatterer, and the incoherent scattering of the amorphous solid water was subtracted. In principle, this procedure puts the coherent scattering on an absolute basis; in our case two uncertainties intrude. First, the absolute mass of the sample studied could not be determined accurately; we have therefore used this mass as an adjustable parameter. Second, and more serious, the Placzek correction is uncertain in that it is not known what mass describes the recoil of a molecule in the solid from a neutron scattering event, or indeed, whether the Placzek correction formalism is valid for an amorphous, deuterium-containing solid. In the simplest approach, the conventional Placzek correction formula was used in the data reduction, but with the recoil mass taken to be an adjustable "effective" mass, $M_{\text{eff}}$. This effective mass was chosen so that the scattering at large $Q$ approaches its asymptotic value. In fact, the corrected scattering for large $Q$ is extremely sensitive to the effective mass, so that this quantity is easy to estimate. We show in Fig. 2 the corrected scattering with $M_{\text{eff}} = 3.0$ atomic mass units (amu) and $M_{\text{eff}} = 6.7$ amu. The former Placzek correction is too large at large $Q$, whereas the latter Placzek correction, which has been used to correct scattering data for liquid water (*4*), is too small. In Fig. 3 we use our best guess that the appropriate mass of water on the substrate is 1.2 g and display the corrected scattering curve for $M_{\text{eff}} = 4.0$ amu. We adopt this curve as the molecular structure factor $S_m(Q)$ for amorphous solid D$_2$O.

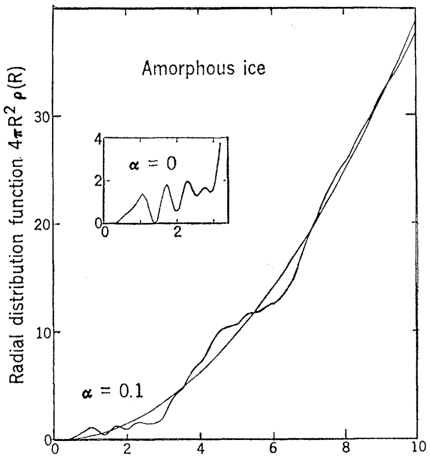


Fig. 4. Radial distribution function for amorphous solid $D_2O$ at 10°K deduced from the scattering function displayed in Fig. 3.

Because neutron scattering is sensitive to both D and O nuclei, the overall diffraction pattern depends on three partial radial distribution functions. Fourier transformation of the data in Fig. 3 gives the radial distribution function (RDF) displayed in Fig. 4. It is related to the partial RDF's, $4\pi R^2 \rho_{\alpha\beta}(R)$, as follows:

$$\begin{aligned}\text{RDF}(R) \equiv 4\pi R^2\rho(R) &= 4\pi R^2[4b_O\bar{b}_D\rho_{OD}(R) \\ &\quad + 4\bar{b}_D{}^2\rho_{DD}(R) + \bar{b}_O{}^2\rho_{OO}(R)] \\ &= 4\pi R^2[0.43\rho_{OD}(R) + \\ &\quad 0.48\rho_{DD}(R) + 0.09\rho_{OO}(R)]\end{aligned}$$

where $\rho_{\alpha\beta}$ is the number density of atom type $\beta$ when viewed from atom type $\alpha$.

In addition, the molecular RDF is related to $S_m(Q)$ by

$$\text{RDF}(R) = 4\pi R^2\rho_0 + \frac{2R}{\pi}\int_0^\infty Q[S_m(Q) - S_m(\infty)] \sin(QR)dQ$$

$$\text{RDF}(R) \cong 4\pi R^2\rho_0 + \frac{2R}{\pi}\int_0^{Q_{\max}} Q[S_m(Q) - S_m(\infty)]e^{-\alpha^2Q^2} \sin(QR)dQ$$

where the last approximation derives from the fact that we cannot measure wave vector transfers larger than $Q_{\max}$. The exponential in the integrand is a convergence factor designed to minimize satellite ripples in the Fourier transform. In Fig. 4, $\alpha = 0.1$ except in the inset, which shows the region of scattering sensitive to the molecular dimensions, where $\alpha = 0$ is used for slightly better resolution. In the equations displayed $R$ is the distance between scatterers, $\rho_0$ is the molecular number density (taken to be the same as that of ice Ih), and

$$S_m(\infty) = \frac{\Sigma b_\alpha{}^2}{(\Sigma \bar{b}_\alpha)^2}$$

defines the normalization. For these calculations we have taken $b_O = 0.577 \times 10^{-12}$ cm and $b_D = 0.65 \times 10^{-12}$ cm.

Because the RDF derived from the experiment is a combination of the three partial RDF's, analysis of the overall RDF is complicated and unique assignment of peaks is impossible except at small distances. Here we see three peaks at 1.00, 1.68, and 2.26 Å; the widths of these peaks are determined by resolution broadening because of the limited $Q$ range covered. We estimate the error in the peak positions to be 3 percent. The first peak is due to the OD separation within a water molecule, and within experimental error is the same as that for ice Ih, that is, 1.015 Å (*5*). This value is common to all condensed phases of water (*6*). The second peak in the RDF can be attributed to a superposition of the intramolecular DD and intermolecular hydrogen bonded O . . . D separations, which are 1.66 and 1.75 Å, respectively, in other hydrogen-bonded tetrahedrally coordinated water structures. The third peak can be attributed to the nearest neighbor intermolecular DD separation, assuming hydrogen bonding, which occurs at 2.30 Å in a condensed-phase tetrahedral arrangement. We conclude that the D$_2$O molecule in amorphous solid water has the same dimensions as in other condensed phases of water and that there is strong evidence for hydrogen bonding. Beyond the third peak specific assignment becomes impossible and we note only that the short-range order in amorphous solid water extends to around 12 Å.

It is important to note that when we use the term "local tetrahedral coordination" we do not imply that all OOO angles are exactly 109°28′. In general, we expect there to be a range of angles, centered around the tetrahedral value, consistent with both "four coordination" and high density, as in amorphous germanium (*7*) and in the several forms of ice (*5, 6*). On the assumption that the intramolecular HOH angle is the same in the vapor and in the condensed phases, this implies the existence of "bent" hydrogen bonds in the amorphous solid. The distribution of intramolecular DOD angles can be measured by neutron scattering techniques if the experimental range can be extended to very large *Q*, since there the molecular form factor dominates the *Q* dependence of the scattering.

For the present we shall not comment further on the detailed structure of amorphous solid water except to emphasize that it has a truly amorphous character; there is no evidence of Bragg-scattering from crystalline material in these neutron scattering data or in the x-ray scattering data. This inference is supported by calculations of the diffraction patterns of polycrystalline samples with extremely small (for example, ten-molecule) crystallites. For these models there is scattering intensity at non-Bragg angles by virtue of incomplete cancellation of interference terms resulting from the very small crystallite size. Both hexagonal and cubic ice crystallite models were tried, and both gave similar, poor agreement with experiment. Most promising as a model for the structure of amorphous solid water is the random network model, which is presented in the report by Alben and Boutron (*8*).

*Note added in proof*: More recent x-ray data show that there are at least two forms of amorphous solid water (9). When deposited at low temperature (~ 10°K), the density is 1.2 g $\mathrm{cm}^{-3}$ and the RDF shows a peak at ~ 3.3 Å; these features persist when the sample is heated to 77°K. When deposited at high temperature (~77°K), the density is 0.93 g $\mathrm{cm}^{-3}$ and the peak in the RDF at 3.3 Å is missing. The control of deposition of amorphous solids is notoriously difficult to standardize; seemingly trivial differences can be important. It is possible that the deposits used for this neutron diffraction study were of the high-temperature form despite the temperature of the substrate. This is suggested by the results of Alben and Boutron's calculations.

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**References and Notes**

1. D. Olander and S. A. Rice, *Proc. Natl. Acad. Sci. U.S.A.* **69**, 98 (1972).
2. C. G. Venkatesh, S. A. Rice, A. H. Narten, *Science* **186**, 927 (1974).
3. W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon, London, 1971); J. E. Enderby, in *Physics of Simple Liquids*, H. N. V. Temperley, Ed. (North-Holland, Amsterdam, 1968), p. 611; I. A. Blech and B. L. Averbach, *Phys. Rev. A* **137**, 1113 (1965); H. H. Paalman and C. J. Pings, *J. Appl. Phys.* **33**, 2635 (1962); D. M. North, J. E. Enderby, P. A. Egelstatt, *Proc. Phys. Soc. Lond. Solid State Phys.* **1**, 784 (1968).
4. D. I. Page and J. G. Powles, *Mol. Phys.* **21**, 901 (1971).
5. N. H. Fletcher, *The Chemical Physics of Ice* (Cambridge Univ. Press, London, 1970).
6. E. Whalley, *Mol. Phys.* **28**, 1105 (1974).
7. See, for example, W. Paul, G. A. N. Connel, R. J. Temkin, *Adv. Phys.* **22**, 529 (1973; *ibid.*, p. 581; *ibid.*, p. 643.
8. R. Alben and P. Boutron, *Science* **187**, 430 (1975).
9 A. H. Narten and S. A. Rice, unpublished work.
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# Continuous Random Network Model for Amorphous Solid Water

Abstract. *Continuous random network models representing amorphous solid water have been constructed. The x-ray and neutron scattering predictions for one type of model agree quite well with experimental results.*

The art of model-building has come to play an important role in our understanding of diverse types of amorphous solids (*1*). This is so because descriptions of amorphous structure based on attenuating the long-range order of crystals or starting from near-neighbor coordination relationships present in the liquid are never precise and calculations from them require many adjustable parameters. By contrast, model structures are perfectly well-defined representations of finite regions within an amorphous sample. Models can be built sufficiently large so that, for structural studies at least, the finite size of the models is not a serious problem.

In this report, we present for the first time predictions for x-ray and coherent neutron scattering for a specific model structure for amorphous solid water (*2*). The model is a continuous random network (CRN), a type of model distinguished by the fact that the loss of correlation between atoms builds up more or less uniformly with separation and does not occur suddenly at grain boundaries or other defects. The starting point for our model was a relaxed version (*3*) of the 519-unit fourfold-coordinated network of Polk and Boudreaux (*4*). This model was built by hand out of plastic and metal tetrahedral units according to various criteria including compactness and the absence of broken bonds or large angular distortions. The model building was stopped at 519 units, since it appeared that the model could be continued indefinitely without any significant change in the average properties. Studies of other examples built according to the same criteria indicate that the Polk-Boudreaux model is fully representative of this type of CRN (*5*).

In our model for amorphous solid water the units of the Polk-Boudreaux model were taken to represent oxygen atoms separated by bonds with an average length of 2.75 Å. The model was then "decorated" with hydrogen atoms, one on each interior bond, in a direct line between the two bonded oxygens, a distance of 1 Å from one oxygen and approximately 1.75 Å from the other (as in ordinary ice Ih). The choice of the near oxygen for each hydrogen was then modified according to a procedure which ensured that the "ice rules" (two near and two distant hydrogens for each oxygen) were satisfied for interior units. The hydrogen positions were then further modified so that the angle formed by an oxygen and its two near hydrogens was exactly the tetrahedral angle. The final model contains 519 atoms of oxygen and 892 atoms of hydrogen and represents an approximately spherical sample of amorphous solid water 32 Å in diameter.

Our calculation for x-ray scattering was carried out as follows. First, the