

# The Freezing Process

## Formation of Ice

The transition between liquid water and ice is one of the most commonly observed events in nature, but like the question of why the sky is blue, the question of why water freezes when it gets cold is one that's rarely given much attention. In fact, like this more famous question, the answer is actually quite surprising to most people; perhaps due to its familiarity. We marvel at the variety and splendid architecture of snowflakes, but give little thought to the magic that occurs when we put a tray of water in the freezer to make ice cubes.

When ice and water are mixed together, then the temperature of the solution will always go to  $0^{\circ}\text{C}$  as long as both liquid and solid are present. Thus we call  $0^{\circ}\text{C}$  the freezing point for water or the melting point for ice, although it's more appropriate to call it the equilibrium point. In fact, if water is cooled to  $0^{\circ}\text{C}$  then it won't freeze; it has to be cooled below  $0^{\circ}\text{C}$  before freezing can occur. Likewise, ice has to be heated slightly above  $0^{\circ}\text{C}$  before melting occurs. Unlike freezing, however, melting will begin as soon as the temperature rises above  $0^{\circ}\text{C}$  no matter how slight the margin. When water is cooled, it often must be taken substantially below the freezing point before ice begins to form. The difference is due to the need for nucleation to occur before an ice crystal can begin to grow. Nucleation refers to the process by which a minimum crystal is formed which can then expand. The continued expansion of the crystal is a process known as growth.

## Nucleation of Ice

### Thermodynamic Considerations:

When ice and water coexist at the freezing point, the amount of ice remains constant as long as no heat is either added or removed from the mixture. At the surface of the crystals, there is a constant interchange of water molecules between the ice and water. If the crystal surface is planar, then the number of molecules which leave the crystal is exactly equal to the number of molecules which join it. If we have a corner on the crystal, then this number will not be equal. The molecules that are part of the crystal at the corner will be less strongly joined to the crystal (they don't have as many neighbors to bond with) and are thus more easily knocked out of the crystal while molecules from the liquid are less likely to join the crystal at the corner. This leads to a net loss of molecules from the corner (melting) at the same temperature for which there is equilibrium on a planar crystal surface. Thus the melting point of a crystal will be a function of the radius of curvature of the crystal. For a given temperature there will be a critical radius which defines the minimum size that a crystal can have and still be stable.

### Derivation of the Critical Radius:

In order to arrive at an expression for the surface tension of a spherical crystal, we first consider the work done by an increase in pressure ( $\Delta P$ ) on a sphere of radius  $r$  when the radius is increased to  $r + dr$ . The work done is given by

$$W = Pdr \times 4\pi r^2 \quad (6.2.1)$$

On the same expanding sphere, if we have a surface tension ( $\sigma$  = free energy per unit area of the interface), then the work done by expanding the sphere is given by

$$W = [4\pi(r + dr)^2 - 4\pi r^2] \sigma \quad (6.2.2)$$

At equilibrium, the surface energy will be equal to the energy of expansion, so combining the two gives

$$P = \frac{2\sigma}{r} \quad (6.2.3)$$

If a solid phase and a liquid phase are in equilibrium, then their free energies per unit quantity are equal, thus there will be no temperature difference across a planar interface between the two. If the interface is curved, however, then a pressure difference must exist to account for the difference in surface energy. The pressure difference  $\Delta P$  just compensates for the departure  $\Delta T$  of the temperature from that which would exist across a planar interface ( $T_f$  = the equilibrium temperature, which is defined as the freezing point if solid and liquid phases are in equilibrium). If the solid phase is incompressible, then  $\Delta P$  is equal to the free energy difference that would exist between solid and liquid at  $T - \Delta T$  if the solid and liquid phases were at the same pressure. The difference in free energy ( $\Delta G_p$ ) is therefore equal to  $\Delta P$ , so that

$$\Delta G_p = \frac{2\sigma}{r^*} \quad (6.2.4)$$

where  $r^*$  is the critical radius at which equilibrium is established. The free energy at a constant pressure ( $\Delta G_p$ ) is given by

$$\Delta G_p = \Delta H - T\Delta S \quad (6.2.5)$$

and since the change in free energy is zero at the equilibrium temperature ( $T_f$ )

$$\Delta S = \frac{\Delta H}{T_f} \quad (6.2.6)$$

Substituting and introducing the latent heat of fusion ( $L_f$ )

$$\Delta G_p = \Delta H - \frac{T\Delta H}{T_f} = \frac{\Delta H(T_f - T)}{T_f} = \frac{L_f \Delta T}{T_f} \quad (6.2.7)$$

Thus we arrive at an expression for the critical radius, the Kelvin equation

$$r^* = \frac{2\sigma T_f}{L_f \Delta T} \quad (6.2.8)$$

There is no way to measure  $\sigma$ , the interfacial tension between water and ice, however, there are methods to infer it. Using a value of  $22 \text{ erg/cm}^2$  we can plot the critical radius as a function of temperature.

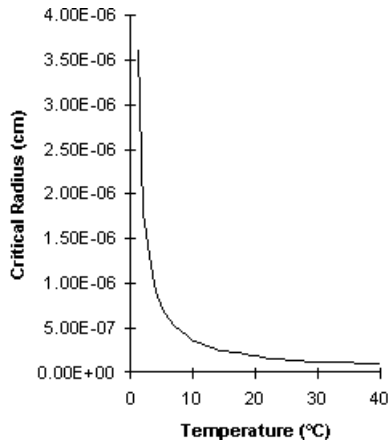


Fig. 6.2.1

Liquid water consists of clusters of molecules which are undergoing constant collisions with other molecules and clusters, sometimes breaking apart and sometimes forming larger clusters. If we cool down pure water, then it follows that we need to obtain a cluster of a size sufficient to match the critical radius or else that particular cluster will not be stable. If we plot the critical radius as a function of temperature (as given by Eq. 6.2.8) then we can see that it's asymptotic at  $0^\circ\text{C}$ --a cluster of infinite radius would be required to be stable. The equation is also asymptotic at a radius of 0, although since we know that water is made out of finite sized molecules, then it follows that there will be a minimum temperature at which the critical radius must exist. We can look at the size of a cluster that is virtually certain to occur just due to fluctuations (if we have a macroscopic quantity of water), and that corresponds to a cluster of about 25 molecules (a radius of about 3 molecules) The critical radius that coincides with this size gives us a temperature of  $-41^\circ\text{C}$ , which is called the homogeneous nucleation temperature (the minimum temperature that pure water can be cooled to before freezing occurs spontaneously).

### Heterogeneous Nucleation:

The difficulty with the above is that if we look at the maximum cluster size that is likely to occur spontaneously (about 250 molecules) then that corresponds to a temperature of about  $-30^\circ\text{C}$ . We know from experience that it's quite difficult to cool water down to that temperature without ice forming and we almost always see freezing occur in water that's only a little below the freezing point. This can be explained on the basis of impurities which exist in the water. If the water molecules wet the surface of an impurity (that is large compared to water molecules) with a

certain contact angle, then a portion of a sphere can form which has the critical radius which will therefore be stable. This type of nucleation is called heterogeneous nucleation.

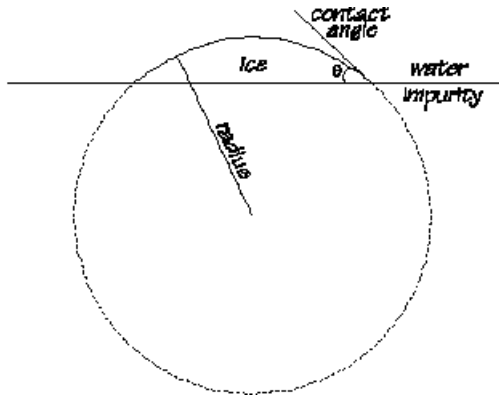


Fig. 6.2.2

By taking up much of the volume that would have been required by an equivalent sphere, the impurity allows a critical nucleus to form out of a cluster that is likely to occur spontaneously. The contact angle ( $\theta$ ) is determined by the adhesive forces present. Although the impurities are usually in the liquid (such as dust particles) there is a phenomenon that occurs with water in glass containers that may be related to this discussion. For clean glass,  $\theta$  is  $0^\circ$ , thus the radius of the equivalent sphere is essentially infinite, resulting in a predicted nucleation temperature of  $0^\circ\text{C}$ . It is often observed that lightly scratching the side of a beaker with a glass thermometer will nucleate water that is only slightly supercooled.

## Growth of Ice Crystals

### Ice Structure:

Once a critical cluster has formed--an ice nucleus--then crystal growth will inevitably proceed as long as the temperature is below the melting point.

### The Water Molecule:

While it's true that water is just plain old  $\text{H}_2\text{O}$ , two hydrogens and one oxygen, the structure that these atoms form when bound together is responsible for all the magnificent properties of water. The hydrogen atoms are covalently bonded to the oxygen, meaning that an electron pair is shared between them. Since the positive charges are constrained within the respective nuclei, the electronic environment of water is determined by the location of the outer electrons. These don't just sit in one place, but may be found in various locations with characteristic probabilities. If we plot the electron density as a cloud around the atoms, then water has the following structure:

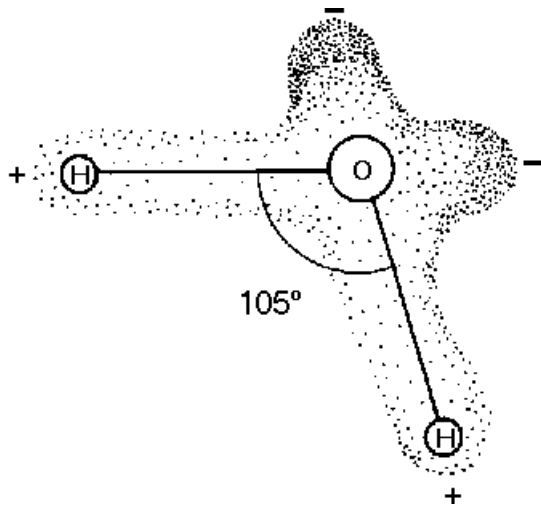


Fig. 6.2.3

We can see that the electrons spend most of their time in two bumps on the surface of the oxygen molecule. This creates a dipole moment in which these two bumps have a slightly negative charge leaving the hydrogen atoms each having a slightly positive charge. Since the charges interact with one another, if we were to view this in three dimensions, we would see an oxygen atom with charge concentrations around a regular tetrahedron which surrounds it, having angles of  $120^\circ$  between the arms.

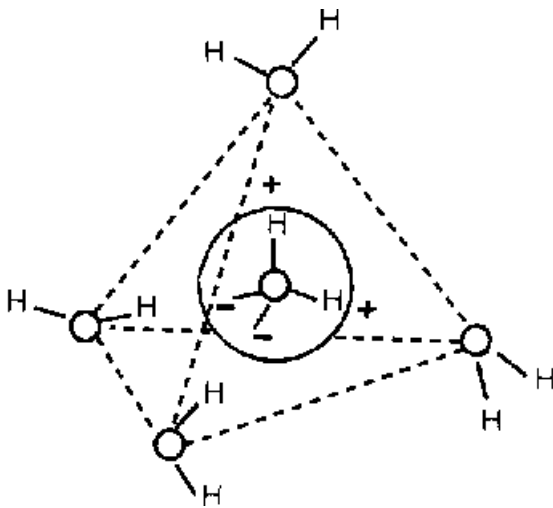


Fig. 6.2.4

When water molecules combine and are allowed to form a structure with the lowest energy, then positive charges will attract negative charges and vice versa. The tetrahedral orientation of charges allows each charge to be paired with an opposite charge when a structure with hexagonal symmetry is formed. The following diagram shows the three dimensional structure of ice, which displays the interlocking hexagon motif that's also characteristic of the structure of diamond.

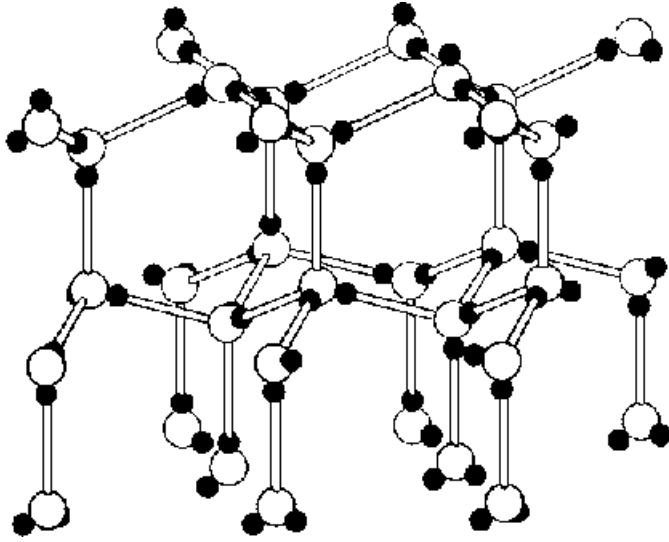


Fig. 6.2.5

The macroscopic crystalline structure takes the form of a hexagonal prism. The following diagram shows the three  $a$  axes which correspond to growth in the direction of the hexagonal face and the  $c$  axis which corresponds to growth in the direction of the prism axis.

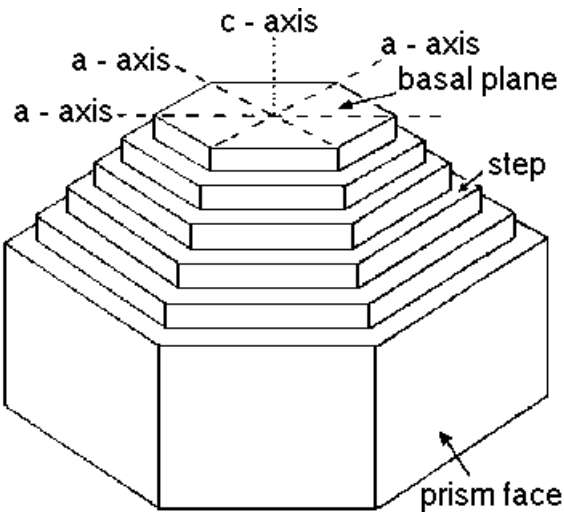


Fig. 6.2.6

One of the most unusual properties of water is that the solid phase is *less* dense than the liquid. Ice actually floats on water. This is fortunate for organisms that live in lakes and rivers which are in freezing climates, as the surface ice provides insulation which prevents the whole lake from freezing, thereby allowing all those organisms to survive the winter. It's also fortunate for those who like cocktails as the ice floating on top of the drink prevents one from quaffing their beverage with undue haste. The reason behind this phenomenon is not well understood and is usually explained as being due to the close packing of clusters.

### **Latent Heat of Fusion:**

When water freezes, there is a large quantity of heat that is liberated by the process. This is the latent heat of fusion, due to the energy that goes into hydrogen bond formation in the crystal. Each water molecule is hydrogen bonded to four other neighboring molecules, each bond having an energy between 10 and 40 kJ/mol. An energy of 80 calories (335 J, but if we recall that a calorie is the amount of heat required to raise the temperature of 1 gram of water by 1°C, then its usefulness here is relevant) is released by the transformation of 1 gram of water at 0°C to ice at the same temperature--this amount of heat would be enough to raise the temperature of the water from 0°C to 80°C!

Once again, a kinetic theory perspective might help to shed some light on the essence of this phenomenon. If we consider the distribution of velocities to correspond to a Maxwell distribution, then we can see that there is a great range of molecular velocities all co-existing at 0°C. We saw previously that only the slow moving molecules are able to join a cluster or crystal and put all their kinetic energy into potential energy of bond formation, thus these are the molecules which are removed from the distribution when ice forms. That changes the distribution of velocities to produce a higher average speed, or a higher temperature. Thus the temperature of the liquid will rise when ice starts to form. Of course, once there are not enough slow molecules left to join the crystal, then the temperature rise will stop. If the temperature was to rise above this level, then there would be too many high-energy molecules which would start breaking molecules out of the crystal (melting). Thus, at the temperature at which the solution finds itself is the one at which the continuing exchange of molecules will be equal in terms of those joining and those leaving the crystal surface.

### **Dynamics of Crystal Growth:**

The crystal structure of ice is such that it does not allow the inclusion of impurities, except within defects in the crystal structure. Thus, when an ice nucleus begins to grow, any solutes which are present in the liquid will be excluded from this growing ice front. If the rate of crystal growth is faster than the rate at which diffusion of the particular solutes can carry them away from the ice front, then a concentration gradient will very quickly form in the liquid which surrounds the ice crystal. The concentrated solute will then lower the freezing point of the solution (see previous section). When a certain amount of ice has formed, then the solution at the interface will have a freezing point equal to the temperature of the interface; at this point, ice growth will be limited by diffusion of the solute away from the crystal. If this situation arises when the solution well away from the ice crystal (in which the solute is not concentrated) is supercooled (at a temperature below the melting point) then this is described as constitutional supercooling. Eventually diffusion will ensure that the system goes to equilibrium, however a situation of instability is created when this occurs.

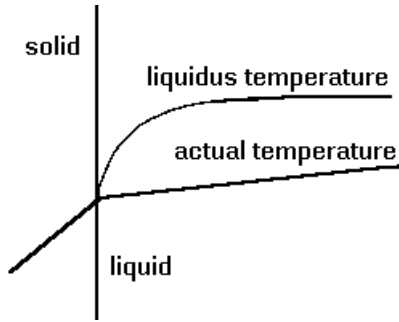


Fig. 6.2.7

The production of heat from crystallization also interferes with crystal growth. The heat is created at the crystal surface and must either be shed through the crystal or through the liquid. The removal of this heat occurs by conduction and can only occur through the liquid if it is supercooled when nucleation occurs. If the latent heat of fusion is conducted away through the ice (e.g. if the crystal is in connection with a heat sink) then the growing crystal will remain essentially smooth any part of the interface which grows beyond the planar front will not be able to lose its heat as quickly as the ice on either side of it, thus these instabilities quickly die out. If the heat is conducted away through the liquid, however, then there are several aspects in which crystal growth is altered. For instance, growth occurs preferentially along the *a* axes compared with growth along the *c* axis. This occurs because of the rise in temperature of the liquid surrounding the crystal. As the molecules become more energetic, they are less likely to join a planar surface where they can only hydrogen bond with a single neighbor. Along the ridges that are seen in fig. 6.2.6, they can bond with at least two neighbors, thus losing more of their kinetic energy to potential energy of bond formation. This is the phenomenon responsible for the hexagonal symmetry that we see in growing ice crystals.

### Cellular Ice Growth:

The existence of constitutional supercooling in advance of a growing ice crystal results in an unstable situation. Since there is a gradient in the degree of supercooling which is maximal a little ways out in front of the interface, a planar ice front will be susceptible to small perturbations. If a local region of the interface advances just slightly ahead of the plane, then its growth rate will increase as well. This is due to the fact that it will now be able to shed its latent heat of fusion to a greater volume of liquid, as well as to liquid which is more supercooled. Such an instability will grow through the supercooled region until the supercooling is reduced to the level at which the rate of growth is limited by the conduction of latent heat once again. In fact, an entire planar interface will form an array of these "cells" when constitutional supercooling occurs.

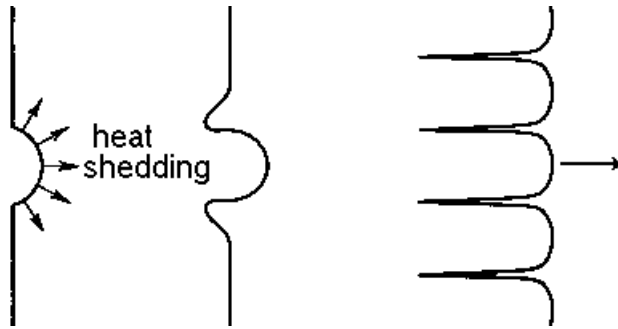


Fig. 6.2.8

### **Dendritic Breakdown:**

Further to the conduction of latent heat, there is also the destabilizing effect of solute exclusion. The cells will exclude solute to the sides as well as in front and the regions between cells will contain concentrated pockets of solute. If the conditions leading to cellular growth are particularly pronounced, then the cells may turn to dendrites--protuberances which start to grow side branches. The sides of the cells become plane fronts in themselves, also subject to the same destabilizing effects of heat conduction and solute exclusion. Since the ice crystal is built on a hexagonal symmetry, then these side branches will follow that symmetry. Once dendritic breakdown (the formation of growing dendrites from a planar interface) occurs, then the excluded solute will be encapsulated in channels that are sandwiched between the growing dendrites. If the freezing is initiated by a single nucleation event, then these channels will all be connected.

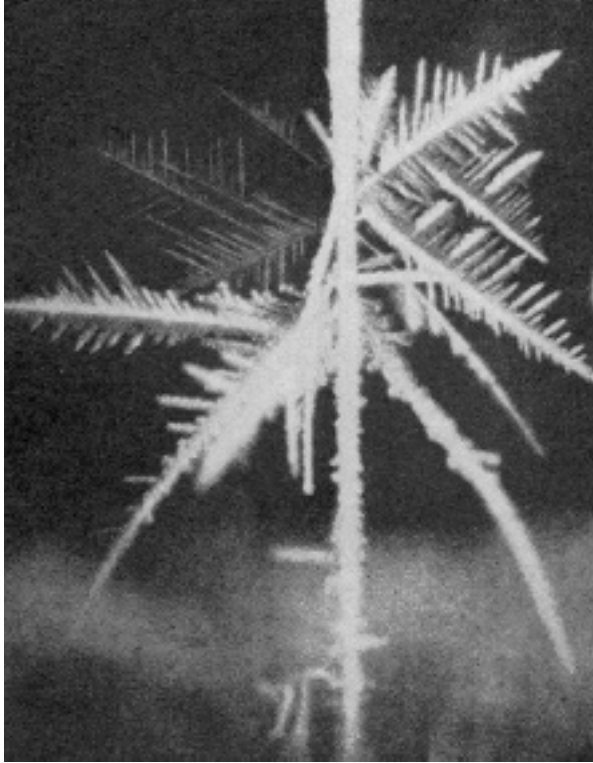


Fig. 6.2.9

### **Recrystallization:**

We saw earlier that the radius of curvature was related to the melting point due to the lowering of the number of bonds which can form at sharp bends in the crystal. This same effect is responsible for the phenomenon known as recrystallization, which is the progressive lowering of the surface free energy of a crystal surface (or the combined energy of the surfaces of many crystals in the same liquid). This occurs by the number of molecules leaving a curved surface being larger than the number of molecules arriving on that surface. The continual exchange of molecules at the interface serves to reduce the curvature of a single crystal (forming a sphere) or to reduce the number of small crystals by adding to the larger crystals. If a system is left long enough, then a single spherical crystal should result (if the geometry of the container permits such a crystal). The highly curved surfaces are present initially due to growth occurring through a constitutionally supercooled environment. There we have cellular or dendritic growth in which the crystals will have a small radius of curvature which are no longer thermodynamically stable once the latent heat of fusion has brought the temperature of the system up to the melting point (or any other manipulation which reduces the supercooling from what was present when the crystal formed).

### **Solidification without Crystallization:**

If a liquid is cooled sufficiently quickly so that nucleation cannot occur (nucleation is a stochastic process that requires fluctuations of a given intensity to occur, thus there is a kinetic

aspect to it) then it is possible to avoid ice formation altogether. This process is called vitrification and results in an amorphous solid, or glass. The liquid is in a metastable state until it gets below a characteristic temperature, the glass transition temperature ( $T_g$ ) which is indicated by a sharp exotherm. The reason for this heat loss is due to the loss of metastable clusters. Those clusters which have more energy than can be held by the bonds which they are able to form will oscillate for a short time and then disintegrate (see kinetic theory section above). Upon reaching the glass transition temperature, this excess energy is lost, thereby stabilizing the clusters. Once below  $T_g$ , the system is not merely a viscous liquid, but is a solid it is in a stable thermodynamic state. Achieving vitrification with pure water requires very small amounts of water and incredibly fast cooling, although with high concentrations of solutes, solutions can be made which can be vitrified relatively easily.

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