Introduction to Materials Science and Engineering
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Lecture - 90
Nucleation

We are discussing the topic of phase formation. And one of the important concepts in phase transformation is Nucleation. So, today we will discuss this idea of nucleation.

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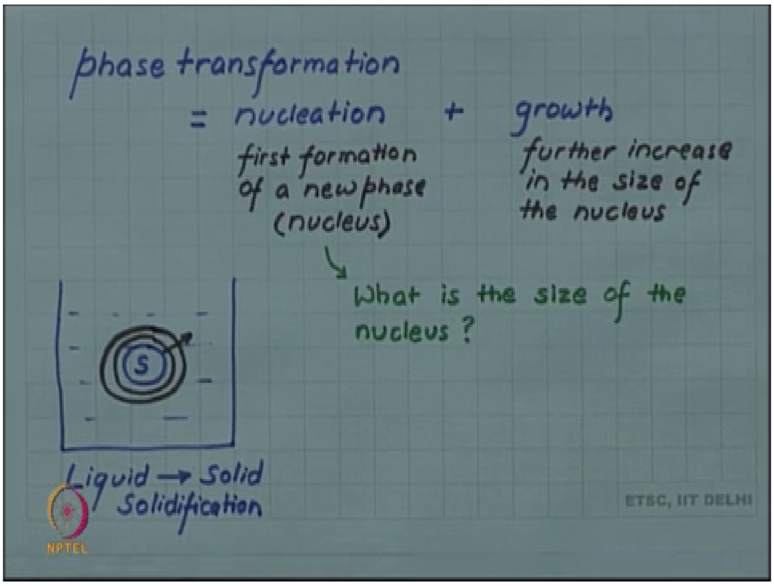

phase transformation
= nucleation + growth

first formation of a new phase (nucleus)

further increase in the size of the nucleus

What is the size of the nucleus ?

Liquid → Solid
Solidification

We have looked at phase transformation. So, phase transformation essentially involves, formation of a new phase in a pre existing phase. So, some pre existing phases is present let us say we have, liquid and in this liquid is going to solidify. So, if we are taking the example of liquid to solid phase transformation, which we call solidification. Let us take this transformation as an example because, this is a familiar transformation.

Now, so, in if liquid is going to solidify, or form solid a solid region has to first form. This first formation of a new phase is called nucleation. So, phase transformation is divided into two stages a stage called nucleation followed by another stage called growth.

So, the first formation of a new phase is called nucleation. So, nucleation is of a new phase so, this region which has formed in the beginning, this is what is called a nucleus.

So, this stage is nucleation after that this nucleus which has formed will continue to increase in size. So, the subsequent increase in size is called growth so, growth in the size of the nucleus.

So, let us look at nucleation in a little bit more detail. So, one important thing which we want to ask that what is the size of the nucleus, the question we want to raise what is the size of the nucleus how large or how small can nucleus be.

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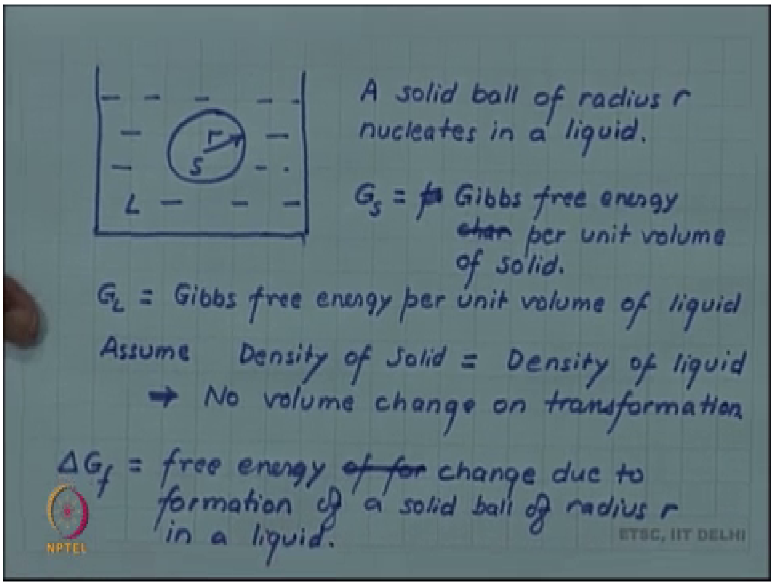

A solid ball of radius r nucleates in a liquid.

G_S = Gibbs free energy ~~chan~~ per unit volume of solid.

G_L = Gibbs free energy per unit volume of liquid

Assume Density of Solid = Density of liquid

→ No volume change on transformation

ΔG_f = free energy ~~of for~~ change due to formation of a solid ball of radius r in a liquid.

So, let us say so, let us analyse the energetics of nucleation process, how the energy of the system is changing, if let us say a solid ball of radius r this is solid forms inside an unstable liquid. So, this is our model nucleus. So, a solid ball of radius r nucleates in a liquid.

So, what will be the changes in energies? So, let us say we have defined let us define G S as let us say Gibbs free energy, Gibbs free energy per unit volume of solid. And let us say G L similar quantity for liquid. So, it is Gibbs per unit volume of liquid and, let us for simplicity assume that there is no density change that is density of liquid is equal to density of solid we assume, this assumption is not essential, but it will keep the mathematical development simpler.

So, we assume this for the moment density of solid is equal to density of liquid, or in other words there is no volume change there is no volume change on transformation.

So, in this case we can see that there is a free energy change on solidification. So, let us try to write that free energy change. So, let me let me call delta G f is the free energy of free energy free energy change due to formation of a solid ball of radius r in a liquid. And let us try to write this free energy change

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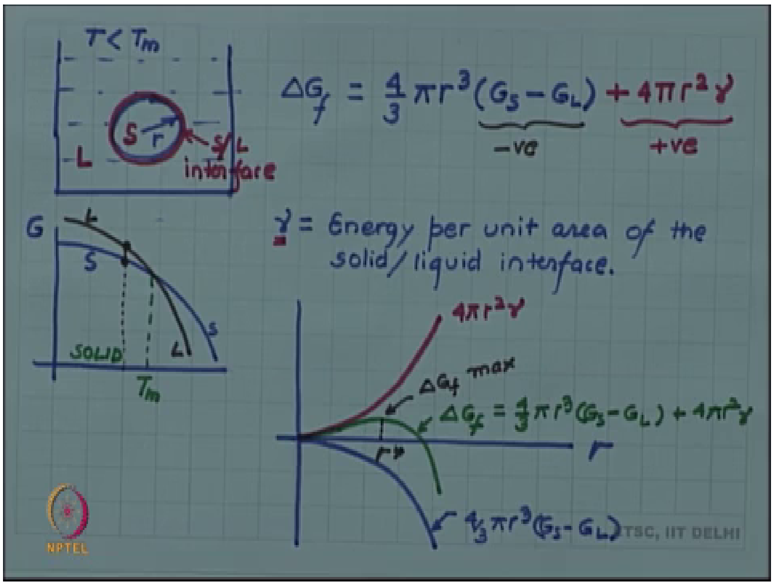

We have this solid ball of radius r, in our liquid and we are trying to write the expression for free energy change. So, since you can see that a ball of radius r solid of ball of radius r has formed. So, you have 4 by 3 pi r cube times G S with the free energy which has been added to the system, but the same volume times G L free energy has been subtracted from the system because so, much of liquid disappeared.

So, if the liquid free energy per unit volume is G L, then 4 by 3 pi r cube G L free energy reduction has taken place because, now we do not have that much of liquid. And corresponding amount of solid has been added. So, this is the change in free energy per unit volume due to the formation of solid of ball of radius r, in terms of the quantities which we have defined. And what is the sign of this?

If we say that liquid is unstable remember. So, that is if we say that the temperature is below T m temperature is below T m remember, the free energy is we had drawn. So, this will be liquid, this will be solid, the intersection point defines the melting point and, below the melting point solid is the stable phase was already stable here. So, if temperature is below T m, if we were working here, then liquid has higher free energy G

L is higher G S is less. So, this term is negative. So, G S minus G L is negative so there is a reduction in free energy and so, this will show that for whatever the radius of radius r maybe, since G S minus G L is negative delta G f will always be negative.

So, a transformation is possible, irrespective of whatever the radius r. We consider but in reality this is not true because we know that it is possible to under cool liquid and to keep it in a metastable form, which shows that the nucleation of solid in some cases is difficult, which means something is obstructing the nucleation to happen. And what is that obstruction?

So, this is not the complete free energy change on the formation, we have to add one more term and what is that term. Let us see you cannot create a ball of radius r, unless and until you also create what is called a solid liquid interface. So, a solid liquid as soon as a ball of radius r of solid is formed, a solid liquid interface is also created and a solid liquid interface will have an energy associated with it.

So, that energy is called the surface energy and, we have met this in the defects chapter. So, there will be a surface energy and let us call gamma, as energy per unit area of the solid liquid interface. And this will always be positive and this positive term has to be added to this expression to complete it.

So, let us add that you can see that for a ball of radius r, the area will be 4 pi r square and since we are seeing that gamma is energy per unit area, we simply multiply this with gamma to give us an additional term. And this additional term by it is very nature you can see is positive. So, this will show that depending on the value of gamma and G S and G L it is not guaranteed that delta G f will be negative whatever the value of r is.

So, let us try to see how free energy varies one, if we once we have taken into account this surface energy. So, let us draw these energy terms as a function of radius r. So, let us first draw in the free energy the volume term. So, that is 4 by 3 pi r cube G S minus T L it is negative. And it varies as r cube so, it will be going down like this. And if we add the surface energy term to this so, the surface energy varies is 4 by power is 4 pi r square gamma.

So, this will be positive and this will be going. And, if we add these two terms and you can see that initially for small r, r square term is dominant, but for large r r cube becomes dominant.

So, initially the curve will follow r square curve and will be going up, but gradually as the radius becomes large the curve will be pulled down, which means you will have. So, this is this is total delta G f 4 by 3 pi r cube G S minus G L r square gamma. So, you can see here now that this curve goes through since initially it was increasing, because of the r square term and, then gradually it starts decreasing. So, there is a radius let us call that critical radius at which delta G f is maximum.

Now, what is the significance of this radius r star, we can see if r is less than r star and we want to increase the size of the solid ball, then delta G f increases. So, this is thermodynamically not a favourable situation that the free energy change increases, with increasing radius.

So, solid balls of radius r will not grow. So, solid balls of radius r less than r star will not grow, but if you have solid balls of radius r larger than r star, then further increase in radius brings the free energy down. So, growth will be possible, if radius is larger than r star.

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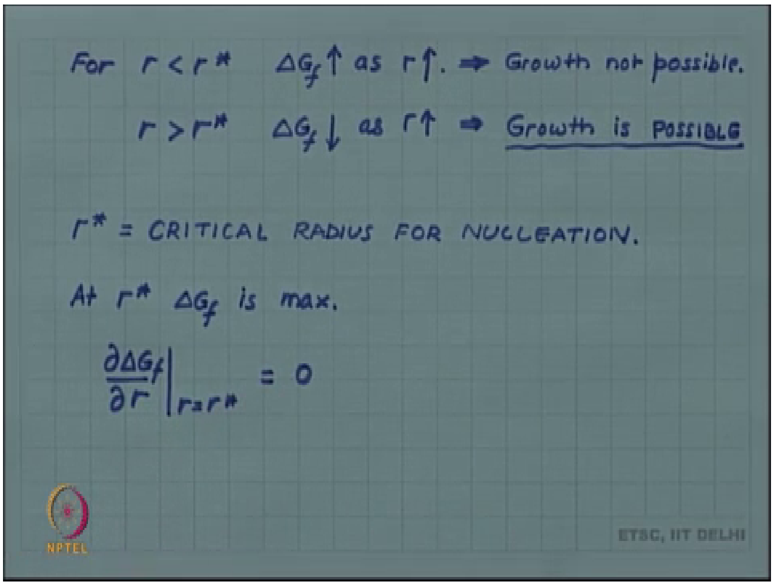

For $r < r^*$ $\Delta G_f \uparrow$ as $r \uparrow$. $\Rightarrow$ Growth not possible.

$r > r^*$ $\Delta G_f \downarrow$ as $r \uparrow$ $\Rightarrow$ Growth is POSSIBLE

r^* = CRITICAL RADIUS FOR NUCLEATION.

At r^* ΔG_f is max.

$$\left.\frac{\partial \Delta G_f}{\partial r}\right|_{r=r^*} = 0$$

So, let us make a note of this observation that therefore, r less than r star delta G f increases as r increases. So, this implies that growth is not possible thermodynamically not possible, but if r is greater than r star, then delta G f decreases as r increases which means growth is now possible growth is possible.

So, which this clearly indicates that the new nucleus which forms has to have at least a minimum radius of r star because, anything less than that the growth is not possible. So, that is why we call this r star critical radius for nucleation. So, nuclei cannot be less than a critical size this is very very interesting result because recall that we are talking about a temperature T, which is less than the freezing temperature. So, even if the liquid is below the freezing temperature solid of radius r, less than r star cannot form. So, one has to assemble a solid ball of radius greater than r star, for it for the growth to be possible.

So, this is the critical radius for nucleation, we can find this in terms of our variables which we introduced. So, recall that we are saying that at r star delta G f is maximum. So, at r star delta G f is maximum, which means the differential coefficient of delta G f with r at r is equal to r star should be 0. So, if we start with our expression and differentiate it with respect to r we can expect to find r star.

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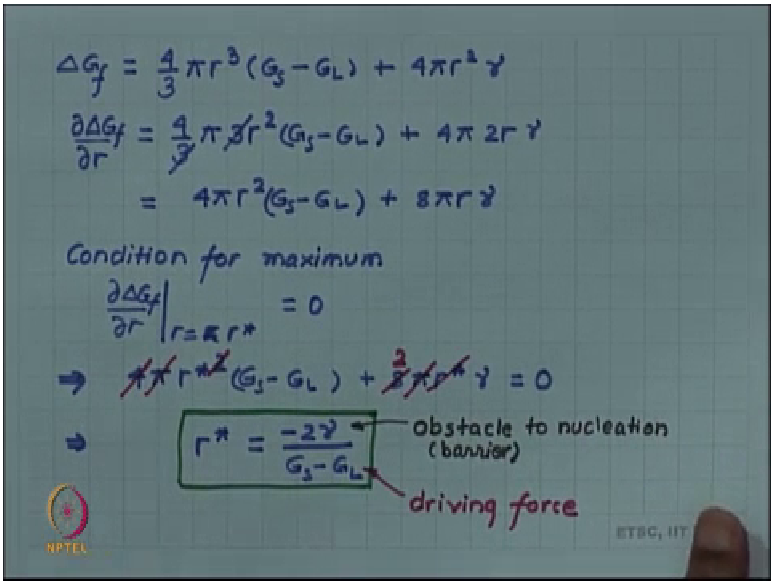

$$\Delta G_f = \frac{4}{3}\pi r^3 (G_s - G_L) + 4\pi r^2 \gamma$$

$$\frac{\partial \Delta G_f}{\partial r} = \frac{4}{\cancel{3}}\pi \cancel{3} r^2 (G_s - G_L) + 4\pi\, 2r\, \gamma$$

$$= 4\pi r^2 (G_s - G_L) + 8\pi r \gamma$$

Condition for maximum

$$\left.\frac{\partial \Delta G_f}{\partial r}\right|_{r = r^*} = 0$$

$$\Rightarrow \cancel{4}\cancel{\pi} r^{*\cancel{2}} (G_s - G_L) + \overset{2}{\cancel{8}}\cancel{\pi}\cancel{r^*}\gamma = 0$$

$$\Rightarrow \boxed{r^* = \frac{-2\gamma}{G_s - G_L}}$$

obstacle to nucleation (barrier)

driving force

So, let us do that you remember delta G f we wrote as sum of two terms the volume term and a surface term. And to apply the condition for maximum we differentiate this. If we differentiate this expression with respect to r, then we get 4 by 3 pi differential coefficient for r cube will be 3 r square minus G L 4 pi for r square, we have 2 r as it is differential coefficient and gamma.

We have 4 pi r square G S minus G L 8 pi r gamma. Now, we apply the condition for maximum which is del delta G f by del r r is equal to r sorry r is equal to r star is equal to 0. So, which means I substitute r star in this expression and set it to 0. So, I do that 4 pi r star square G S minus GL 8 pi r star gamma is equal to 0. So, you can see now we can cancel many times pi cancels, r star also cancels with the cancellation of a square here and 4 cancels with 8 here 2. So, we get an expression for r star as 2 gamma by G S minus G L with the minus sign minus 2 gamma by G S minus G L.

You recall that G S minus G L itself is negative. So, that is why we have a minus sign there. So, r star gives you a positive radius. Now, if you think about it. So, this G S minus G L is the driving force, this is what is finally, making the transformation possible. So, it coming in the denominator is justified in the sense that higher is the driving force is smaller is the critical radius. So, which means you have if driving force is high, then nucleation is easier you have to assemble a smaller number of atoms; you have to form a smaller critical radius for nucleation to happen. So, more the driving force is smaller is the radius.

On the other hand you can see that gamma is on in the numerator, this gamma is actually an obstacle to nucleus. And we saw that the surface energy term, the surface energy term was making a positive contribution to delta G f which is thermodynamically not liked. If the transformation has to happen, you want to reduce the free energy and not increase the free energy and 4 pi r square gamma, was trying to increase the energy of the system.

So, this is in a kind an obstacle to nucleation, obstacle or barrier you can call so, large larger is this barrier, larger is r star this is again understandable because, if more is the barrier nucleation becomes difficult and that is reflected in the fact that you have to assemble larger number of atoms now, make a larger radius of ball for nucleation to happen.

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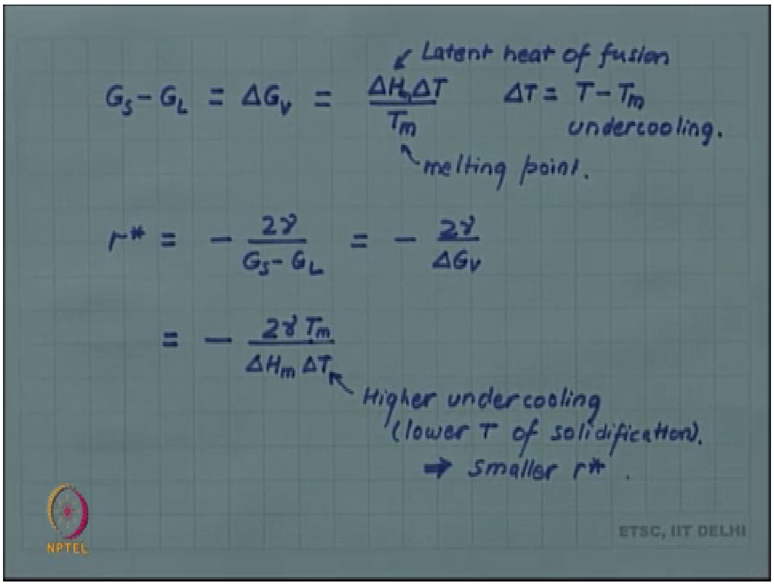

Latent heat of fusion

$$G_s - G_L = \Delta G_v = \frac{\Delta H_m \Delta T}{T_m} \qquad \Delta T = T - T_m$$

undercooling.

melting point.

$$r^* = -\frac{2\gamma}{G_s - G_L} = -\frac{2\gamma}{\Delta G_v}$$

$$= -\frac{2\gamma T_m}{\Delta H_m \Delta T}$$

Higher undercooling (lower T of solidification).

⇒ Smaller r^*.

We can we have recalled that we had formulated an expression for this G S minus G L. So, G S G L which we can call as delta G V and we had shown that this is nothing, but delta H delta T by T m, where delta T was T minus T m. This was under cooling and, there I can write it as delta H m. So, this is the latent heat of fusion and, this is the melting point. We had derived this expression in a previous video.

So, if you use this we can see how critical radius will depend upon temperature. We can write r star minus 2 gamma G S minus G L delta G V delta H m delta T T m. So, this is another way of now seeing that of course, gamma will also vary gamma will also vary with the temperature. For the moment if we neglect the variation of gamma, then we can see higher is the under cooling higher under-cooling means lower temperature will imply smaller r. So, lower is the temperature of solidification smaller is the critical radius.