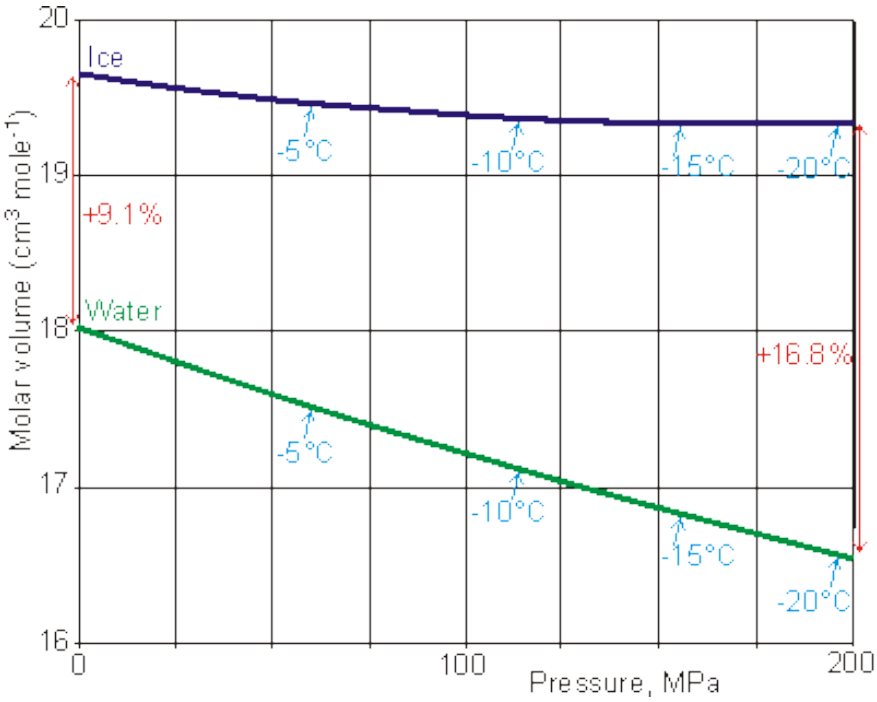
Explanation of the Density Anomalies of Water (D1-D22)

- **The density of ice increases on heating (up to 70 K)**
- **Water shrinks on melting**
- **Pressure reduces ice's melting point**
- **Liquid water has a high density that increases on heating (up to 3.984 °C)**
- **The surface of water is denser than the bulk**
- **Pressure reduces the temperature of maximum density**
- **There is a minimum in the density of supercooled water**
- **Water has a low coefficient of expansion (thermal expansivity)**
- **Water's thermal expansivity reduces increasingly (becoming negative) at low temperatures**
- **Water's thermal expansivity increases with increased pressure**
- **The number of nearest neighbors increases on melting**
- **The number of nearest neighbors increases with temperature**
- **Water has unusually low compressibility**
- **The compressibility drops as temperature increases up to 46.5 °C**
- **There is a maximum in the compressibility-temperature relationship**
- **The speed of sound increases with temperature up to 74 °C**
- **The speed of sound may show a minimum**
- **'Fast sound' is found at high frequencies and shows an discontinuity at higher pressure**
- **NMR spin-lattice relaxation time is very small at low temperatures**
- **The NMR shift increases to a maximum at low (supercool) temperatures**
- **The refractive index of water has a maximum value at just below 0 °C**
- **The change in volume as liquid changes to gas is very large**

D1 The density of ice increases on heating (up to 70 K)

Most solids expand and become less dense when heated. Hexagonal, cubic and amorphous ices all become denser at low temperatures. However, all expand slightly with cooling at all temperatures below about 70 K [209a] with a minimum thermal expansivity at about 33 K (expansion coefficient (α) ~ -0.000003 K^{-1}). This appears to be due to alteration in the net bending motion of three tetrahedral hydrogen bonded molecules with temperature, as higher frequency modes are reduced [209b]. This is a similar but unrelated phenomenon to the maximum density anomaly that occurs in liquid water. Interestingly, the density maximum for hexagonal ice is at about 72 K at ambient pressure and this is the maximum temperature for its catalyzed phase transition to ice XI. Over the range 80-160 K, the density of high-density (HDA) amorphous ice decreases on isobaric heating above ~0.35 GPa but increases below this pressure [1688]. [**Anomalies page : Back to Top**]

D2 Water expands on freezing (compare liquid argon shrinks 12% on freezing)



It is usual for liquids (like ethanol) to contract on freezing and expand on melting. This is because the molecules are in fixed positions within the solid but require more space to move around within the liquid.

When water freezes at 0 °C its volume increases by about 9% under atmospheric pressure. If the melting point is lowered by increased pressure, the increase in volume on freezing is even greater (for example, 16.8% at -20 °C [561]). Opposite is shown the molar volumes of ice and water along the melting point curve [561].

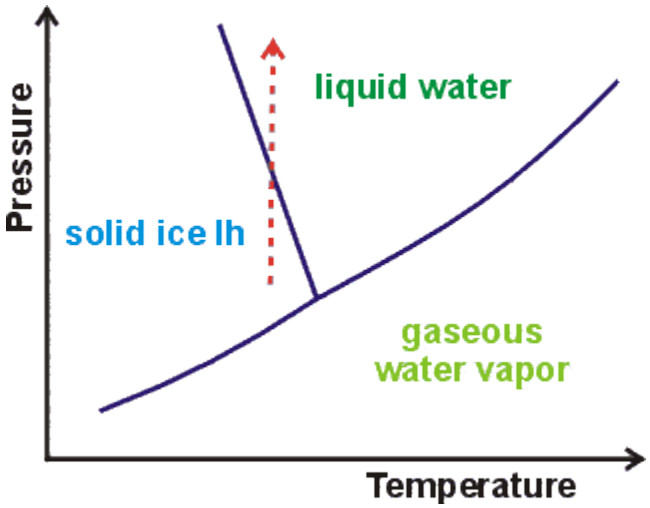
The structure of ice (Ih) is open with a low packing efficiency where all the water molecules are involved in four straight tetrahedrally-oriented hydrogen bonds; for comparison, solid hydrogen sulfide has a face centered cubic closed packed structure with each molecule having twelve nearest neighbors [119]. On melting, some of these ice (Ih) bonds break, others bend and the structure undergoes a partial collapse, like other tetrahedrally arranged solids such as the silica responsible for the Earth's crust floating on the outside of our planet. This is different from what happens with most solids, where the extra movement available in the liquid phase requires more space and therefore melting is accompanied by expansion.

In contrast, it should be noted that the high-pressure ices (ice III, ice V, ice VI and ice VII) all expand on melting to form liquid water (under high pressure). It is the expansion in volume when going from liquid to solid, under ambient pressure, that causes much of the tissue damage in biological organisms on freezing. In contrast, freezing under high pressure directly to the more dense ice VI may cause little structural damage [535].

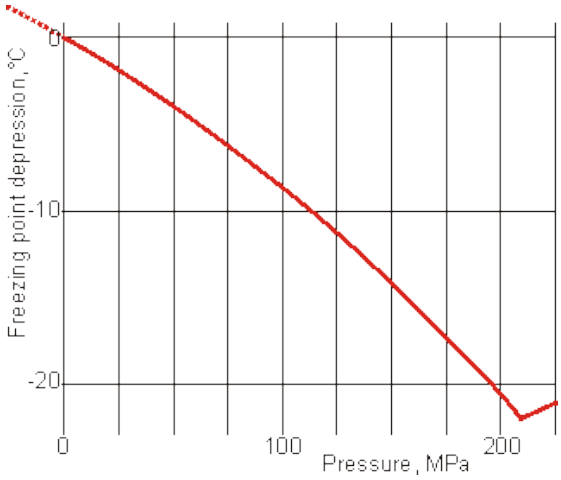
An interesting phenomenon, due to the expansion on freezing, is the formation of thin ice spikes that occasionally grow out of (pure water) ice cubes on freezing [564a]. This phenomenon appears to be a general property of any material that expands on freezing [564b].

As sea ice floats on water, displacing its own weight of water, it is generally thought that when such ice melts (caused for example by global warming), the level of the water as a whole should not rise.[j] However as the ice melts to give fresh (not salty) water which is less dense than the salty sea water, a very small rise in sea level does occur. This has been estimated as 50 μm rise for the 750 km^3 of ice melted each year from our polar ice sheets [1662]. [**Anomalies page : Back to Top**]

D3 Pressure reduces ice's melting point (13.35 MPa gives a melting point of -1 °C)



Increasing pressure normally promotes liquid freezing, shifting the melting point to higher temperatures. This is shown by a forward sloping liquid/solid line in the phase diagram. In water, this line is backward sloping with slope 13.46 MPa K^{-1} at 0 °C, 101.325 kPa. As the pressure increases, the liquid water equilibrium shifts towards a collapsed structure (for example, CS) with higher entropy. This lowers the melting free energy change ($\Delta G=\Delta H-T\Delta S$) such that it will be zero (that is, at the melting point) at a lower temperature.



The minimum temperature that liquid water can exist without ever freezing is -21.985 °C at 209.9 MPa; at higher pressures water freezes to ice-three, ice-five, ice-six or ice-seven at increasing temperatures. Stretching ice has the reverse effect; ice melting at +6.5 °C at about -95 MPa negative pressure within stretched microscopic aqueous pockets in mineral fluorite [243].[a]

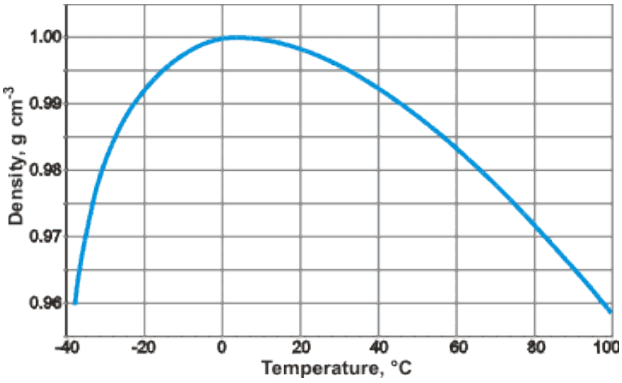
It should be noted that ice skating (or skiing) does not produce sufficient pressure to lower the melting point significantly, except at very sharp edges, or involving powdered ice on the ice surface. The increase in slipperiness is normally generated by frictional heating, perhaps initially involving the ultra-thin surface layer of disorganized and weakly held frozen water (see [1238] for a review). The underlying slipperiness of water and ice can be explained by the two state model [1859] that aids the formation of a slipping plane on confinement. The slipperiness of wet surfaces is greatest when one surface is hydrophilic and the other hydrophobic and least when both surfaces are hydrophilic [2085].

If the increase in volume on freezing is prevented, an increased pressure of up to 25 MPa may be generated in water pipes; easily capable of bursting them in Winter[b]. An interesting question concerns what would happen to water cooled below 0 °C within a vessel that cannot change its volume (isochoric cooling). Clearly if ice forms, its increased volume causes an increase in pressure which would lower the freezing point at least until the lowest melting point (-21.985 °C) is reached at 209.9 MPa.[e] A recent thermodynamic analysis concludes that ice nucleation cannot arise above -109 °C during isochoric cooling [1053], which is close to the upper bound of the realm of deeply supercooled water (-113 °C), so it is unclear if ice would ever freeze in such a (unreal) system.

Melting ice, within a filled and sealed fixed volume, may result in an apparently superheated state where the metastable iso-dense liquid water is stretched, relative to its equilibrium state at the (effectively) negative pressure, due to its cohesiveness. Consequently, the ES⇌CS equilibrium is shifted towards the more-open ES structure. [**Anomalies page : Back to Top**]

D4 Liquid water has a high density that increases on heating (up to 3.984 °C)

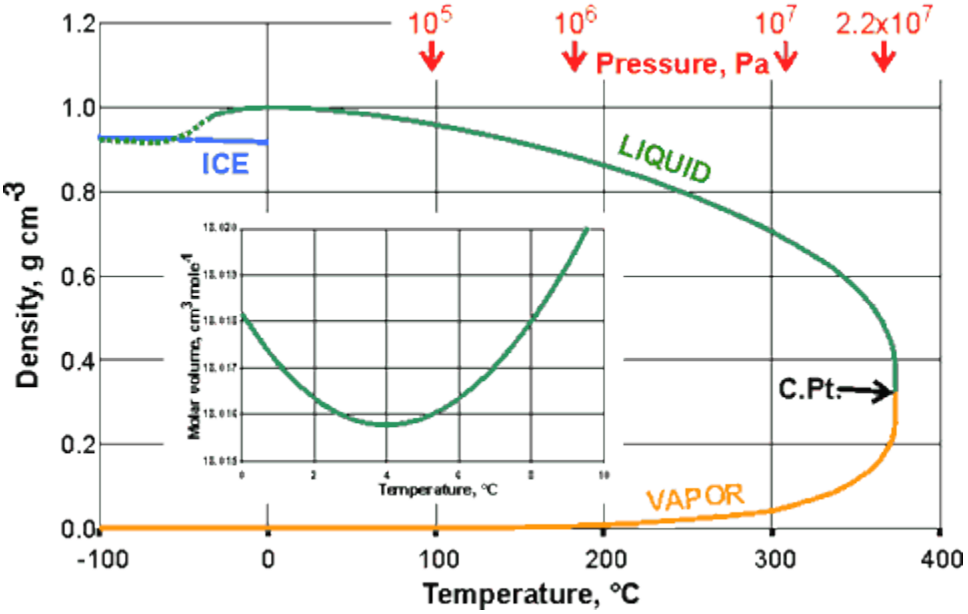
The high density of liquid water is due mainly to the cohesive nature of the hydrogen-bonded network, with each water molecule capable of forming four hydrogen bonds.[g] This reduces the free volume and ensures a relatively high-density, partially compensating for the open nature of the hydrogen-bonded network. Its density, however, is not as great as that of closely packed, isoelectronic, liquid neon (1207 kg m^{-3} at 27 K, with molar volume 92.8% of water). It is usual for liquids to expand when heated, at all temperatures. The anomalous temperature-density behavior of water can be explained as previously [13, 14, 1354] utilizing the range of environments within whole or partially formed clusters with differing degrees of dodecahedral puckering.[c] The zero point kinetic energy of liquid water also has a maximum at ~4 °C due to the density maximum [2038].



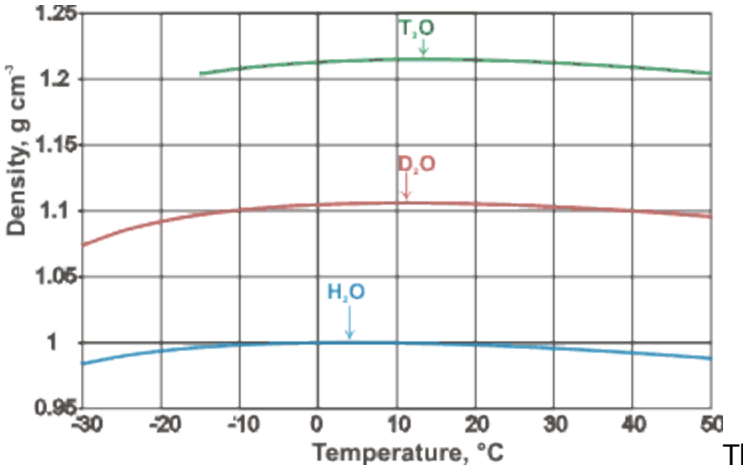
The density maximum (and molar volume minimum) is brought about by the opposing effects of increasing temperature, causing both structural collapse that increases density and thermal expansion that lowers density. Counter-intuitively, the distance between the water molecules decreases [1489] as the density decreases as the supercooling temperature is lowered, the decrease in density being primarily due to the reduction in nearest neighbors. At lower temperatures there is a higher concentration of ES whereas at higher temperatures there is more CS and fragments, but the volume they occupy expands with temperature. The change from ES to CS as the temperature rises is accompanied by positive changes in both entropy and enthalpy due to the less ordered structure and greater hydrogen bond bending respectively.

The density maximum ensures that the bottoms of freezing freshwater lakes generally remain at about 4 °C and unfrozen. The change in density with temperature causes an inversion in cold water systems as the temperature is raised above about 4 °C. Thus in water below about 4 °C, warmer water sinks whereas when above about 4 °C, warmer water rises. As water warms up or cools down through 4 °C, this process causes considerable mixing with useful consequences such as increased gas exchange.

Shown below is the variation of the density of ice, liquid water, supercooled water and water vapor, in equilibrium with the liquid, with temperature (the orthobaric density).

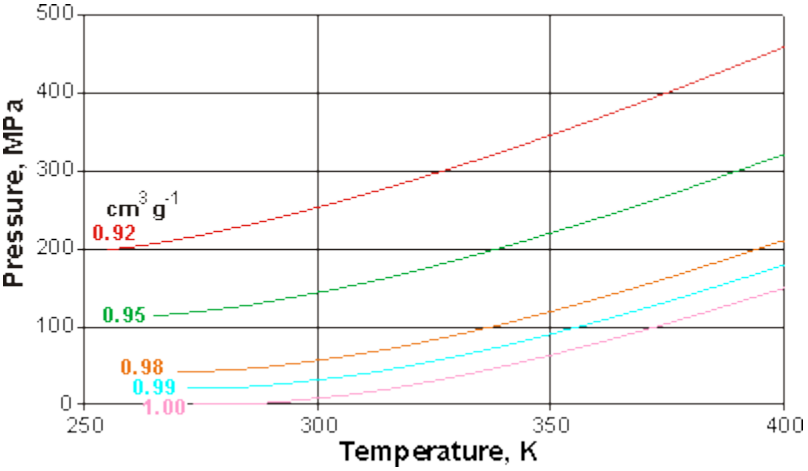


The diagram helps explain why liquid water cannot exist above the critical point (C.Pt.). Also shown (inset) is the variation of the molar volume of liquid water with temperature about the density maximum (at 3.984 °C). Note the unusual and rapid approach of the densities of supercooled water and ice (estimated at -50 °C, 100 kPa [580]) at about the homogeneous nucleation temperature (~-45 °C, 101 kPa). This approach moves to lower temperatures at higher pressures, seemingly absent at ~200 MPa [561] (seebelow, D5).



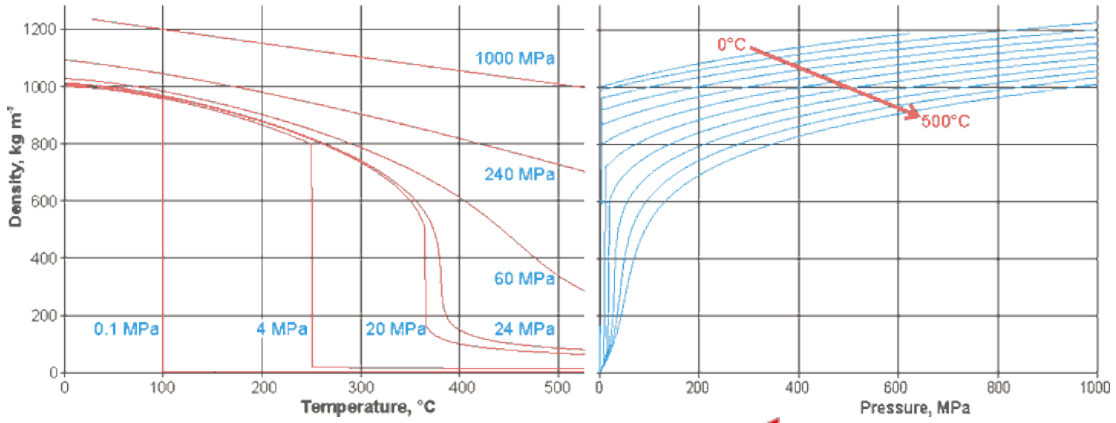
The occurrence of a density maximum, as in water, is sometimes if only rarely found (or predicted) in other liquids , such as He, Te, BeF_2, Si and SiO_2 for a variety of reasons. Opposite is shown the densities and density maxima (mouse over for molar volumes, molar volume minima) of H_2O, D_2O and T_2O compared.

The effect in liquid He^4 is thought due to zero point energy and a similar reason has been put forward for water [1301] although, in practical terms, this presents a related if alternative approach to that above.



Inversely related to changes in densities are the changes in volumes. Opposite are shown pressure-temperature curves of liquid water at constant volume; showing the change in pressure that would occur with temperature using a (theoretically ideal) constant volume container. There is a minimum in the curve only for volumes greater than 0.986 cm^3 g^{-1}. The data were obtained from the IAPWS-95 equations [540].

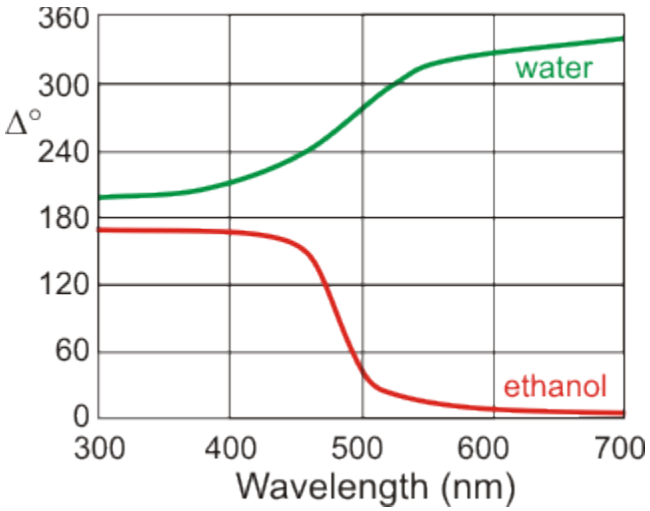
Below shows the variation of density of liquid water with temperature and pressure. At low temperatures the right-hand curves continue (metastably) for several MPa of negative pressure [1887].



[Anomalies page : Back to Top]

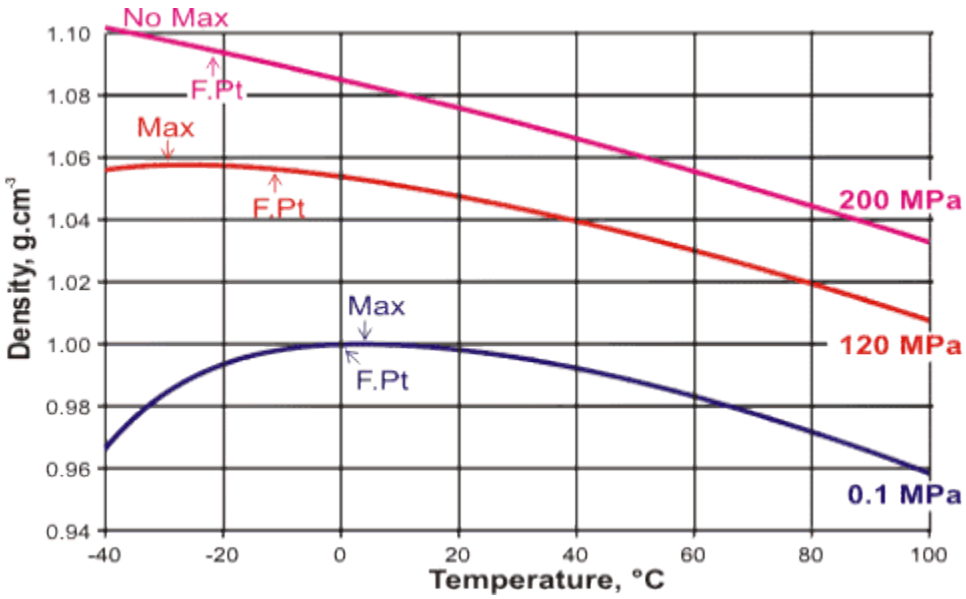
D5 The surface of water is denser than the bulk

Ellipsometry [1482]



The structure of the surface of water generates much controversy and presents a confused picture. However both thermodynamics and experimental evidence suggest that, at lower temperatures and in contrast to the situation with other liquids, the surface in contact with the air is more dense than the bulk liquid. Thermodynamics (seeelsewhere) can be used to derive $\left(\frac{dA}{dV}\right)_{TPn}$; a measure of a difference in density between the surface density and bulk density. This shows that surface water density varies less with temperature than the bulk at low temperatures and equals it at 3.984 °C. The refractive index of the surface of water at 22 °C has been shown to be higher than that of the bulk and opposite in behavior to other liquids (for example, ethanol) [1482]. Thus this surface water appears to behave like water at a lower temperature, and hence has higher density.[i] Related to this phenomenon is the anomalously fast and efficient intermolecular vibrational energy transfer processes at aqueous interfaces [1816]. [Anomalies page : Back to Top]

D6 Increased pressure reduces the temperature of maximum density



Increasing pressure shifts the waterequilibrium towards a more collapsed structure (for example, CS). So, although pressure will increase the density of water at all temperatures (flattening the temperature density curve), there will be a disproportionate effect at lower temperatures.
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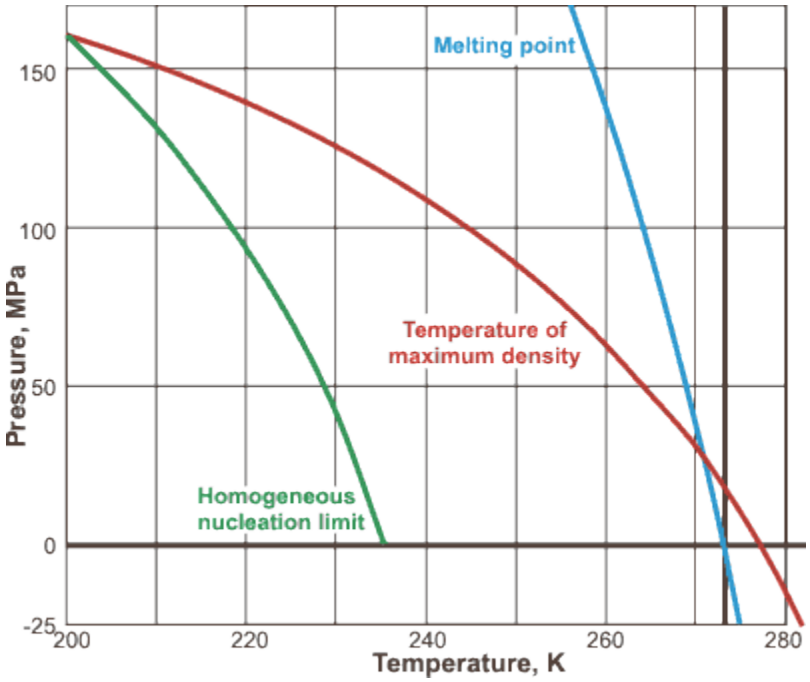
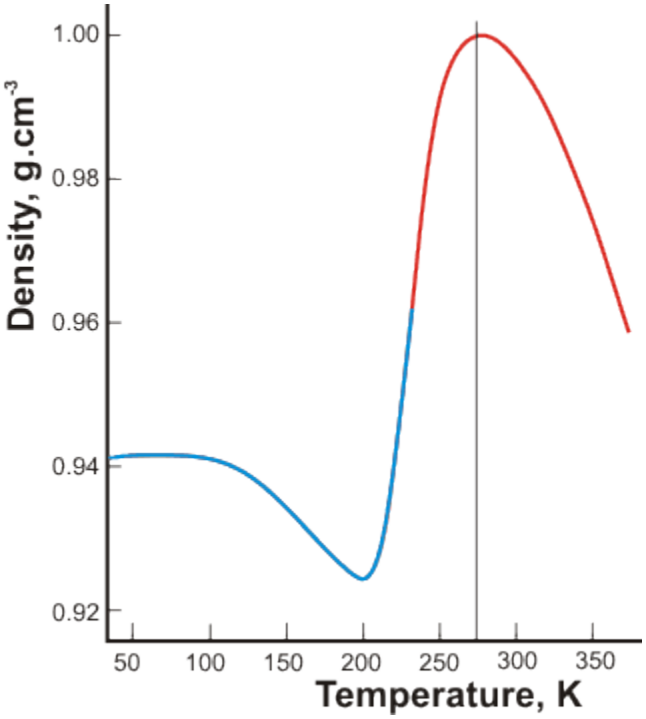


The result is a shift in the temperature of maximum density to lower temperatures. At high enough pressures the density maximum is shifted to below 0 °C (at just over 18.84 MPa). Above 28.33 MPa it cannot be observed above the melting point (now at 270.97 K), except in supercooled water [1860], and it cannot be observed at all above about 200 MPa where it encounters the homogeneous nucleation limit. The stronger and more linear hydrogen bonding in D_2O gives rise to a 25% smaller shift in the temperature of maximum density (from 11.185 °C at 0.1 MPa) with respect to increasing pressure [726].

Under negative pressure (that is, increased stretching of liquid water) the temperature of maximum density increases to about 320 °C (~-180 MPa, 922.8 kg m^{-3}) [1945]. However, the temperature of maximum density shows this as a maximum with respect to pressure in this negative pressure region [419], as the hydrogen bonds are stretched beyond breaking point at higher negative pressures.

A similar effect may be caused by increasing salt concentration, which behaves like increased pressure in breaking up the low-density clusters. Thus in 0.36 molal NaCl the temperature of freezing and maximum density coincide at -1.33 °C. Higher salt concentrations reduce the temperature of maximum density such that it is only accessible in the supercooled liquid. Lowering the temperature of maximum density is not a colligative property as both the nature and concentration of the solute[d] affects the degree of lowering. [**Anomalies page : Back to Top**]

D7 There is a minimum in the density of supercooled water



At a temperature below the maximum density anomaly there must be a minimum density anomaly so long as no phase change occurs, as the density increases with reducing temperature at much lower temperatures. This was first seen in simulations [498] and is expected to lie below the minimum temperature accessible on supercooling (232 K, [215]) and close to where both maximum ES structuring and compressibility occur, with the liquid density close to that ofhexagonal

ice (latterly confirmed [871]). It is evident that most anomalous behavior must involve a quite sudden discontinuity at about the homogeneous nucleation temperature (~228 K, where the densities of supercooled water and ice approach) as the tetrahedrally arranged hydrogen bonding approaches its limit (two acceptor and two donor hydrogen bonds per water molecule) and no further density reduction is possible without an energetically unfavorable stretching (or breaking) of the bonds. By use of optical scattering data of confined water and a model that divides the liquid water into two forms of low and high density, the density minimum has been proposed to lie at 203±5 K [1325], shown opposite, redrawn from [1722] where the blue line show determinations on confined water.

A density minimum at 210 K has been experimentally determined in supercooled D_2O contained in 1-D cylindrical pores of mesoporous silica [1195]. Although possibly related, density values obtained for confined water cannot be taken as necessarily giving the density minimum for the bulk supercooled liquid however [2045]. [**Anomalies page : Back to Top**]

D8 Water has a low thermal expansivity (0.00021/ °C, cf. CCl_4 0.00124/ °C at 20 °C)

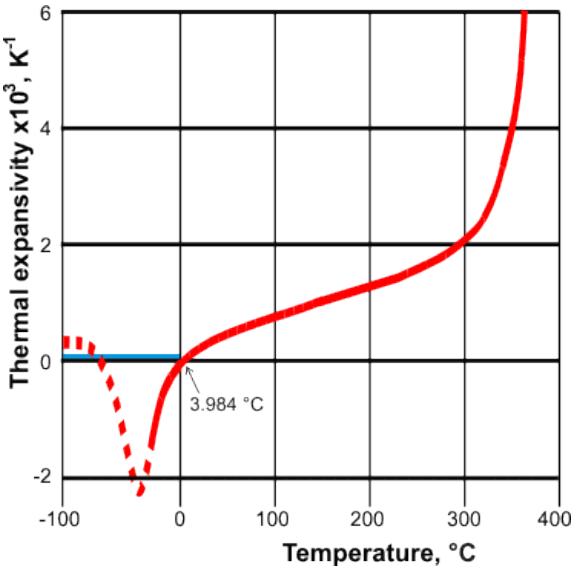
The thermal expansivity is zero at 3.984 °C, being negative below and positive above (see density and expansivityanomalies). As the temperature increases above 3.984 °C, the cluster equilibrium shifts towards the more collapsed structure (for example, CS), which reduces any increase in volume due to the increased kinetic energy of the molecules. Normally the higher the volume a molecule occupies, the larger is the disorder (entropy).

Thermal expansivity (α_P);

$$\alpha_P = [\delta V/\delta T]_P/V \propto <(\Delta V)(\Delta S)>_{TPN}$$

depends on the product of the fluctuations in these factors.[h] In water, however, the more open structure (for example,ES) is also more ordered (that is, as the volume of liquid water increases on lowering the temperature below 3.984 °C, the entropy of liquid water reduces). [**Anomalies page : Back to Top**]

D9 Water's thermal expansivity reduces increasingly (becoming negative) at low temperatures.

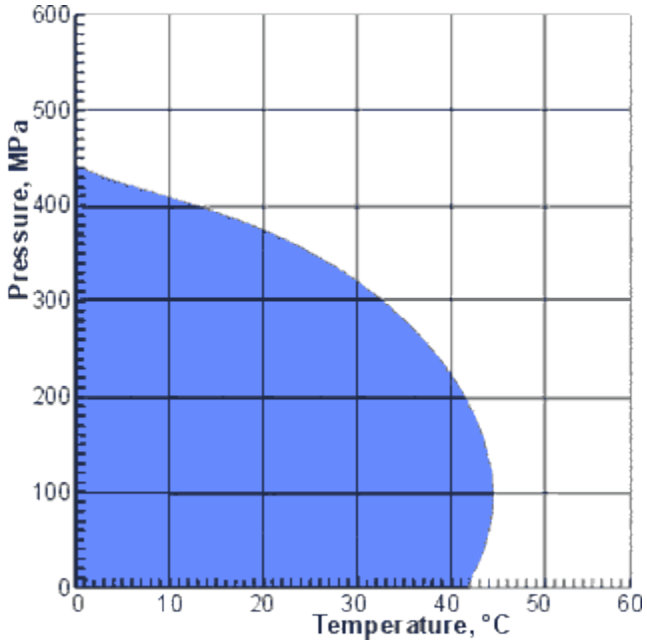


It is usual for liquids to expand increasingly with increased temperature.

Supercooled and cold (< 3.984 °C) liquid water bothcontract on heating [68]. As the temperature decreases, the cluster equilibrium shifts towards the expanded, more open, structure (for example, ES), which more than compensates for any decrease in volume due to the reduction in the kinetic energy of the molecules. It should be noted that this behavior requires that the thermodynamic work (dW) equals -pΔV rather than the usual +pΔV (pressure times change in volume) [404]. The behavior expected, if water acted as most other liquids at lower temperatures, is shown as the dashed line opposite. The blue line shows the expansivity of ice. Also, for water and other materials with negative thermal expansivity, both $\left(\partial S/\partial V\right)_T$ and $\left(\partial S/\partial V\right)_U$ are negative [1147] whereas normally both are positive.

The expansivity-temperature curve crosses the zero expansivity line at the maximum and minimum in the densisity-temperatue curve [1970]. The thermal expansivity reaches a minimum (when most of the liquid water is in the expanded, more open, structure. Then, the expansivity increases to positive values on lowering the temperature further, in line with the more normal behavior of materials, if sufficiently low temperatures could be reached. This minimum phenomenon has been shown to occur in confined liquid water at about 225 K [1604b]. [**Anomalies page : Back to Top**]

D10 Water's thermal expansivity increases with increased pressure.



The thermal expansion of water (α_P) increases with increased pressure up to about 44 °C in contrast to most other liquids where thermal expansion decreases with increased pressure. This is due to the collapsed structure of water having a greater thermal expansivity than the expanded structure and the increasing pressure shifting the equilibrium towards a more collapsed structure.

Opposite is shown (blue area) the range of temperatures and pressures where the thermal expansion increases with increased pressure. Expansivity-temperature curves, drawn at increasing pressures, all cross at ~42 °C ±5 °C (α_P = 0.44 x 10^{-3} K^{-1}) (mouse over Figure above) [1970]. Note

that 42 °C is also the temperature when the compressibility change with temperature has a minimum that is independent of pressure.This follows from the relationship $\left(\frac{\partial \alpha_P}{\partial P}\right)_T = -\left(\frac{\partial K_T}{\partial T}\right)_P$ [2081] [Anomalies page : Back to Top]

D11 The number of nearest neighbors increases on melting

Each water molecule in hexagonal ice has four nearest neighbors. On melting, the partial collapse of the open hydrogen bonded network allows nonbonded molecules to approach more closely so increasing this number. Normally in a liquid the movement of molecules, and the extra space they find themselves in, means that it becomes less likely that they will be found close to each other; for example, argon has exactly twelve nearest neighbors in the solid state but only an average of about ten on melting. [Anomalies page : Back to Top]

D12 Nearest neighbors increase with temperature

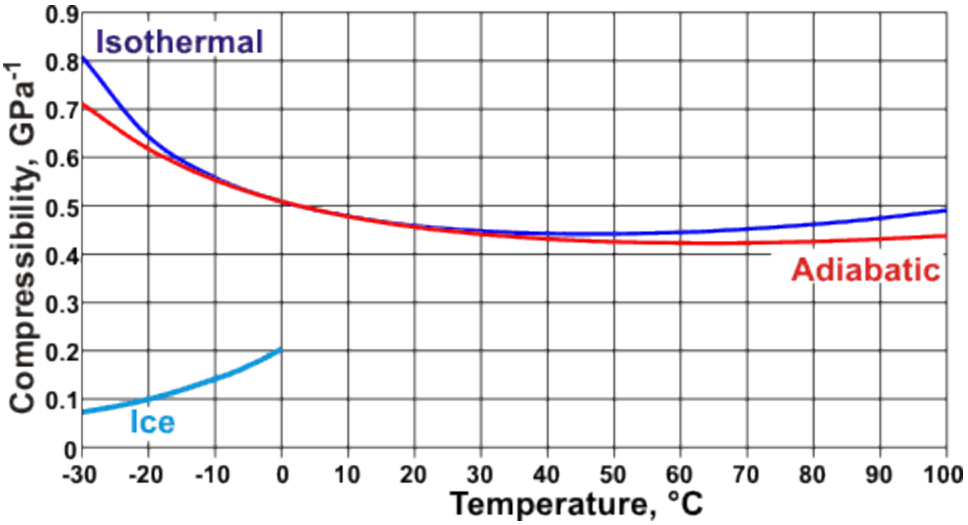
If a water molecule is in a fully hydrogen-bonded structure with strong and straight hydrogen bonds (such as hexagonal ice) then it will only have four nearest neighbors. In the liquid phase, molecules approach more closely due to the partial collapse of the open hydrogen bonded network. As the temperature of liquid water increases, the continuing collapse of the hydrogen bonded network allows nonbonded molecules to approach more closely so increasing the number of nearest neighbors. This is in contrast to normal liquids where the increasing kinetic energy of molecules and space available due to expansion, as the temperature is raised, means that it becomes less likely that molecules will be found close to each other. [Anomalies page : Back to Top]

D13 Water has unusually low compressibility (0.46 GPa^{-1}, compare CCl_4 1.05 GPa^{-1}, at 25 °C)[f]

Although commonly erroneously thought to be incompressible, water has been understood to be compressible for over 250 years [2023]. It may be thought that water should have a high isothermal compressibility ($\kappa_T = -[\delta V/\delta P]_T/V$) as thelarge cavities in liquid water allows plenty of scope for the water structure to collapse under pressure without water molecules approaching close enough to repel each other. The deformation causes the growth in the radial distribution function peak at about 3.5 Å with increasing or pressure [51] (and temperature [50]), due to the collapsing structure. The low compressibility of water is due to water's high-density, again due to the cohesive nature of the extensive hydrogen bonding. This reduces the free space (compared with other liquids) to a greater extent than the contained cavities increase it. At low temperatures D_2O has a higher compressibility than H_2O (for example, 4% higher at 10 °C but only 2% higher at 40 °C [188]) due its stronger hydrogen bonding producing an ES⇌CS equilibrium shifted towards the more-open ESstructure. Also noteworthy is that solutions of highly compressible liquids, such as diethyl ether (1.88 GPa^{-1}) in water, reduce the compressibility of the water, as they occupy its clathrate cavities. Water ices also have low compressibilities, reportedly mainly due to the lengthening of the O-H covalent bond as the O···H-O hydrogen bond is compressed [1809]. [Anomalies page : Back to Top]

D14 Compressibility drops as temperature increases (up to a minimum at about 46.5 °C)

In a typical liquid the compressibility decreases as the structure becomes more compact due to lowered temperature. In water, the cluster equilibrium shifts towards the more open structure (for example, ES) as the temperature is reduced due to it favoring the more ordered structure (that is, ΔG for ES⇌CS becomes more positive). As the water structure is more open at these lower temperatures, the capacity for it to be compressed increases [68].



The adiabatic compressibility lies below the isothermal compressibility except at thetemperature of maximum density where they are equal.

The effect is not a simple dependency on density, however, or else the minimum at 46.5 °C for isothermal (that is, without change in temperature) compressibility[h]

$\kappa_T = -[\delta V/\delta P]_T/V$

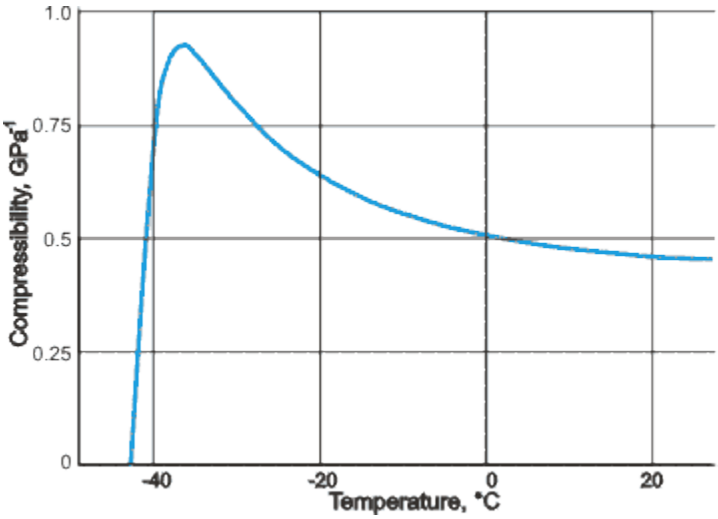
$\kappa_T = [\delta \rho/\delta P]_T/\rho \propto <(\Delta V)^2>_{TPN}$

and the minimum at 64 °C for adiabatic (that is, without loss or gain of heat energy, also called isentropic) compressibility ($\kappa_S = -[\delta V/\delta P]_S/V$ [112]) would both be at the density minimum (4 °C). Relationships between κ_T and κ_S aregiven elsewhere.
Compressibility depends on fluctuations in the specific volume (or density) and these will be large where water molecules fluctuate between being associated with a more open structure, or not, and between the different environments within the water clusters [1899]. At high pressures (for example, ~200 MPa) this compressibility anomaly, although still present, is far less apparent [706]. It remains, however at about the same temperature (~42 °C ±5 °C) [1970], in line with the maximum extent of the diffusion anomaly. Note that 42 °C is also the temperature when all the expansivity-temperature curves, drawn at increasing pressures, cross. This follows from the relationship $\left(\frac{\partial \alpha_P}{\partial P}\right)_T = -\left(\frac{\partial K_T}{\partial T}\right)_P$[2081].

Unusually, the very large differences in compressibility between supercooled water and hexagonal ice increases further as the temperature is lowered even as their densities are approaching similar values.

Some other liquids, such as formamide (also extensively hydrogen bonded), show a compressibility minimum. [**Anomalies page : Back to Top**]

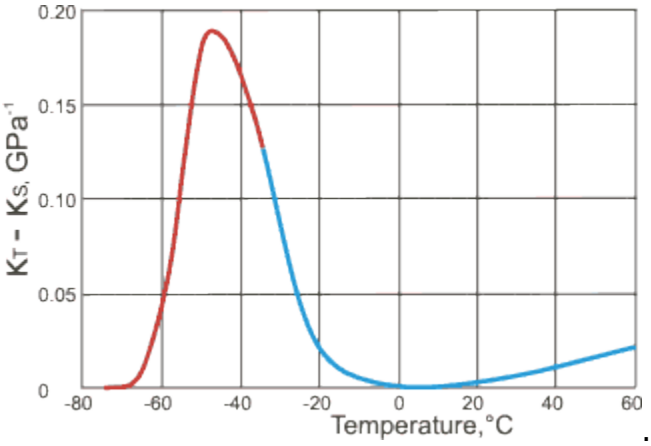
D15 There is a maximum in the compressibility-temperature relationship



At sufficiently low temperature, there must be a maximum in this compressibility-temperature relationship, so long as no phase change occurs, as the compressibility decreases with reducing temperature at much lower temperatures.. This is expected to lie just below the minimum temperature accessible on supercooling (232 K, [215]) close to the temperature of minimum density. The graph right is from [1794].

There is also a maximum in the difference between the adiabatic (κ_T) and isoentropic (κ_S) compressibilities [1982], see below. where the blue line is bulk water and the red line is from confined water, and

$$\kappa_T - \kappa_S = \frac{\alpha^2 T}{\rho C_P}$$



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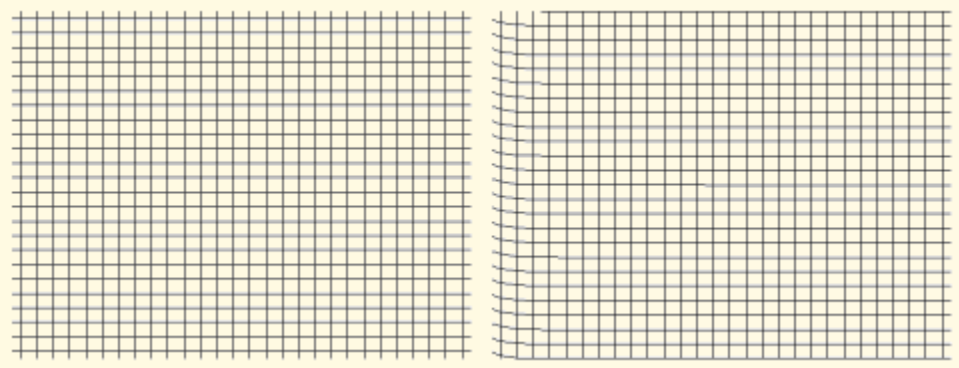
D16 Speed of sound is slow and increases with temperature (up to a maximum at 74 °C)

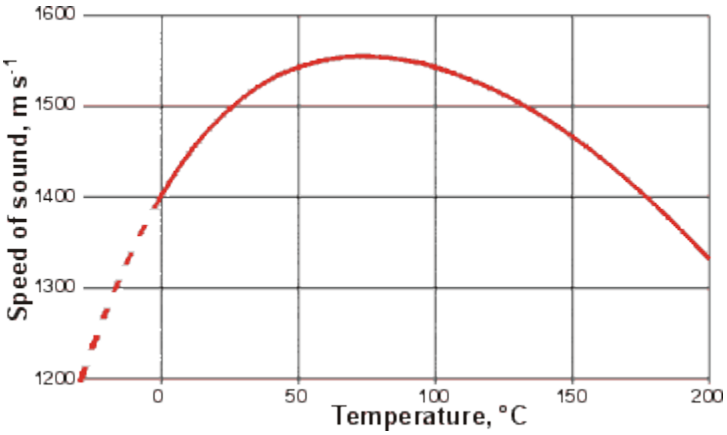


Sound is a longitudinal pressure wave, whereby the energy is propagated as deformations in the media but the molecules then return to their original positions and are not propagated. The propagation of a sound wave depends on the transfer of vibration from one molecule to another. Transverse waves may form at the surface of liquid water (ripples, ocean waves) but do not persist in bulk liquid water.

Longitudinal wave **Transverse wave**

In a typical liquid, the speed of sound is faster (see fast sound) and decreases as the temperature increases, at all temperatures. The speed of sound in water is over four times greater than that in air (~340 m s^{-1}).

The speed (u) is given by $u^2 = 1/\kappa_S\rho = [\delta P/\delta\rho]_S$ [802] where κ_S is the adiabatic compressibility, ρ is the density and P the pressure. The anomalous nature of both these physical properties is described above (compressibility, density).

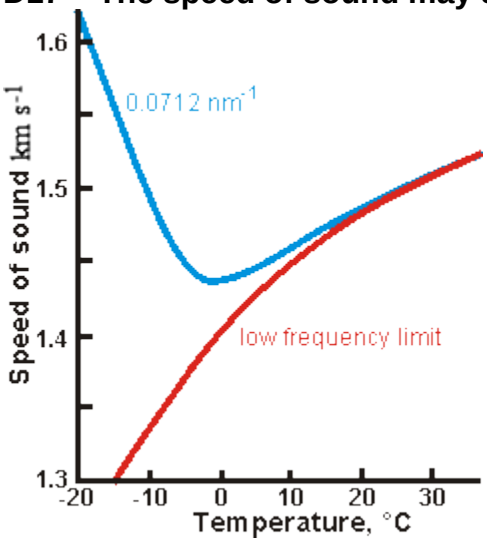


At low temperatures both compressibility and density are high, so causing a lower speed of sound. As the temperature increases the compressibility drops and goes through a minimum whereas the density goes through a maximum and then drops [67]. Combination of these two properties leads to the maximum in the speed of sound. Increasing the pressure increases the speed of sound and shifts the maximum to higher temperatures, both in line with the effect on the density. The supercooled data has been calculated for the graph, right.

The presence of salt causes small shifts in the temperature maximum in line with the Hofmeister series; reducing the temperature at higher concentrations. Ionic kosmotropes cause a slight increase in the temperature maximum at low concentrations [921].

There is a discontinuity in the pressure response to sound velocity that occurs at 290 MPa and 293 K consistent with gradual phase transition to interpenetrating hydrogen bonded networks at the higher pressures, as seen with other anomalies [1374]. The sound velocity in supercritical water is given in [1625]. [**Anomalies page : Back to Top**]

D17 The speed of sound may show a minimum



Depending on the frequency, there may be a minimum in the speed of sound with respect to temperature at low temperatures [568]. Although this may be thought due to compensation in the changes in density decrease and compressibility increase with lowering temperature, this is not apparent in thecalculated data above. It is most likely due to the increasing strength of its hydrogen bonding and consequential transition to 'fast sound' at lower frequencies (see below). The data opposite is from [1151]. There may be a minimum in the speed of sound with respect to density (-12 °C, ~1320 m s^{-1}, ~0.98 g cm^{-3}) at low temperatures with a maximum at even lower density (-12 °C, ~1350 m s^{-1}, ~0.94 g cm^{-3}) [2056].

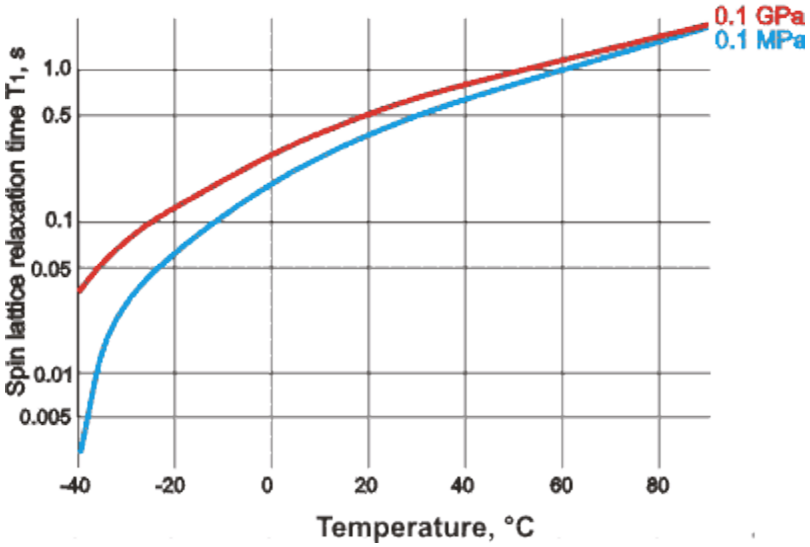
The speed of sound in the oceans has a minimum at about 1000 m where the increase in speed due to increasing pressure balances the decreasing speed with drop in temperature. Sound waves are trapped and propagate horizontally in thisSOFAR channel. [**Anomalies page : Back to Top**]

D18 'Fast sound' is found at high frequencies and shows an discontinuity at higher pressure

Water has a second sound 'anomaly' (called 'fast sound') concerning the speed of sound. Over a range of high frequencies (> 4 nm^{-1}) liquid water behaves as though it is a glassy solid rather than a liquid and sound travels at about twice its normal speed (~3200 m s^{-1}; similar to the speed of sound in ice Ih). There is little effect of temperature below 20 °C [1151]. At lower temperatures the speed of sound increases from its low frequency value towards the high frequency value (i.e. 'fast sound') at lower frequencies, giving rise to a minimum in the temperature-speed of sound relationship [1151] (see above). 'Fast sound' is not a true anomaly as this behavior is what might be expected from a typical liquid, whereas the (hydrodynamic) lower speed of sound (~1500 m s^{-1}) is due to the hydrogen bonding network structure of water.However, there is a discontinuity anomaly at a density of about 1.12 g cm^{-1} (~300 MPa at 273 K) that may indicate a structural rearrangement [644, 655],

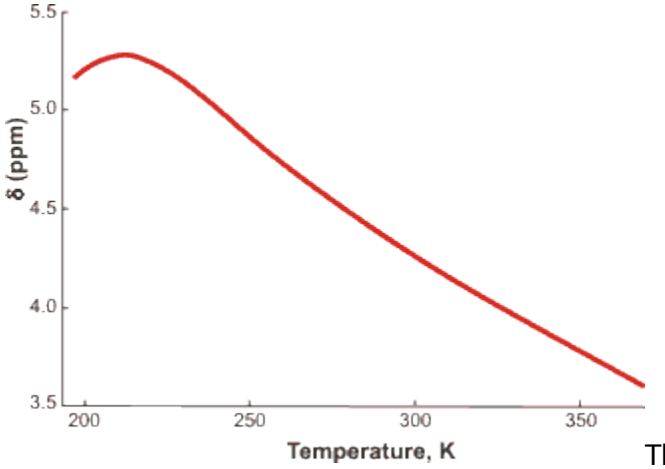
due to the gradual phase transition to interpenetrating hydrogen bonded networks at the higher pressures, as seen with other anomalies. [**Anomalies page : Back to Top**]

D19 NMR spin-lattice relaxation time is very small at low temperatures



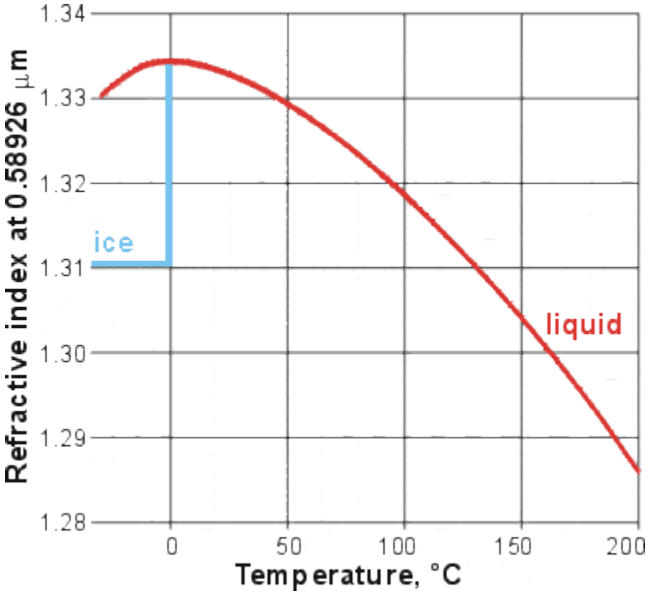
NMR spin-lattice relaxation time depends on the degree of structure. As the water cluster equilibrium shifts towards a stiffer, tetrahedrally organized, structure (for example, ES) as the temperature is lowered, the NMR spin-lattice relaxation time reduces far more than would otherwise be expected [53a]. This effect can be partially reversed by increasing the pressure, which reduces the degree of structure. [**Anomalies page : Back to Top**]

D20 The NMR shift increases to a maximum at low (supercool) temperatures



The NMR shift increases to a maximum at about 214 K in confined water [1496]. It is likely that the same effect will be found in supercooled unconfined water. The variation in NMR chemical shift with temperature correlates with water's hydrogen bonding and its logarithmic temperature derivative is related to the specific heat andits anomaly [1496]. [**Anomalies page : Back to Top**]

D21 The refractive index of water has a maximum value at just below 0 °C.



The refractive index of water (λ = 589.26 nm) rises from an estimated 1.33026 at -30 °C to a maximum value at just below 0 °C (1.33434) before falling ever increasingly to 1.31854 at 100 °C [310]. This may be explained by the mixture model [60] applied to the change from ES to CS as the temperature rises; ES possessing a lower refractive index than CS. Most of the effect is due to thedensity difference between ES and CS. Higher density produces higher refractive index such that the refractive index temperature maximum lies close to the density maximum, with the small difference due to the slightly different effect of temperature on the specific refractions of ES and CS. Although not considered anomalous, it is interesting to note that ice has the lowest refractive index (1.31, λ = 589 nm) of any known crystal.

A related phenomenon is the pressure derivative of the refractive index (isothermal piezo-optic coefficient, $(\delta n/\delta p)_t$), which anomalously shows minima dependent on the wavelength used. [**Anomalies page : Back to Top**]

D22 The change in volume as liquid changes to gas is very large.

Water is one of the lightest gasses but forms a dense liquid. The volume change is the greatest known (except for metals) at 1603.6 fold, at the boiling point and standard atmospheric pressure. This change in volume allows water to be of great use in the steam generation of electrical power. [**Anomalies page : Back to Top**]

Footnotes

[a] There is some dispute over whether such a negative pressure can be reached [917]. [Back]

[b] Pipes burst due to the rapid formation of a network of feathery dendritic ice [1798] enclosing water which then expands on freezing within a now restricted volume to generate the required pressure [354]. The curious phenomenon of hot water pipes bursting more often than cold water pipes ([959, 1416]) is due to the differences in this dendritic ice formation causing blockage in the pipes at low percentage ice formation. [Back]

[c] The change in density is almost mirrored by the size of ortho-positronium bubbles, which are affected by the free volume available and show a minimum at 8 °C [826]. *ortho*-Positronium consists of a positron - electron pair with parallel spins [826], created here by positron irradiation of water. [Back]

[d] The depression in the temperature of maximum density is linearly related to concentration for most solutes (ethanol and methanol are exceptional giving a slight increase in the temperature of maximum density at low concentrations) [1037], as discovered in 1839 by Despretz. Urea solutions behave strangely, producing a temperature of maximum density at up to ten molal concentration, with a minimum temperature of maximum temperature (258.6 K) at about six molal [1506].[Back]

[e] It would be impossible to reach this pressure in a container, unless pressure was also exerted from the outside, due to the pressure induced expansion of the vessel. Water sealed in a steel cylinder in 1871 by Boussingault was still liquid at -18 °C. [Back]

[f] Others take a contrary view, stating that water's compressibility is twice that expected [53b]. This difference is down to the viewpoint and different theoretical expectations. In both cases, water's compressibility is unexpected; either being greater than expected due to water's open structure or less than expected (in spite of its open structure) due to the cohesive nature of its extensive hydrogen bonding. [Back]

[g] In liquid methanol (CH_3OH) the oxygen atoms are 3% closer than they are in liquid water but its density is 21% less than water, due to methanol only able to form only two hydrogen bonds per molecule. [Back]

[h] The full expressions are

$$\kappa_T = -[\delta V/\delta P]_T/V = [\delta \rho/\delta P]_T/\rho = <(\Delta V)^2>_{TPN} / k_B TV$$

$$\alpha_P = [\delta V/\delta T]_P/V = <(\Delta V)(\Delta S)>_{TPN} / k_B TV = <(\Delta V)(\Delta H)>_{TPN} / k_B T^2 V$$

where κ_T, α_P, k_B, P, T, N, ρ, V, H and S are the isothermal compressibility, thermal expansion, Boltzmann constant, pressure, temperature, number of molecules, density, volume, enthalpy and entropy respectively; the <> brackets indicate the fluctuations in the values about their mean values.

(see [1481]) [Back]

[i] A higher refractive index is indicative of higher density or greater hydrogen bond strength (at equal density). Structured water has higher specific refraction and refractive index for its density [60] but the effect of density changes on the refractive index outweighs that of the specific refraction differences due to water structuring; thus, ice has a density of 91.7% of water and refractive index of 98.2% of water. The thermodynamics confuses this view as at 22 °C thermodynamic arguments suggest the surface is less dense than the bulk (if rather less so than other liquids). The opposing views may be reconciled by consideration of the different depths probed by the two methods. [Back]

[j] There is an interesting discussion over the change in height of pure water on the melting of floating ice cubes [1776]. [Back]

Source:http://www1.lsbu.ac.uk/water/explan2.html