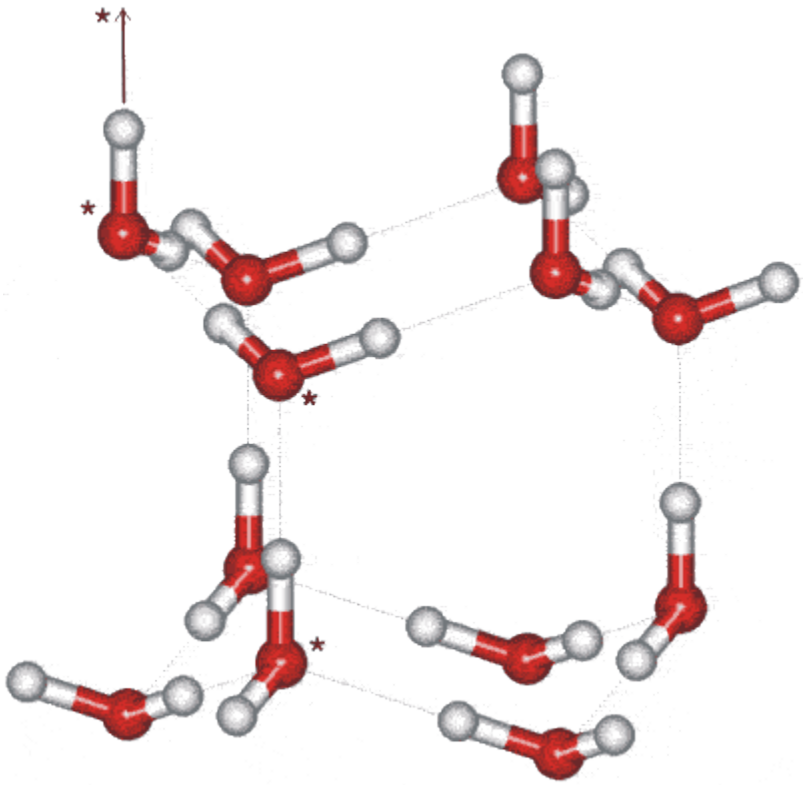
Hexagonal Ice (Ice Ih)

- Some physical properties
- Ice nucleation and growth
- Is ice slippery?

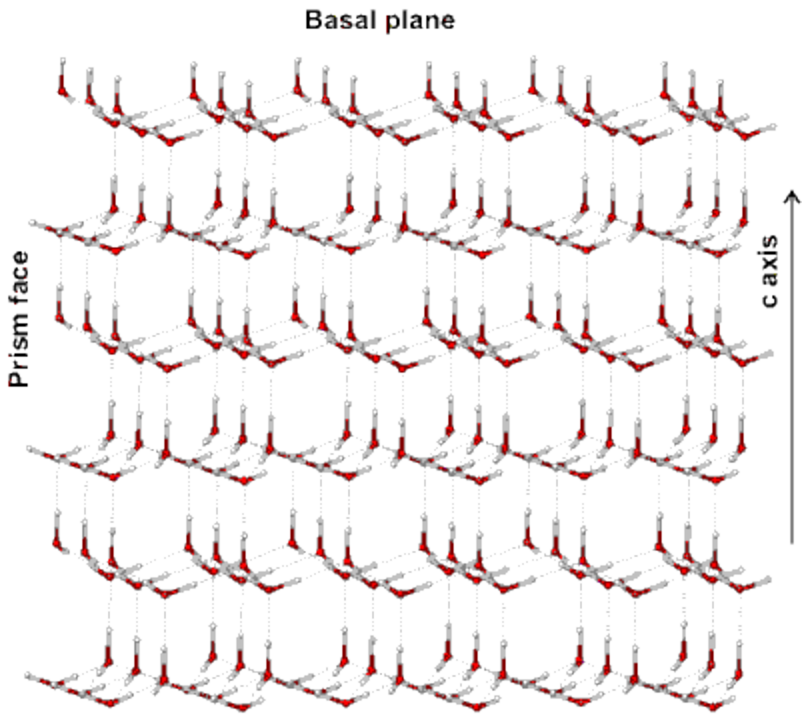
Hexagonal ice (ice Ih) [1969]. is the form of all natural snow and ice on Earth (see Phase Diagram), as evidenced in the six-fold symmetry in ice crystals grown from water vapor (that is, snow flakes).



Hexagonal ice (Space group $P6_3/mmc$, **194**; symmetry D_{6h}, Laue class symmetry 6/mmm; analogous to β-tridymite silica or lonsdaleite) possesses a fairly open low-density structure, where the packing efficiency is low (~1/3) compared with simple cubic (~1/2) or face centered cubic (~3/4) structures[a] (and in contrast to face centered cubic close packed solid hydrogen sulfide).

The crystals may be thought of as consisting of sheets lying on top of each other. The basic structure consists of a hexameric box where planes consist of chair-form hexamers (the two horizontal planes, opposite) or boat-form hexamers (the three vertical planes, opposite). In this diagram the hydrogen bonding is shown ordered whereas in reality it is random,[b] as protons can move between (ice) water molecules at temperatures above about 130 K [1504].

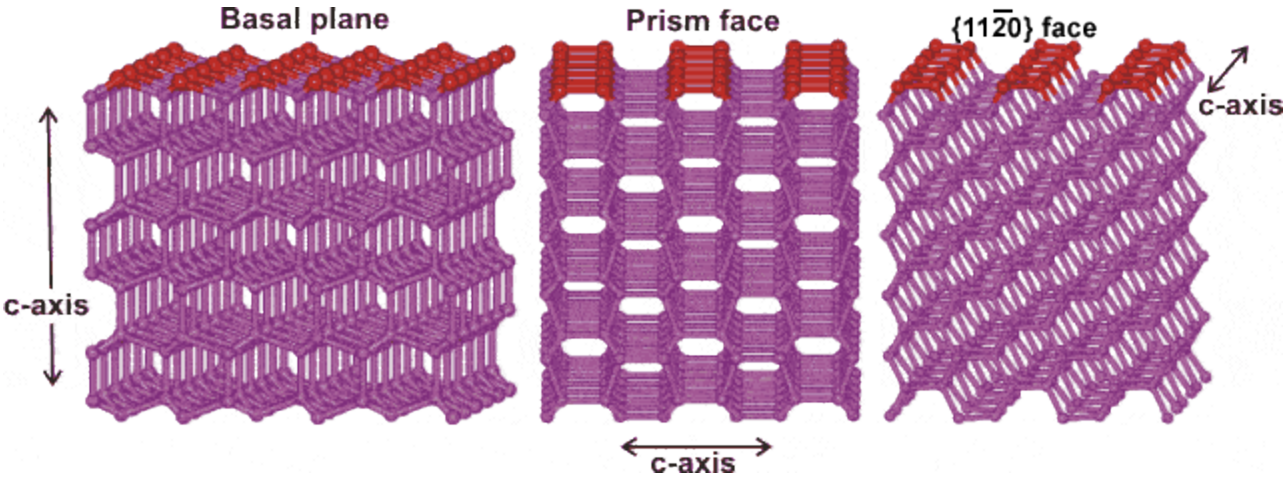
The water molecules have a staggered arrangement of hydrogen bonding with respect to three of their neighbors, in the plane of the chair-form hexamers. The fourth neighbor (shown as vertical links opposite) has an eclipsed arrangement of hydrogen bonding.

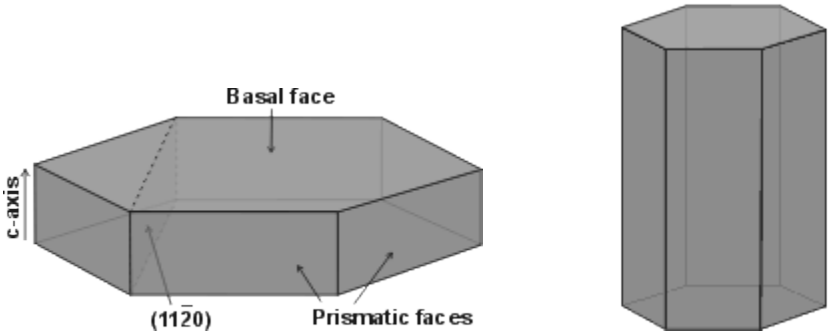


There is a small deviation from ideal hexagonal symmetry as the unit cell[c] is 0.3 % shorter in the c-direction (in the direction of the eclipsed hydrogen bonding, shown as vertical links in the figures). All molecules experience identical molecular environments.

There is space enough inside each box to hold aninterstitial water molecule. Although this is generally not thought to occur, interstitial water molecules have been recently found by neutron diffraction of effectively-powdered ice [154].

Hexagonal ice has triple points with liquid and gaseous water (0.01 °C, 612 Pa), liquid water and ice-three (-21.985 °C, 209.9 MPa) and ice-two and ice-three (-34.7 °C, 212.9 MPa). The dielectric constant of hexagonal ice is 97.5 [94].
The melting curve for hexagonal ice is given by $P_m = 6.11657x10^{-4} - 414.5 \times \left(\left(\frac{T_m}{273.16} \right)^{8.38} - 1 \right)$ MPa [1320][g]. TheIAPWS release on the equation of state for hexagonal ice is available. Some simple equations relating the variation of the physical properties with temperature of hexagonal ice and its aqueous slurries are available [1665].[h] The hardness of ice varies with the temperature, increasing from about or below that of gypsum (≤2 on Mohs scale) at 0 °C to about that of feldspar (6 on Mohs scale) at -80 °C [2097], an anomalously large change in abolute hardness (>24 times) with temperature.





Hexagonal ice crystals form hexagonal plates and columns where the top and bottom faces are basal planes {0 0 0 1}, and the six equivalent side faces are called the prism faces {1 0 -1 0}[di] . Secondary prism faces {1 1 -2 0} [dii] may be formed down the planes formed by the sides of the chair structures.

Hexagonal ice shows anomalous reduction in thermal conductivity with increasing pressure (as do cubic ice and low-density amorphous ice) but different from most crystals. This is due to changes in the hydrogen bonding decreasing the transverse sound velocity [617].

The hydrogen bonding in the surface of hexagonal ice is predicted to be more ordered than that within the bulk structure [1529].

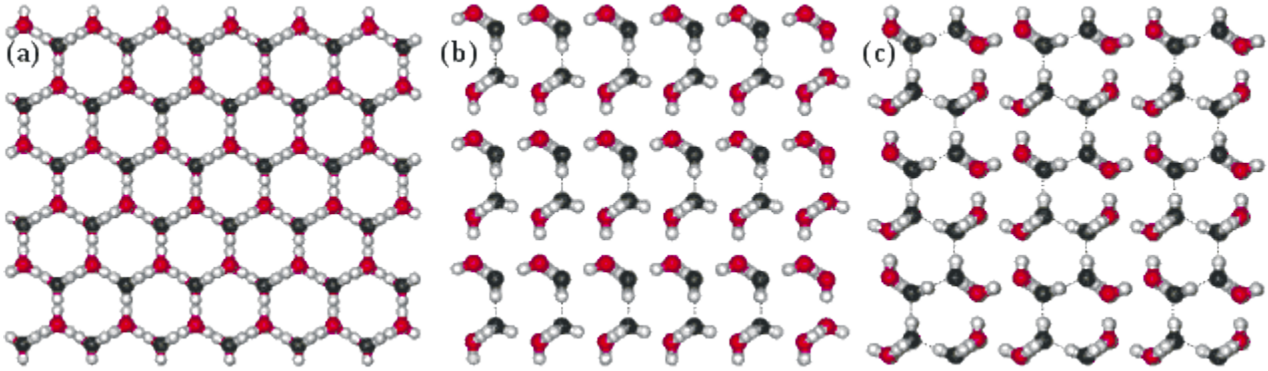
Interactive structures of hexagonal ice (Jmol) are available. [**Back to Top**]

Ice nucleation and growth

The minimum number of water molecules necessary for ice nucleation is about the same (i.e. 275±25) as that required for a complete icosahedral cluster (i.e. 280) [1931]. Ice nucleation occurs greatly enhanced, by a factor of 10^{10}, at the air-water surface rather than within bulk water [914]. Hexagonal ice crystals may form by (slowly) growing in the direction of the c-axis (S1 ice) as inside vertical freezing pipes or where ice crystals grow down vertically from crystal platelets nucleated on still water with their c-axes vertical, and where sideways growth is prevented but axial growth allowed. Alternatively they may grow more rapidly from the prism faces (S2 ice), as at the disturbed randomly-directed surface of rapidly freezing or agitated lakes. Growth from the {1 1 -2 0} faces is at least as fast as that from the prism faces but such growth turns these faces into prism faces [827]. Ice crystal growth data has been critically examined elsewhere. The relative speeds of this

crystal growth, on the different faces depend on the ability of these faces to form greater extents of cooperative hydration. The temperature of the (supercooled) surrounding water determines the degree of branching in the ice crystal. Crystal growth is limited by the rate of diffusion at a low degree of supercooling (i.e < 2 °C; giving rise to more branching) but limited by the kinetics of growth at higher degrees of supercooling (i.e. > 4 °C; giving rise to needle-like growth) [883]. The hexagonal crystal structure, the different growth characteristics of the crystal faces and the temperature of the surrounding (supercooled) water are behind the flat six-pointed shapes of snowflakes [1916].

Solutes cannot be incorporated into the ice Ih structure at ambient pressure[f] but are expelled to the surface or the amorphous ice layer between the microcrystalline ice crystals. This may be made use of when purifying water (for example, degassing) using successive freeze-thaw cycles. Some solutes (for example, chaotropic ions such as NH_4^+ and Cl^-) are incorporated more easily into freezing ice than others (for example, kosmotropic ions such as Na^+ and SO_4^{2-}), so removing them from the remaining thin films of liquid between the crystals. This may result in the electrical charging of the surface due to surface water dissociation balancing the remaining charges (which also may give rise to electromagnetic emission) and changes in the pH of the residual liquid films (for example, $(NH_4)_2SO_4$ becomes more acidic [1010] and NaCl becomes more alkaline [1089]).



Views perpendicular to the faces of the ice (1h) crystal showing the next layer attached (with O-atoms black). (a) Slow growing basal {0 0 0 1} face (viewing down the c-axis); where only isolated water molecules attach. (b) faster growing {1 0 -1 0} prism face (viewing down the a-axis), where pairs of newly-attached water molecules may hydrogen bond to each other; one hydrogen bond/two water molecules. (c) Fastest growing {1 1 -2 0} (secondary prism) face, where chains of newly-attached water molecules may cooperatively hydrogen bond to each other; one hydrogen bond/water molecule. These form ridges which divide and encourage conversion into two prism faces. [**Back to Top**]

Is ice slippery?

Although ice is often perceived as 'slippery' (for example, ice skating), it is also very 'sticky' (for example, the difficulty in removing ice from from car windscreens, the compaction of snow to form 'snowballs' and the ease with which two ice cubes stick together). The underlying slipperiness of ice can be explained by the tetrahedral open structuring [1859] of the liquid water surface that aids the formation of a slipping plane on confinement, whereas its 'stickiness is due to the refreezing of liquid water confined between ice surfaces. Capillary condensation of liquid water between a tungsten tip and a hydrophobic graphite surface using a friction force microscope has been proposed to form a sticky 'ice' at room temperature [1033].[e] These different perceptions depend on the speed of the relative movement between the surfaces and the presence and properties of the ultra-thin layer of

quasiliquid water/amorphous ice on the crystalline surfaces [937] that may be 10 nm thick or greater [1303]. This surface layer is easily melted further by frictional heating (so leaving trails behind the skates) with the low thermal conductivity of ice reducing the loss of heat. There is good evidence that the surface layer is indistinguishable from normal liquid water with a thickness that depend upon the temperature (that is, the further below the freezing point, the thinner the layer; it being many nm thick at -1 °C but has disappeared at about -38 °C). Hexagonal ice is a very soft material (1.5 on Moh's scale) being scratched by most crystalline solids except soapstone, $Mg_3Si_4O_{10}(OH)_2$. The surface is liquid below 0 °C due to the pressure melting caused by the one-sided attractive interaction with the underlying solid ice [1686]. [**Back to Top** ▲]

Footnotes

[a] The exact packing efficiency for ice Ih is low (~ $\frac{\pi}{48\times\left\{\sin\left[\frac{\cos^{-1}(1/3)}{2}\right]\right\}^3}$ ~ 0.34, ~1/3) compared with simple cubic ($\frac{\pi}{6}$ = 0.5236, ~1/2) or true face centered cubic ($\frac{\pi}{3\sqrt{2}}$ = 0.7408, ~3/4) structure [811]. [Back]

[b] In all these structural diagrams the hydrogen bonding is ordered whereas in reality it is random and constantly changing (obeying the 'ice rules'). As the H-O-H angles are about 106.6º [717], the hydrogen bonds are not straight (although shown so in the figures). Although each water molecule is shown symmetricaly situated, thermal motion causes a broad range of the hydrogen bond energies giving noticeable instantaneous asymmetry around the crystallographic sites [2095].

Although the proton order in bulk ice is disordered, the surface of the ice probably has a preference for proton order in terms of stripes of dangling H-atoms and O-lone pairs [1551]. [Back]

[c] The unit cell may be considered as a group of four molecules (three shown starred in the top figure, with the fourth linked as indicated). The crystallographic c-axis is in the vertical direction. The hexagonal crystal has unit cell dimensions 4.5181 Å (a) and 7.3560 Å (c) (90º, 90º, 120º, 4 molecules, at 250 K) [382]. In a perfect crystal the 'c' cell parameter would be 2√(2/3) times the 'a' cell parameter (that is, 7.3780 Å). The cell dimensions for D_2O are 4.5216 Å (a) and 7.3627 Å (c) [382], with its c-axis very slightly less affected. [Back]

[d] (i) There are six prism face planes around the hexagonal crystal; going anticlockwise {0 1 -1 0} {-1 1 0 0} {-1 0 1 0} {0 -1 1 0} {1 -1 0 0} {1 0 -1 0}. (ii) There are six such secondary prism face planes across similar diagonals in the hexagonal crystal; going anticlockwise {1 1 -2 0} {-1 2 -1 0} {-2 1 1 0} {-1 -1 2 0} {1 -2 1 0} {2 -1 -1 0}.[Back]

[e] Such confined meniscus water has been shown to possess 10^6-10^7 times greater viscosity than bulk water [1304]. [Back]

[f] However, the close match of the crystal lattice constants between hexagonal ice and hexagonal β-AgI makes the AgI an effective ice nucleating agent. Similarly the hydrogen bonded salt NH_4F (with hexagonal unit cell l dimensions 4.37 Å (a) and 7.17 Å (c)) can also form mixed crystals [1568]. The poor solubility of solutes in hexagonal ice does not extend to the high pressure ices, where salts may be incorporated into the crystal lattice. [Back]

[g] There seems to be an error in the published equation, where the denominator is given as 273.15. [Back]

[h] The variation of some physical properties of ice may be given in terms of the temperature (T, °C) [1665]:

Density of ice (kg m^{-3}) = 917 – 0.13 x T
Specific heat of ice (kJ kg^{-1} K^{-1}) = 2.12 + 0.008 x T
Thermal conductivity of ice (W m^{-1} K^{-1}) = 2.21 – 0.012 x T
Enthalpy of ice (kJ kg^{-1}) = –332.4 + T (2.12+0.008 x T)

Source:http://www1.lsbu.ac.uk/water/ice1h.html