Anomalous properties of water

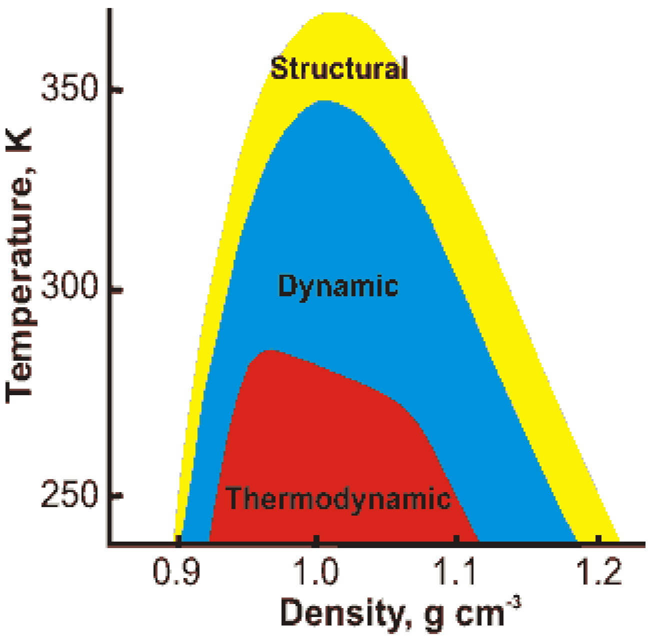
The range of anomalous properties of water

The anomalous properties of water are those where the behavior of liquid water is quite different from what is found with other liquids [1414].[a] Frozen water (ice) also shows anomalies when compared with other solids. Although it is an apparently simple molecule (H_2O), it has a highly complex and anomalous character due to its intra-molecular hydrogen bonding (see [1530] for example). As a gas, water is one of lightest known, as a liquid it is much denser than expected and as a solid it is much lighter than expected when compared with its liquid form. It can be extremely slippery and extremely sticky at the same time.[f] An interesting history of the study of the anomalies of water has been published [1542].

As liquid water is so common-place in our everyday lives, it is often regarded as a 'typical' liquid. In reality, water is most atypical as a liquid, behaving as a quite different material at low temperatures to that when it is hot. It has often been stated (for example, [127]) that life depends on these anomalous properties of water. In particular, the high cohesion between molecules gives it a high freezing and melting point, such that we and our planet are bathed in liquid water. The large heat capacity, high thermal conductivity and high water content in organisms contribute to thermal regulation and prevent local temperature fluctuations, thus allowing us to more easily control our body temperature. The high latent heat of evaporation gives resistance to dehydration and considerable evaporative cooling. Water is an excellent solvent due to its polarity, high dielectric constant and small size, particularly for polar and ionic compounds and salts.[b] It has uniquehydration properties towards biological macromolecules (particularly proteins and nucleic acids) that determine their three-dimensional structures, and hence their functions, in solution. This hydration forms gels that can reversibly undergo the gel-sol phase transitions that underlie many cellular mechanisms [351]. Water ionizes and allows easy proton exchange between molecules, so contributing to the richness of the ionic interactions in biology.

At 4 °C water expands on heating **or** cooling. This density maximum together with the low ice density results in (i) the necessity that all of a body of fresh water (not just its surface) is close to 4 °C before any freezing can occur, (ii) the freezing of rivers, lakes and oceans is from the top down, so permitting survival of the bottom ecology, insulating the water from further freezing, reflecting back sunlight into space and allowing rapid thawing, and (iii) density driven thermal convection causing seasonal mixing in deeper temperate waters carrying life-providing oxygen into the depths. The large heat capacity of the oceans and seas allows them to act as heat reservoirs such that sea temperatures vary only a third as much as land temperatures and so moderate our climate (for example, the Gulf stream carries tropical warmth to northwestern Europe). The compressibility of water reduces the sea level by about 40 m giving us 5% more land [65]. Water's high surface tension plus its expansion on freezing encourages the erosion of rocks to give soil for our agriculture.

Notable amongst the anomalies of water are the opposite properties of hot and cold water, with the anomalous behavior more accentuated at low temperatures where the properties of supercooled water often diverge from those of hexagonal ice.[c] As (supercooled) cold liquid water is heated it shrinks, it becomes less easy to compress, its refractive index increases, the speed of sound within it increases, gases become less soluble and it is easier to heat and conducts heat better. In contrast as hot liquid water is heated it expands, it becomes easier to compress, its refractive index reduces, the speed of sound within it decreases, gases become more soluble and it is harder to heat and a poorer conductor of heat. With increasing pressure, cold water molecules move faster but hot water molecules move slower. Hot water freezes faster than cold water and ice melts when compressed except at high pressures when liquid water freezes when compressed. No other material is commonly found as solid, liquid and gas.[d]



The anomalies of water appear as a hierarchy of effects with different bounds [169]. These are shown indicatively opposite as derived from modeling, not experimental data. The 'Structural' bounds indicate where water is more disordered when compressed, the 'Dynamic' bounds indicate where diffusion increases with density, and the 'Thermodynamic' bounds show where there is a temperature of maximum density; with the data from [169] shifted upwards 38 K to give the correct temperature of maximum density under standard pressure. As density always increases with increasing pressure, a similar relationship holds with pressure along the horizontal axis.

Sometimes apparently unpredictable or unexpected properties of liquid water may be due to variations in the dissolved gas concentrations [1948], a factor that is difficult to control and easy to overlook. Atmospheric gasses dissolve in water and then form nanobubbles and microbubbles some of which may expand and rise back to the surface. This process causes continuous, but somewhat chaotic, changes in the gaseous concentrations over significant time periods (» 100 s) and consequently continuous changes in the hydrogen-bonded structuring within the water [1948]. Such artifacts are thought to be absent in the anomalous properties described below. [Back to Top]

Water phase anomalies [e]

1. Water has unusually high melting point. [Explanation]
2. Water has unusually high boiling point. [Explanation]

3. Water has unusually high critical point. [Explanation]
4. Solid water exists in a wider variety of stable (and metastable) crystal and amorphous structures than other materials. [Explanation]
5. The thermal conductivity, shear modulus and transverse sound velocity of ice reduce with increasing pressure. [Explanation]
6. The structure of liquid water changes at high pressure. [Explanation]
7. Supercooled water has two phases and a second critical point at about -91 °C. [Explanation]
8. Liquid water is easily supercooled but glassified with difficulty. [Explanation]
9. Liquid water exists at very low temperatures and freezes on heating. [Explanation]
10. Liquid water may be easily superheated. [Explanation]
11. Hot water may freeze faster than cold water; the Mpemba effect. [Explanation]
12. Warm water vibrates longer than cold water. [Explanation]
13. Water molecules shrink as the temperature rises and expand as the pressure increases. [Explanation]

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Water density anomalies

1. The density of ice increases on heating (up to 70 K). [Explanation]
2. Water shrinks on melting. [Explanation]
3. Pressure reduces ice's melting point. [Explanation]
4. Liquid water has a high density that increases on heating (up to 3.984 °C). [Explanation]
5. The surface of water is denser than the bulk. [Explanation]
6. Pressure reduces the temperature of maximum density. [Explanation]
7. There is a minimum in the density of supercooled water. [Explanation]
8. Water has a low coefficient of expansion (thermal expansivity). [Explanation]
9. Water's thermal expansivity reduces increasingly (becoming negative) at low temperatures. [Explanation]
10. Water's thermal expansivity increases with increased pressure. [Explanation]
11. The number of nearest neighbors increases on melting. [Explanation]
12. The number of nearest neighbors increases with temperature. [Explanation]
13. Water has unusually low compressibility. [Explanation]
14. The compressibility drops as temperature increases up to 46.5 °C. [Explanation]
15. There is a maximum in the compressibility-temperature relationship. [Explanation]
16. The speed of sound increases with temperature up to 74 °C. [Explanation]
17. The speed of sound may show a minimum. [Explanation]
18. 'Fast sound' is found at high frequencies and shows an discontinuity at higher pressure. [Explanation]
19. NMR spin-lattice relaxation time is very small at low temperatures. [Explanation]
20. The NMR shift increases to a maximum at low (supercool) temperatures [Explanation]
21. The refractive index of water has a maximum value at just below 0 °C. [Explanation]
22. The change in volume as liquid changes to gas is very large. [Explanation]

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Water material anomalies

1. No aqueous solution is ideal. [Explanation]
2. D_2O and T_2O differ significantly from H_2O in their physical properties. [Explanation]
3. Liquid H_2O and D_2O differ significantly in their phase behavior. [Explanation]
4. H_2O and D_2O ices differ significantly in their quantum behavior. [Explanation]
5. The mean kinetic energy of water's hydrogen atoms increases at low temperature. [Explanation]
6. Solutes have varying effects on properties such as density and viscosity. [Explanation]

7. The solubilities of non-polar gases in water decrease with temperature to a minimum and then rise. [Explanation]
8. The dielectric constant of water is high. [Explanation]
9. The relative permittivity shows a temperature maximum. [Explanation]
10. Proton and hydroxide ion mobilities are anomalously fast in an electric field. [Explanation]
11. The electrical conductivity of water rises to a maximum at about 230 °C. [Explanation]
12. Acidity constants of weak acids show temperature minima. [Explanation]
13. X-ray diffraction shows an unusually detailed structure. [Explanation]
14. Under high pressure water molecules move further away from each other with increasing pressure; a density-distance paradox. [Explanation]

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Water thermodynamic anomalies

1. The heat of fusion of water with temperature exhibits a maximum at -17 °C. [Explanation]
2. Water has over twice the specific heat capacity of ice or steam. [Explanation]
3. The specific heat capacity (C_P and C_V) is unusually high. [Explanation]
4. The specific heat capacity C_P has a minimum at 36 °C. [Explanation]
5. The specific heat capacity (C_P) has a maximum at about -45 °C. [Explanation]
6. The specific heat capacity (C_P) has a minimum with respect to pressure. [Explanation]
7. The heat capacity (C_V) has a maximum. [Explanation]
8. High heat of vaporization. [Explanation]
9. High heat of sublimation. [Explanation]
10. High entropy of vaporization. [Explanation]
11. The thermal conductivity of water is high and rises to a maximum at about 130 °C. [Explanation]

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Water physical anomalies

1. Water has unusually high viscosity. [Explanation]
2. Large viscosity increase as the temperature is lowered. [Explanation]
3. Water's viscosity decreases with pressure below 33 °C. [Explanation]
4. Large diffusion decrease as the temperature is lowered. [Explanation]
5. At low temperatures, the self-diffusion of water increases as the density and pressure increase. [Explanation]
6. The thermal diffusivity rises to a maximum at about 0.8 GPa. [Explanation]
7. Water has unusually high surface tension. [Explanation]
8. Some salts give a surface tension-concentration minimum; the Jones-Ray effect. [Explanation]
9. Some salts prevent the coalescence of small bubbles. [Explanation]
10. The molar ionic volumes of salts show maxima with respect to temperature. [Explanation]

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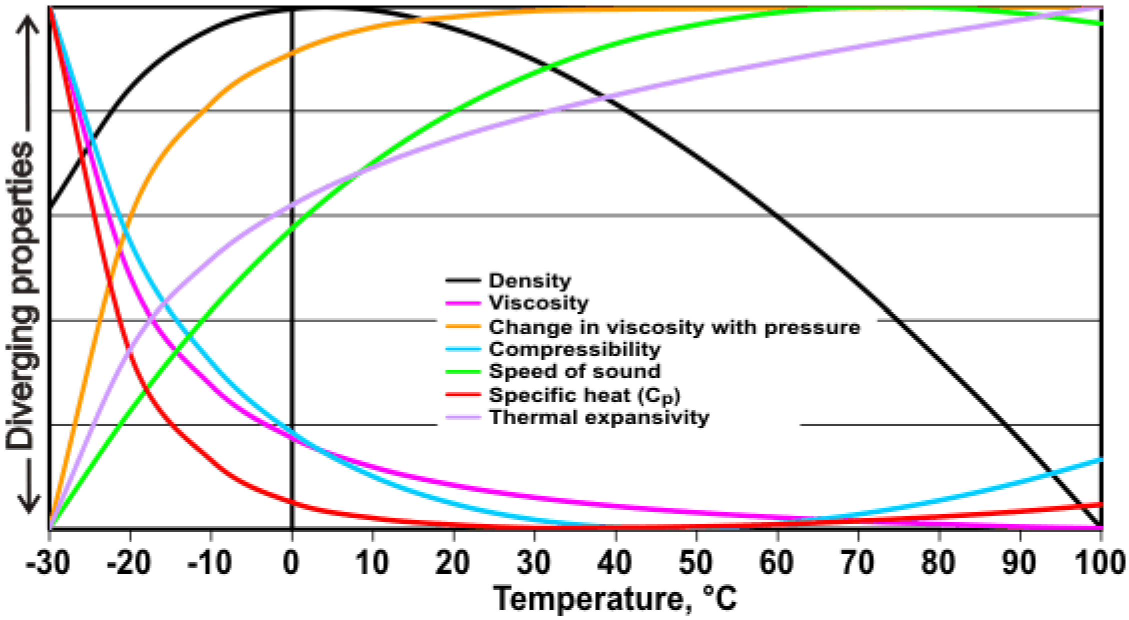

The figure left shows some of the anomalous properties of liquid water that are related to temperature. The graph uses data that have been scaled between their maximum and minimum values within this range (seeoriginal data).

Note, in particular, the different behaviors at high and low temperatures.

Footnotes

[a] Whether or not the properties of water are seen to be anomalous depends upon the materials used in the comparison and the interpretation of the term 'anomalous'. For example, it could well be argued that water possesses exactly those properties that one might deduce from its structure (see for example, [402]). Other tetrahedrally interacting liquids, such as liquid Si [1835], SiO_2 and BeF_2 have many similar 'anomalies' [1814], as do other materials where mixed phases may arise, such as liquid Te [1538]. Comparisons between water, liquid sodium, argon and benzene appear to Franks [112] to indicate several of the properties given above as not being anomalous. However, these materials are perhaps not the most typical of liquids. My list gives the unusual properties generally understood to make liquid water (and ice) stand out from 'typical' liquids (or solids). See [242] for a review concentrating on the non-anomalous properties of water; that is, those that are the 'same' as for other liquids. At higher temperatures (>315 K) the thermodynamic properties of water may be considered close to 'normal' for a liquid [1638]. Note that properties that are compared at ambient pressure or along the vapor/liquid line may be seen as anomalous whereas under isopycnic (isodensity) conditions no (anomalous) maximum or minimum values may be found (for example, no specific heat minimum, speed of sound maximum or compressibility minimum are found at constant water density of 1 g cm^{-3} ; see line on phase diagram). [Back]

[b] It is therefore very difficult to obtain really pure water (for example, < 5 ng g^{-1} solute). For a review of aqueous solubility prediction, see [744]. Note that (hexagonal) ice, in contrast, is a very poor solvent and this may be made use of when purifying water (for example, degassing) using

successive freeze-thaw cycles. The excellent solvent properties of water, together with its non-toxic nature, make water a preferred solvent for many chemical reactions [1566]. [Back]

[c] Some scientists attribute the low temperature anomalous nature of water to the presence of a second critical point; an interesting if somewhat unproductive hypothesis as a sole explanation (as the attribution mixes cause with effect, as agreed by others [1859]). Water's anomalies do not require this as an explanation, although it does seem likely. [Back]

[d] The temperature range of 'hot' and 'cold' water varies in these examples; see the individual entries for details. [Back]

[e] The anomalies of water are divided into groups but, clearly, some anomalies may be included under more than one topic and there may not be universal agreement for the groupings shown. The 'number' of anomalies depends on which ones are chosen and whether related anomalies (such as reciprocal variations including molar volume and density) are grouped together or as separate phenomena. [Back]

[f] This is easily shown with two wet glass panes. If one sheet is placed horizontally on top of the other other then the sheets easily slip over each other horizontally (i.e. very slippery) whilst it being almost impossible to separate the sheets vertically (i.e. very sticky). [Back]

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