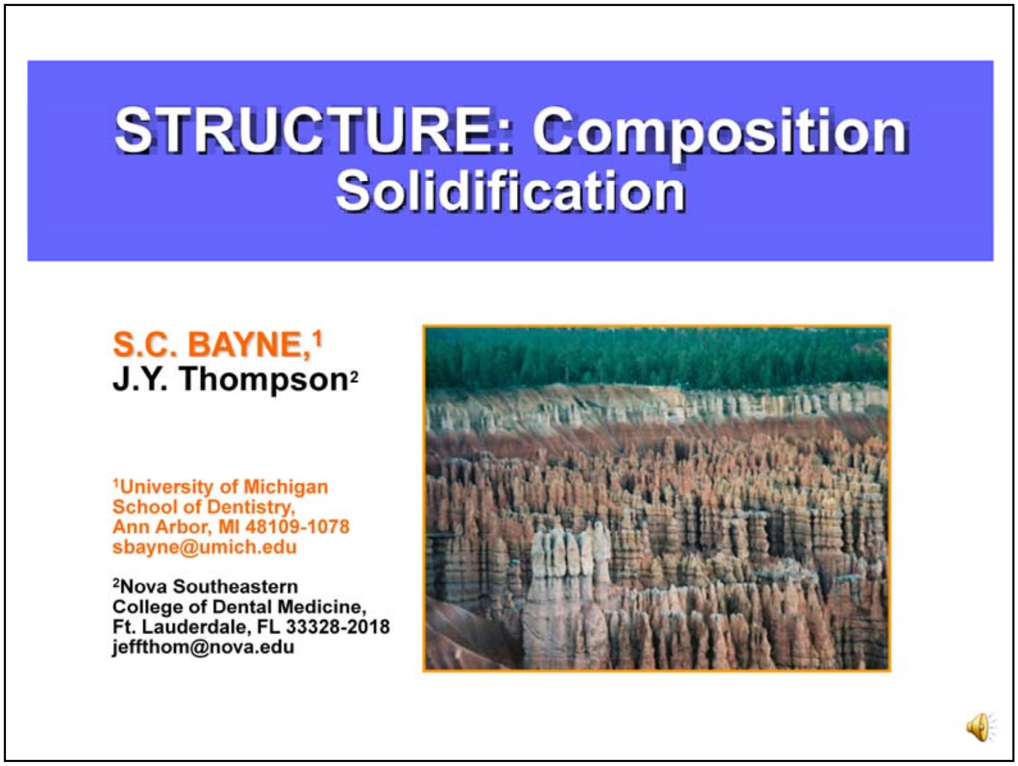
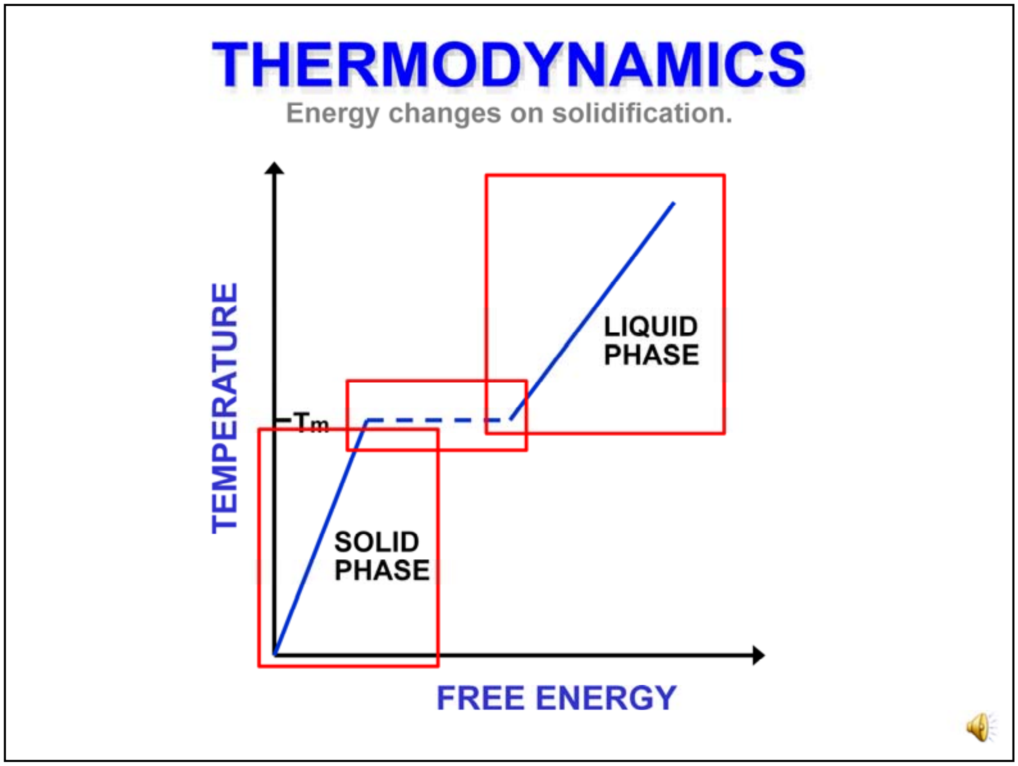


The composition of a material can involve a range of element types, bonded together with different primary and secondary bonding patterns, and with a range of phases depending on the relative solubility of the components. For all metals, many ceramics, and some polymers the solid state is crystalline so understanding these solid involves understanding how they crystallize from the liquid to the solid.

As we have already seen, crystallization allows the material to lower its energy. Crystallization requires that the material have sufficient thermal energy over a long enough time for the process to occur. The formation of the first little bit of stable organized solid is called a nucleus. Solidification depends on nucleation and then growth of crystals composition. There are two types of nucleation, homogeneous and heterogeneous, and these are the focus of this module. By controlling those processes you can dramatically affect the number of crystal and pattern of those crystal – affecting the final properties of the solid.



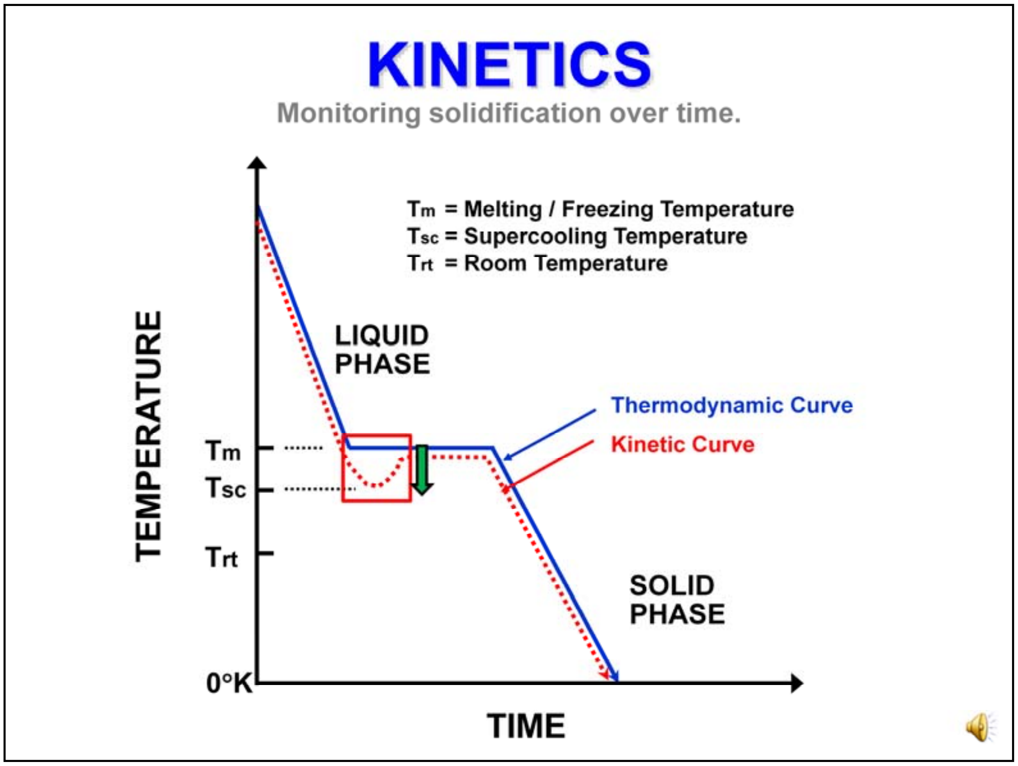
If you looked solely at the energetics of solidification, you would predict that everything occurred neatly at the freezing or melting temperature. We will use the abbreviation Tm to mean the temperature for melting or freezing. Tm implies that you are going up, but can also be used to talk about events when the temperature is going down.

[CLICK] Look at the graph above for the total energy of a system like water. Start in the upper right hand corner and follow the line downward. As you decrease the temperature, the total energy of the system decreases in a linear fashion. The heat capacity of the liquid (dE/dT) is the slope of the line.

[CLICK] At the Tm, the energy drops dramatically before the temperature continues to drop. This corresponds to the reduction in energy as disorganized liquid atoms or molecules become organized and reduce their energy. This is the energy of crystallization.

[CLICK] After crystallization is complete, the temperature starts to drop again. The heat capacity (dE/dT) for the new solid is different than for the liquid and so the slope of the line is different. The energy continues to decrease to absolute zero.

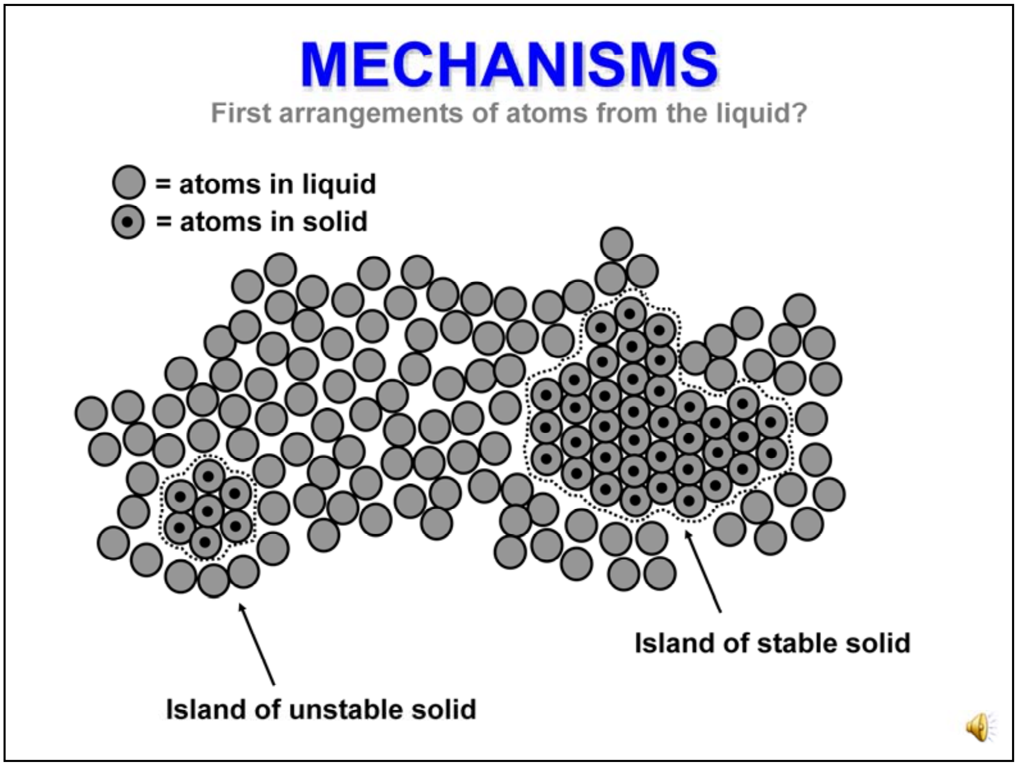
This is the ideal situation for T versus E, which we call the thermodynamic curve. If you monitor the T versus t (time) instead you observe aberrant behavior at the Tm when freezing is trying to occur. Let’s consider that next.



The blue curve that corresponds to the THERMODYNAMIC curve. Instead of T versus E, let's graph T versus t (time). **[CLICK]** What really happens on cooling is the red curve – which we call the KINETIC curve because it is related to time. On cooling from a high temperature, the cooling drops below the Tm, then recovers to the Tm, remains at Tm, and then begins to drop again. What is happening?

[CLICK] Well, the reason that T drops below Tm is because the liquid supercools and does not freeze right away. It is waiting for local organized regions of material to form that are stable enough to grow into crystals and truly start the process of solidification. As soon as solidification starts, the first energy released raises the temperature back up to Tm and crystallization continues. Once it is complete the temperature starts to drop again.

[CLICK] Supercooling is the rule for all materials being cooled. The extent of supercooling can be significant and represent up to 20% of the Tm (in degrees Kelvin). If the Tm is 1500 K, then the supercooling might be up to 300 K and solidification might not start until 1200 K.

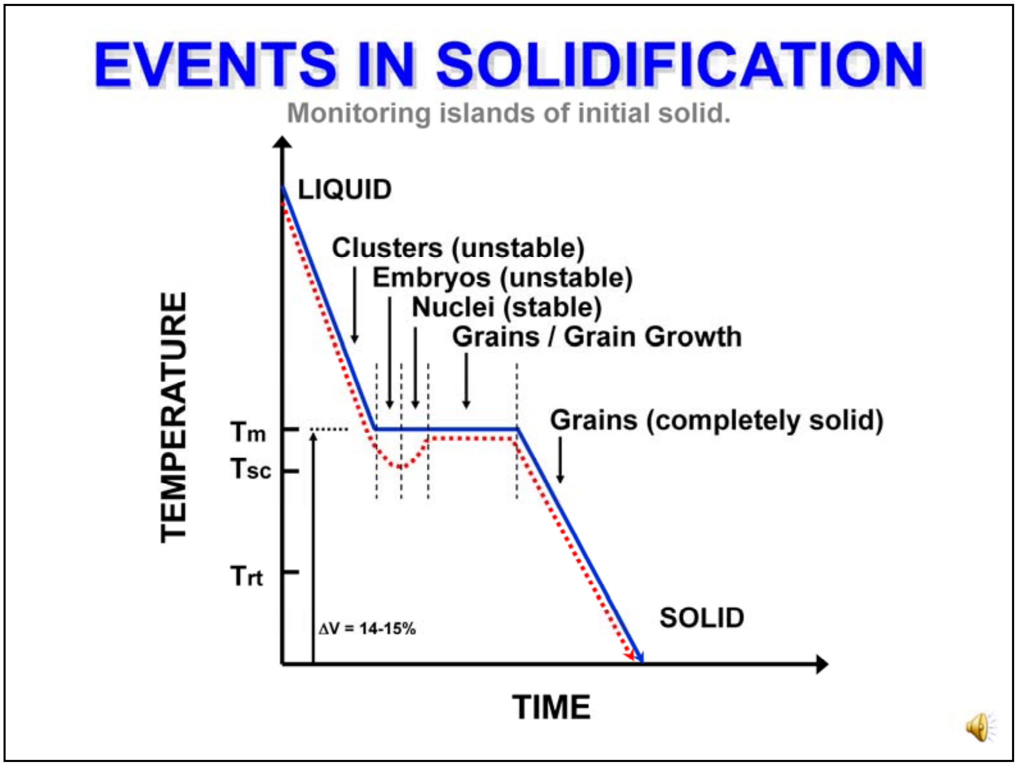


Now let's look at the what is happening on an atomic scale.

As the temperature cools down around Tm, very small regions of liquid will randomly get arranged into small islands called "clusters" **[CLICK]** but be energetically unstable because the T is still above the Tm. At or below Tm, islands continue to form called embryos but also tend to be unstable. Small amounts have a huge surface area to volume. The atoms inside the embryos are lower in energy but the surface atoms are actually at higher energy and overall this piece is not stable. Unless the embryo is very large it will not be energetically favorable to remain as solid.

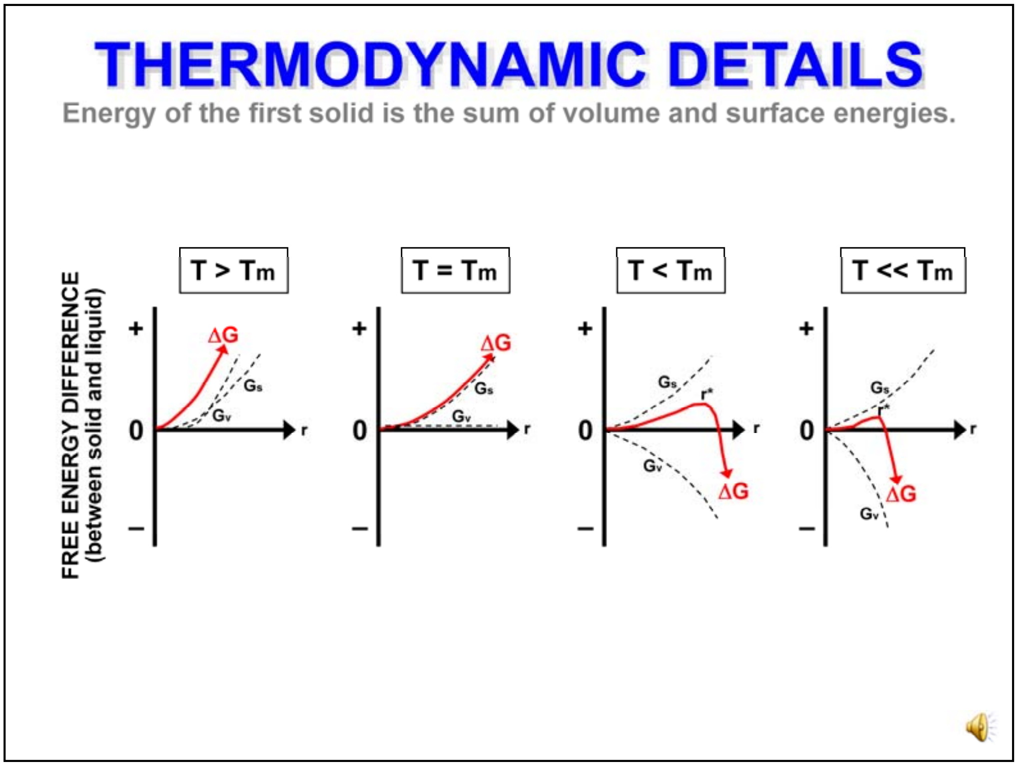
At sufficient supercooling, the energetics change and favor smaller and smaller islands being stable. These islands are called nuclei. **[CLICK]** They persist and continue to grow – causing solidification. The number of crystals which form in the solid is directly proportional to the number of nuclei which form. Solids with fewer but large crystals, have different properties than ones with many and smaller ones.

When crystals were first discovered they were viewed with low power light microscopes and the crystals looked like grains of sand. The name has remained ever since. We refer to crystals in solid as grains – and refer to their relative sizes as grain sizes.



Here is a map of the tendencies toward solidification. **[CLICK]** Clusters exist above Tm. **[CLICK]** Embryos exist at or below Tm. **[CLICK]** Nuclei exist well below Tm and are stable. **[CLICK]** Nuclei grow into grains. **[CLICK]** Once the solid is formed, it continues to uniformly decrease in temperature, again.

Another process, which we will explore later in more detail, is change in volume with changing temperature. As a liquid cools, it shrinks. Crystals occupy less space. **[CLICK]** All materials shrink about 14-15% on cooling from their Tm to down to absolute zero. Those with very high Tm values, shrink less per degree. The rate of shrinkage is called the “coefficient of thermal contraction or expansion.” It is linear but has different values for the liquid phase and the solid phase.



This explanation on this slide of the free energy (E) for events during crystallization is NOT required for this course but is presented for completeness. <u>You can skip over this material if you like</u>.

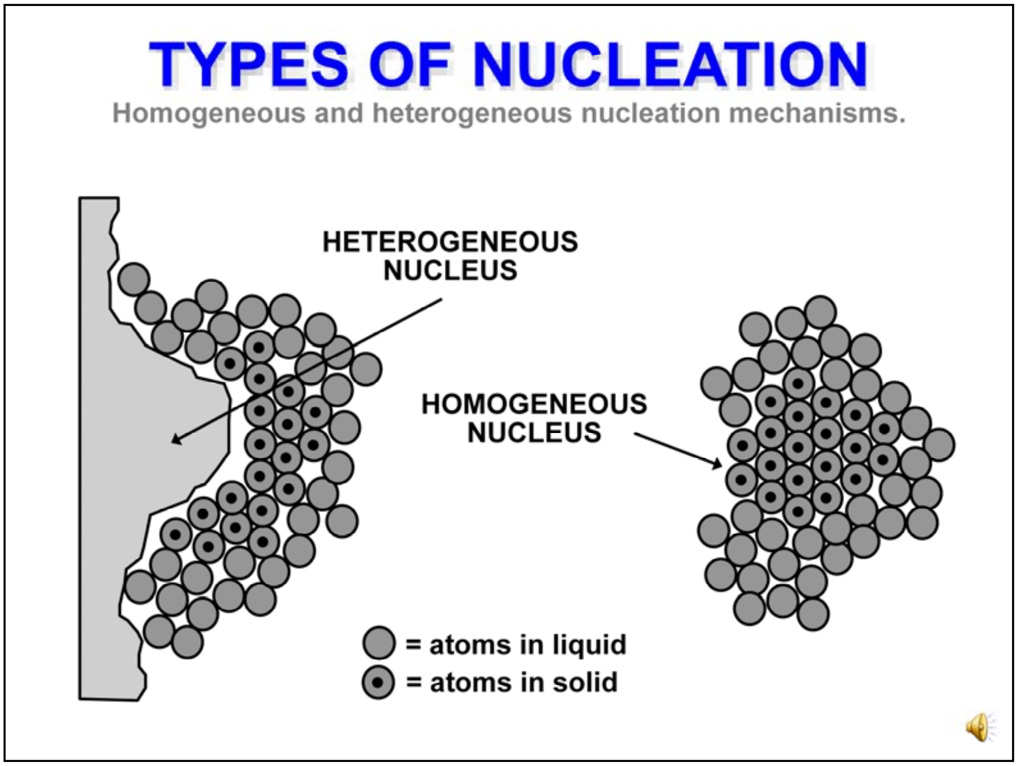
The explanation is presented for LIQUID above Tm (T>Tm), LIQUID at Tm (T=Tm), LIQUID slightly below Tm (T<Tm), and LIQUID well below Tm (T<<Tm). Let's look at each case. The total energy of the system is the energy of the volume (Gv) of material that is solid and the extra energy of the surface atoms (Gs). Surface atoms always have slightly higher energy because they cannot share their bonds with material above the surface like the ones in the bulk. Positive energy on the y-axis represents energies above that for solidification. There is a curve plotting the Gv and Gs for the radius (x-axis) of any organized piece of material.

T>Tm: For CLUSTERS at all sizes the energy (G) is positive and not negative. Clusters are unstable and disappear.

T=Tm: For EMBRYOS, at all sizes the energy (G) is positive. EMBRYOs are not stable.

T<Tm: For EMBRYOS only at very large sizes (which is improbable) is the net energy (G) is negative.

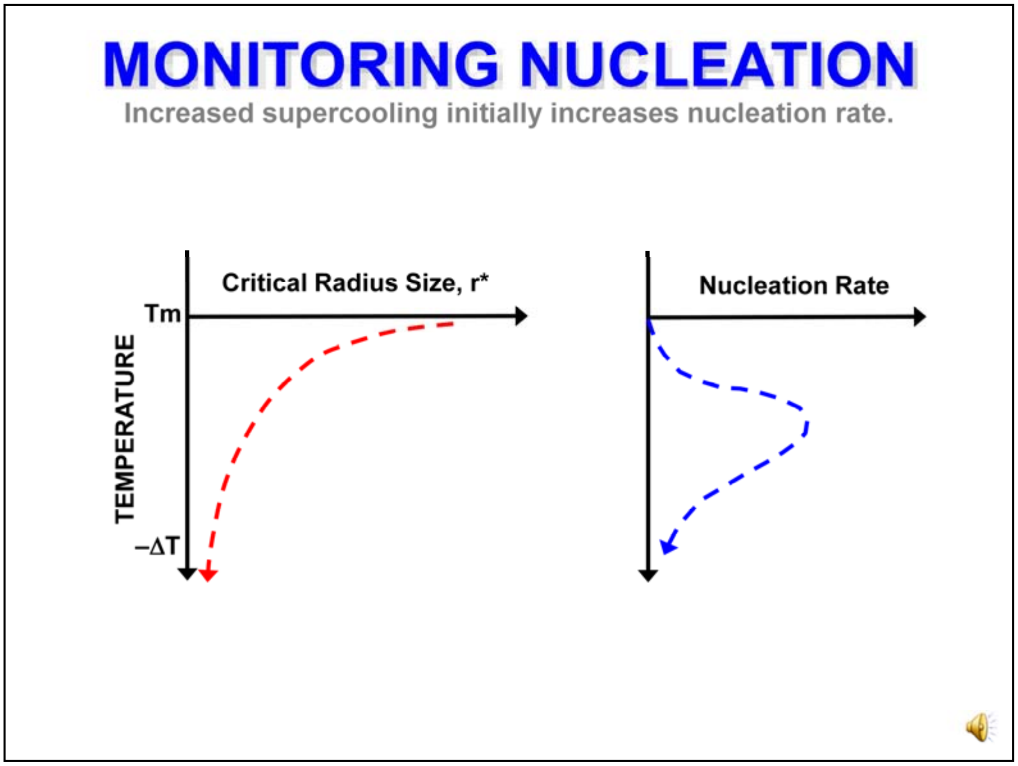
T<<Tm: For NUCLEI, at relatively small sizes, the energy (G) is negative and these islands are stable and grow into GRAINS.



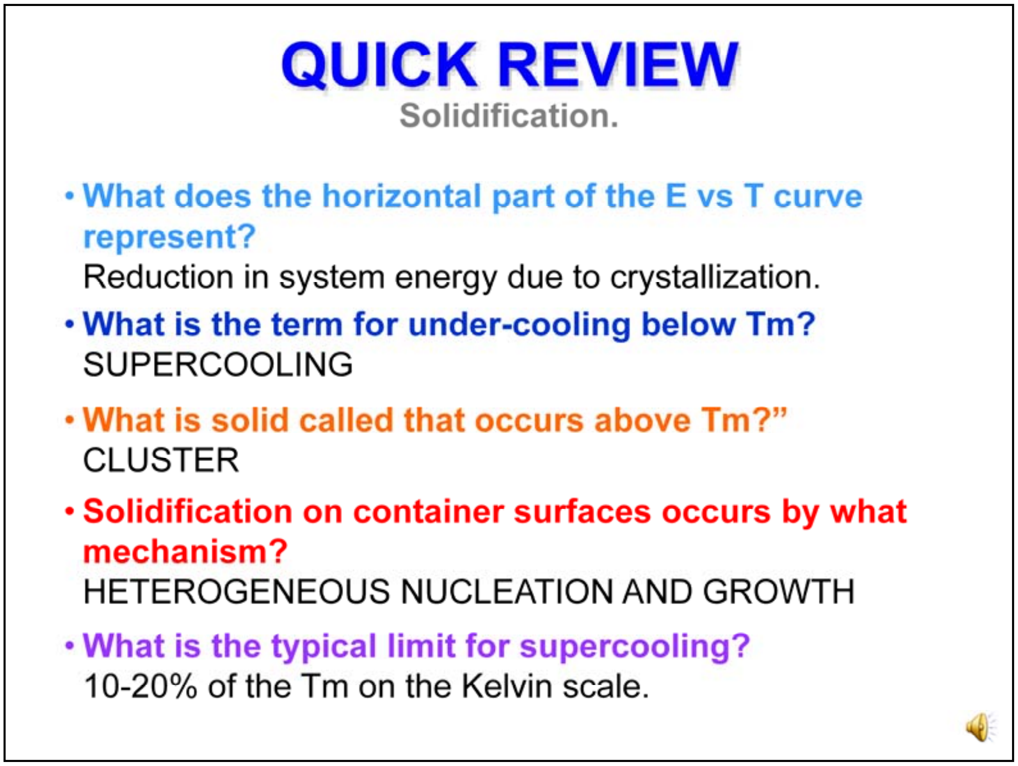
What we have described thus far is called HOMOGENEOUS NUCLEATION. It occurs within the liquid. Additionally, nuclei may also form at boundaries of the container for any liquid or at the surfaces of contaminants suspended in the liquid. These foreign surfaces are large enough to act as stable nuclei. These surfaces are called HETEROGENEOUS NUCLEI and material forming on these surfaces grows into normal grains. **[CLICK]**

In the real world both processes occur. Heterogeneous nucleation occurs first and if material is still not fully crystallized as supercooling proceeds, you observe homogeneous nucleation as well.

All transitions occur by nucleation. Bubbles form in champagne by nucleation. Rain drops form in clouds by nucleation. Hydroxyapatite crystals form during embryogenesis by nucleation. All transitions and changes of state occur by nucleation.



As shown in the previous slide, as the degree of supercooling increases, the critical radius size for a stable NUCLEUS gets smaller and smaller. That is why you do not tend to get supercooling below 20% of the absolute Tm. **[CLICK]** The odds of nucleation and grow rapidly increase with continuing supercooling but then falls off due to the decreasing thermal energy to get atoms to move around.



Here is a quick review of the concepts from this module.

[CLICK] (1) What is the horizontal portion of the E vs T thermodynamic curve represent?
[CLICK]

[CLICK] (2) What is the correct term for under-cooling below Tm?
[CLICK]

[CLICK] (3) What is first solid called that occurs above Tm?
[CLICK]

[CLICK] (4) Solidification on container surfaces occurs by what mechanism?
[CLICK]

[CLICK] (5) What is the typical limit for supercooling?
[CLICK]

THANK YOU.