Basics of Materials Engineering
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Lecture - 63
Kinetics of Phase Transformations
(Homogeneous Nucleation)

Welcome back. In this class we will discuss about thermal processing and heat treatment of steels.

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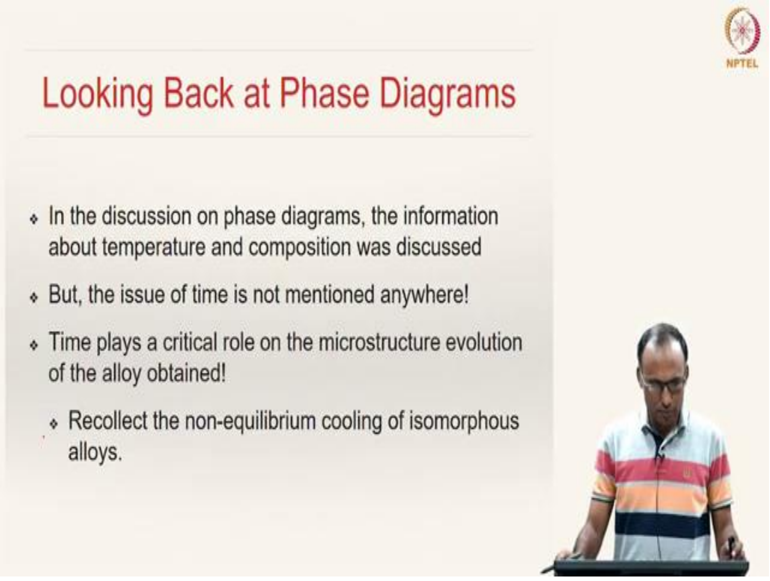

Looking Back at Phase Diagrams

- In the discussion on phase diagrams, the information about temperature and composition was discussed
- But, the issue of time is not mentioned anywhere!
- Time plays a critical role on the microstructure evolution of the alloy obtained!
  - Recollect the non-equilibrium cooling of isomorphous alloys.

Let us have a quick look back at phase diagram and see what we have discussed. In the discussion on phase diagrams, we primarily paid attention to the information about the temperature and composition. We have discussed for a given composition of an alloy when we are cooling it down how the microstructure evolves.

However, we have not actually discussed anywhere, the time that is required to convert a liquid phase to a solid state and at each and every instance, the time taken for the transformation to complete, at a given temperature.

The aspect of time is not studied anywhere during the discussion on phase diagrams; however, time plays a critical role in the microstructure evolution of the alloy of any composition that we are looking at - for instance, in binary phase diagrams.

We had a discussion on the effect of time for one specific case i.e., non-equilibrium cooling of isomorphous alloys, where we have shown that the microstructure during non-equilibrium cooling of an isomorphous alloy is different from the microstructure obtained through equilibrium cooling.

The major difference between equilibrium cooling and non-equilibrium cooling is the time involved or the amount of time that we are providing for the system to cool down at a given temperature. Hence, time is the key for real microstructure evolution during the solidification.

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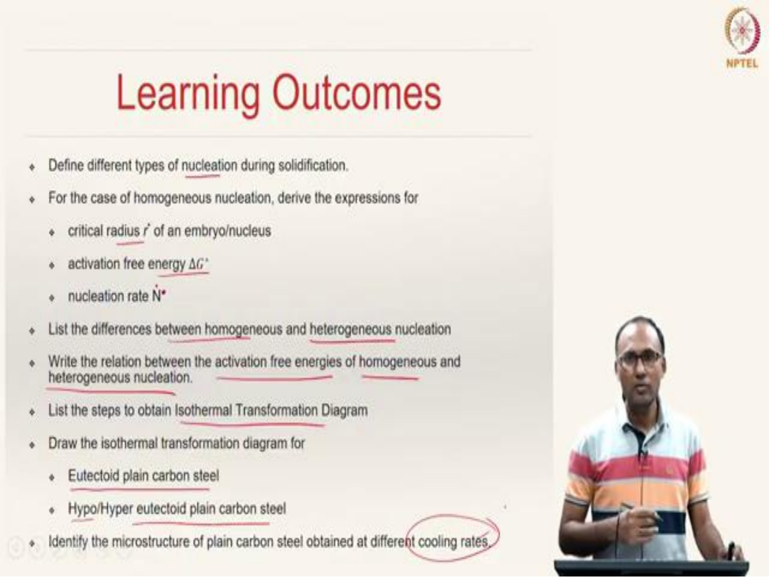

Learning Outcomes

- Define different types of nucleation during solidification.
- For the case of homogeneous nucleation, derive the expressions for
  - critical radius r^* of an embryo/nucleus
  - activation free energy ΔG^*
  - nucleation rate $\dot{N}^*$
- List the differences between homogeneous and heterogeneous nucleation
- Write the relation between the activation free energies of homogeneous and heterogeneous nucleation.
- List the steps to obtain Isothermal Transformation Diagram
- Draw the isothermal transformation diagram for
  - Eutectoid plain carbon steel
  - Hypo/Hyper eutectoid plain carbon steel
- Identify the microstructure of plain carbon steel obtained at different cooling rates.

In this module, we will pay attention to this aspect of time and understand how the microstructure evolution is going to get affected because of the time that is involved during the transformation. The learning outcomes of this module are – firstly, we will discuss about the fundamentals of this microstructure evolution.

The microstructure evolution from liquid state to solid state is governed by two phenomena; one is nucleation, followed by growth. We need to understand different types of nucleation during solidification. We should be able to define different types of nucleation during solidification.

For the case of homogeneous nucleation, we will be deriving the expression for critical radius $r^*$of a nucleus or embryo, activation free energy ΔG^*, and the nucleation rate $\dot{N}$. At the end of this module, we should be able to list the differences between homogeneous nucleation and heterogeneous nucleation.

You should be able to write the relation between the activation free energies of homogeneous nucleation and heterogeneous nucleation - how their activation free energies are related. We will talk about important concept called isothermal transformation diagram and while we are talking about isothermal transformation diagram, we should be able to list various experimental steps that one needs to undertake in order to generate such an isothermal transformation diagram.

We should be able to draw the isothermal transformation diagram for eutectoid plain carbon steel, hypo and hyper eutectoid plain carbon steels and identify the microstructure of plain carbon steel obtained at different cooling rates - that is the key. The time aspect is coming here and we will be able to see how the microstructure is evolving when we have different cooling rates.

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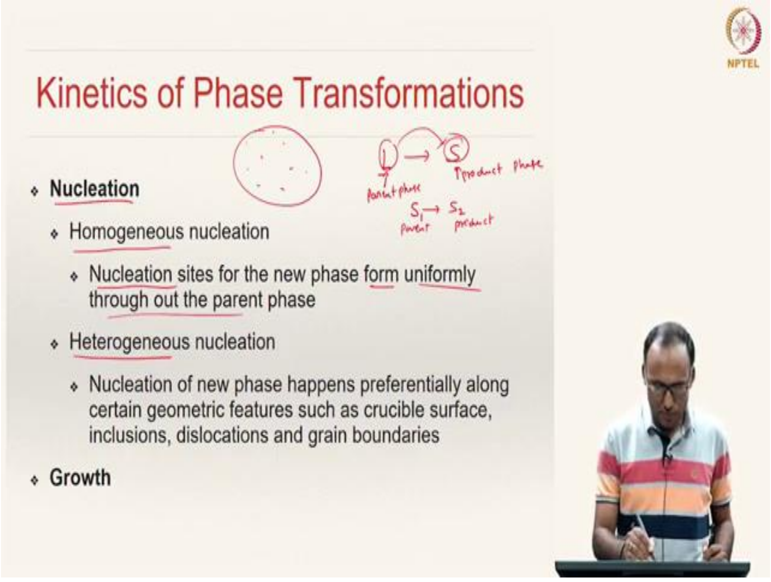

Kinetics of Phase Transformations

- Nucleation
  - Homogeneous nucleation
    - Nucleation sites for the new phase form uniformly through out the parent phase
  - Heterogeneous nucleation
    - Nucleation of new phase happens preferentially along certain geometric features such as crucible surface, inclusions, dislocations and grain boundaries
- Growth

To begin with, we will study about the kinetics of phase transformation. Phase transformation essentially means 2 aspects; firstly, you should have nucleation of the product phase. Let us say, have a liquid phase to solid phase transformation.

This liquid phase is called parent phase and solid phase is called product phase, if the phase transformation is happening from liquid state to solid state. As we have seen in the discussion on phase diagrams, we also have phase transformations happening within the solid state. For instance, eutectoid reaction and peritectoid reaction are the transformations that are happening within the solid state; that means, phase transformation need not always happen from liquid to solid, but it can also happen within solid state.

If it is happening from solid state 1 to solid state 2, then this is what is called our parent phase and this is our product phase. During the transformation from a parent phase to product phase, at an appropriate temperature, you have the nucleation of the product phase system. For instance, whenever we are solidifying a liquid, the nuclei of solid should form at the freezing temperature or solidification temperature.

There are two kinds of nucleation; homogeneous nucleation and heterogeneous nucleation. What do we mean by homogeneous nucleation? If the nucleation sites for the new phase, let us say in this case solid phase, form uniformly throughout the parent phase; that means, let us say this is our liquid, here the nucleation of the solid phase should happen uniformly throughout the parent phase - then such a nucleation is called homogeneous nucleation

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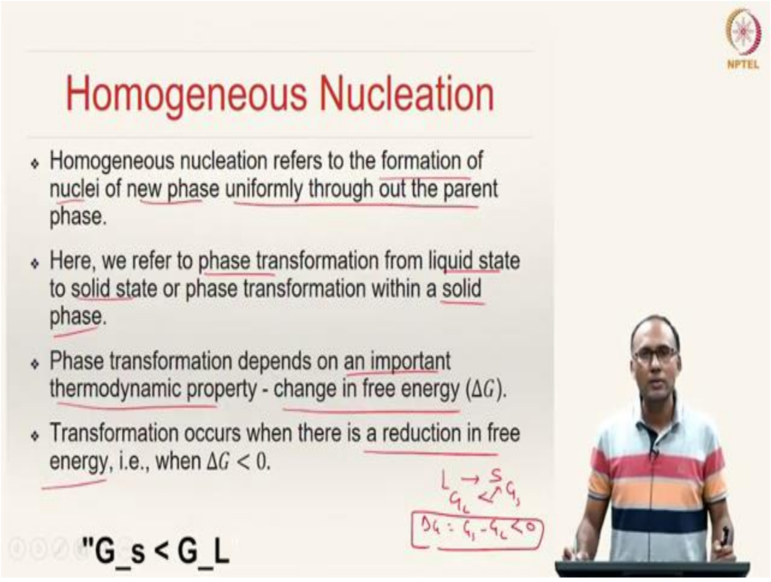

Homogeneous Nucleation

- Homogeneous nucleation refers to the formation of nuclei of new phase uniformly through out the parent phase.
- Here, we refer to phase transformation from liquid state to solid state or phase transformation within a solid phase.
- Phase transformation depends on an important thermodynamic property - change in free energy (ΔG).
- Transformation occurs when there is a reduction in free energy, i.e., when $\Delta G < 0$.

"G_s < G_L

In other words, there should not be any preference for the nucleation; there should not be any preferential sites for the beginning of nucleation. Such a nucleation is called homogeneous nucleation.

In heterogeneous nucleation, nucleation of the new phase happens preferentially along certain geometric features. For instance, if you are solidifying a liquid metal in a crucible, the crucible surface may be one of the favorable positions where nucleation can begin. Sometimes you may have inclusions and the inclusion surfaces can be favorable nucleation sites.

Similarly, if you have a system where a certain amount of liquid has transformed to solid, there may be some dislocations and grain boundaries that are generated - they can also be states of heterogeneous nucleation. However, within a solid state, if you have transformation from one solid state to another solid state, the grain boundaries and dislocations can act as preferential sites for nucleation.

In principle, you can have these two kinds of nucleation - homogeneous and heterogeneous nucleation. Once the nucleation of a product phase begins, this nucleus has to grow in order to finish the complete transformation. The next stage is growth stage. Let us now try to understand or spend some time understanding homogeneous nucleation and derive certain important expressions that we have discussed in the learning outcomes.

As we have already mentioned, the homogeneous nucleation refers to the formation of nuclei of new phase or product phase uniformly throughout the parent phase. There is no preference whatsoever for the location where the nuclei have to form. Here, we will be discussing about the phase transformation from liquid state to solid state or within solid phase. But the discussion that we are having can be applied to any phase transformation.

The phase transformation depends on an important thermodynamic property called change in free energy. A phase transformation from one phase to another phase occurs only when there is a reduction in free energy, what is the meaning of that?

At a given temperature, a liquid is transforming to solid; that means, the solid’s free energy is less than the liquid’s free energy. $\Delta G = G_{\mathrm{S}} - G_{\mathrm{L}} < 0$. Phase transformation happens from one phase to another phase only when the change in free energy is negative.

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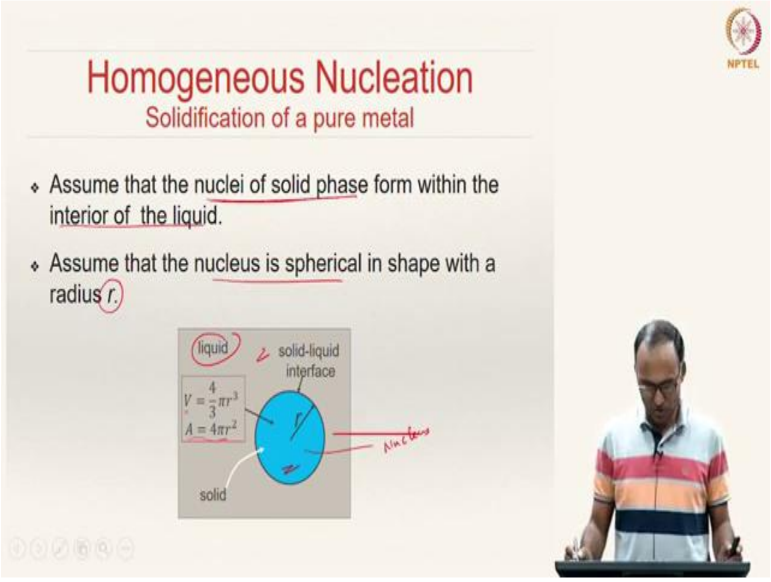

Homogeneous Nucleation

Solidification of a pure metal

- Assume that the nuclei of solid phase form within the interior of the liquid.
- Assume that the nucleus is spherical in shape with a radius r.

Let us now look at the solidification of a pure metal under homogeneous nucleation. Assume that this grey area that I am showing here is the liquid. Let us assume that the nuclei of solid phase, we are paying attention to one nucleus, but there are several such nuclei formed uniformly throughout the liquid phase because it is homogeneous nucleation - but we are paying attention to one such nuclei.

Assume that the nuclei of solid phase form within the interior of the liquid. If you have liquid pool, you are assuming that the nucleus is forming within the interior, it is not forming on the boundary.

We are assuming that the nucleus is having a spherical shape. However, the methodology that we are developing can be applied to any other shape too. To make the discussion simple, we are going to assume the nucleus to be of spherical shape with radius r.

As shown here, the blue color represents the nucleus or solid and the grey color represents the liquid. The boundary of the sphere, in 2D is shown as a circle; this is the solid liquid interface. The volume and surface area of the sphere are,

$$V = \frac{4}{3}\pi r^3$$

$$A = 4\pi r^2$$

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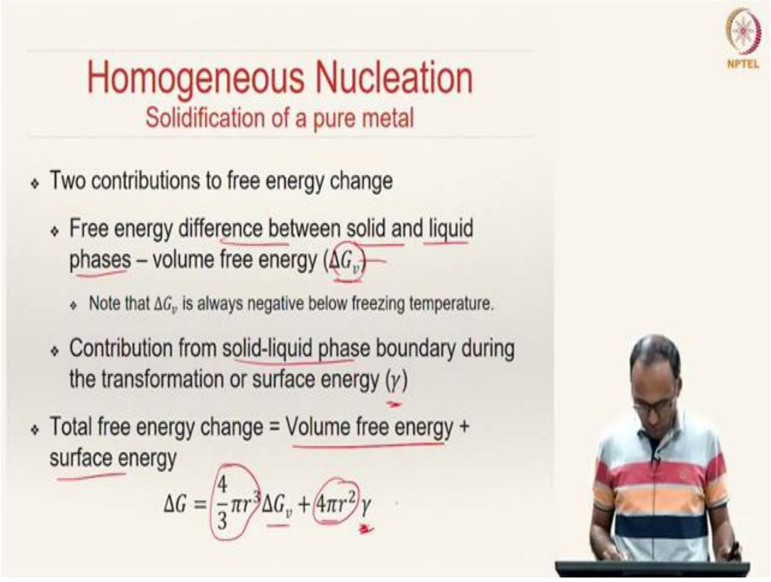

Homogeneous Nucleation

Solidification of a pure metal

- Two contributions to free energy change
  - Free energy difference between solid and liquid phases – volume free energy (ΔG_v)
    - Note that ΔG_v is always negative below freezing temperature.
  - Contribution from solid-liquid phase boundary during the transformation or surface energy (γ)
- Total free energy change = Volume free energy + surface energy

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

When we have system like that, there will be two contributions to free energy change. First contribution is the free energy difference between solid and liquid phases, which is going to be negative; that is what we are calling volume free energy.

ΔG_v is the volume free energy which is negative if at all the phase transformation is happening as the solid phase free energy should be less than the liquid phase free energy.

One contribution is from the volume and another contribution is from the boundary or surface; that is called surface energy. The total free energy change is equal to volume free energy plus surface energy.

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

The first term is the volume free energy, which is volume times free energy change. The second term is the surface area times γ, where γ is the surface energy associated with the interface boundary between solid and liquid.

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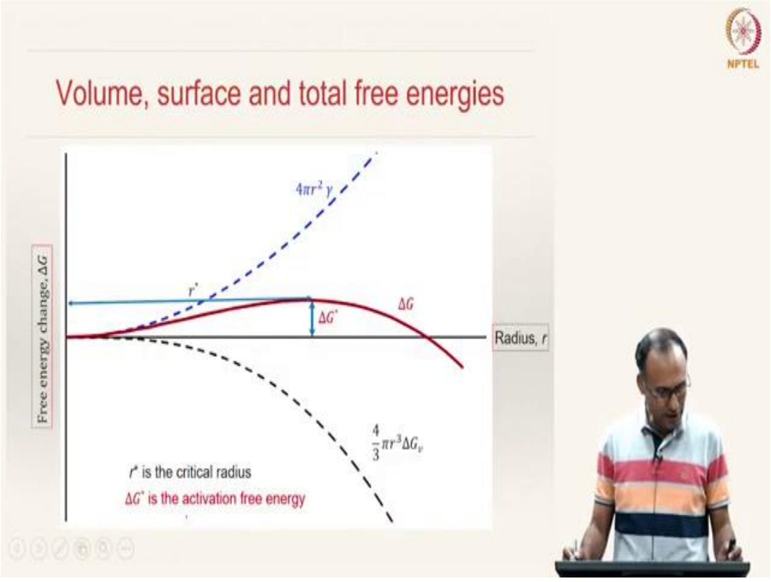

Volume, surface and total free energies

r^* is the critical radius

ΔG^* is the activation free energy

Let us plot the quantities volume free energy, surface energy and the total quantity. Note that volume free energy a is negative quantity, whereas surface energy is a positive quantity. The dashed blue line represents the surface energy term, i.e., $4\pi r^2\gamma$. The dashed black line represents the free energy volume free energy term, i.e., $\frac{4}{3}\pi r^3\Delta G_v$. The sum of these two quantities is described by the solid red line which shows a maximum and then decreases.

Please note that this free energy ΔG is plotted as a function of the radius of the nucleus. Up to here, the free energy is increasing and then it is decreasing. Let us try to understand what is the meaning of that.

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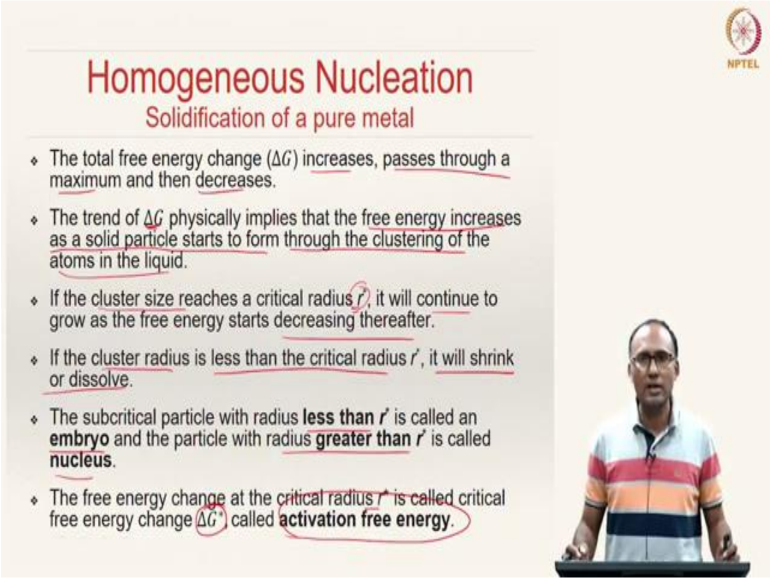

Homogeneous Nucleation

Solidification of a pure metal

- The total free energy change (ΔG) increases, passes through a maximum and then decreases.
- The trend of ΔG physically implies that the free energy increases as a solid particle starts to form through the clustering of the atoms in the liquid.
- If the cluster size reaches a critical radius r^*, it will continue to grow as the free energy starts decreasing thereafter.
- If the cluster radius is less than the critical radius r^*, it will shrink or dissolve.
- The subcritical particle with radius **less than r^*** is called an **embryo** and the particle with radius **greater than r^*** is called **nucleus**.
- The free energy change at the critical radius r^* is called critical free energy change (ΔG^*) called **activation free energy**.

The total free energy change increases, passes through a maximum and then decreases. So, this trend of ΔG physically implies that the free energy increases as a solid particle starts to form through the clustering of the atoms in the liquid. What happens when the solid particle is starting to form? The atoms from the liquid state should be coming together and start clustering to form a nucleus. When such a process is happening, the free energy change ΔG first increases and then decreases.

If the cluster size reaches a critical radius r^* i.e., this distance, the nucleus will continue to grow as the free energy now starts decreasing thereafter. If the clustering of atoms from the liquid state to solid state reaches a critical size r^*, that is when the nucleus continues to grow because ΔG starts decreasing.

However, if the cluster radius -- cluster radius means, the radius of this cluster of atoms which are trying to form a nucleus -- is less than the critical radius, then what happens? Because it is not energetically favorable, it cannot be stable and hence, it will shrink or dissolve. If it is less than r^*, a further increase will result in the increase of total free energy, which is not an energetically favorable situation.

The subcritical particle with radius less than r^* is called embryo; so that means if the particle size is less than r^*, the embryo which will eventually dissolve or shrink. The particles with radius greater than r^* are called nucleus. At the critical radius r^*, the free energy change is ΔG^*.

The free energy change corresponding to the critical radius r^* is what we call critical free energy change ΔG^* or it is also called activation free energy and that is important.

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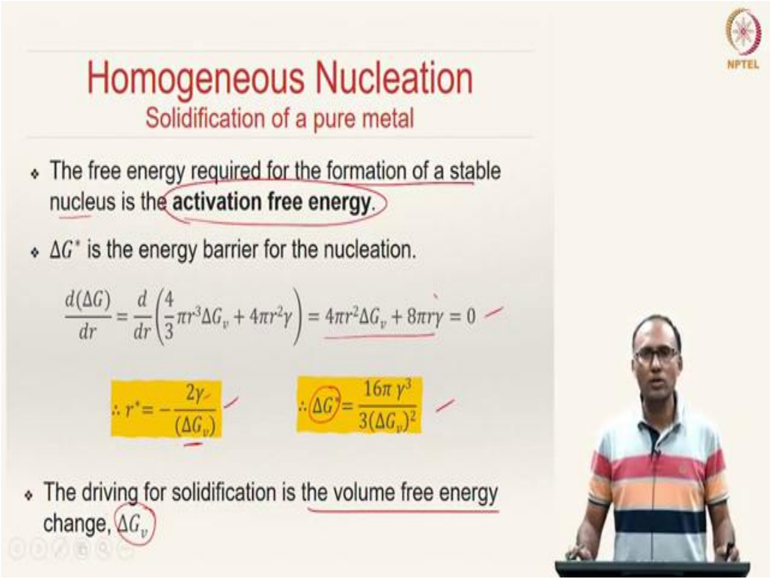

Homogeneous Nucleation

Solidification of a pure metal

- The free energy required for the formation of a stable nucleus is the **activation free energy**.
- ΔG^* is the energy barrier for the nucleation.

$$\frac{d(\Delta G)}{dr} = \frac{d}{dr}\left(\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma\right) = 4\pi r^2 \Delta G_v + 8\pi r \gamma = 0$$

$$\therefore r^* = -\frac{2\gamma}{(\Delta G_v)} \qquad \therefore \Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

- The driving for solidification is the volume free energy change, ΔG_v

The free energy required for the formation of stable nucleus is what we call activation free energy. This is the free energy change required to form a stable nucleus; otherwise, the nucleus will be unstable and will again dissolve.

We have seen ΔG is a function of r, and ΔG^*corresponds to the maximum value of ΔG.

$$\frac{d(\Delta G)}{dr} = \frac{d}{dr}\left(\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma\right) = 4\pi r^2 \Delta G_v + 8\pi r \gamma = 0$$

$$\therefore r^* = -\frac{2\gamma}{\Delta G_v}; \Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$

The critical radius depends on the surface energy and the volume free energy of the system. The critical free energy change or the activation free energy can be found by substituting the value of r^* in the expression for $\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$.

The driving force for the solidification is the volume free energy ΔG_v. If you have less activation free energy, it is much easier for the formation of nucleus.

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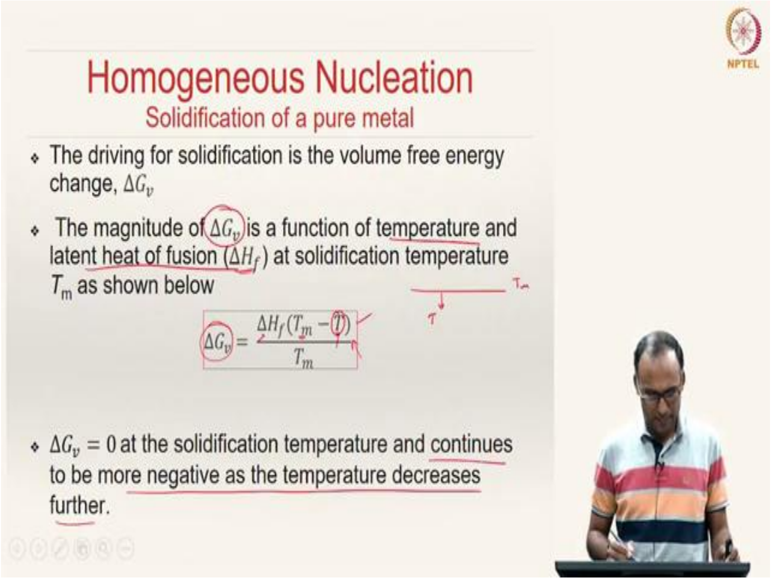

Homogeneous Nucleation

Solidification of a pure metal

- The driving for solidification is the volume free energy change, ΔG_v
- The magnitude of ΔG_v is a function of temperature and latent heat of fusion (ΔH_f) at solidification temperature T_m as shown below

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

- $\Delta G_v = 0$ at the solidification temperature and continues to be more negative as the temperature decreases further.

The magnitude of volume free energy ΔG_v is a function of temperature and latent heat of fusion, ΔH_f.

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

In the above expression, T_m is the solidification/melting temperature, T is the temperature at which we are trying to find out the volume free energy. So, volume free energy is a function of temperature.

At the solidification temperature i.e., when $T_m = T$, $\Delta G_v = 0$. We know that ΔH_f is negative, because it is the latent heat of fusion; that means its heat not supplied, but heat is lost by the system and hence it is negative.

As T reduces, i.e., as the difference $T_m - T$ increases, ΔG_v becomes more negative. So, at solidification temperature, it is 0 and continues to be more negative as temperature T decreases further.

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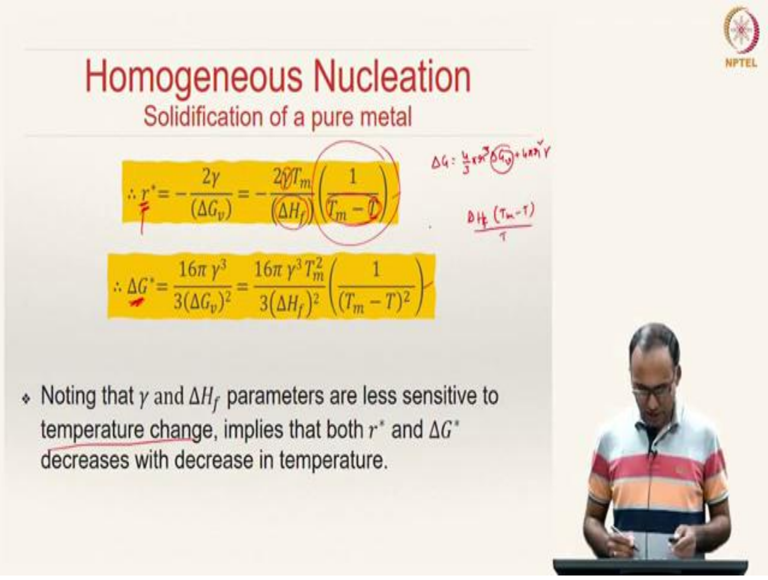

Homogeneous Nucleation

Solidification of a pure metal

$$\therefore r^* = -\frac{2\gamma}{(\Delta G_v)} = -\frac{2\gamma T_m}{(\Delta H_f)}\left(\frac{1}{T_m - T}\right)$$

$$\therefore \Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} = \frac{16\pi\gamma^3 T_m^2}{3(\Delta H_f)^2}\left(\frac{1}{(T_m - T)^2}\right)$$

$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$

$\frac{\Delta H_f (T_m - T)}{T}$

- Noting that γ and ΔH_f parameters are less sensitive to temperature change, implies that both r^* and ΔG^* decreases with decrease in temperature.

We can now write r^* and ΔG^* in terms of latent heat of fusion and temperature.

$$r^* = -\frac{2\gamma}{\Delta G_v} = -\frac{2\gamma}{\Delta H_f}\left(\frac{1}{T_m - T}\right)$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} = \frac{16\pi\gamma^3 T_m^2}{3(\Delta H_f)^2}\left(\frac{1}{(T_m - T)^2}\right)$$

The quantities surface free energy i.e., γ and latent heat of fusion delta i.e., H_f are usually less sensitive to temperature change. They are sensitive, but they are not very strong functions of temperature.

From the above expressions, if we assume γ and ΔH_f are constants (they do not change with temperature), as you reduce the temperature T, r^* and ΔG^* also reduce.

As you are reducing this number, this difference increases; as a result, this fraction reduces and hence you will have lower value of r^*. In the expression $\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$, upon substituting $\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$, we obtain ΔG as a function of temperature.

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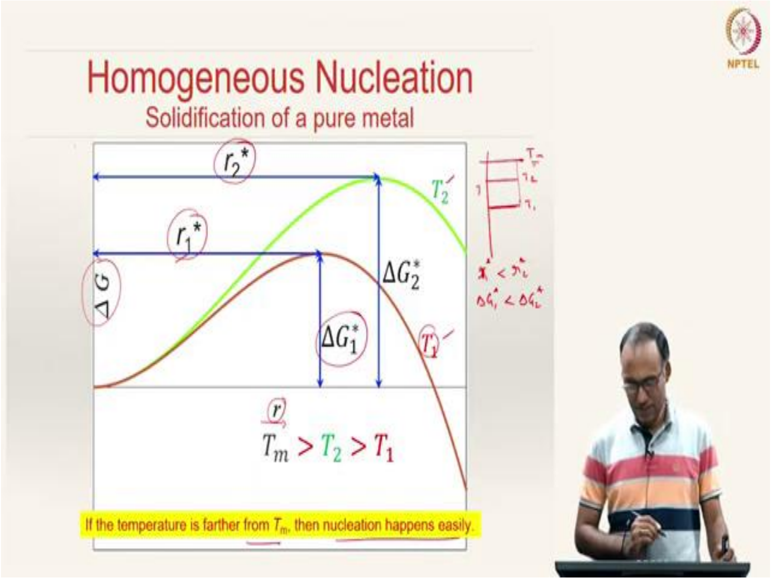

Homogeneous Nucleation

Solidification of a pure metal

$T_m > T_2 > T_1$

If the temperature is farther from T_m, then nucleation happens easily.

Once we find the expression for ΔG, we can plot ΔG as a function of r for different values of temperatures. Let us say T_m is somewhere up here, where $\Delta G_v = 0$.

Let us plot ΔG as a function of r at two different temperatures such that $T_m > T_2 > T_1$, then we can clearly see as the temperature reduces, r^* reduces.

You can see that $r_1^* < r_2^*$ and $\Delta G_1^* < \Delta G_2^*$. At lower temperatures, it is much easier for the nucleation to happen. If the temperature is far away from the freezing temperature, then the critical radius and activation free energy are less. Hence, the nucleation happens more readily at temperatures far below the solidification temperatures. So, if the temperature is farther from T_m, nucleation happens easily.

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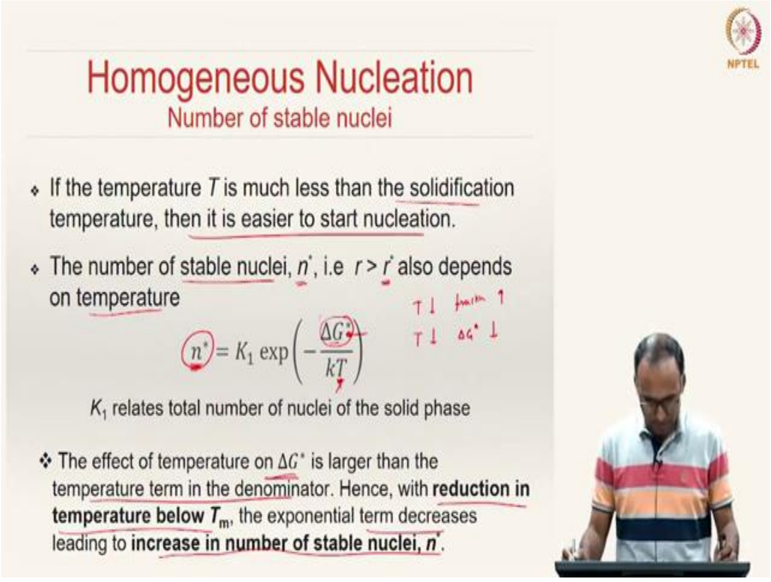

Homogeneous Nucleation

Number of stable nuclei

- If the temperature T is much less than the solidification temperature, then it is easier to start nucleation.
- The number of stable nuclei, n^*, i.e $r > r^*$ also depends on temperature

$$n^* = K_1 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

$T \downarrow$ fractn $\uparrow$

$T \downarrow$ $\Delta G^* \downarrow$

K_1 relates total number of nuclei of the solid phase

- The effect of temperature on ΔG^* is larger than the temperature term in the denominator. Hence, with **reduction in temperature below T_m**, the exponential term decreases leading to **increase in number of stable nuclei, n^***.

So far, we have focused our attention to the nucleation of one particle. Because we are talking about homogeneous nucleation, the number of such stable nuclei n^* -- whenever we are saying stable nuclei n^*, that means for all these n^* nuclei, the radius is greater than r^*(which also depends on temperature).

n^* can be expressed as a function of ΔG^* and the temperature. For a given temperature, we know ΔG^*, which is also a function of temperature T.

$$n^* = K_1 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

With reduction in temperature, ΔG^* reduces. This term in the exponential has the effect of temperature on the numerator as well as on the denominator.

If you reduce the temperature, this entire quantity is increasing if you keep ΔG^* constant. Let us carefully look at it. Normally, ΔG^* is a function of temperature. However, for the sake of argument, let us say ΔG^* is constant. Then, as you reduce the temperature, this fraction increases.

Let us now forget about the effect of temperature. As you reduce temperature, ΔG^* reduces. The numerator term has an effect which is opposing the effect that is caused by the denominator term; because the temperature is also going to affect and ΔG^* is also a function of temperature.

The effect of temperature, however, is larger on ΔG^*. Hence, with a reduction in temperature below T_m, the exponential term decreases - that means this term decreases.

However, there is a negative here, and as a result the number of stable nuclei n^* increases; that means as you go away from the solidification temperature, as you go down, the number of stable nuclei also increases. The nucleation is easier and the number of stable nuclei also will be more as you go away from the solidification temperature.

So, that is the concept that we need to understand that, the number of stable nuclei increases as you reduce the temperature from the solidification temperature.

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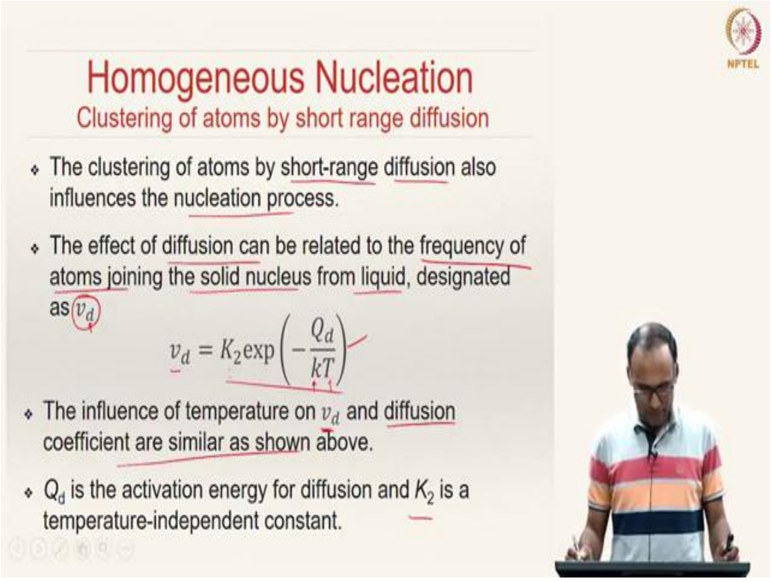

Homogeneous Nucleation

Clustering of atoms by short range diffusion

- The clustering of atoms by short-range diffusion also influences the nucleation process.
- The effect of diffusion can be related to the frequency of atoms joining the solid nucleus from liquid, designated as v_d

$$v_d = K_2 \exp\left(-\frac{Q_d}{kT}\right)$$

- The influence of temperature on v_d and diffusion coefficient are similar as shown above.
- Q_d is the activation energy for diffusion and K_2 is a temperature-independent constant.

Another important aspect during nucleation -- we know that the nucleation happens by clustering of atoms within the liquid state to form a solid nucleus. So, the clustering of atoms happens by short range diffusion which also influences the nucleation process. That means, we need to also take into consideration of the fact that, how many atoms are coming and attaching to the already clustered solid surface.

The effect of this short-range diffusion can be related to the frequency of atoms joining the solid nucleus from liquid. That basically represents the short-range diffusion of the atoms for clustering. This is basically described by the frequency of atoms joining the solid state from the liquid state and this frequency is designated by v_d, the d (in the subscript) is to represent diffusion.

This can be expressed similar to the diffusion coefficient.

$$v_2 = K_2 \exp\left(-\frac{Q_d}{kT}\right)$$

The influence of temperature on the frequency of atoms joining the nucleus and the diffusion coefficients are similar as shown by this equation. In the above expression, Q_d is the activation energy for diffusion, K_2 is a temperature independent constant, k is the Boltzmann constant and T is temperature in absolute Kelvin.

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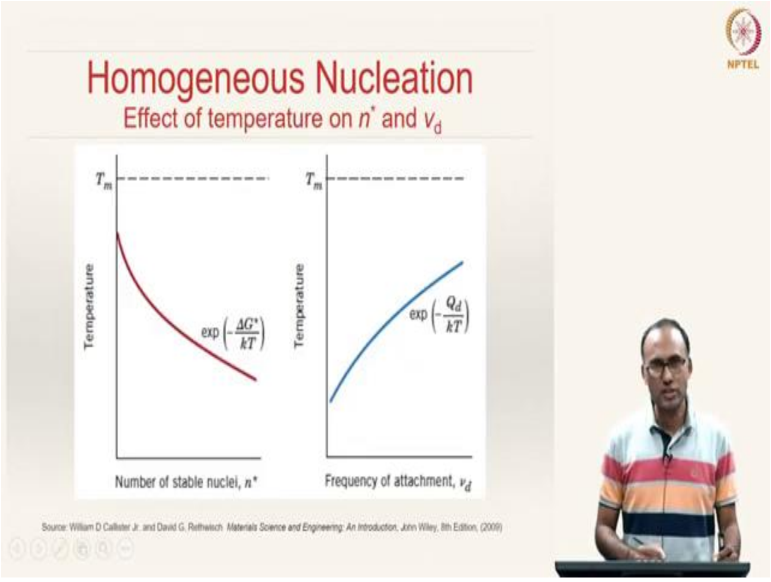

Homogeneous Nucleation

Effect of temperature on n^* and v_d

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

The nucleation is dependent on both the number of stable nuclei and also the frequency at which the atoms from liquid state are coming and getting attached to the solid nucleus.

If you would plot the number of stable nuclei n^* and the frequency of attachment v_d, they are having mutually opposing effects. On the x-axis, we are showing nucleation; so at high temperatures it is low, whereas at high temperatures the diffusion or the frequency of attachment is high.

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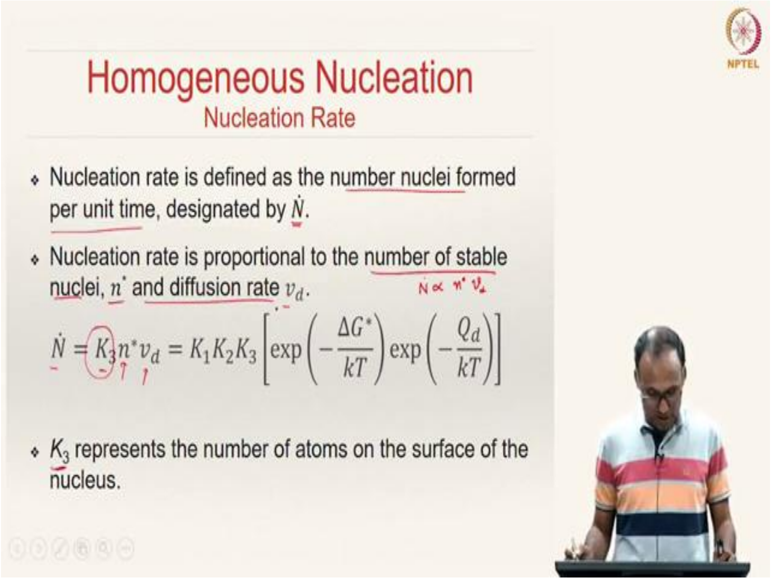

Homogeneous Nucleation

Nucleation Rate

- Nucleation rate is defined as the number nuclei formed per unit time, designated by $\dot{N}$.
- Nucleation rate is proportional to the number of stable nuclei, n^* and diffusion rate v_d.

$\dot{N} \propto n^* v_d$

$$\dot{N} = K_3 n^* v_d = K_1 K_2 K_3 \left[\exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{Q_d}{kT}\right)\right]$$

- K_3 represents the number of atoms on the surface of the nucleus.

Let us now define another term called nucleation rate. What do we mean by nucleation rate? The number of nuclei formed per unit time is what is called nucleation rate designated by $\dot{N}$. The nucleation rate is proportional to the number of stable nuclei and the diffusion rate or the frequency at which the atoms from liquid state are coming and attaching to the solid state. So, it is proportional to n^* and v_d.

$$\dot{N} \propto n^* v_d = K_3 n^* v_d = K_1 K_2 K_3 \left[\exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{Q_d}{kT}\right)\right]$$

In the above expression, K_3 is the proportionality constant for nucleation rate, and it represents the number of atoms on the surface of the nucleus.

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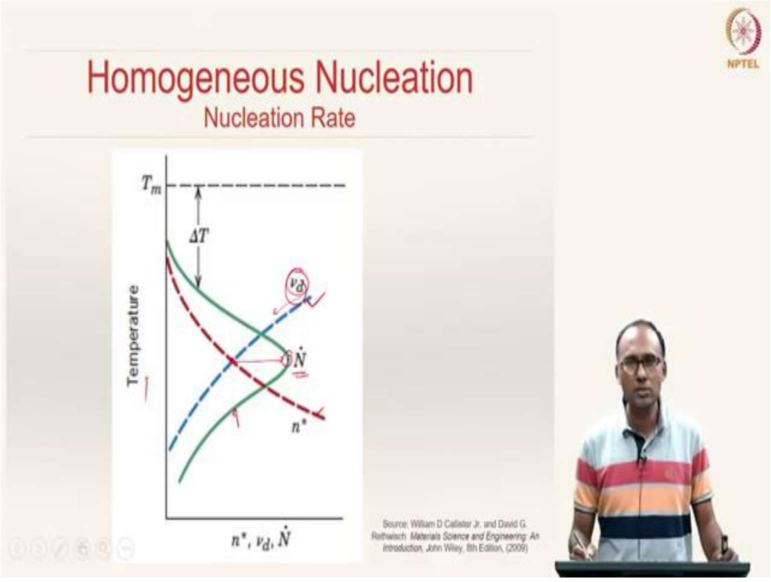

Homogeneous Nucleation

Nucleation Rate

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Let us now plot how the nucleation rate changes as a function of temperature. On the y-axis, we are showing temperature, on the x-axis, we are showing the green curve; this is our nucleation rate and this we have already plotted, but we are plotting it on the same graph - n^* is the number of stable nuclei as a function of temperature and also the diffusion or the frequency of attachment of atoms as a function of temperature.

As you can see, n^* increases as you decrease the temperature, v_d decreases as you decrease the temperature. The combined effect i.e., the product of these two things is what we are calling nucleation rate and this is shown by the green curve.

As you are reducing the temperature, the nucleation rate starts increasing and then reaches a maximum and then decreases. The maximum value of this nucleation rate will happen approximately when the number of stable nuclei n^* and v_d will be equal. So, around this temperature where they are meeting, and around the same temperature you will have maximum value of nucleation rate.

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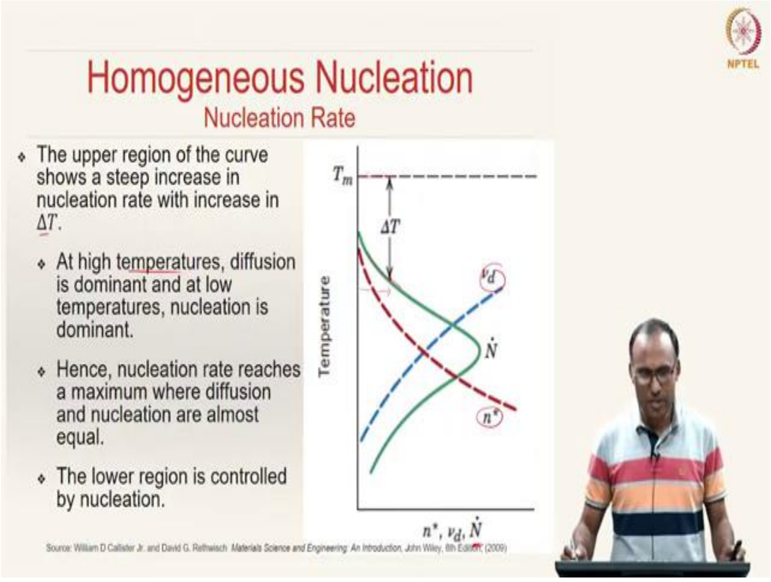

Homogeneous Nucleation

Nucleation Rate

- The upper region of the curve shows a steep increase in nucleation rate with increase in ΔT.
  - At high temperatures, diffusion is dominant and at low temperatures, nucleation is dominant.
  - Hence, nucleation rate reaches a maximum where diffusion and nucleation are almost equal.
  - The lower region is controlled by nucleation.

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition (2009)

The upper region of this nucleation rate curve shows a steep increase; you can see that there is a steep increase in the nucleation rate with decrease in ΔT.

Here, ΔT is the temperature difference between the solidification temperature and the temperature at which are we are calculating the nucleation rate. As you are increasing ΔT or as we are decreasing the temperature (both are equivalent), the nucleation rate first increases.

As we know, at high temperatures as we can see, diffusion is dominant and at low temperatures nucleation is dominant. Hence as expected, the nucleation rate reaches a maximum, where diffusion and nucleation rates are almost equal. The lower region is controlled by nucleation, and the upper region is controlled by diffusion, or the lower region is limited by diffusion and the upper region is limited by nucleation.

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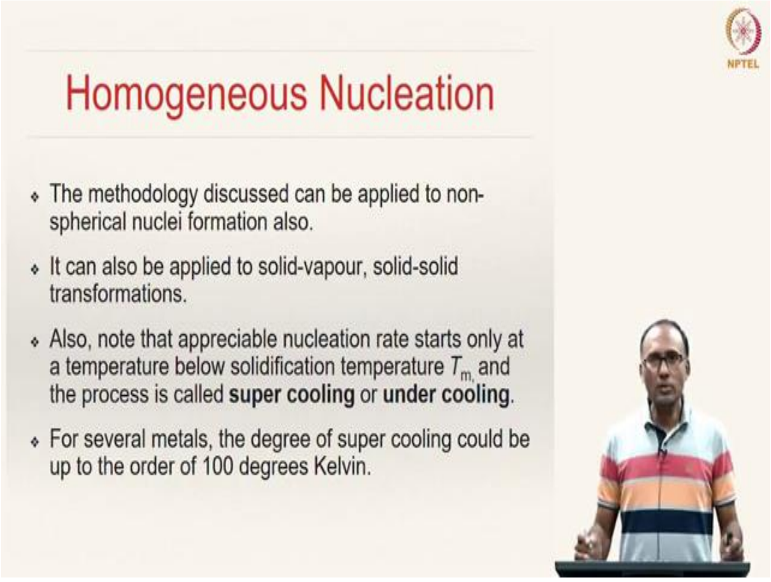

Homogeneous Nucleation

- The methodology discussed can be applied to non-spherical nuclei formation also.
- It can also be applied to solid-vapour, solid-solid transformations.
- Also, note that appreciable nucleation rate starts only at a temperature below solidification temperature T_m, and the process is called **super cooling** or **under cooling**.
- For several metals, the degree of super cooling could be up to the order of 100 degrees Kelvin.

The methodology that we have discussed need not necessarily be applicable only for spherical nuclei; it can be applied for non-spherical nuclei also. It can also be applied to other phase transformations like solid-vapor, solid-solid and so on. Note that in this previous graph, up to this temperature away from T_m, you do not have a reasonable/appreciable amount of nucleation rate.

The nucleation rate starts picking up after certain temperature below our freezing temperature. The appreciable nucleation rate starts only at a temperature below solidification temperature T_m and the process of bringing the temperature below the solidification temperature for creation of nucleation is called super cooling or under cooling. The amount of temperature by which we are reducing the temperature from the solidification temperature is what we call degree of under cooling or degree of super cooling.

For several metals, the degree of super cooling could be of the order of 100 K; for several metals for homogeneous nucleation if you would calculate, the degree of super cooling would be around few 100 K. The ΔT that we are talking about is the degree of super cooling.

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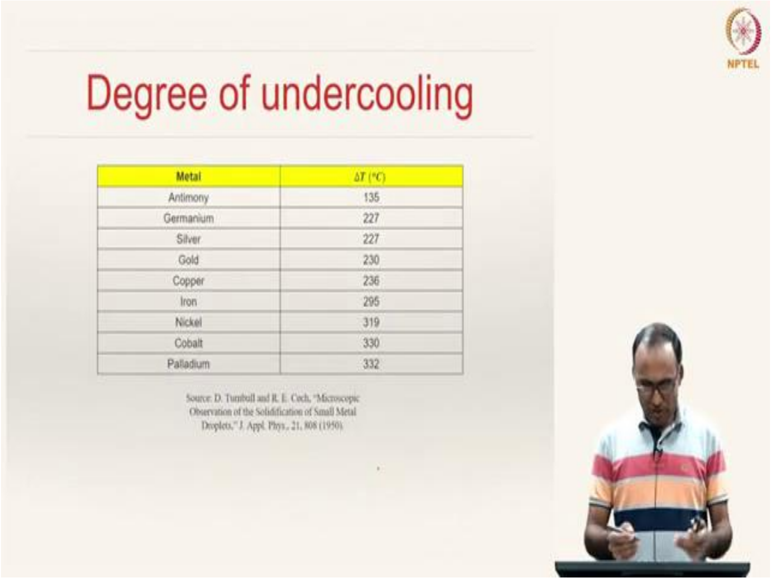

Degree of undercooling

Metal	ΔT (°C)
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

Source: D. Turnbull and R. E. Cech, "Microscopic Observation of the Solidification of Small Metal Droplets," J. Appl. Phys., 21, 808 (1950).

This table here shows the degree of under cooling for several metals. For instance, in the case of iron, for the nucleation rate to have an appreciable number, you need to under cool pure iron to almost 300 K or 300° degrees C, below the solidification temperature.