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 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 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.

JACK WENZEL*
C. U. LINDERSTRØM-LANG
Research Establishment Risø,
Roskilde, Denmark
STUART A. RICE
Department of Chemistry and
James Franck Institute, University of
Chicago, Chicago, Illinois 60637

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.
10. J.W. and S.A.R. are grateful to Dr. Alan Mackintosh for arranging the use of the facilities at Risø, and J.W. and C.U.L.-L. would like to thank the staff of the Physics Department, Risø, for discussions and technical support. In addition, J.W. would like to thank Dr. G. Tourrand of Centre d'Etudes Nucleaires du Saclay, France, for hospitality during a stay at Saclay, where preliminary data analysis was carried out. This research was supported by a grant from the National Science Foundation (GP 32910X) and by the Danish Atomic Energy Commission. S.A.R. also wishes to acknowledge partial support of this research by the general National Science Foundation Materials Research Laboratory grant at the University of Chicago. This report is abstracted from the Ph.D. thesis of J.W., Department of Chemistry, University of Chicago.

* Present address: Atomic Energy Research Establishment, Harwell, Didcot, Oxon OXII ORA, England.

23 August 1974

■

Continuous Random Network Model for Amorphous Solid Water

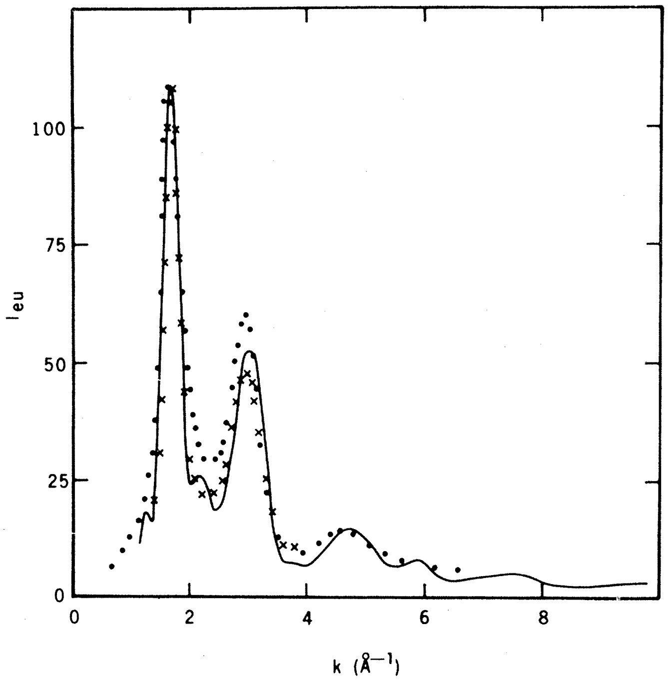
Abstract. *Continuous random network models representing amorphous solid water have been constructed. The x-ray and neutron scattering predictions for one type of model agree quite well with experimental results.*

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



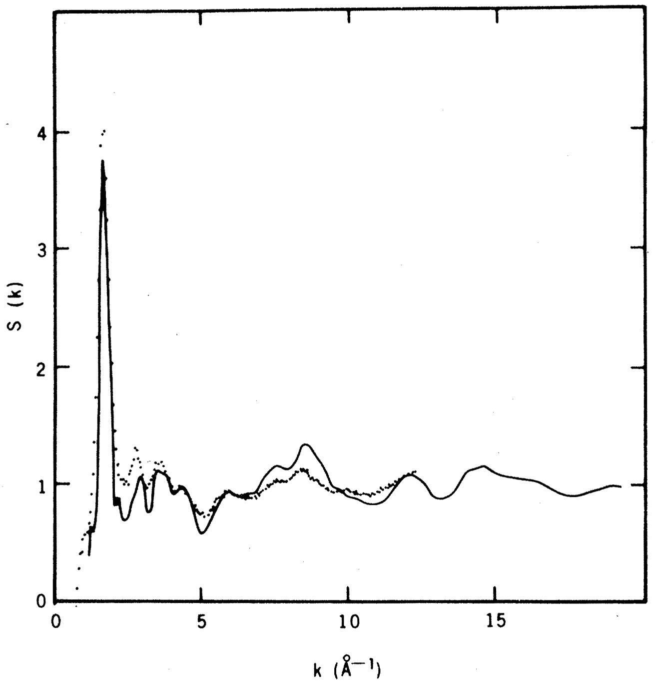


Fig. 1 (left). Comparison of calculated x-ray scattering $I_{eu}(k)$ in electron units per H_2O for amorphous solid water (solid line) with the experimental results of Dowell and Rinfret (*8*) (X) and of Bondot (*9*) (•), both normalized to have the same maximum values as the theoretical curve. Wave vector $k = 4\pi \sin\theta/\lambda$. The data of (*8*) were originally given as relative intensities and were converted to relative I_{eu}. The symbols used to represent the data of (*8*) and (*9*) describe the data but are not actual data points. Fig. 2 (right). Comparison of the calculated neutron structure function $S(k)$ with data points of Wenzel *et al.* (*12*) for amorphous solid heavy water D_2O.

pair distribution functions for hydrogen-hydrogen, hydrogen-oxygen, and oxygen-oxygen pairs were computed in histogram form with a bar width of 1/20 of the oxygen-oxygen near-neighbor distance. These functions were then corrected for the finite size of the models by reference to the difference between the pair distributions for finite uniform spheres, with the sphere being of different radii for the two types of atoms, and the pair distributions for an infinite uniform sample (*6*). The corrected pair distribution functions together with x-ray form factors for neutral oxygen and hydrogen were used to compute the scattering in electrons units (*7*), according the "exact method" described by Warren (*7*). The calculated curve as a function of wave vector k ($= 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength) compared with two sets of experimental data (*8, 9*) is shown in Fig. 1. The agreement is generally good. Except for the subtle structure near 2.2 and 5.3 Å^{-1}, the calculation is within the range of variation of the different experimental results. The results of recent x-ray experiments of Venkatesh *et al.* (*10*) appear to be quite different from the data shown in Fig. 1. We believe that this reflects a fundamental difference in microscopic structure between the sample of Venkatesh *et al.* (*10*) and those which agree with the model presented here.

The coherent neutron scattering for the model was calculated from the corrected pair distribution functions according to standard methods (*11*). Since deuterium (^2H) is a far better coherent scatterer than protium (^1H), and accordingly since experiments have been done on D_2O, we used scattering lengths appropriate to D_2O ($b_D = 0.65$,

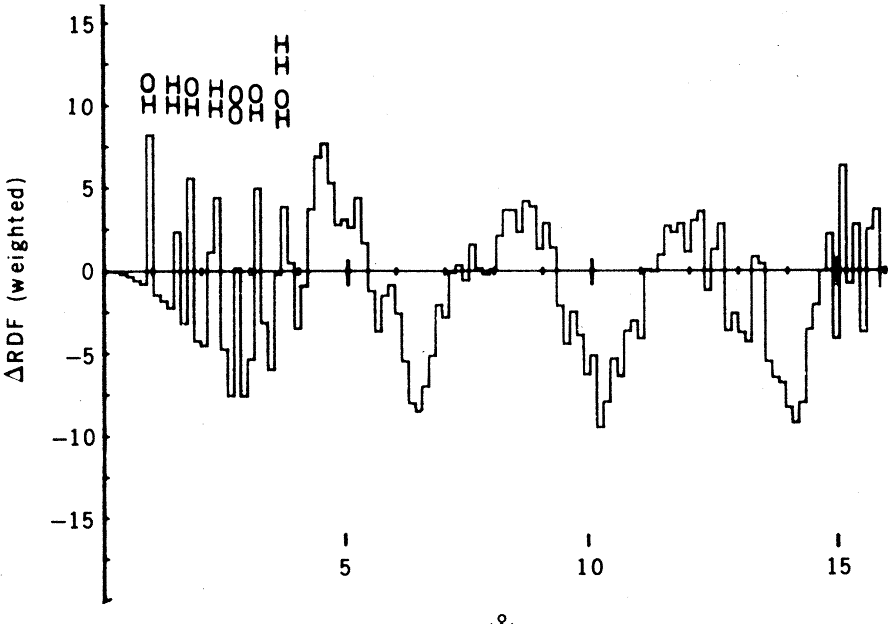


Fig. 3. Model radial distribution function ΔRDF(r), with the smooth parabolic background subtracted, weighted appropriately for neutron scattering for amorphous solid heavy water D_2O. The first few peaks are labeled according to the pairs (HH, OH, or OO) with which they are associated.

$b_0 = 0.577$) (*11*). The resulting structure function, normalized to unity for uncorrelated scattering, is shown in Fig. 2, compared with the experimental data of Wenzel *et al.* (*12*). The overall agreement is excellent. Even the small discrepancies can be understood; the overestimate of the oscillations in $S(k)$ for large k is due to the static nature of the model, whereas the displacement of the experimental points from the theoretical curve at low k could be due to experimental correction factors.

A striking feature of both the neutron and x-ray experimental results is the strong first peak at $k = 1.7$ Å^{-1}. It can be shown that the presence of this peak in the calculated results is due to an anisotropic layer structure which extends over a distance of at least the order of 15 Å in the Polk-Boudreaux type of CRN model (*13*). It would thus appear that this type of relatively long-range order is present in typical samples of amorphous solid water. It should be emphasized that none of the peaks in $S(k)$ for $k < 8$ Å^{-1} can be ascribed to intramolecular scattering, and that the structure observed and calculated for small k is determined by relatively long-range correlations.

In Fig. 3 we show the excess (above a smooth parabolic background) of the weighted radial distribution function (RDF) for a slightly modified version of the model. (Here the H_2O groupings were taken to have the same shape as gas-phase H_2O molecules.) This weighted RDF determines the neutron scattering $S(k)$ according to the relation:

$$S(k) = \int_0^{r_c} \Delta\mathrm{RDF}(r)\,\frac{\sin kr}{kr}\,dr$$

where r_c is a cutoff distance taken as 20 Å. The first few interatomic separations give rise to well-defined peaks labeled according to the pairs of atoms involved. The oscillatory behavior for large r with period ~ 3.7 Å corresponds to the sharp peak in $S(k)$ at $k = 1.7$ Å^{-1} discussed above.

In order to examine the sensitivity of our results to the properties of the Polk-Boudreaux model, we have constructed another random network which incorporates as much as possible large cages such as occur in the clathrate hydrates (*2, 14*). The near-neighbor coordinations in this model are essentially the same as those of the Polk-Boudreaux model, but there are differences in the longer-range correlations (distances greater than 10 Å). We find that the strong first peak is not reproduced by the cage model. We have also carried out calculations for a version of the Polk-Boudreaux model with one hydrogen for each bond, but placed without regard to the ice rules. This model also does not agree with experiment nearly as well as the original model.

RICHARD ALBEN*
PIERRE BOUTRON

Laboratoire de Magnétisme du Centre National de la Recherche Scientifique, Avenue des Martyrs, 38000-Grenoble, France

References and Notes

1. See, for example, J. D. Bernal, *Proc. Roy. Soc. Ser. A* **280**, 299 (1964); R. J. Bell and P. Dean, *Nature (Lond.)* **212**, 1354 (1966); D. E. Polk, *J. Non-Cryst. Solids* **5**, 365 (1971).
2. A more detailed account of this work will be published elsewhere (R. Alben and P. Boutron, *J. Chem. Phys.*, in press).
3. P. Steinhardt, R. Alben, M. G. Duffy, D. E. Polk, *Phys. Rev. B* **8**, 6021 (1973).
4. D. E. Polk and D. S. Boudreaux, *Phys. Rev. Lett.* **31**, 92 (1973).
5. P. Steinhardt, R. Alben, D. Weaire, *J. Non-Cryst. Solids* **15**, 199 (1974).
6. A. Guinier and G. Fournet, *Small-Angle Scattering of X-Rays* (translated by C. B. Walker) (Wiley, New York, 1956), p. 10.
7. B. E. Warren, *X-Ray Diffraction* (Addison-Wesley, Reading, Mass., 1969), pp. 1–4, 135–142.
8. L. C. Dowell and A. P. Rinfret, *Nature (Lond.)* **188**, 1144 (1960).
9. P. Bondot, *C. R. Hebd. Seances Acad. Sci. Ser. B Sci. Phys.* **265**, 316 (1967).
10. C. G. Venkatesh, S. A. Rice, A. H. Narten, *Science* **186**, 927 (1974).
11. G. E. Bacon, *Neutron Diffraction* (Oxford Univ. Press, London, ed. 2, 1962).
12. J. Wenzel, C. U. Linderstrøm-Lang, S. A. Rice, *Science* **187**, 428 (1975).
13. P. Chaudhari and J. Graczyk, *J. Non-Cryst. Solids*, in press; R. Allen, P. Steinhardt, D. Weaire, in *Tetrahedrally Bonded Amorphous Semiconductors*, M. H. Brodsky, S. Kirkpatrick, D. Weaire, Eds. (Conference Proceedings, American Institute of Physics, New York, 1974), vol. 20, p. 213.
14. G. A. Jeffrey and R. K. McMullan, *Progr. Inorg. Chem.* **8**, 43 (1967).

* United States–France Exchange of Scientists Fellow, 1974; permanent address: Department of Engineering and Applied Science, Yale University, New Haven, Connecticut, 06520.

29 August 1974

Enzymatic Characterization of Soluble Organic Phosphorus in Lake Water

Abstract. *Although the concentration of soluble organic phosphorus in lake water often exceeds that of orthophosphate severalfold, little is known of its composition. By using enzyme assays it was determined that up to 50 percent of the organic fraction is hydrolyzable by phytase. The enzymatically degradable material consists of both low and high molecular weight fractions.*

During periods of maximal algal growth the concentration of orthophosphate in natural waters approaches nondetectable levels. During such algal blooms organically bound phosphorus often constitutes 85 to 99 percent of the total soluble phosphorus (*1*). Nucleic acids (*2*) and nucleotides (*3*) have been identified as minor constituents of naturally occurring organic phosphorus; the preponderant portion, however, is undefined. Furthermore, the potential availability of organic phosphorus for algal growth is virtually unknown.

Because the ability of various organic phosphorus compounds to satisfy algal growth requirements depends on their susceptibility to enzymatic liberation of orthophosphate (*4*), we characterized naturally occurring soluble organic phosphorus by incubation with different enzymes and measurement of the orthophosphate released. Enzymes employed included (i) alkaline phosphatase, (ii) phosphodiesterase and alkaline phosphatase, incubated sequentially, and (iii) phytase (a nonspecific phosphatase capable of hydrolyzing phytic acid). We determined that up to 50 percent of the soluble organic phosphorus is hydrolyzable by phytase, the hydrolysis kinetics of the degradable fraction being identical to that of myoinositol hexaphosphate.

Two small lakes of mesotrophic and highly eutrophic nutrient enrichment status (*5*) were studied between March 1973 and April 1974. Four-liter samples were obtained from the upper 1 m and were immediately passed through membrane filters and subjected to cation exchange. Because the soluble organic phosphorus content seldom exceeded 40 μg of PO_4 per liter we concentrated samples by partial freezing (*6*). After concentration by a factor of 10 to 12, recovery of soluble phosphorus routinely exceeded 80 percent.

The enzymes employed included commercial preparations (Sigma) of alkaline phosphatase and phosphodiesterase, and a phytase which we extracted and purified from wheat bran (*7*). They were added (at 0.04 to 0.06 mg of protein per milliliter) to con-