



Amorphous Solid Water: An X-ray Diffraction Study

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shown in Fig. 1C. The upper zone gradually builds up, and the advanced front ablates back. The zone of maximum velocity moves down from the upper region to the front as a wave (see Fig. 2C). The surge ends after this wave passes through the front of the glacier, and the position of the maximum velocity reverts to the upper region once more.

Onset of surge. For a given glacier (that is, for specified values of b and a) the onset of the surge depends on the values of ϕ and η . For a given η a certain critical value of ϕ separates surging from nonsurging conditions. Thus ϕ and η can be found to match real glaciers.

Size of the surge. The distance and speed of the surge can be increased by lowering η . From laboratory measurements of the flow law of ice it is apparent that realistic values of η will give rise to realistic values of surge speed and distance of advance. For greater sophistication, power law or hyperbolic sine functions could be used, but at this stage we are still attempting to find the appropriate order of magnitude.

Duration of the surge. The duration decreases as η decreases, when the ϕ value is set just above the critical value. Thus it is possible to vary the duration of the surge over a wide range. For the example chosen in Figs. 1 and 2 the change in length of 8 km occurs over 2 years.

Period of the surge. The main factors influencing the period of the surge cycle include the profiles of a and b , and the parameters ϕ and η . The length of the period is not simply related to the accumulation rate because it also depends on the magnitude of the surface lowering caused by the surge.

Shift of the equilibrium line. If a is changed to reduce the steady-state glacier size, a surging glacier can be changed to a nonsurging glacier that reaches a new steady state with a reduced length. Increasing the accumulation on a surging glacier increases the magnitude of the surge and also shortens its period.

Change in bedrock profile. A steeper bedrock gives rise to surges at lower ice thicknesses and lower velocities. For two glaciers that have the same curve of balance versus elevation, the steeper glacier will be shorter and thinner than the less steep glacier.

We believe that the simple program presented here can be used to match

real glacier surges to the first order of magnitude by suitable choice of the unknown parameters. Higher order approximations should be possible by refinements to the existing model. The matching of the model with real glaciers gives a method of determining the unknown parameters. We expect that the flow law and the lubrication functions eventually will be found to be general properties of ice and to be much the same for all temperate glaciers, with minor variations due to other influences such as bedrock properties and geothermal heat flux. The model developed here also provides a new way of treating the large-scale basal sliding of glaciers in which τ_b and V_b are not directly related at a point but are both determined instead by the properties of the whole glacier.

Finally, in our model no special physical conditions other than a and b distinguish surging from nonsurging glaciers. All glaciers are subject to the same laws. Some glaciers for their given situation reach the stage for which, through frictional lubrication, the basal sliding becomes dominant and the fast

mode sets in. For surging glaciers the accumulation cannot keep up the flow in the fast mode; thus the flow runs out and reverts to the low sliding or slow mode, and the glacier builds up once more.

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Amorphous Solid Water: An X-ray Diffraction Study

Abstract. Water vapor that condenses on a metal surface at 10°K forms a non-crystalline phase of estimated density 1.2 grams per cubic centimeter. X-ray diffraction data of high precision and resolution have been analyzed to yield oxygen atom pair correlation functions. The positional correlation in amorphous solid water extends over only a few molecular radii, and the radial distribution of near-neighbor oxygen atoms in amorphous solid water is qualitatively different from that found in the low-pressure ice modifications. Amorphous solid water is a useful material for liquid water models because it can be studied under conditions such that the effects of static disorder and thermal excitation can be separated.

Despite intensive study for many years, our understanding of the properties of water is primitive. Two factors have contributed heavily to the difficulties encountered. First, water is a polyatomic fluid with strong directional molecular interactions. The available statistical mechanical theories of the liquid state are inadequate for the description of water, and thus theory has not been of much use as a guide to experiment. Second, in the normal condition, at room temperature and atmospheric pressure, positional and orientational disorder in water are hopelessly intermixed with the effects of thermal excitations; hence experimental studies have not yet made it possible to separate the roles of static

disorder and dynamical disorder and have been inadequate to guide the development of a theory of the properties of the liquid.

In view of the situation described, Olander and Rice (1) sought for a model of water that could be studied under conditions such that the effects of static disorder and thermal excitation could be separated. They suggested that amorphous solid water might be such a model material.

Amorphous solid water was first reported by Burton and Oliver (2) in 1935, and a few studies of this material have been reported during the succeeding four decades (3). In most of these studies the solid was produced by the condensation of water vapor on

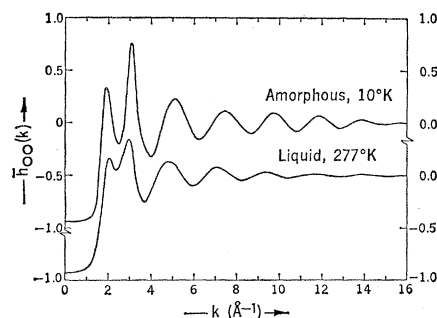


Fig. 1. Structure functions for water descriptive of oxygen atom pair interactions, derived from x-ray diffraction.

metal surfaces under vacuum in the temperature range $77^\circ\text{K} < T < 153^\circ\text{K}$. Immediately above 153°K cubic ice is always the dominant form. Ghormley (4) was the first to use temperatures of deposition below 77°K , and Olander and Rice (1) developed a method of preparation in the temperature range $20^\circ\text{K} < T < 55^\circ\text{K}$ in which the deposits were completely free of crystalline ice. Olander and Rice emphasized the importance of slow deposition and very low temperature; it now appears that most deposits obtained at or above 77°K may have been contaminated with crystalline ice.

We here report the first (5) x-ray diffraction study of pure amorphous solid water at 10°K . The solid was produced by the very slow (~ 4 mg/hour) condensation of water vapor on the horizontal surface of a copper single crystal attached to a liquid-helium Dewar and mounted in an x-ray diffractometer designed for the study of noncrystalline materials (6). The surface (2 by 2 cm) of the copper crystal was carefully aligned to minimize Bragg scattering, and deposition was ended (after 2 weeks) when the sample had reached a thickness of about 1 mm. The diffraction pattern was measured with the use of a divergent beam of $\text{MoK}\alpha$ x-rays, with a graphite monochromator mounted in the diffracted beam. The measurements were carried out over a period of 15 days, during which time no systematic changes in the diffraction pattern were observed. In addition to the study at 10°K reported here, we have also carried out two diffraction measurements of the amorphous material at 77°K . Analysis of the 77°K data, although as yet incomplete, indicates no qualitative changes in the structure of amorphous solid water from that re-

ported here for the lower temperature.

From the x-ray data, structure and correlation functions descriptive of molecular centers (oxygen atoms) have been derived. The results are shown in Figs. 1 and 2, together with the corresponding curves for liquid water (7) near the melting point. The structure function, $h_{00}(k)$, for amorphous solid water (Fig. 1) shows no trace of the sharp Bragg peaks characteristic of crystalline materials.

Oxygen atom pair correlation functions, $h_{00}(r)$, for amorphous solid and liquid water are compared in Fig. 2. Significant features of the curve for amorphous solid water may be summarized as follows:

1) The positional correlation between oxygen atoms extends over only a few molecular radii.

2) The first peak in $h_{00}(r)$, characteristic of nearest neighbors, is completely resolved, and can be described by a single Gaussian distance distribution centered at 2.76 \AA with a root-mean-square variation of 0.1 \AA . The area under this peak corresponds to four oxygen atom pair interactions.

3) A sharp maximum at 3.3 \AA corresponding to about one oxygen atom pair is clearly resolved. Since for tetrahedral coordination interactions with second neighbors are centered around 4.5 \AA (where a well-defined maximum is observed in Fig. 2), we conclude that this peak is part of a complex first-coordination sphere.

The first and third conclusions stated above indicate that the amorphous solid material is distinctly different from the low-pressure ice phases I_H and I_C . Furthermore, these crystalline phases have densities near 0.93 g cm^{-3} , whereas we estimate [from the initial slope of $rh(r)$] that the microscopic density of the amorphous material is of the order of 1.2 g cm^{-3} .

In the correlation function for liquid water, the upper bound of the first maximum is not well resolved, and it is not clear whether the barely resolved shoulder near 3.6 \AA can be related to the peak at 3.3 \AA in the curve for the amorphous material. Otherwise, the correlation functions for amorphous solid and liquid water (Fig. 2) show many similarities, the maxima in the curve for liquid water being shifted to slightly larger distances and very much broadened by comparison with the positions of the maxima in the curve for amorphous solid water. Narten and

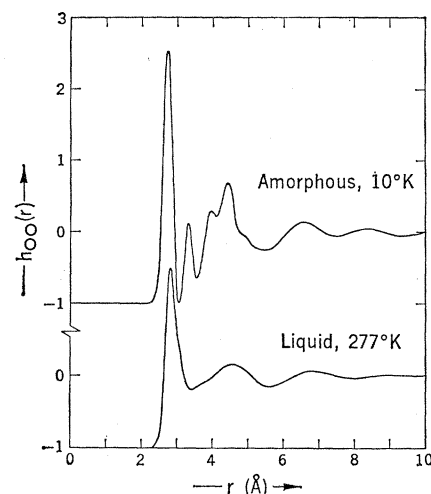


Fig. 2. Correlation functions for molecular centers (oxygen atoms). The peak near 3.3 \AA is a unique feature of amorphous solid water.

Levy have shown (8) that in the liquid, as in the amorphous material, the first coordination shell of a water molecule is complex and cannot be described by tetrahedral coordination alone. Additional evidence in support of a similarity between liquid and amorphous solid water has been obtained from ongoing spectroscopic studies (9).

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10. X-ray data collection and reduction were done at Oak Ridge National Laboratory (operated by Union Carbide Corporation for the U.S. Atomic Energy Commission). C.G.V. and S.A.R. were supported under NSF grant GP 32910X.

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