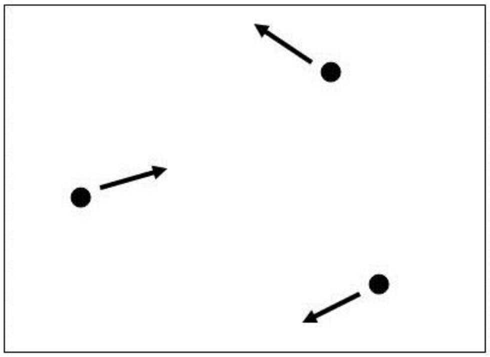
Crystallization - A Primer (with pictures and minimal equations)

The High Temperature Gas Phase - recalling the importance of thermal motion.
Recall what you already know about the gaseous state. The molecules are very sparsely situated with a typical molecule such as N_2 occupying about 1000 times its own molecular volume. They are flying around at a tremendous speed - on average - for our N_2 they are traveling at average speeds of about 500 m/sec at room temperature, about a third of the speed of a rifle bullet (see e.g., W. Moore, *Physical Chemistry*, Table 4.2, p 124).

It might be worth reflecting on how the situation in a gas would appear if you shrank so small that the N2 molecule appeared as large as a basketball. At such a magnification there would be only about ten basketballs flying around in a space the size of a typical room (3mx3mx2.5m). Of course they would be bouncing around at a tremendous velocity and you wouldn't want top be in that room. They would be hitting the wall of this room very frequently (which produces the "pressure" of the gas in its container. The velocity, or thermal motion, would be dependent on the temperature. In fact the thermal energy of this motion, $\frac{1}{2} mv^2$ depends almost linearly on the temperature, when expressed in degrees Kelvin. (T(K) = T(C) + 273.17). In fact, the Kelvin temperature is essentially a measure of the thermal energy of a gas, and for an ideal gas represents a means to define the temperature.

Thermal energy = $\frac{1}{2} mv^2 = 3/2\ kT$ (where k is the Boltzmann constant)

The higher the temperature the more rapid the motion!

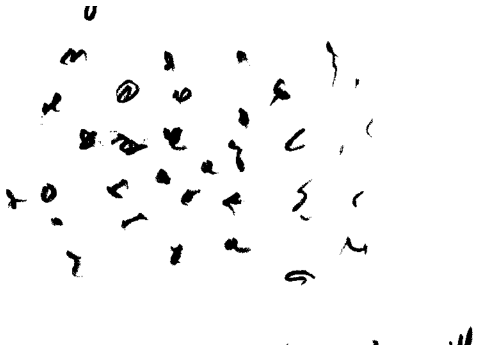


In gaseous state:
- Fast moving molecules
- random motions
- very sparse with lots of free space

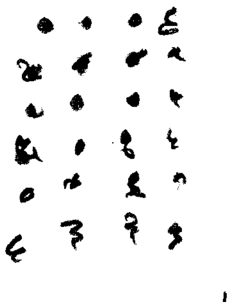
But molecules all have some level of attraction for one another and, as the temperature is reduced and thermal motions subside, the molecules will eventually begin to express their desire to be in closer contact with one another. This coming-together occurs because it reduces the energy of the system as a result of this force of attraction. That is what having a force of attraction actually means. In the language of physics, the force of attraction is the reduction of the energy (potential) with shrinking separation (or $F= -dU/dx$).

At high temperature the molecules are moving in a fast and chaotic manner; almost total randomness in this sparse gas prevails. But as the system is cooled and the molecules slow down, they eventually reach a point in temperature where the attraction of being together (and its associated energy lowering) balances and overcomes the urge to be apart, and the first drop of liquid begins to form. The liquid is a much denser state with the molecules residing much closer to one another than in the gas, about 10 ten times closer on average, although still moving and jostling about. Much of the randomness remains in the positions of the molecules as they jostle about in a denser, more confined space.

As the temperature of the liquid is reduced still further the molecules may slow down enough to achieve the even more energetically favorable state of the positionally ordered, crystalline state. In the crystal state the molecules are in fixed positions relative to one another, at least on average. The positional ordering of the crystalline state is referred to as “long- range” . By **long range order** we mean that if we know the position of one atom, we can with fair confidence know the position of the other atoms, five, ten ore even one hundreds of atoms away. It is like the seats in a large auditorium, their positions and inter atomic spacing are fixed relative to one another over many rows of atoms. Within the “seats” (or crystal lattice positions), there may be some jiggling of the atoms, but the average positions of the molecules in a crystal are very fixed relative to one another. And the molecules lose their freedom to rotate unhindered. The difference between the ordering in the liquid and crystalline states is illustrated in the figure below.



Liquid
Molecules relatively close together
but not ordered - essentially random
motion is not constrained
Greater disorder



Crystalline Solid
very ordered
close together
closer than in liquid (H2O exception)
motions within “cells”
Lower Energy

It must be emphasized that the highly ordered state of the crystal can only be achieved once the thermal motions (temperature) has been reduced enough to allow the molecules to settle down into this more energetically favorable and more ordered state of the crystal.

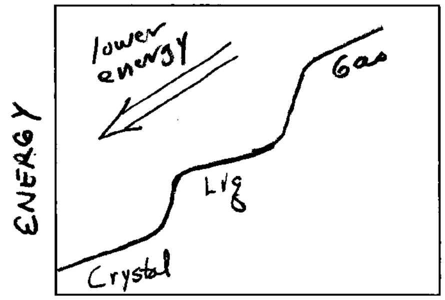
It should also be noted that while the crystal becomes the more favorable state below the melting temperature, T_m, **reducing the temperature below T_m is not a sufficient condition to ensure that crystals will form**, at least in short order. That’s because there are some barriers that the molecules must overcome in the process of forming the first tiny raft of crystals in a sea of liquid. The formation of these first tiny crystals is referred to as Nucleation, the topic of our discussion to follow. These barriers to the formation of the first baby crystal nuclei are what allow many liquids to be cooled below their freezing points without freezing, phenomena referred to as **super cooling**.

In contrast to the supercooling , when the temperature of a crystalline solid is raised from a low temperature to a temperature above T_m, the liquid will begin to form almost immediately once the T_m is reached. That's because going from the ordered to the disordered state occurs more naturally (the 2nd law of thermodynamics*) with no appreciable barrier. Going to disorder happens much more easily that the reverse, a concept most of us can appreciate from both intuition and experience.

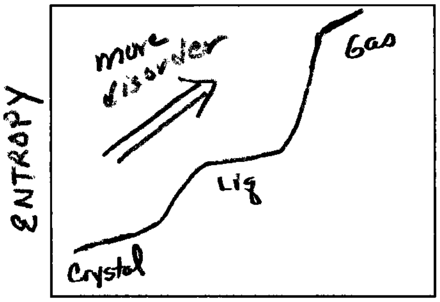
The Driving Forces of Nature:
There are some very fundamental principles of science (thermodynamics in particular) contained in the previous comments. There are two fundamental and opposing driving forces involved in this competition between the gas and liquid equilibrium (or the liquid solid equilibrium). They are:

A. The tendency to lower energy, like water always running down hill to reduce it's gravitational energy. So the formation of a liquid from a gas or the formation of a crystal from a liquid results from a lowering of the "internal" energy of the collection of molecules as they come closer together. Their coming closer together is a more energetically favored situation as is their becoming more organized in a regular array

B. **The tendency to maximum disorder**, such as the diffusion of ink spreading away from the drop placed in a dish of clear water. So the formation of gas from a drop of liquid greatly increases the randomness or disorder of the molecules. A similar increase in disorder occurs as the ice cube melts into liquid water. This concept of disorder is captured in a thermodynamic variable called the **entropy**, denoted the symbol S.

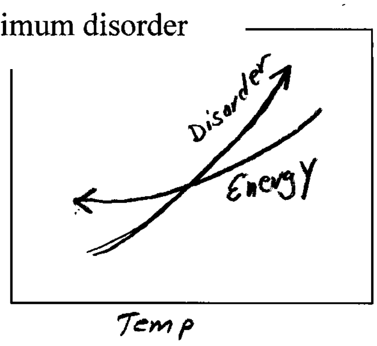


Tendency to minimum energy



Tendency to maximum disorder

Higher temperature will always drive to the disordered state while lowering the temperature will in general be necessary to favor the more ordered, lower energy forms. It is the balance of these two fundamental driving forces which occurs at the transition temperatures (T_{vapor} of T_{melt}).



* The second law of thermodynamic can be stated in many different, but equivalent ways. A simple form is that natural processes in isolation will always tend to greater disorder.

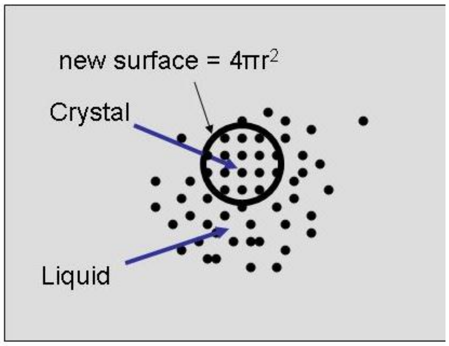
This can be expressed in a special energy function which combines both tendencies in a single quantity. That special energy is referred to as the "**Free Energy**" and in the specific and usual case where temperature and pressure are fixed, the appropriate function is the called the **Gibbs free energy**, G, given by

$$\mathbf{G= H - TS}$$

where H is the internal energy function called the Enthalpy and S is the entropy, our disorder function. Notice how this free energy is the difference between an energy H (called the enthalpy) and a temperature dependent disorder term (-TS). Notice also that the disorder term has temperature as a factor, and thus will become more dominant as the temperature increases.

What is involved in crystal formation?

1. First the temperature must be low enough that the crystal is stable relative to the liquid, that is, below the liquid-crystal equilibrium temperature, $T_{crystal}$, also referred to as T_{melt}. (You may already know that in the language of free energy, this is the temperature at which the free energy of the liquid is equal to the free energy of the crystal.)
2. **Nucleation:** First, an initial, tiny crystal nucleus must form within the liquid - this is referred to as Nucleation. We will find that forming this first small crystal nucleus takes some "extra" energy - the energy to form the initial "seed" for growth. This extra energy serves as a barrier to the beginning of crystal formation and growth. The barrier can be viewed as the extra energy required to create the new surface between the crystal on the liquid.



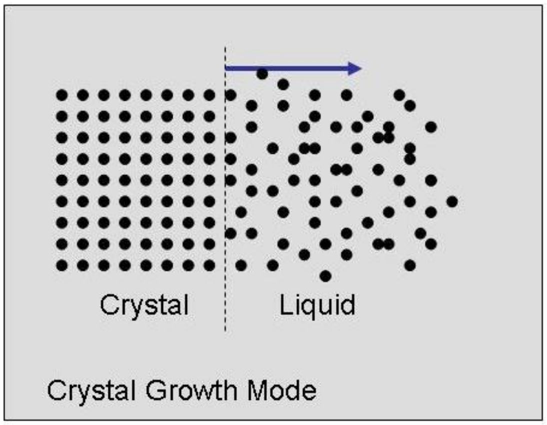
Nucleation of a crystal phase in Liquid

Because of this barrier to forming the first crystal nuclei, many liquids can be cooled quite a few degrees below their crystallization (or melt) temperature before any crystals can be observed to form in the solution. This situation is referred to as **supercooling**, where the solution is actually unstable relative to the crystal formation, but it simply can't find a means to get there - at least not right away. This is directly analogous to the situation of a solution of crystals dissolved in a solvent being brought to a temperature below the solubility limit. There we refer to this unstable condition as supersaturation.

The crystal formation depicted in the picture above is referred to as **homogeneous** nucleation, where the first tiny crystal nucleus must form directly within the liquid with no other interfaces to assist in the transition. An alternative is for the first crystals to form or nucleate on existing interfaces, such as the container wall, on foreign particles in the solution or even at the surface of air bubbles within the liquid. Nucleation on such foreign interfaces is referred to as **heterogeneous** nucleation. Heterogeneous nucleation is by far the more commonly observed process, as it provides a much lower energy path to crystal formation. True homogeneous nucleation can dominate only in the absence of these heterogeneous sites. The nucleation rates for both homogeneous and heterogeneous nucleation depend very strongly on the degree of under cooling.

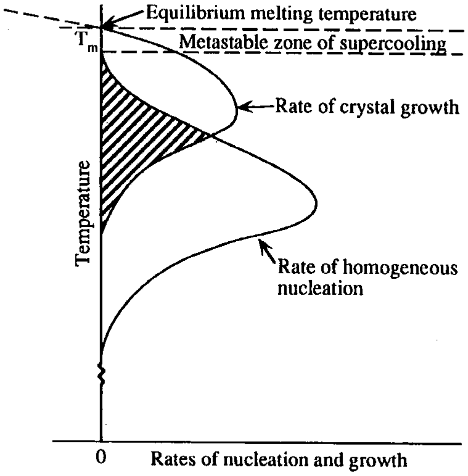
3. Crystal Growth

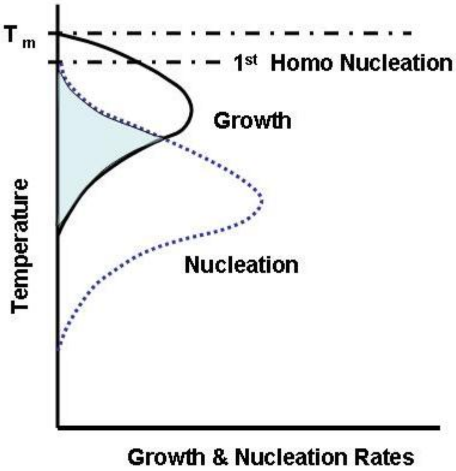
Once a small crystal seed has formed, (either from homogeneous or heterogeneous nucleation), it will continue to grow by advancing the crystal/liquid interface. Here the obstacle is no longer the creation of new interface but is limited more by the rate at which molecules can move in, align and grow new crystal layers. This is referred to as crystal growth step and its rate is also very temperature dependent.



Crystal Growth figure:

While the crystal growth and nucleation rates are both temperature dependent, they can have very different rates depending on the temperature. The difference between the temperature dependence of these two important crystallization processes is illustrated in the figure below.





Typically the crystal growth rate has its maximum at higher temperatures (approaching the melting temperature) where the solution is less viscous and molecules can move about more easily. The nucleation rates tend to maximize at somewhat lower temperature than the growth maximum. It is the under cooling which provides the driving force for both of these processes, but each in a slightly different fashion. It is the increasing viscosity with lower temperatures that provides the opposing effect, creating the maximum. As lower temperatures the supercooled liquid becomes too viscous for either nucleation or crystal growth to occur in any reasonable time. If one can cool the solution into this high viscous, lower temperature range fast enough to avoid the crystallization, then a glass can be formed instead. That is why glass formation and crystal formation are intimately intertwined.

One can also utilize this difference in nucleation and growth rates to control the size and quantities of crystals within a glass. Scientist and glass manufacturers utilize specific temperature profiles to first nucleate crystals followed by a period of higher temperature for the subsequent growth. These steps are also part of the process for making fudge, the creamy texture of which results from the presence of many tiny sugar crystals.