

Liquid State of Low-Density Pressure-Amorphized Ice above Its T_g

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Experiments using a blunted conical indenter show that the low-density amorphous solid form of pressure-amorphized ice deforms under load and behaves like a viscous liquid near 143 K, much before its rapid crystallization to cubic ice. Since a mechanical stress biases the molecular diffusion of a fluid undergoing a Newtonian deformation, the observation puts into question the basis for an earlier [*J. Phys. Chem.* **1995**, *99*, 11584] conclusion that water near 140 K is no more fluid than cubic ice. It is pointed out that the profile of the dielectric relaxation rate–temperature plot of supercooled water seriously disagrees with that of the computer-simulated diffusion coefficient in the 206–284 K range (0.966–0.984 g/mL density) and that there is an unusually large discrepancy between the recently determined diffusion coefficient of a 33 molecule thick layer of water at 155 K and the value deduced from the equation obtained from computer simulation.

Introduction

Based on their isotopic exchange kinetics studies of vapor-deposited, 0.1 mol % 2-naphthol containing amorphous solid water (ASW), Fisher and Devlin¹ concluded that the dominant mobility in ASW below 125 K is orientational and characterizable as motions of the orientational defects and protons in an essentially completely H-bonded network. They extrapolated these conclusions and inferred that fluidity is not expected for ASW (and other amorphous solid states of water) when warmed above its glass–liquid transition temperature of 136 K,^{2–4} any more than it is expected for cubic ice above its glasslike transition observed near 140 K.⁵ Therefore, the small increase in the heat capacity observed near 136 K for both sintered-and-annealed ASW⁴ and hyperquenched glassy water (HGW)^{2,3} and at 130 K for *Ida*^{6,7} (the low-density amorph obtained by pressure-collapsing hexagonal ice⁶ and cubic ice⁷ at 77 K and then heating to 130 K at 1 bar⁸) may also arise from the random diffusion of L-defects in a completely H-bonded structure. The premise was that this heat capacity increase, ΔC_p , is quantitatively similar to the ΔC_p observed for cubic ice near 140 K,⁵ and various ice clathrates at different temperatures,^{9,10} and is qualitatively similar to that observed for other orientationally disordered solids.^{11,12} Hence, the dominant mobility in an almost completely H-bonded network formed by water molecules in the structure of ASW seemed essentially orientational, characterizable as motions of the Bjerrum^{13,14} and ionic defects.¹⁵

The glass–liquid transition temperature, T_g , refers to that temperature, T , at which the viscosity on *heating* a glass has decreased to $\sim 10^{13}$ P (fluidity = reciprocal viscosity) and the glass softened on one's time scale of observations. At $T > T_g$, the state is said to be fluid. So, the validity of the conclusion¹ may be tested by determining whether water at $T > T_g$ deforms under a load. But there is a difficulty in ascertaining the deformation of ASW and HGW by flow under a concentrated load of an indenter, as their millimeter thick samples are often porous. Annealing in a vacuum reduces this porosity, as well as the strain energy, thus rendering a sample suitable for calorimetric^{2–4} and dielectric studies.^{16,17} (Whether that makes it suitable also for deformation studies is not known.) Alternatively, water's self-diffusion coefficient may be determined

in the as-prepared ASW or HGW samples and be compared against that of cubic ice. This is an indirect approach and one in which the self-diffusion may be considerably accelerated by the internal stresses if the samples are thin films deposited on a substrate to which the material adheres. Scott et al.¹⁸ measured the desorption rate from 33 molecule thick amorphous H₂O and D₂O films and concluded that isotopic mixing occurs as a result of the water molecule's translational diffusion. They deduced that the self-diffusion coefficient of water in these thin films, which presumably contained no cubic ice at 155 K, is $10^{-16 \pm 1}$ m²/s, about 10^6 times the extrapolated value for hexagonal ice at 155 K.¹⁸ They also deduced that the viscosity of water at 155 K is 10^5 P.¹⁸ In view of its estimated viscosity of $\sim 10^{12}$ P at 136 K, this value appears rather low, as it implies that there is a 7 order of magnitude increase in viscosity on cooling from 273 to 155 K and an identical increase on cooling from 155 to 136 K.

On the contrary, *Ida* samples are nonporous and more stable against crystallization on heating at 30 K/min in the 130–148 K range than ASW and HGW (see the DSC scans and discussion in refs 2, 4, 6, and 7), thus making *Ida* suitable for observing its deformation and ultimately penetration by an indenter. The study reported here shows that at $T > T_g$ an indenter deforms and penetrates a ~ 3 mm thick *Ida* sample, and not the cubic or hexagonal ice of a similar thickness at the same temperature. Thus, the state of water at 143 K is mechanically soft, like a viscous liquid in which translational diffusion is required even when the network structure is assumed to be unbroken, as for example in the deformation of SiO₂ and network structure polymers above their respective T_g 's, but not the non-Newtonian deformation of a plastic crystal or the ices.

Experimental Method and Results

A dynamic mechanical analyzer, Perkin-Elmer DMA-7, was originally intended for use in determining the deformation of the samples, as it was used by us before for the internal friction studies and deformation of hexagonal ice approaching the melting point.¹⁹ For deformation studies by DMA-7, a flat sample is mounted on the precooled metal stage, and the linear

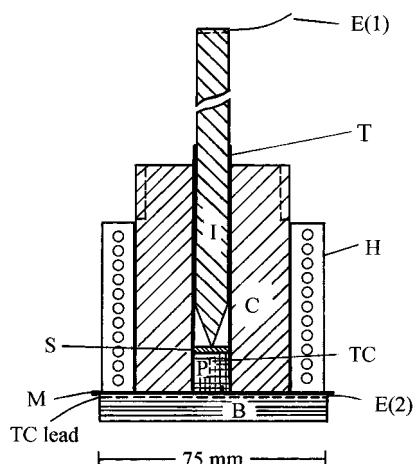


Figure 1. Drawing of the assembly used for preparing the samples and studying their deformation. The labeling is as given in the text.

displacement of a wedge-shaped load resting on the sample is measured continuously during the heating of the sample.

To prepare the sample, a piston–cylinder apparatus was used. It was similar in design to that used earlier for the preparation of high-density amorphous form (hda) by pressurizing hexagonal ice to ~ 20 kbar at 77 K.^{6,7,20–22} The samples were recovered by pushing the plug and the sample through the bottom of the cylinder into liquid N_2 , as in earlier studies.^{6,7,20–22} The hda and lda samples thus recovered were broken and of irregular shape, which made it difficult to place them flat on the cold metal stage below the wedge-shaped load of the DMA-7. In addition the sample's pieces also contained small cracks that had formed during the process of their sudden and explosive extraction through the bottom of the pressure vessel. Some of the samples further cracked during manipulating them on the cold stage and on loading. This made the handling of the sample for deformation studies by DMA-7 tedious and difficult, and after many unsuccessful attempts in manipulating the irregular-shaped, albeit sufficiently large, samples on the precooled stage (occasionally immersed in liquid N_2), the use of the DMA-7 for deformation measurement was discontinued. Another method was devised such as to allow detection of the lda's deformation under the load of an indenter's mass without removing the sample from the piston–cylinder apparatus.

The piston–cylinder apparatus used for preparing hda was then modified, as shown in Figure 1. The cylinder (C) acting as a pressure vessel was lined with a ~ 0.8 mm thick Teflon tube (T), and the diameter of the bottom plug (P) was reduced to provide a radial clearance of 0.5 mm. The latter was jammed into the cylinder by pushing through the Teflon tube liner. The piston's diameter was reduced to provide a radial clearance of $200\ \mu\text{m}$ between it and the Teflon liner at 298 K, and its surface and faces were polished to $1\ \mu\text{m}$ finish, to allow the piston's removal from the cylinder with relative ease at low temperatures. The cylinder was itself slid into an electrically insulated shell (H) containing an axially wound Nichrome heater wire to allow regulated heating of the lda (S) resting atop the plug at the bottom of the cylinder. The shell covered 75% of the vessel's height, allowing the 25% of the top height to accept the wrench needed for the removal of the piston. The entire assembly resting on the metal base (B) was submerged in liquid N_2 contained in an insulated metal container, which in turn was mounted on the platen of a 30 ton hydraulic press and insulated both thermally and electrically (by mica sheet M) from the press. A copper–constantan thermocouple (TC) was placed at a distance of ~ 1 mm from the outer flat surface of the bottom

plug, inside a coaxially drilled bore in it. The hda samples were prepared by pressurizing hexagonal ice at ~ 77 K, and lda was prepared by heating hda to 130 K while maintaining a pressure of ~ 80 bar. After lda had formed, the piston was tapped several times and then removed from the vessel by turning it with pliers.

For penetration experiments, a ~ 10 cm long, ~ 10 mm diameter polished steel rod was tapered to a 45° cone, and the point of the cone was blunted to provide a ~ 0.8 mm diameter flat surface. This acted as an indenter (I), which was kept immersed in liquid N_2 . After the piston was gently pulled out of the cylinder containing the sample under study, the indenter (I) was inserted through the Teflon liner (T) with a radial clearance of ~ 0.3 mm until it rested on the lda itself resting atop the plug (P) at the bottom of the cylinder. The indenter moved relatively freely through the Teflon liner and exerted a pressure of ~ 10 bar on the sample. The two surfaces, (i) the blunted indenter's (~ 0.8 mm diameter) and (ii) the plug's (~ 12 mm diameter), which sandwiched the sample, acted as parallel plate electrodes of a capacitor. Two electrical leads, one attached to the plug (E_2) and the second to the indenter (E_1), formed the terminals at which the capacitance and resistance for 1 kHz frequency were measured by means of a computer-interfaced General Radio 1689 Digibridge. The sample's temperature was measured to ± 0.2 K, simultaneously with the leads (TC lead). When the indenter, under its own weight, sank into the sample during heating, the capacitance between the two terminals increased first slowly and then rapidly, and the electrical resistance decreased in a similar manner, short-circuiting the two terminals and halting abruptly the data collection. The capacitance of this size sample was < 0.02 pF. To increase the sensitivity of the measurements, the connectors' and leads' capacitance was allowed to remain high, ~ 0.3 pF. It should be stressed that the capacitance reported here is *not* useful for determining the dielectric permittivity of the samples and that electrical resistance measurements could also yield information on the penetrability of the sample, but the resistance at 125 K of the samples was immeasurably high.

The operation of the assembly was tested first by using *cis*-decalin, whose T_g is 134 ± 2 K.²³ A measured volume of *cis*-decalin was injected into the Teflon tube lined pressure vessel at 298 K to provide a ~ 3 mm thick sample on top of the plug. The cylinder was then cooled to ~ 90 K by pouring liquid N_2 on it. The indenter rod already cooled to ~ 77 K was inserted. Electrical connections were made to the GR 1689 assembly and to the temperature measurement and control programmer. The sample was allowed to come to a thermal equilibrium at 125 K, while collecting data, and then heated at 2 K/min from 125 to 160 K. Figure 2 shows a plot of the capacitance against the temperature. It shows a rapid increase at ~ 140 K before short-circuiting. Under its own weight, the indenter penetrated *cis*-decalin's ~ 3 mm thick sample at ~ 140 K.

Next, a ~ 2 mm thick layer of hexagonal ice was formed atop the plug inside the pressure vessel kept in a freezer at 253 K, by injecting a measured amount of water. The surface of the ice formed was convex, and it was melt-flattened by using a warm piston. The indenter at 253 K was inserted and the assembly cooled to ~ 90 K. The capacitance and resistance were then measured during the heating of hexagonal ice. No short-circuiting occurred until 272 K when ice began to partially melt and soften, thus allowing the indenter to reach the plug. The plot of the capacitance measured in this experiment is excluded from Figure 2.

Experiments were then performed in a similar manner on lda. Typical plots of the measured capacitance are shown in Figure

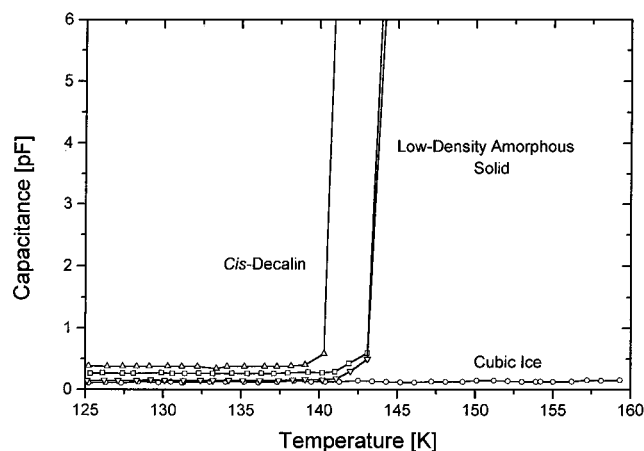


Figure 2. Plots of the capacitance measured against temperature. The almost vertical increase indicates that the sample has been penetrated by the indenter and is fast approaching short circuit.

2. The capacitance increased rapidly near 142 K at 2 K/min heating. After that, the sample short-circuited. Measurements on four different samples gave a temperature of the capacitance increase and short-circuiting as 142 ± 0.8 K. This variation, which is mainly an experimental error, also contains the effects due to the variation in the thickness of the lda samples.

Similar experiments were performed on cubic ice, which was prepared by heating lda.⁶ Since lda became powdery on crystallization by blooming out at 1 bar, it was necessary to prepare cubic ice from lda under pressure. Thus, in one experiment, the pressure on hda was decreased to ~ 0.5 kbar at 77 K, and the sample was then rapidly heated to 160 K, during which the pressure rose to ~ 0.8 kbar at ~ 160 K. The pressure was then reduced to 1 bar, the cylinder cooled to ~ 90 K, the piston removed, and the indenter inserted. The sample was then heated. The measured capacitance is plotted also in Figure 2. There is no indication for deformation of cubic ice up to 160 K. To summarize, lda becomes deformable and penetrable at ~ 142 K, in the same manner as *cis*-decalin at ~ 140 K. This shows that, like other glasses, lda becomes a viscous liquid on heating above its T_g .

We realize that the rate of penetration of a suitably designed indenter could have led to the determination of viscosity, η , of water from the knowledge of the pressure exerted by the indenter and its rate of penetration. Alternatively, calibration of an indenter's penetration rate for a fixed pressure for various liquids of known viscosity near their glass transition temperature over this temperature range could have been used to determine η of water from our experiments. This was not done, because η of a sufficiently stable, supercooled liquid near its T_g in the 130 K range is not available for calibration. So, the viscosity of water near 142 K remains undetermined.

Discussion

Because a large surface-to-volume ratio alters a material's properties, it is worth inquiring whether the self-diffusion coefficient, D , and η of bulk water samples can be justifiably compared with the values deduced for nanometer thick layers deposited on a substrate. Since the magnitudes of D and η determine the overall rate of crystallization, this may be done by examining whether the crystallization kinetics and solid/liquid-phase coexistence of bulk water differ from those of its nanometer thick layers.

Desorption rate measurements of 33 molecules thick layers have yielded D of $10^{-16 \pm 1}$ m²/s, from which the inferred value

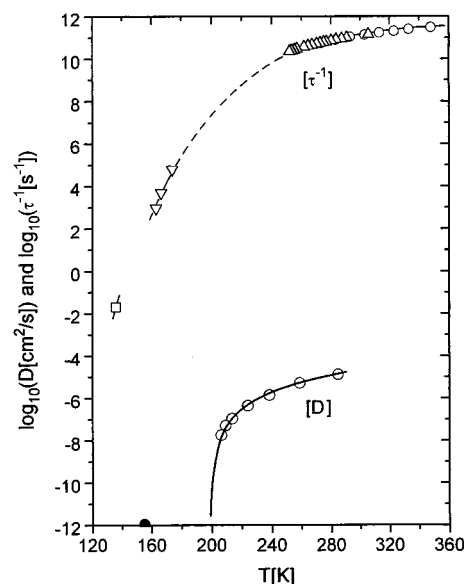


Figure 3. Reciprocal of the average dielectric relaxation time, $\langle \tau \rangle$,²⁸ the self-diffusion coefficient, D , deduced from measurements on a 130 nm thick film¹⁸ (shown by the filled circle at 155 K), and the calculated D of water²⁷ plotted against the temperature.

of η is 10^5 P for water at 155 K.¹⁸ Similar desorption rate measurements of nanometer thick deposited layers also show that the crystallization rate of ASW varies with the layer's thickness and the nature of the substrate^{24,25} and that the crystallization rate constant for 50 nm thick layers deposited on amorphous carbon substrate is twice as much²⁵ as that for 1–5 μm thick samples studied by Hage et al.²⁶ Also, water and cubic ice are found to coexist near 155 K.²⁴ These indicate that D and η of water deduced from measurements on micrometer or millimeter thick samples may not be comparable with those deduced for the nanometer thick layers. Furthermore, the conditions of water/cubic ice coexistence are found to differ in different nanometer thick layer's studies^{24,25} as are their desorption rate against temperature curves.¹⁸ It also seems remarkable that η of water will increase from 10^{-2} P at 273 K to 10^5 P at 155 K¹⁸ and then from 10^5 to 10^{12} P (again 7 orders of magnitude) on cooling to 136 K, the T_g of annealed ASW for 30 K/min heating.⁴ For these reasons, interpretations of experiments on micrometer thick or bulk samples are to be done differently from those for nanometer thick films adhered to a substrate.

Figure 3 shows the temperature dependence of (i) the self-diffusion coefficient, D , as determined from desorption measurements on 33 molecule thick layers of ASW, (ii) D , computer-simulated²⁷ over a temperature range 284.5–206.3 K (density = 0.984–0.966 g/mL) from a model for molecular diffusion, and (iii) $\langle \tau \rangle^{-1}$, the measured average dielectric relaxation rate for bulk samples.²⁸ (Because of the known limitations of the Stokes–Einstein equation, $\langle \tau \rangle$ was not converted to D .) Figure 3 shows that the profile of the $\langle \tau \rangle^{-1}$ plot is inconsistent with the profile of the computer-simulated D plot. The latter follows the equation²⁷ $D = 13.93[(T/198.7) - 1]^{2.73}$, which implies that water's structural arrest occurs at 198.7 K. This is contrary to the experiment. Furthermore, the measured value at 155 K¹⁸ seems inconsistent with that calculated from this equation.

Finally, it should be stressed that the deformation of lda reported here, and the significantly fast self-diffusion in the 33 molecule thick layer of water at 155 K,¹⁸ have little effect on the validity of the conclusion that the Bjerrum (orientational)

defects and ionic defects determine the isotopic exchange kinetics in ASW in the 120–125 K range.¹ Rather, this study and that in ref 18 show that an extrapolation of that conclusion¹ to water above 140 K was misleading and that self-diffusion, which likely involves²⁹ broken H bonds in water above its T_g , is significantly fast.

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