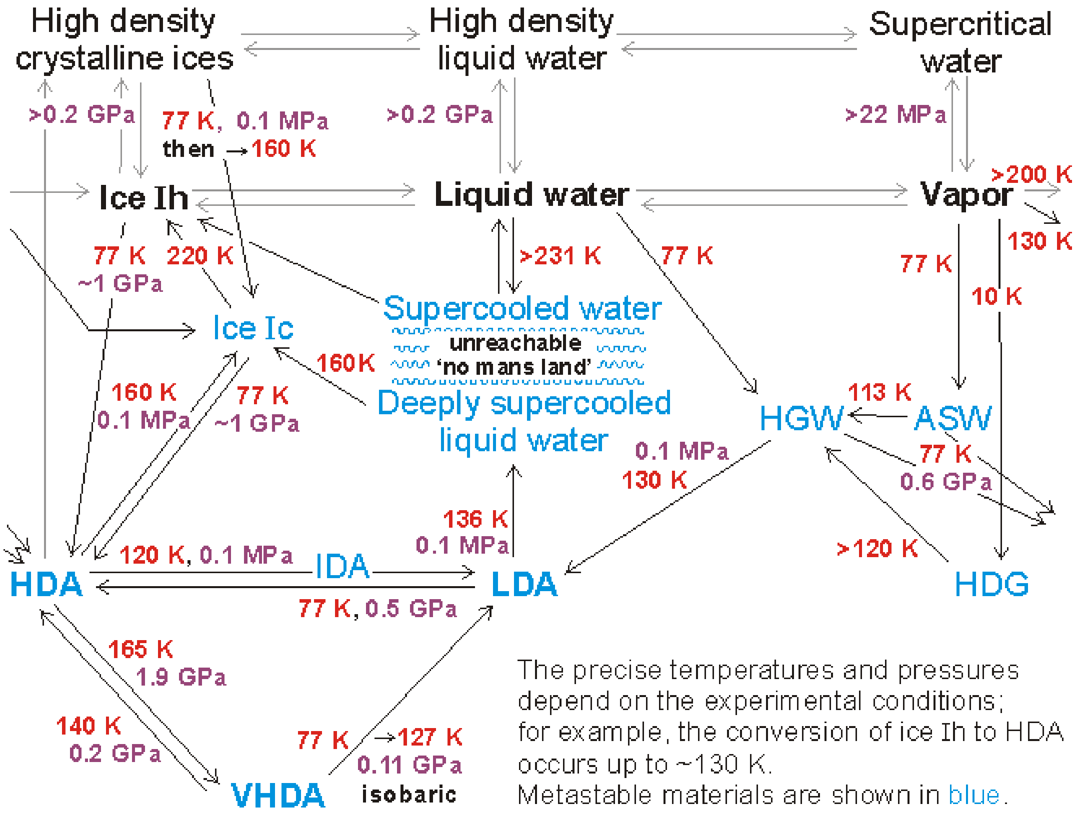
Amorphous Ice and Glassy Water

- **Cold metastable water**
- **Ultraviscous water and the glass transition temperature**
- **Low-density amorphous ice (LDA)**
- **High-density amorphous ice (HDA)**
- **Very-high density amorphous ice (VHDA)**

Cold metastable water

Cooling liquid water below its normal freezing point normally forms solid hexagonal ice. If it is very pure and cooled carefully, the liquid water supercools to about -42 °C.[e] If cooled very rapidly liquid water forms a glass, for example, hyperquenched glassy water (HGW, [312e]). HGW is formed by the rapid spraying of a fine jet of µm-sized water droplets into very cold liquefied gas (for example, propane), or onto a very cold solid substrate, about or below 80 K or by cooling capillary tubes containing bulk liquid water (~100 µm diameter) with liquid helium at 4.2 K [1005]. These methods all involve cooling rates of greater than 10^5 K s^{-1}. These glasses have some structural and thermodynamic similarity with liquid water at 273 K, due to their methods of formation and amorphous properties. A similar material is amorphous solid water (ASW), formed from the slow deposition of water vapor, at < 2 nm s^{-1}, on a very cold metal crystal surface below 120 K [900]. ASW (also called low density glass, 0.94 g cm^{-3}) contains voids and dangling hydrogen bonds, which are removed by annealing under vacuum when the glass converts to material indistinguishable from HGW or low density amorphous ice (LDA, 0.94 g cm^{-3}) at slightly higher temperatures. High density glassy water (HDG, 1.1 g cm^{-3}), formed by vapor deposition at 10 K [692] and subject to cosmic ray irradiation,[d] may be the commonest form of water in the universe. Notably, this 10 K ice had greatly increased numbers of water molecules held at van der Waals distances (~3.3 Å), giving it a higher density, which are not present if the vapor is deposited at 77 K. Recently much interest has been shown in the high density amorphous ices, high-density ice (HDA, 1.17 g cm^{-3} at 0.1 MPa) and very-high density ice (VHDA, 1.26 g cm^{-3} at 0.1 MPa), formed from LDA or crystalline ices. These last three amorphous ices (LDA, HDA and VHDA) occupy three distinct megabasins in the energy landscape [1719] but are not required to obey the 'ice rules', may contain a significant number of dangling bonds and their structures may depend on the preparative method and thermodynamic history with well-relaxed (annealed) samples showing higher thermal stability [1953]. Amorphous ices have been reviewed [1122, 1543, 1719] and their vibrational [1202] and diffraction scattering data compared [1546]. It was found by neutron scattering that ASW, LDA and HGW were structurally very similar [1546]. The HDA → LDA phase transition has been examined [1635, 1682].

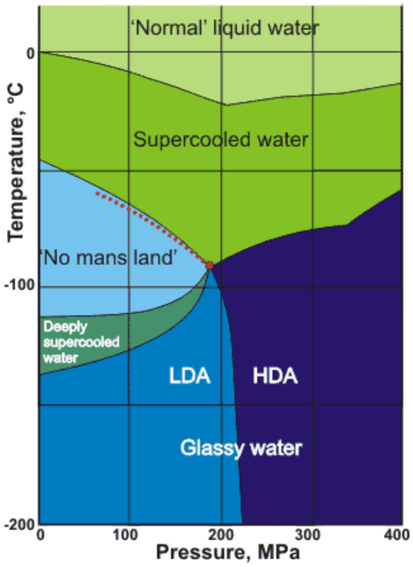
Solid water can thus exist in a number of non-crystalline forms (glasses), which have specific physical characteristics such as density and vibrational spectra. Although often treated as though they are homogeneous, there is no support for this assumption with many natural glasses being clearly heterogeneous on the nano or micro scale with two or more separate phases [993]. As amorphous material, they mostly behave as glasses, which behave as liquid depending on the time scale of observation. Many, but not all, of the transformations are shown below (mostly from [569]). All the amorphous solids can be recovered to ambient pressure (0.1 MPa) at 77 K (liquid nitrogen) where they are (meta)stable for extended periods. While different preparations of the same density may have similar properties, it is likely that materials prepared by very different routes may differ. Some may simply be mechanically collapsed ice whereas others may have structures related to liquid water [1682], with transformations between these forms on annealing being possible but not obligatory. There is no evidence that any of these amorphous ices are actually microcrystalline although they are sometimes proposed as such. There are comprehensive reviews of the amorphous phases of ice and their transitions [569, 2033], an interesting simulation study of this polymorphism [590] and a critical review of the experimental data; particularly the diffraction data [1544].



The precise temperatures and pressures depend on the experimental conditions; for example, the conversion of ice Ih to HDA occurs up to ~130 K.
Metastable materials are shown in blue.

[Back to Top]

Ultraviscous water and the glass transition temperature



The metastable phase diagram above is mainly guesswork, based on the few data available. The 'phases' may be stable for hours or days. Metastable 'phase lines' may move with the direction and time taken of condition changes. The red dot represents a (disputed) position for the second critical point of water [580]. The line where there is maximum fluctuations (the 'Widom' line) is disputed but may follow close to the upper bound of 'No man's land' and end in thesecond critical point at higher temperature and lower pressure than given above as indicated by the dotted line.Liquid water also changes structure at about 200 MPa and possible interference by VHDA is neglected although its phase line is unknown.

A highly viscous deeply supercooled liquid water phase can be formed from either solid LDA or solid HDA indicating an extension of 'normal' supercooled liquid water with structural similarities. The transformation occurs on warming amorphous LDA to about 136 K [74, 137] or heating solid HDA at 1 GPa from approximately 130 K [1770]. The transformation of HDA is reversible with the low-temperature high-density liquid water phase vitrifying on subsequent cooling [1770]. X-ray diffraction has shown the transition of ultraviscous liquid phases of LDA and HDA at about 140 K and 0.2 GPa [1762]. Ultraviscous liquid HDA can exist down to 116 K under ambient pressure [2048].

This ultraviscous deeply supercooled water has a consistency variously described as "soft toffee" [312c] or "molten sherbet" [868], has a viscosity 15 orders of magnitude greater than the normal liquid [1840] but still has a million-fold greater self-diffusion (at the still very low values of 2.2 x 10^{-19} m^2 s^{-1} at 150 K [334] and ~1 x 10^{-16} m^2 s^{-1} at 160 K [1840]) than crystalline ice. The hundred-fold higher viscosity than that expected from its diffusivity may indicate the presence of long-lived crystallites within the deeply supercooled liquid [868]. The relationship between these supercooled waters is not easily investigated as there is an unobtainable 'no man's land' in the physical conditions where no liquid phase can be found [1903]; although ESR indicates that a small fraction of the water molecules may be 'free' coexisting with cubic ice between about 160-230 K [1005]. The very existence of deeply supercooled liquid water, between about 136-160 K, is evidence that the glass transition temperature is the lower of those proposed (136 K, [312]), although characterized by only a small change in specific heat due to the high degree of strong hydrogen bonding in the liquid. Deeply supercooled low density liquid water is one of the strongest liquids known with heat capacity steps of < 1 JK^{-1}. Deeply supercooled high density liquid water gives a different glass transition temperature of 116 K [2048].

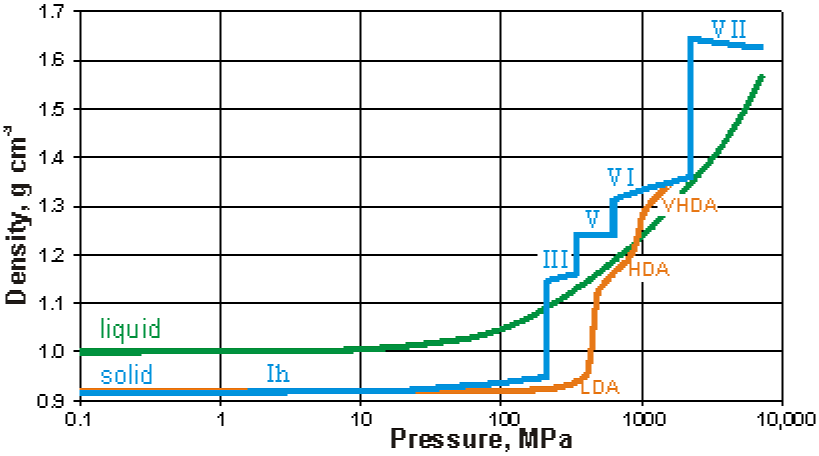
Deeply supercooled liquid water may be formed when amorphous ices are 'annealed' at temperatures above 136 K. This lower density deeply supercooled liquid water is a good solvent for inert gas (Xenon) atoms but a very poor solvent for salt (LiCl) [1120]. In addition, it has an excess entropy(1-2 kJ mol^{-1} K^{-1}) much smaller than the entropy difference between liquid water and crystalline ice at 0 °C (22 mol^{-1} K^{-1}) and an enthalpy of crystallization at 150 K (~1.35 kJ mol^{-1}) also much smaller than the heat of crystallization of liquid water (~6 kJ mol^{-1}) both indicating a high degree of tetrahedral order via intermolecular hydrogen bonding [1840].These properties indicate ES-like qualities and elsewhere I present a possible molecular explanation. At higher temperatures (~165 K) LiCl becomes very soluble, at high concentrations forming a deeply supercooled solution, as its interactions with ultraviscous water overcome the strong water-water interactions present at lower temperatures [1225]. [**Back to Top** ▲]

Low-density amorphous ice (LDA)

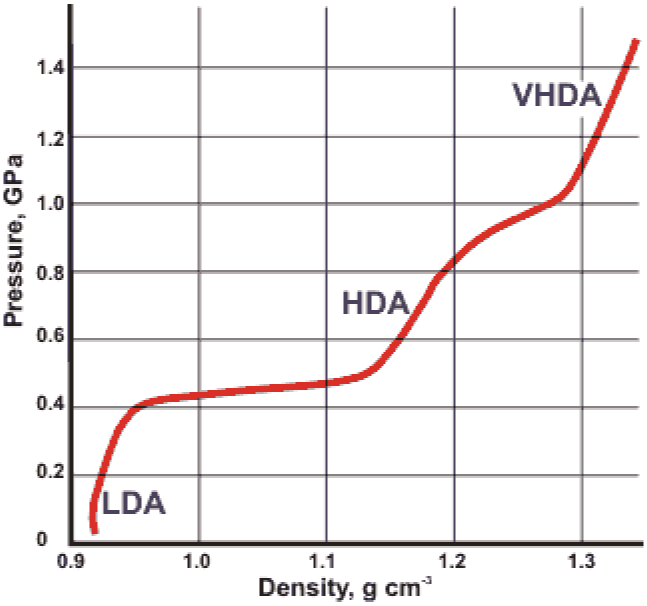
LDA may be prepared from glassy water, as above, or by warming high-density amorphous ice (HDA) to just above 120 K at atmospheric pressure (Note however that some preparations of LDA differ from others; in particular, LDA-I is obtained by isobaric warming of HDA at ambient pressure and LDA-II is obtained by isothermal decompression of VHDA at 143 K). It is stable for months at 77 K and ambient pressure but transforms into cubic ice at about 150-160 K. The structure is unknown but consistent with LDA having an open structure (primarily like ES) and structurally [718, 1284] and thermodynamically related to supercooled liquid water. It has a similar density to ES of 0.94 g cm^{-3} (LDA of D_2O has a density of 1.04 g cm^{-3} at 0.1 MPa), and has tetrahedrally arranged hydrogen-bonded water molecules with four nearest-neighbors and clathrate cages (evidence presented elsewhere). The dielectric relaxation time for LDA is 100-1000 seconds at 130 K, which is two orders of magnitude greater than that of VHDA, and indicates that the ice rules are preventing more rapid orientational mobility [1447] similar to that found in the crystalline ices. The oxygen pair correlation function is similar to that of supercooled liquid water [43], but the thermal conductivity behavior appears to differ [617] with LDA showing behavior more similar to a crystalline material rather than an amorphous glass [617, 1155]. Although similarities exist, LDA is likely to have a somewhat different structure to ASW or HGW, which both show different glass transition behavior. [**Back to Top** ▲]

High-density amorphous ice (HDA)

HDA may be prepared by submitting low-pressure ices (Ih, Ic, XI[a] or LDA) to high pressure (~1.0 GPa, ice Ih; ~0.5 GPa, LDA) at low temperatures (for example at 125 K, see below from [1122]). As with LDA some preparations of HDA differ from others. It is stable for months at 77 K and ambient pressure. HDA has a density of 1.17 g cm^{-3} at 0.1 MPa (1.31 g cm^{-3} at 1.0 GPa; HDA of D_2O has density of 1.30 g cm^{-3} at 0.1 MPa). The structure is unknown and varies between preparations and probably consists of a mixture of constrained frozen material. The material appears to be heterogeneous on a length scale of nanometers [995]. However, the available data is not inconsistent with HDA (made from LDA) having primarily the structure of crushed CS; the main feature appearing to be a puckering (collapsing) that increase the number of water molecules in the first coordination shell.[b]



Note that the liquid water (from the IAPWS-95 equations [540]) and ice data is from the phase line and the temperature varies whereas the amorphous ice line is variation with pressure only.



The collapsing puckering of convex clathrate-type structures in the LDA → HDA conversion involves a potential energy barrier which may explain the difficulty of the reverse HDA → LDA conversion at low temperatures (for example, 77 K) and sometimes put down as a 'lynch pin' effect due to the presence of the extra (non-hydrogen bonded) water molecule within the inner O···O coordinated shell.[c] Once a clathrate cage has puckered, there exists a larger potential energy barrier to changes in puckering (for example, from a tetrahedral to octahedral arrangement). Therefore as the initial puckering is expected to vary from site to site dependent on the strength (and weakness) of surrounding hydrogen bonding, HDA formed this way is expected to be somewhat disordered. As HDA's structure appears to vary during annealing [394] (producing intermediate density amorphous ices, IDA [718] and in contrast to several early papers describing a first-order (meaning abrupt and direct) transition between LDA and HDA, see [569]), with preparation method [618b] (particularly with respect to time [618c]) and starting material [618d], data from diffraction and vibrational spectroscopy has to be interpreted carefully. A more stable annealed form of HDA, e-HDA, has been prepared by annealing at about 0.2 GPa [1544]. This material appears to be homogeneous, completely converts to ice IX (the low temperature form of ice III) on warming to ~170 K at 100 MPa and is the best candidate for the solid form of high density liquid water [2071]. An interesting property of HDA is that the thermal conductivity decreases from that of ice Ih, ice Ic or LDA during their pressurized densification, as usually the thermal conductivity of materials increases with increasing pressure [618b]. [**Back to Top** ▲]

Very-high density amorphous ice (VHDA)

VHDA (first recognized in 2001 [693]) may be prepared by submitting high-density amorphous ice (HDA) at 77 K to isobaric heating to 160 K at 1.15 GPa [421]. On isobaric annealing of HDA between 0.3 and 1.9 GPa (with temperature increasing from 77 K), VHDA appears to have formed at 0.8 GPa with changes in density at higher pressures being due to elastic compression [935]. The LDA ⇌ e-HDA ⇌ VHDA transitions are reversible [1533]. D_2O behaves similarly to H_2O, but with crystallization, to a mixture of high pressure ices, taking place above 143 K rather than 140 K [1534]. Dielectric spectra indicates that VHDA can form a metastable ultraviscous water state at 1 GPa and above 140 K [1160], but this liquid has unexpected properties compared with liquid water supercooled past the ice VI phase boundary and may be the high density equivalent of the deeply supercooled low-density water described earlier. As VHDA is formed from HDA by a process of structural relaxation (also known as rHDA), it has been considered a more stable form of HDA [845].

It shows a greater extent of structuring than HDA and LDA [675] and is stable for months at 77 K and ambient pressure. It has a density of 1.25 g cm^{-3} at 0.1 MPa (1.37 g cm^{-3} at 1.4 GPa), which may be indicative of the presence of some ring penetration such as occurs in the similarly dense ice six, although a simulation indicates otherwise [747].[c] The dielectric relaxation time for VHDA is a couple of seconds at 130 K, which is two orders of magnitude less than that of LDA, and indicates that the close proximity of non-hydrogen bonded water molecules allow more rapid orientational mobility [1447].

Changes from HDA may occur by increased ordering, producing the more dense structure. Interestingly there is a density-distance paradox with the nearest water-water distances increasing from 2.75 Å to 2.80 Å to 2.83 Å as the density increasess for LDA, HDA and VHDA respectively; this increase due to the increase in the number of non-hydrogen-bonded water molecules in the first hydration shell from zero to one to two respectively [421, 1055], these water molecules easing the network outwards in a manner seen in high-density liquid water. Interestingly, when warmed at different pressures between 0.3 and 2 GPa, VHDA recrystallizes into only the proton disordered ices III, IV, V, XII, VI and VII in order of increasing pressure, but not into the proton ordered phases such as ice II [756] (in apparent contrast to HDA which can form ice IX [932]). Recent molecular dynamics simulation indicates that HDA may evolve continuously into VHDA and densification causes an increase in hydrogen-bonded rings containing 8-10 water molecules, due to more efficient packing [747], like ice-twelve with its 7- and 8- membered rings and similar density. If higher pressure is used (2 - 4 GPa) on HDA then high pressure ices (ice-seven or ice-eight) are formed. VHDA shows structural similarities to high-pressure cold (>0.2 GPa, < 273 K; cooled and supercooled high-density liquid water) and hot water (to 6.5 GPa and 670 K [1001]) but possesses more extensive ordering. Much has been made of the possibility of a phase transition line between supercooled metastable liquid forms of LDA (called low density liquid, LDL) and VHDA (called high density liquid, HDL, and often referred to as the liquid phase of HDA before VHDA was discovered) existing at high pressure. Such a situation is expected to end in a second (metastable) critical point [419, 432, 580]. The existence of this scenario is difficult to prove, and is disputed, but is capable of (but not necessary for) explaining many of the low-temperature anomalies of liquid water. [**Back to Top** ▲]

Footnotes

[a] The transformation with pressure of ice XI (and ice VIII) has been modeled [749]. [Back]

[b] CS has a density of 1.00 and has 1/4 of its water dodecahedra puckered relative to ES (density 0.94 g cm^{-3}). Full puckering of the remaining three water dodecahedra would give a density of 0.94 + 4 x 0.6 = 1.18 g cm^{-3}, which is similar to the density of HDA of 1.17 g cm^{-3}. If this puckering of the water dodecahedra is random with respect to the number of inner water molecules, this would produce a more disordered structure than LDA in line with the thermal conductivity data [617] and the recent finding of HDA's lack of a unique structure [618]. [Back]

[c] The activation energy for the HDA → LDA transition has been estimated as equivalent to about one hydrogen bond [792a], with that for the VHDA → LDA transition being equivalent to about two hydrogen bonds [792b]. The non-hydrogen-bonded water molecules may be due to separate interpenetrating hydrogen bonded networks or a crushed hydrogen bonded structure where nearby water molecules are linked by both hydrogen bonding to third water molecules further away. [Back]

[d] A similar material may be prepared from low density glass by lowering the temperature to 12 K, when irradiated with 2-3 electron Å^{-2} at ambient pressure [957]. A glass of intermediate density

(1.04 g cm^{-3}) has been found using cooling rates of 110-271 K s^{-1} on diamond [972] and by modeling [498], and which may be related to the collapsed structure of water (CS) mentioned elsewhere. [Back]

[e] A review of the supercooling process is given at [1573]. [Back]

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