Relaxation Time of Water's High-Density Amorphous Ice Phase

Ove Andersson

Department of Physics, Umeå University, S-901 87 Umeå, Sweden
(Received 15 April 2005; revised manuscript received 28 June 2005; published 9 November 2005)

Dielectric relaxation spectroscopy of pressure amorphized hexagonal ice shows that water's high-density amorphous form relaxes in ~1 s at 140 K and 1 GPa and that the relaxation is virtually unaffected by pressure. This indicates that the amorph is an ultraviscous liquid above 140 K, the same as would be obtained by supercooling water at 1 GPa through its ice VI phase boundary, and that the glass transition temperature is independent of pressure and close to that of amorphous solid water produced at atmospheric pressure.

Water exhibits many unusual properties, such as a density maximum at 4 °C and increasing compressibility and heat capacity upon cooling of the liquid state [1]. Moreover, the viscosity of supercooled water decreases initially upon pressurization, and, at high pressures, its free energy becomes smaller than that of hexagonal ice, which results in melting of the ice upon isothermal pressurization. It is likely that many or all of water's unusual features have a common origin, but still there is no well-established unifying model that can account for its abnormal low temperature behaviors. The finding of two amorphous states of water, high- and low-density amorphous ices, which are produced via pressure induced amorphization at low temperatures [2,3], may provide an important step towards such a model [1]. Existence of these states implies the possibility of two liquid states of water and a second critical point, which has also been observed in simulations [1]. A second critical point at low temperatures may explain the unusual behaviors in properties upon cooling. Positive or negative proofs for the liquid states are, therefore, important for progressing the understanding of water's low temperature properties. Although the amorphous ices have been studied in a vast number of investigations using various probes, experimental results that equivocally establish existence of the liquid counterparts have not been found. Such proof requires the detection of the transition between the two amorphs and the liquid states, i.e., their glass transitions. The finding of the glass transition for the states would also firmly establish the amorphous nature of these states, which has occasionally been questioned. The puzzling lack of unambiguous glass transition anomalies in the amorphous ices has been discussed in a recent critical evaluation of the experimental results [4].

High-density amorphous (HDA) ice is produced by pressurizing hexagonal or cubic ice at 77 K to ~1.5 GPa [2], whereas low-density amorphous (LDA) ice is formed by heating HDA at ambient pressure up to 125 K [3]. Neutron and x-ray scattering studies have shown that HDA converts to LDA isothermally at different temperatures, beginning at ~95 K, in several stages with well defined kinetics at each temperature [5]. In order to study slow intrinsic HDA kinetics at low pressures, it might therefore be necessary to keep HDA below 95 K, or perhaps at even lower temperatures [6], to avoid slow conversion to LDA. At pressures above ~0.1 GPa, the HDA to LDA transition is avoided [7], but at sufficiently high temperature the sample will inevitably crystallize unless special precautions are taken to suppress crystallization, such as using emulsified water [8]. If HDA is heated at high pressures in the 0.5–1.9 GPa range, then it densifies gradually to a lower energy states or "relaxed states of HDA" [9], where the one of highest density has been referred to as very high-density amorphous (VHDA) ice [10]. The structure of HDA at ambient pressure, which has been given complementary descriptions [11,12], contains one interstitial water molecule within the first shell [11], and that of VHDA two interstitial water molecules in a fully tetrahedrally bonded hydrogen network [13].

In this Letter, we report the first, *in situ*, dielectric relaxation spectroscopy study of bulk HDA just below its crystallization point, where a glass transition is expected but has not been observed. For a strongly polar substance, such as water, dielectric spectroscopy is a much more sensitive method than thermal methods for cases where the heat capacity step at the glass transition is small. Consequently, a glass transition that remains undetected or weak in thermal measurements, due to the small heat capacity change, can easily be observed by dielectric measurements. It is here shown that HDA exhibits a relaxation process with a relaxation time τ of ~1 s at 140 K and 1 GPa, indicating that it is in an ultraviscous (ergodic) liquid under these extreme conditions. This result supports qualitatively the recent conclusion [14] of a connection between high-pressurized liquid water and the relaxed state of HDA and indicates that the normal glass transition of HDA is just below 140 K.

The study was performed by using two dielectric cells, one a parallel plate capacitor of nominally 139 pF air capacitance and another concentric electrode capacitor of 19 pF. The change in geometry of the latter up to 1 GPa is insignificant when the pressure is hydrostatic [15]. The

capacitor was placed inside a 37 mm internal diameter Teflon container, which itself closely fitted inside the high-pressure cylinder of internal diameter 45 mm of a high-pressure assembly [16], and then connected to a Solartron 1260 impedance analyzer. The Teflon cell was filled with ca. 25 ml of pure water (tissue-culture grade water supplied by Sigma or water purified by using Milli-Q® Ultrapure WaterSystems) or water doped with a minute amount of KOH (1.7×10^{-4} mole fraction). (The KOH doping decreases the dielectric relaxation time in ice Ih due "to the release of water molecules from the ice rule" [17] so that the relaxation can be studied during the path towards amorphization, but those results will be published elsewhere. In the course of the experiments with the KOH dopant, the unexpected relaxation behavior of HDA was established. As described below, the failure rate in these experiments is very high, and the demonstrated insignificant effect of doping on the relaxation behavior of HDA justifies the use of the data also for the doped water to obtain a more complete picture. The reason for the lack of doping effect might be due to the amorphous structure of HDA, which makes the ice rules irrelevant, and/or segregation of the dopant during pressurization.) The cell was sealed with a tightly fitting, 5 mm thick Teflon cover and the piston inserted. The whole assembly was placed in a vacuum chamber and load was applied [16]. The pressure in the cell was determined from the ratio of load to area to which a correction for friction was applied. This correction had been previously established in a separate, *in situ*, experiment by using the pressure dependence of the resistance of a manganin wire. Temperature was varied by using a built-in helium cryostat equipped with a heater, and pressure on the sample was computer-monitored continuously. Their accuracy was ±0.3 K and ±0.05 GPa.

The high-pressure vessel, containing water at ~0.04 GPa, was cooled from 298 K to about 100 K. Thereafter, its temperature was raised and stabilized at 125–130 K, which took a total of 10 h. The pressure was then raised at the average rate of 0.1 GPa/h. The heating rate was typically 15 K/h and cooling rate 10 K/h, near 150 K. Thus, one set of experiments took a continuous period of several days. The temperature difference between the sample and the Teflon cell wall [differential thermal analysis (DTA)] was measured continuously to determine water's transformation. Because of frequent rapid crystallization during pressurizing from 0.8 to 1.1 GPa, the ice-amorphization range, the success rate in these experiments was only ~20%. In total, five experiments were successful in obtaining HDA ice: three with pure water, which were used for measurements at pressures below 0.1 GPa and at 1 GPa, and two with KOH-doped water, which were used for measurements at 0.4 and 1 GPa.

Figure 1 shows that the capacitance C' measured for 1 MHz frequency increases at 0.75 GPa in a stretched sigmoid shape manner as hexagonal ice at ~130 K amorphizes to a high-density amorphous ice, in agreement
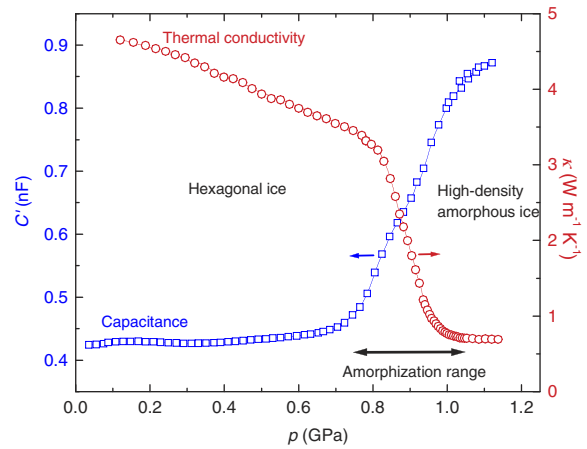

FIG. 1 (color online). The dielectric capacitance at 1 MHz frequency of KOH-doped hexagonal ice (see experimental details) and thermal conductivity at ~130 K [18] is plotted against the pressure.

with previous results [18]. Pressure was then decreased to 1 GPa, and the sample at this pressure was heated while recording the dielectric spectra (Fig. 2). The spectra at 130 K show only the high frequency part of a relaxation peak. As temperature is increased, the peak shifts to a higher frequency and finally appears in the spectra above 140 K. The decrease in the height of the dielectric loss ε'' peak (or C'' peak) at higher temperature shows that both the pure and doped samples (see experimental details) begin to crystallize on heating above ~150 K. Simultaneously recorded DTA data (not provided here) showed a small, slowly growing exothermic effect which reached a local maximum at ~150 K, thus verifying nucleation or onset of a slow crystallization, which accelerated above 150 K. It has been shown previously that VHDA crystallizes to ices VI and XII on slow heating near 1 GPa [19].
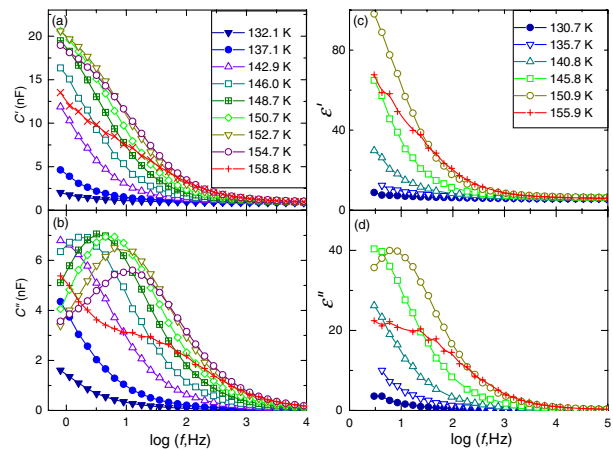

FIG. 2 (color online). The dielectric loss spectra for: (a),(b) KOH-doped HDA and (c),(d) pure HDA at 1 GPa at different T.

In most studies, HDA has been produced by pressure amorphization of ice at 77 K. On heating at pressures above 0.8 GPa [10], it densifies to VHDA in a time-dependent manner [9,10]. Since the pressurizing rate used here is 80 times slower than the rate used before [10] and heating took a 20 times longer period than before [10], we consider that 100% VHDA at 1 GPa was formed here at temperature well below 150 K, where HDA has transformed to ∼90% VHDA using the higher rates (Fig. 3 in Ref. [10]).

The fitting of relaxation functions to the ε' and ε'' spectra of pure and doped VHDA at 150.8 and 148.7 K is shown in Figs. 3(a) and 3(b). The spectra are best described by a symmetrical τ distribution function given by Cole and Cole [20]: $\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (i\omega\tau_{cc})^{1-\alpha}]$, where $\omega(= 2\pi f)$ is the angular frequency and τ_{cc} is the Cole-Cole relaxation time. This type of distribution has been found for water also in the range 273–323 K [21]. The fitted value for the static permittivity ε_0 for the pure amorph is 140 at 146 K.

For both pure and KOH-doped VHDA (Fig. 4), τ is 30 ± 5 ms at 150 K, where τ is calculated from the reciprocal of the ε''-peak frequency, i.e., $\tau = (2\pi f_{peak})^{-1}$. This demonstrates that the minute amount of doping has an insignificant effect on τ. The small value of τ is astonishing, because VHDA has been inferred to be an amorphous solid under these conditions and, therefore, its τ should be greater than 1 ks. Instead, it is of order of the value typically observed for ultraviscous liquids.

Also included in Fig. 4 are the data for τ obtained at 0.41 GPa for doped VHDA. The small difference between τ at 1.0 and 0.41 GPa shows that the activation volume for the relaxation process, $\Delta V^* = RT(\partial \ln\tau/\partial p)_T$, where R is the gas constant, is very small. A calculation yields $\Delta V^* = 0.5$ cm^3 mol^{-1} at 145 K. The unusually weak pressure dependence for τ, and the corresponding small ΔV^*, are in qualitative agreement with viscosity results for water at 273 K [22]. The viscosity decreases on compression up to 0.15 GPa and then increases and reaches the same value at 0.3 GPa as that at 0.1 MPa. The tendency for decrease in viscosity is most pronounced and continues up to higher pressures at the lowest temperature, in the investigated range of 258–283 K, which suggests that at 145 K this tendency would persist and could be even more pronounced.

The relaxation spectra of VHDA on heating at a low pressure (below 0.1 GPa) were also measured. In this case, the sample transformed before a relaxation peak could be observed, in agreement with previous findings that HDA transforms slowly to LDA near 100 K and rapidly around 125 K.

Structures of the state of HDAs with different densities have been found to consist of a tetrahedrally coordinated fully hydrogen-bonded network but with extra (interstitial) H_2O molecules within the first shell of the tetrahedral structure. There is approximately one interstitial H_2O molecule in the structure of HDA, and two interstitial molecules in the structure of VHDA at atmospheric pressure [13]. These (non-hydrogen-bonded) interstitial H_2O molecules distort the tetrahedrally hydrogen-bonded structure of the two amorphs. Such unbonded water molecules are absent in a continuous random network structure model
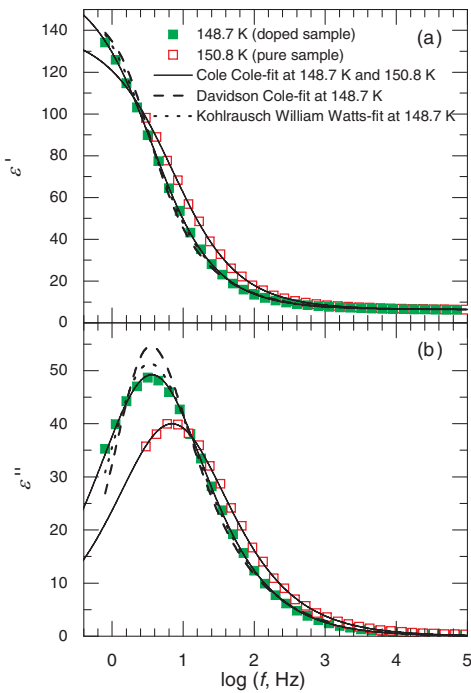

FIG. 3 (color online). Analysis of the permittivity and loss spectra in terms of a distribution of relaxation times for frequencies less than 10^3 Hz, as indicated. For the KOH-doped sample, the measured values were converted to ε' and ε'' by using the cell constant, $C_g = C_\infty$ (KOH-doped water)$/\varepsilon_\infty$ (pure water) at 130 K. The best fit parameters of the Cole-Cole function are $\alpha = 0.29$ and $\varepsilon_0 = 164$, $\varepsilon_\infty = 6.4$, and $\tau_{CC} = 0.044$ s. The corresponding data for pure water at 150.8 K are $\alpha = 0.30$ and $\varepsilon_0 = 132$, $\varepsilon_\infty = 6.4$, and $\tau_{CC} = 0.022$ s.
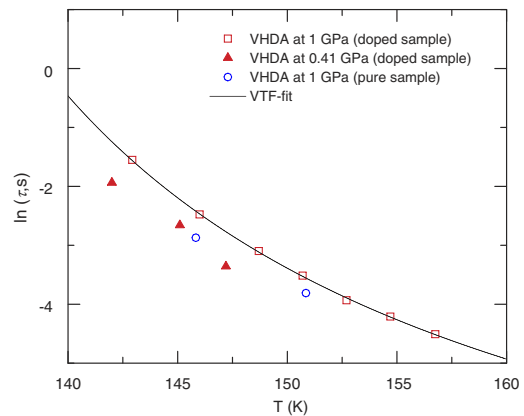

FIG. 4 (color online). The relaxation time at 1 and 0.41 GPa, as indicated. The line is the best fit of the Vogel-Tamman-Fulcher function $\ln\tau = -9.81 + [204.0/(T - 118.2 \text{ K})]$.

P H Y S I C A L   R E V I E W   L E T T E R S

for ambient liquid water, but they are a part of the structure in its two-state model. Because of ~40% higher density of VHDA at 1 GPa, their population is greater, and lack of hydrogen bonding makes them energetically distinguished from those in a tetrahedrally bonded structure. It has been suggested that an increasing occupancy of the interstitial position can account for the structural difference between liquid water, HDA, and VHDA at ambient pressures [13]. The abnormal pressure dependence of the viscosity near the freezing point may, therefore, be associated with this structural change and the accompanying weakening of the hydrogen-bonded structure.

Since both reorientational and translational motions of H_2O molecules in liquid water with tetrahedral bonding require breaking and reforming of hydrogen bonds, the two processes are concomitant. In fact, it has been shown that the Stoke-Einstein relations [23] are valid down into the supercooled liquid temperature range [24,25]. Moreover, it has been shown that the dielectric τ and the structural τ estimated from the T_g endotherm for amorphous solid water obtained by rapid cooling at atmospheric pressure are of the same order of magnitude at ambient pressure and 136 K [26]. The τ is estimated as ~35 s at 136 K [26], which agrees well with results for T_g obtained from a study of the molecular diffusion [27]. The data for VHDA at 1 GPa (Fig. 4) yield $\tau \sim 1$ s by a short extrapolation to 140 K. The structures of HDA, VHDA, and their intermediate states are apparently similar to that of liquid water [11–13]. We therefore conclude that onset of reorientational motions observed at low temperature should be linked to the vitrification of the amorph. This would mean that VHDA exhibits a glass transition before crystallization commences, which is the normal behavior of glassy states.

In summary, the results for the dielectric relaxation of VHDA indicate that VHDA at 1 GPa is in a metastable equilibrium state at temperatures above 140 K, i.e., an ultraviscous water state. This state would be achieved if water at 1 GPa could be supercooled through its ice VI phase boundary to ~140 K. But here the state has been achieved via an irreversible path of pressure amorphization of hexagonal ice. Its τ of ~1 s at 140 K, which is virtually independent of pressure, provides a new picture of the dynamics of the high-density amorph and is a significant step in relating it to liquid water at ambient pressures.

[1] P. G. Debenedetti, J. Phys. Condens. Matter **15**, R1669 (2003).

[2] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **310**, 393 (1984).

[3] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **314**, 76 (1985).

[4] M. M. Koza, B. Geil, H. Schober, and F. Natali, Phys. Chem. Chem. Phys. **7**, 1423 (2005).

[5] C. A. Tulk, C. J. Benmore, J. Urquidi, D. D. Klug, J. Neuefeind, B. Tomberli, and P. A. Egelstaff, Science **297**, 1320 (2002).

[6] M. M. Koza, H. Schober, H. E. Fischer, T. Hansen, and F. Fujara, J. Phys. Condens. Matter **15**, 321 (2003).

[7] G. P. Johari and O. Andersson, J. Chem. Phys. **120**, 6207 (2004).

[8] O. Mishima, J. Chem. Phys. **121**, 3161 (2004).

[9] C. G. Salzmann, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. **6**, 5156 (2004).

[10] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. **3**, 5355 (2001).

[11] J. L. Finney, A. Hallbrucker, I. Kohl, A. K. Soper, and D. T. Bowron, Phys. Rev. Lett. **88**, 225503 (2002).

[12] S. Klotz, G. Hamel, J. S. Loveday, R. J. Nelmes, M. Guthrie, and A. K. Soper, Phys. Rev. Lett. **89**, 285502 (2002).

[13] J. L. Finney, D. T. Bowron, A. K. Soper, T. Loerting, E. Mayer, and A. Hallbrucker, Phys. Rev. Lett. **89**, 205503 (2002).

[14] N. Giovambattista, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. **94**, 107803 (2005).

[15] G. P. Johari, A. Lavergne, and E. Whalley, J. Chem. Phys. **61**, 4292 (1974).

[16] O. Andersson, B. Sundqvist, and G. Bäckström, High Press. Res. **10**, 599 (1992).

[17] S. Kawada, J. Phys. Soc. Jpn. **57**, 3694 (1988).

[18] G. P Johari and O. Andersson, Phys. Rev. B **70**, 184108 (2004).

[19] S. Klotz, G. Hamel, J. S. Loveday, R. J. Nelmes, and M. Guthrie, Z. Kristallogr. **218**, 117 (2003).

[20] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[21] K. Okada, M. Yao, Y. Hiejima, H. Kohno, and Y. Kajihara, J. Chem. Phys. **110**, 3026 (1999).

[22] T. DeFries and J. Jonas, J. Chem. Phys. **66**, 896 (1977).

[23] H. J. V. Tyrrell and K. R. Harris, *Diffusion in Liquids* (Butterworth, London, 1984).

[24] H. R. Pruppacher, J. Chem. Phys. **56**, 101 (1972).

[25] C. Rønne, L. Thrane, P.-O. Åstrand, A. Wallqvist, K. V. Mikkelsen, and S. R. Keiding, J. Chem. Phys. **107**, 5319 (1997).

[26] G. P. Johari, Phys. Chem. Chem. Phys. **7**, 1091 (2005).

[27] R. Souda, Phys. Rev. Lett. **93**, 235502 (2004).