Fundamentals of Materials Processing (Part–1)

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Lecture Number 05

Kinetics of Solidification (Homogeneous)

Okay welcome back students! So last lecture we were discussing about the thermodynamics of solidification. Hopefully those were not tough contents in thermodynamics. I can understand that thermodynamics may not be the desired suit for most of you but still I kept the thermodynamics to the minimum. Something that you need to be aware in if you are learning about solidification. Okay, so thermodynamics is one aspect to understand.

Another aspect in most of the times when we are talking about thermodynamics, which will only tell you, which is a more desirable or what is the most theoretically possible condition, but it does not tell you how and if at all the transformation takes place. There we need to get into kinetics, or in this case, nucleation. So today we will be talking first about nucleation.

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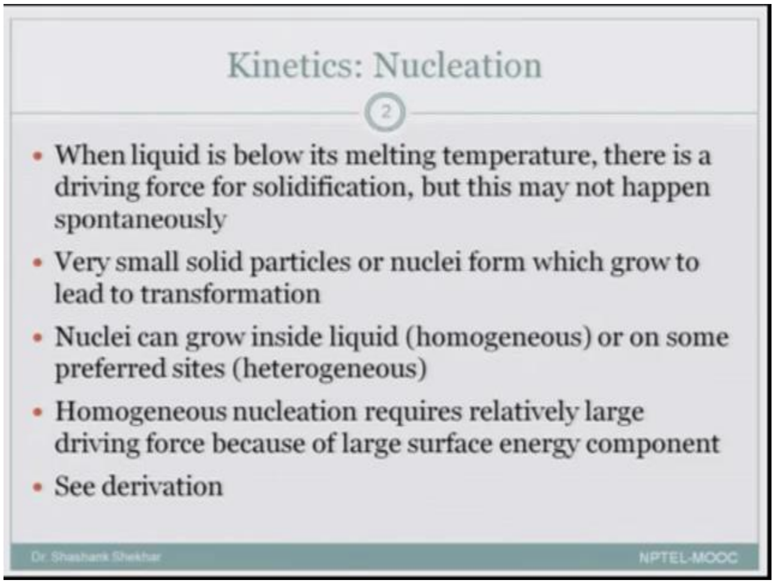

Kinetics: Nucleation

2

- When liquid is below its melting temperature, there is a driving force for solidification, but this may not happen spontaneously
- Very small solid particles or nuclei form which grow to lead to transformation
- Nuclei can grow inside liquid (homogeneous) or on some preferred sites (heterogeneous)
- Homogeneous nucleation requires relatively large driving force because of large surface energy component
- See derivation

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Okay. So like I said, when liquid is below its melting temperature, there is a driving force for solidification, which we got to know from thermodynamics. But this may, this solidification or this transformation may not happen simultaneously. Very small solid particles or nuclei (formed) in the liquid, which then grow and then (com) when they completely submerge or when they completely eat away the liquid, then you have the complete transformation. Nuclei can grow inside liquid, that is just inside anywhere, randomly inside the liquid, which will be called homogeneous nucleation, or at some preferred sites, most likely the mould sites; if you have kept a mould, then that nucleation will take place at those preferred sites, and in that case it is called heterogeneous nucleation.

Homogeneous nucleation requires relatively large driving force, and that is what we will start with, we will begin with to understand, when we look at the some of the equations related to nucleation. Okay, so let us get to some board work. Okay let us say we have a liquid like this.

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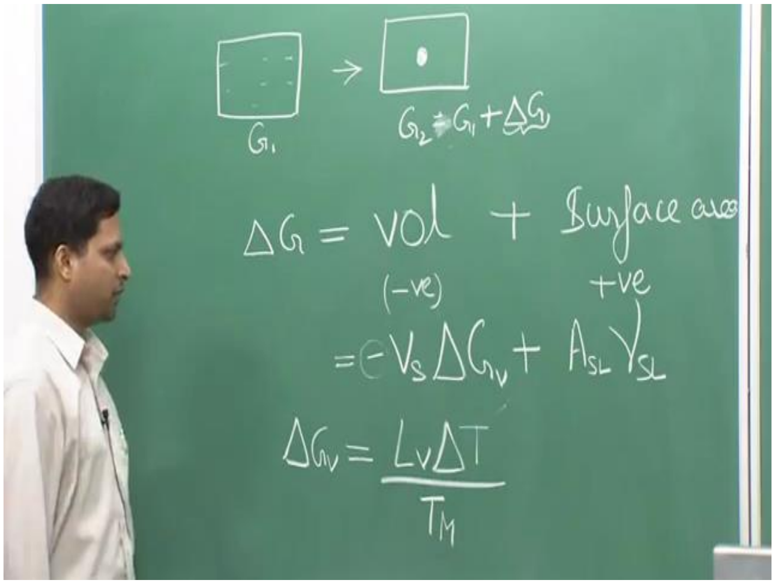

So this is a box inside which we have liquid; so this is all liquid. And then, you reduce the temperature below the melting point and some, at some particular temperature below the melting point. It need not happen exactly when at the melting point when you are reducing the temperature. At some temperature below the melting point which is also called as under-cooling, you may start to see some nuclei, small very small, these are microscopic in size. Now, thermodynamically, if we say that this is the free energy of the system G1, then G2 is equal to G1 plus delta G, where delta G is the change in the free energy because some of the liquid has transformed into this solid.

Now this transformation delta G, which led to this free energy change, delta G, it can be negative or positive, depending on the size of the nuclei. So that is what we will first look at. What is this delta G, what is this change in delta G, what are the two components that you think will contribute to this change in the energy delta G. there will be actually two components; one will be the volume component, and the other will be the surface area. Now what is this volume component? When the transformation is taking place, you remember from our class on thermodynamics, that when liquid transforms to solid at temperature below the melting point, then free energy is released. So this will be a in effect, negative free energy, or there will be negative change.

However, when this solid has formed, a surface area has also been created. Now this surface area, or you you remember that surface always has some energy, so there is some surface energy related to it. So surface energy times surface area is that energy term that we are talking about here. So it is adding to the change in the free energy; so this is a positive term. So this is increasing the overall energy. And when, this starts to dominate, that is when you have the transformation actually taking place. So if we want to write it in more formal way, this will become minus VS, where volume, VS is the volume that has formed. Delta GV is the change in the free energy because of this form, formation per unit. Volume plus ASL, we are, ASL is the area that is formed, and gamma SL which is the surface energy, solid liquid surface energy.

Now here, remember (look) see that we have already said or already put a negative term over here, which means that we are taking this to be a positive quantity, even though the change in energy is negative. So, just, this just makes the equation or understanding simpler; so we will keep it that way. So our delta GV will remain positive, but in in effect the overall energy change is negative. Now, you remember from the previous lecture also, there was equation where we said that if LV is the latent heat of fusion, then delta GV can be written as, where delta T is the under-cooling that is the temperature, change in the temperature below or you can say difference from melting point to the actual point at which you are, and TM is the melting point, LV is the latent heat of fusion. So GV can be given like this.

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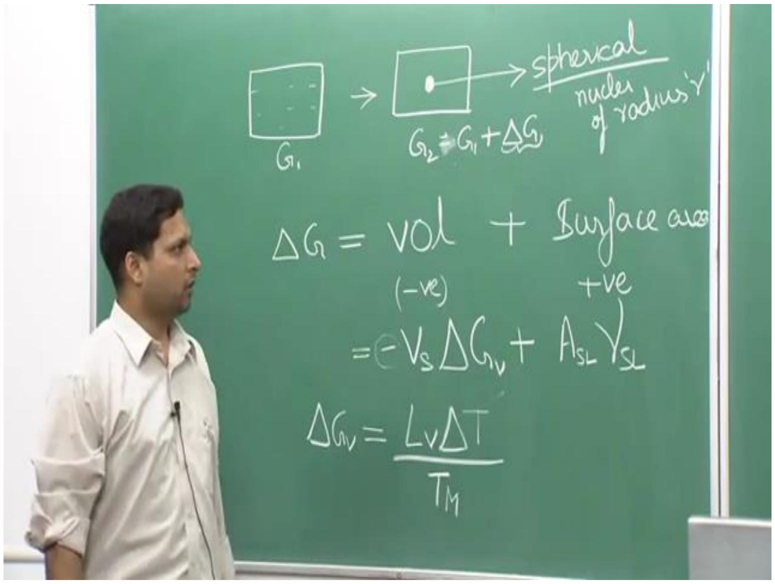

And therefore, this equation becomes; okay if I even if before I go over there, let me assume that the nuclei that are forming are spherical in shape. This is an assumption, remember. This is spherical in shape. So, this taking into account a spherical form, we can find the volume, we can find the area, and we know this GV. So we can write it like this; where r is the radius, spherical nuclei of radius r, some arbitrary value r. We do not know yet, what is that value r, we will get to know very soon. So this is the form, and since we are taking a spherical, so we will put a subscript r over here, so this becomes delta Gr, or the change in the free energy for a spherical nuclei that is forming. So this is how it will look like. Now, what next?

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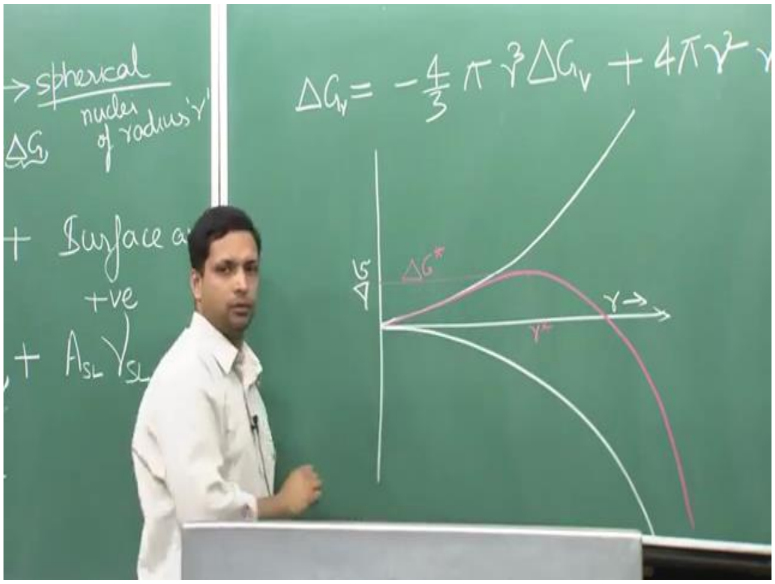

Let us plot this energy. Now what you will see is that the first term is proportional to r cube, while the second term is proportional to r square. So this, the positive term is proportional to r square, and the negative term is proportional to r cube. And when that is the form, what happens is that lower values r square, this term will dominate and at higher values this term will dominate. So it will have something like this, and where on the x-axis you have radius, size changing radius. Over here, you can say this is delta G; so this started from 0 even though it may not look like but just remember that we are starting from 0. And over here, this drops down very fast, because it is proportional to r cube.

So if we draw the sum of these two, how it would look like? It would look like, something like this. Why? Because initially it is being dominated by the r square term, it increases; and thereafter it is dominated by the r cube term, and then it starts to decrease. Therefore, it has a maxima, and at some value r; let us call that r star, and at that r star, there will be a value, which we, let us say denote by delta G star. Now, if you look at the form of the equation, you should be able to determine the value of r star, and delta G star. So let us; we will not derive this part, we will leave the mathematics to you. I will just put the final value of these r star and delta G star.

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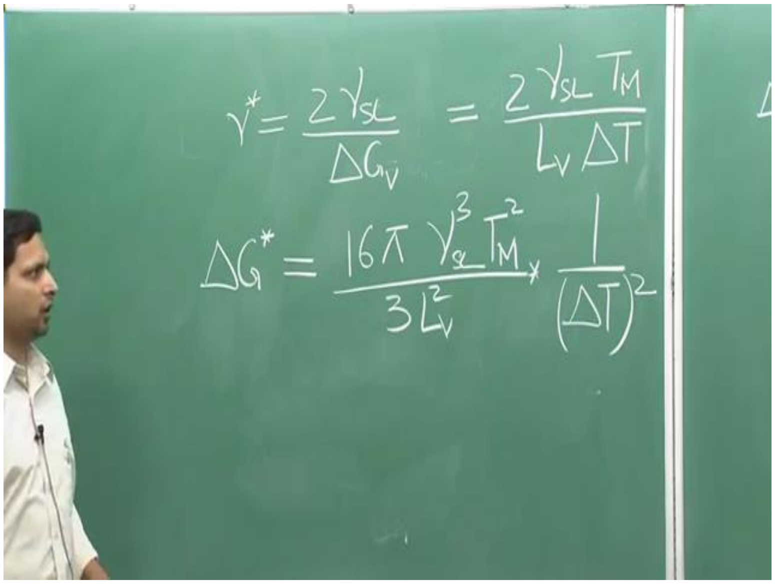

$$r^* = \frac{2\gamma_{SL}}{\Delta G_v} = \frac{2\gamma_{SL} T_M}{L_v \Delta T}$$

$$\Delta G^* = \frac{16\pi \gamma_{SL}^3 T_M^2}{3L_v^2} \times \frac{1}{(\Delta T)^2}$$

So, what will be the r star value? And how do you obtain this? Just by maximizing this delta GV in terms of r value. You will be able to get a delta, d delta GV by dr equal to 0, and you will be able to get critical value of r, which we are terming as r star. And you can show that this is the r star value. And if we again go back and put the delta GV in terms of LV, we can write it as; so let me erase that part properly, the there is no gamma over here which we are seeing over here. So this is the r star value.

Okay now, similarly if you put this r star value in over here, you will get delta G, or for this particular r star, and that will be called as delta G star. So this delta G star can be written like. So this is how delta G star would look like, and I have, as I said, I have left the mathematics to you; this is not very difficult exercise, you can very easily show this. In fact, what you should be trying is that instead of taking a spherical radius, try and do it using say, a cuboidal (radius) sorry, not a radius, spherical nuclei, instead of spherical nuclei, try and take a cubical nuclei, or some other form of that, a simpler form for which the surface area and the volume does not get complicated.

Now here there are couple of things to note. One you will note that r star is proportional to gamma SL, and delta G star is proportional to gamma SL cube; this will become very important very soon. I will leave that part for now. Another (thing) another thing that is important is r star is proportional to 1 over delta T, while delta G star is proportional to 1 over delta T square, meaning, if you increase the delta T, or increase the under-cooling, delta G star drops very fast; on the other hand, delta, if you increase delta T, r star also decreases, although not at the same rate. Both of these would imply that the probability of nucleation increases when you increase delta T. We will get that get to that in a moment.

But before that, what does the change in temperature what do you, what can you say from these equation about this curve when we change the temperature? So this is, let us say, this is the delta G plot that you get at some particular temperature T1, and I will erase the rest of the part.

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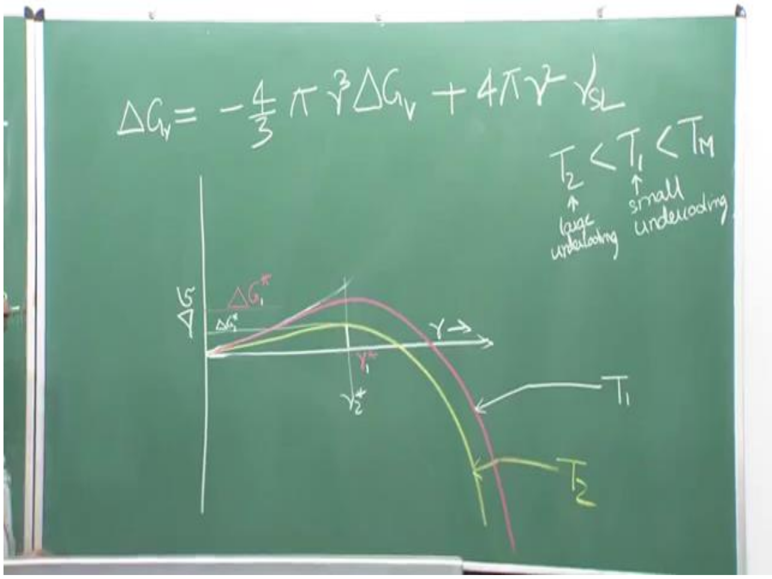

So let us say this is some temperature T1. This is how the delta G looks like. Now if we increase the under-cooling, or the temperature becomes lower than T1, so we have T2. So let us say something like T2 is less than T1 is less than TM. So, here you have small under-cooling, and here you have large under-cooling. So, from here, what do we know when large, there is larger under-cooling? That is when delta T is large, r star should decrease. So this r star value, which is over here, it should come down, somewhere over here. Now, this equation also tells that delta G star should decrease even faster with increase in delta T. So delta G star should now be even smaller, in fact, the magnitude of decrease in delta G star should be larger than the magnitude of decrease in r star. So it should be something like, let me use still different colour, something like this.

So, the yellow curve is for T2. What I am trying to show here is that, so, this is our; so this is r1 star, and this is r2 star, and, correspondingly this becomes delta G1 star and this becomes delta G2 star. So, what I am trying to show here is that when when you decrease the temperature, or when you increase the under-cooling, r star has decreased from r1 star to r2 star by some magnitude, and even by a larger magnitude, delta G star has increased, or dropped, sorry not increased. Now although I did not explicitly mention, but from your earlier courses, you would understand what is the significance of r star and delta G star. r star is the size, or the critical size of the nucleus, (if you) beyond which you can say that the (liq) liquid has transformed into solid.

For example, let us say, (we have) we are at this particular temperature T1, and solid and the liquid items come together to form a nuclei of this size, exactly of this size. If, you add one more atom, or just a little bit increase the radius, then what do you see, delta G starts to drop; meaning, the total change in energy becomes, starts to become negative. Hence, this will become a stable entity. So, this cannot, or this will have very low probability of again going back or getting dissolved into the liquid.

On the other hand, let us say that you have a radius somewhere over here. Now, the (size) the cluster that has formed with such a radius over here, if you add a atom to this, what is happening, the delta G is increasing; so it is becoming more relatively more and more unstable. On the other hand if you take away one atom, it becomes more stable, why? Because delta G has (incre) dropped.

Therefore, in this, if a radius, the cluster sizes of this radius, it has a higher tendency or higher probability to decrease in size, and lower probability to increase in size. On the other hand, if you are over here, it has a higher probability to increase in size, because then it becomes permanent solid or once it has become higher than that, it has the tendency to retain that configuration, or that solid nuclei, it does not want to get back, because that will require more energy. So that is the significance of delta G and delta G star and r star. Now let us look at again we were talking about the probability of nucleation.

So, how do we quantify this term ‘probability of nucleation’. One thing we understand is that r star decreases when we increase under-cooling, or sorry when we increase the under-cooling then the delta T becomes large and large. The (under) the probability or the the size of the, the critical size of the radius becomes smaller and smaller. So one thing one can say is that the it is very larger probability to find a critical nucleus with smaller radius, and much lower probability to find critical radius with larger nucleus. But let us have it in a more, much more quantitative way.

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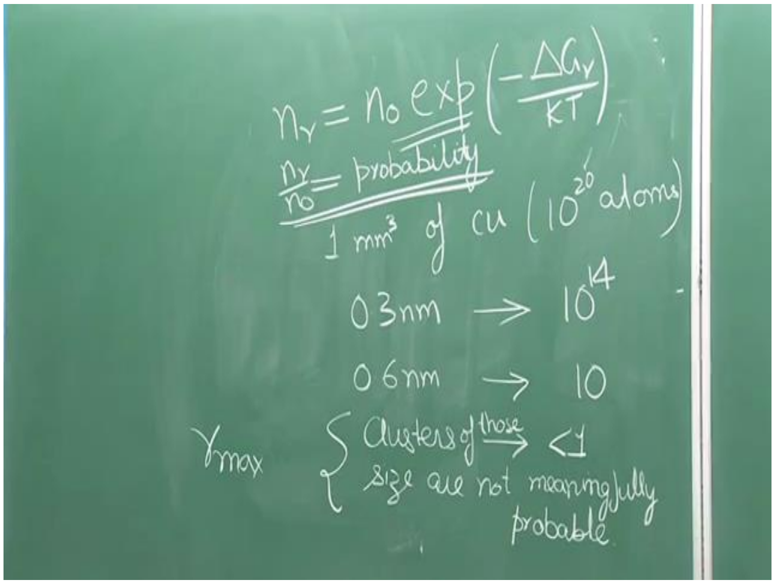

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{KT}\right)$$

$$\frac{n_r}{n_0} = \text{probability}$$

1 mm^3 of cu (10^{20} atoms)

0 3nm → 10^{14}

0 6nm → 10

r_{max} { Clusters of those → <1 size are not meaningfully probable

So let us say n0 is the total number of atoms per unit volume, and nr is the number of cluster with size of with size r. So we can say nr is equal to n0 minus delta Gr by KT. So this equation tells you that how many cluster of size r you will find in a liquid which contains n0 atoms per unit volume, when the energy related to formation of this cluster size is delta Gr. Now, this equation, what does this equation tell us? One thing, it tells us, you remember that over here what was happening?

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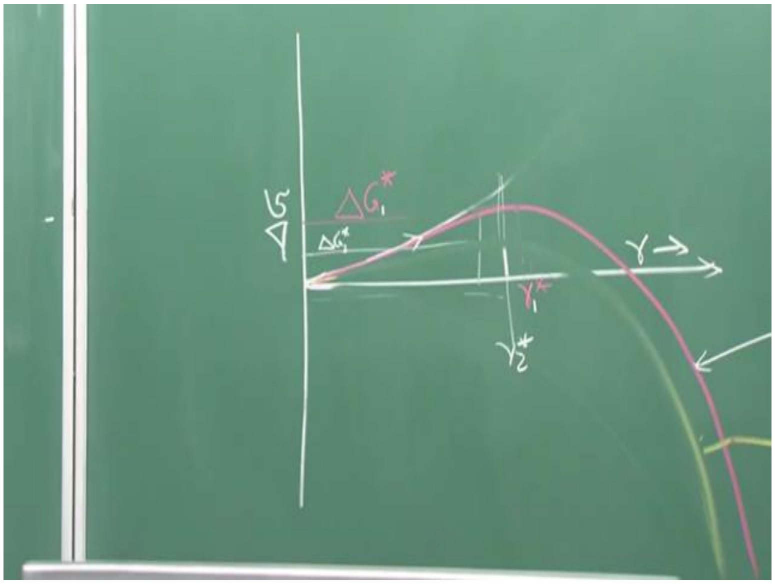

If you go from zero radius to the critical radius r star; so for sake of simplicity, I will again remove the yellow plot that we had over here. Now if you keep increasing in this direction, delta, as you keep increasing r size, the size, the delta G star; or not delta G star but the delta Gr keeps increasing. Therefore this term keeps increasing which is a positive entity, because overall, we made it negative by putting a negative sign. So this is becoming more and more large, and therefore, nr will become smaller. The number of clusters with a larger radius will become smaller and smaller.

As an example, if we take, for example 1 millimeter cube of copper which has approximately 10 to power 20 atoms; so n0 is our 10 to power 20 divided by the volume. If we take this kind of a size, and then, if we are looking for nucleus of size, say point 3 nanometer, and compare it with number of nucleus with size point 6 nanometer, the change in the size is not very large one; it is just double, but look at the number of clusters that you can find.

A cluster of this size, you would find approximately 10 to power 14. But, a (siz) cluster of this size, you may find only 10, because of his exponential term. Because of this exponential term, this probability or this number of cluster (siz) now number of cluster of a given size drops (ex) exponentially, because of this exponent terms. It decreases very very fast.

And, nr over n0, you can say is effectively the probability. Now you see, we have increased just from point 3 nanometer to point 6 nanometer, and the amount of, and the number of clusters that you can find has decreased from 10 to power 14 to 10. If we go, if we go on like this, very soon, you would see that the number of clusters may actually reduce less than 1, in which case it means, that clusters of those size are not meaningfully probable. So, we can say there is rmax value that you can find for a given liquid, for a given size, and for a given delta T condition. So there is a maximum size of cluster that you can find. Now that is a very important concept, because now we will see what happens to this rmax.

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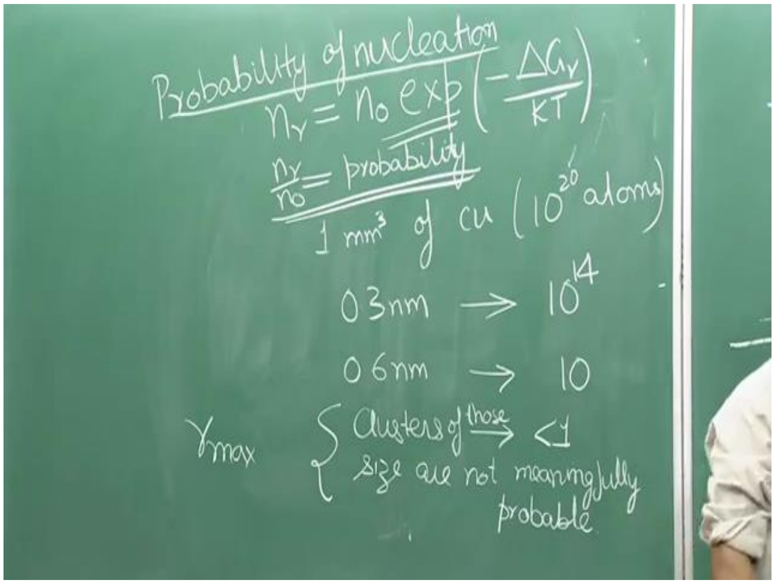

Probability of nucleation

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{KT}\right)$$

$\frac{n_r}{n_0}$ = probability

1 mm^3 of Cu (10^{20} atoms)

0 3nm → 10^{14}

0 6nm → 10

r_{max} { Clusters of those → <1 size are not meaningfully probable

It is not very difficult to show that if you plotted rmax, it will increase, where on the x-axis, you have delta T, so you are increasing the under-cooling, and over here, you have the size. So, if you keep increasing the under-cooling, your rmax, the maximum size that is possible keeps increasing, meaning there are higher and higher probability of getting even larger size radius, larger size clusters. And at the same time, the r star, the size r star, when you remember it from our previous equation, we showed that r star is proportional to 1 over delta T; so this is how this 1 over delta T term would look like; meaning all, what it is saying is, let us look at this particular condition.

If you are at this, some delta T1 condition; if you are at a very small, which is a very small value; if you are at a very small under-cooling, the maximum size of cluster that can form is this. But, for solidification, the critical size of radius that you need is this, which is larger than the maximum possible. So this kind of cooling is, or this kind of at this particular condition, solidification is not possible. Now let us get to this place at a larger under-cooling; delta T2. So at this particular under-cooling, the maximum possible cluster size is this. And all you need to get the solidification is a much smaller radius, or much smaller cluster size. Therefore, it implies that over here, you can easily get solidification, but here, it is almost not possible to get solidification.

So there must be a critical value of the delta T, where you can start to get solidification, and that delta T is this. So we will denote this by delta TN, meaning, it is this particular temperature where actual nucleation will start to take place. So, remember if you are at a smaller under-cooling, the maximum size that is possible is smaller than the required critical size. Only when you go to under-cooling which is larger than delta TN, that your maximum size possible, maximum cluster size possible is larger than the critical size required for solidification; and hence, only when you are at under-cooling larger than this, that you will be able to get solidification. So this is what we were talking about, probability of nucleation. There is one more equation related to this, which is about nucleation rate.

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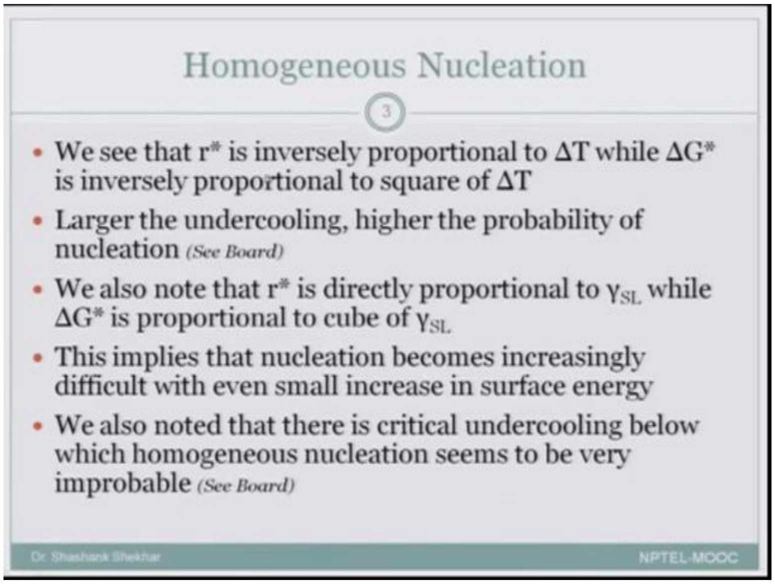

Homogeneous Nucleation

3

- We see that r^* is inversely proportional to ΔT while ΔG^* is inversely proportional to square of ΔT
- Larger the undercooling, higher the probability of nucleation *(See Board)*
- We also note that r^* is directly proportional to γ_{SL} while ΔG^* is proportional to cube of γ_{SL}
- This implies that nucleation becomes increasingly difficult with even small increase in surface energy
- We also noted that there is critical undercooling below which homogeneous nucleation seems to be very improbable *(See Board)*

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But before that, let us let us gather what we have talked so far. So, we saw that r star, which is the critical radius, is inversely proportional to delta T, while delta G star is inversely proportional to square of delta T. So delta G star is dropping at a much larger rate, which means that larger the under-cooling, higher the probability of nucleation, and we saw that on the board. We also noted that r star is directly proportional to gamma SL, while delta G star is proportional to cube of gamma SL; meaning both these terms are increasing with surface energy. The larger the surface energy, both of these terms will increase, which means you will need a larger critical radius, you will need a larger delta G to get the solidification. So it is very very sensitive to surface energy. This implies that nucleation becomes increasingly difficult with even small increase in surface energy.

We also noted that there is critical under-cooling below which homogeneous nucleation seems to be very improbable. That we saw over here which is this delta TN; so below this, we saw that it is improbable to have a solidification, and only a when you have under-cooling beyond this, that you will get a nucleation and hence, solidification. And we will also look at the nucleation rate in the next class. So we will end over here, but in the next class we will continue, and finish the homogeneous nucleation with what is called the nucleation rate, and then we will go on to the heterogeneous nucleation.