Structure of Materials
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Lecture - 38
Chapter - 08
Phase Transformations

Let us start Phase Transformations in detail, using the example of solidification of a pure metal.

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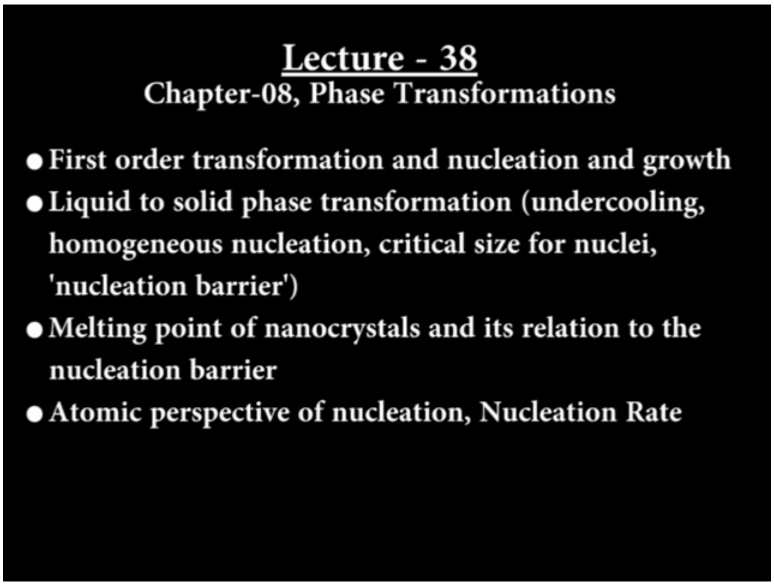

Lecture - 38

Chapter-08, Phase Transformations

- First order transformation and nucleation and growth
- Liquid to solid phase transformation (undercooling, homogeneous nucleation, critical size for nuclei, 'nucleation barrier')
- Melting point of nanocrystals and its relation to the nucleation barrier
- Atomic perspective of nucleation, Nucleation Rate

This is a indeed a simple illustrative examples.

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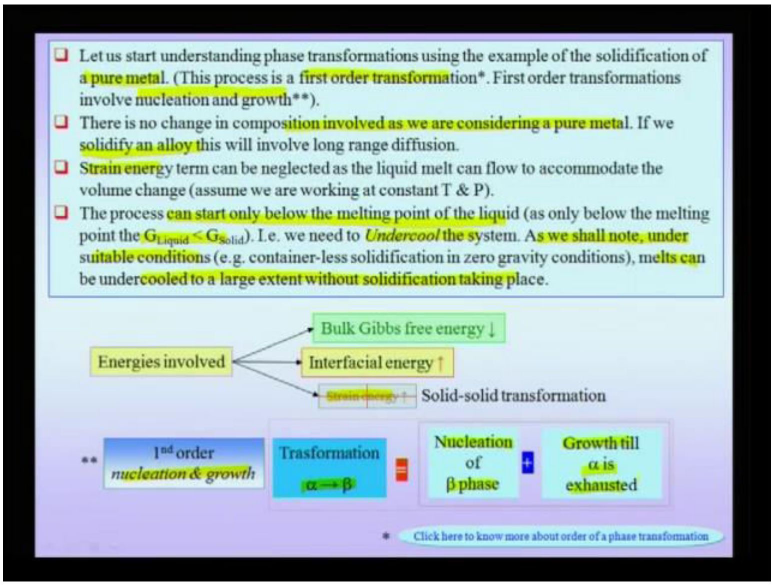

- ❑ Let us start understanding phase transformations using the example of the solidification of a pure metal. (This process is a first order transformation*. First order transformations involve nucleation and growth**).
- ❑ There is no change in composition involved as we are considering a pure metal. If we solidify an alloy this will involve long range diffusion.
- ❑ Strain energy term can be neglected as the liquid melt can flow to accommodate the volume change (assume we are working at constant T & P).
- ❑ The process can start only below the melting point of the liquid (as only below the melting point the $G_{Liquid} < G_{Solid}$). I.e. we need to *Undercool* the system. As we shall note, under suitable conditions (e.g. container-less solidification in zero gravity conditions), melts can be undercooled to a large extent without solidification taking place.

Energies involved → Bulk Gibbs free energy ↓

Energies involved → Interfacial energy ↑

Energies involved → ~~Strain energy ↑~~ Solid-solid transformation

** 1st order *nucleation & growth*

Trasformation $\alpha \rightarrow \beta$ = Nucleation of β phase + Growth till α is exhausted

* Click here to know more about order of a phase transformation

But, some of the important points we note here, are applicable to other kind of phase transformations as well. This is the first order phase transformation, though here we are not defining in detail what is meant by the order of a transformation. And but, important point we need to notice that, such first order phase transformations involve nucleation and growth. That means, the phase transformation has two steps, one is nucleation, another is growth and what is meant by this nucleation and what is growth, we will see in considerable detail very soon.

Since, we are talking about solidification of a pure metal, there is no change in composition involved. And this on the other hand suppose, I solidify a alloy, it could also mean that, we have already seen the isomorphous phase diagram. There is a continuous change in compositions to the two phase region and therefore, it will involve long range diffusion. But, in the simple example there is no long range diffusion, just we are talking about nucleation and growth and we will see some illustrative figures to understand this a little more detail.

Strain energy term can be neglected, we have seen this strain energy term we understood the origin of that strain energy term but, you can safely neglect that term here because, you are working at constant temperature and pressure. And this is a liquid to solid phase transformation and therefore, we need not talk about strain energy and this can be safely neglected from the Gibbs free energy of the process. This process obviously, can start only below the melting point because, only below the melting point, is the free energy of the liquid lower than that of the solid.

In other words, there is at all any propensity for the system to solidify and this automatically implies, we have to use under cool the system. That means, we have to take it below the bulk melting point and this phenomena or this process is called under cooling. And as we shall see later and maybe we can note now that, under suitable conditions melts can be under cooled to a large extent without solidification taking place. That means suppose, I take molten pool of nickel and I take it below it is melting point, I can keep on cooling it to a lower and lower temperatures.

And if there is no for instance suppose, this is under a zero gravity conditions and you do not have a container, in which it is held under such circumstances, it is been possible to under cool systems more than 100 degrees Celsius. So, we have to understand the mystery that, why is such under cooling possible, is not it that below the melting point, the material should solidified or the more fundamental question is the melting point also the freezing point and some of these things, we will understand very soon.

Now, I pointed out that, this nucleation and growth process involves for instance suppose, I am talking about an alpha to beta phase transformation or in the present case, the liquid to solid phase transformation involves nucleation of a solid phase for instance. And the growth of the phase till the alpha phase is exhausted, that would complete my phase transformation and therefore, such a phase transformation can be thought of as nucleation followed by growth.

Now, why do we have to actually split this process into two steps, one involving the term called nucleation, one involving the term called growth and in this context, let me point out the term nucleation is a technical term.

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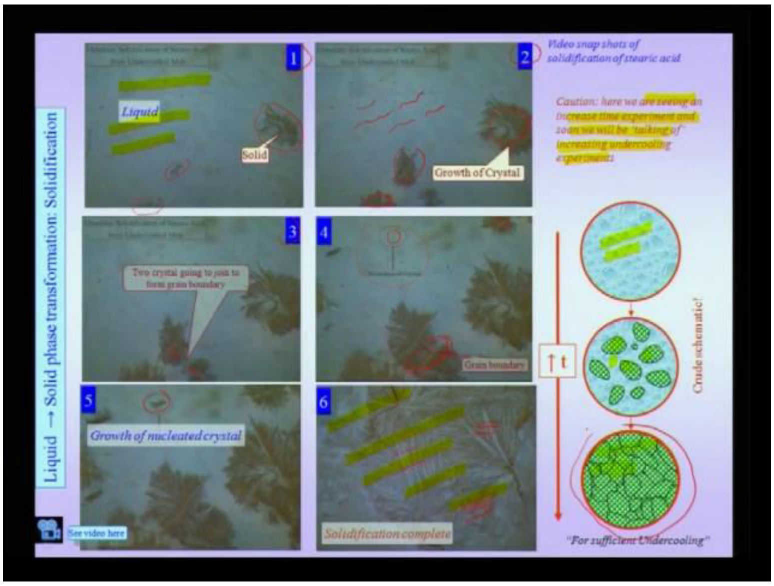

Liquid → Solid phase transformation: Solidification

Video snap shots of solidification of stearic acid

Caution: here we are seeing an increase time experiment and soon we will be "talking of" increasing undercooling experiment!

Crude schematic!

"For sufficient Undercooling"

So, to understand this process, let us see the solidification of stearic acid from an under cool melt. Initially what happens of course, there is a liquid pool here and this whole region is the liquid and in this liquid pool you will notice, that there are small regions of crystalline phase forming. So, these is my crystalline stearic acid, there is also a small crystal here and there is a another crystal here and this crystal grows, if you wait long enough.

Here of course, we are doing a solidification experiment, in which of course, system is being cooled and we are not at a constant temperature, we just cooling the system and alloying solidification to take place. But, this is an illustrative and nice example to understand, how a two phase mixture can coexist at any point of time. So, at any point of time, you can notice whether there is a solidified phase here, there is a solid phase in this region, there is a solid phase in this region but then, there is also this liquid pool which exists here.

So, the liquid and solid phase are coexistent at this point of time and as you progress in time so, this is step 1 in time, this is step 2 in time you go to step 3 in time you would notice that, some of the crystallites grow and joint and they lead to the formation of a green boundary. Because now, this is a boundary between two crystals and that can be called a green boundary. Parallelly you can notice that, some of the preexisting crystallites grows but, new crystallites are also forming.

That means, for instance in this region, you would have noticed a crystallite which is formed, here new nucleus is forming as that we are seeing in figure number 4. And this nucleus at a later point of time grows, slowly you would notice that, as we are waiting long enough and of course, we are also falling in temperature the cooling experiment then, most of the liquid melt has got transformed into solid. So now, in figure number 6, you would notice that, all these are crystals now.

So, this is crystal, this is another crystal and this is another crystal and most of the liquid phase is gone away and we have many green boundaries between these crystalline regions, which are all single crystals but, separated from other such single crystals by a boundary as shown is schematically in figure 4. So, it is clear that, phase transformation is taking place from the liquid to solid and if you are cooling the system below the melting point then, you would notice that, the fraction of the solid is increasing with time.

A important point to note is that, here we are seeing an increasing time experiment and soon, we will be talking about increasing under cooling experiment. So, we will have to be very very careful that, when it is just a schematic to understand the point that, how solid and liquid phase coexist, how a nucleation of a second phase or the solid phase takes place or the crystal takes place in the melt, how such crystallites grow in the melt and how finely they join together to finally, form an entire, as in picture 6 almost a completely a crystalline phase of course, this is a poly crystal.

The reason for choosing stearic acid of course, is the low melting compound and added to the fact that, it is also transparent so that, we can easily see the growth of these dendrites and this dendritic kind of solidification. So, a schematic of this process is shown in the figure on the right hand side that, you have the liquid then, at a lower at increasing time, you have a solid phase forming and with the crystalline phase which is coexisting with the liquid and finally, of course, you have a poly crystalline solid, as in the bottom most figure here.

So, you have a poly crystalline solid here and as I told you, all this can only happen if you are below the melting point in other words, if you under cool the system. Of course, you get go and cooling the system, as in the current experiment or you could hold it at a constant under cooling and wait for and see that, what happens. So, this is the schematic with which or a actual experiment carried out but, as an illustrative example, we have considered this.

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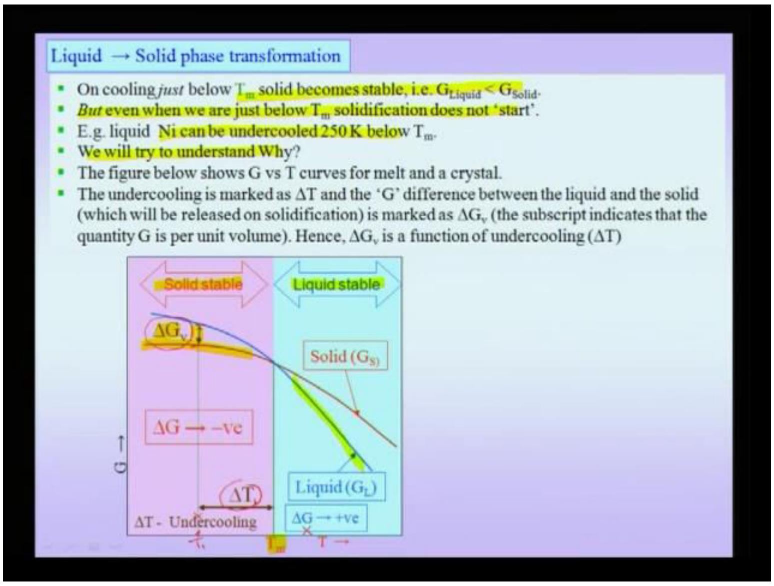

Liquid → Solid phase transformation

- On cooling *just* below T_m solid becomes stable, i.e. $G_{Liquid} < G_{Solid}$.
- *But* even when we are just below T_m solidification does not 'start'.
- E.g. liquid Ni can be undercooled 250 K below T_m.
- We will try to understand Why?
- The figure below shows G vs T curves for melt and a crystal.
- The undercooling is marked as ΔT and the 'G' difference between the liquid and the solid (which will be released on solidification) is marked as ΔG_v (the subscript indicates that the quantity G is per unit volume). Hence, ΔG_v is a function of undercooling (ΔT)

Now, let us see, talk about the liquid to solid phase transformation in more detail and we known that, below the melting point, the solid phase becomes more stable, the liquids free energy is lower than the solids free energy. If you see the diagram below, this is the melting point T m, above the melting point it is a liquids free energy which is lower and below the melting point, there is a solids free energy which is lower so, this is of course, the definition of the melting point itself.

So, liquid is stable on the right hand side, the blue region in the figure and the solid is stable below the melting point in the region shaded pink. Now suppose, I am at a certain enter cooling that means, I am at a certain temperature, which I can call T 1 and at this T 1, temperature here I can note that, that means I am at a certain under cooling. That means, somehow I have instantaneously gone from the molten solid say, above the melting point somewhere here, at this temperature to a temperature T 1 where, I am under a certain under cooling, maybe I can subscript it as delta T 1.

Now, at this delta T 1, the liquid free energy is here, the solids free energy is here that means, if this liquid transforms into solid, I have a benefit of delta G subscript v, this subscript v indicates that, I am under cooling. I mean, this is the volume free energy that means, per unit volume of the material, how much free energy benefit I get when the solidification takes place. Now, the important point is that, even if you are just below the melting point, solidification does not start, this is something which we will talk about in detail in the coming slides.

But, if suppose, I am at this T 1 which is at delta T 1 under cooling, solidification does not start. In fact, liquid nickel has been under cooled to about 250 degrees Celsius below the melting point under suitable conditions. Why is that systems get under cooled so much, what is that, which is sort of impending the solidification, these are the questions we will try to understand in the coming slides. And as you have seen here, that the whole reason that the liquid needs to turn into a solid is this delta G v term, which we have considered at an under cooling of delta T 1.

That means, I am under cooling delta T 1, there is propensity for the system to lower it is Gibbs free energy by forming as crystalline solid from the melt.

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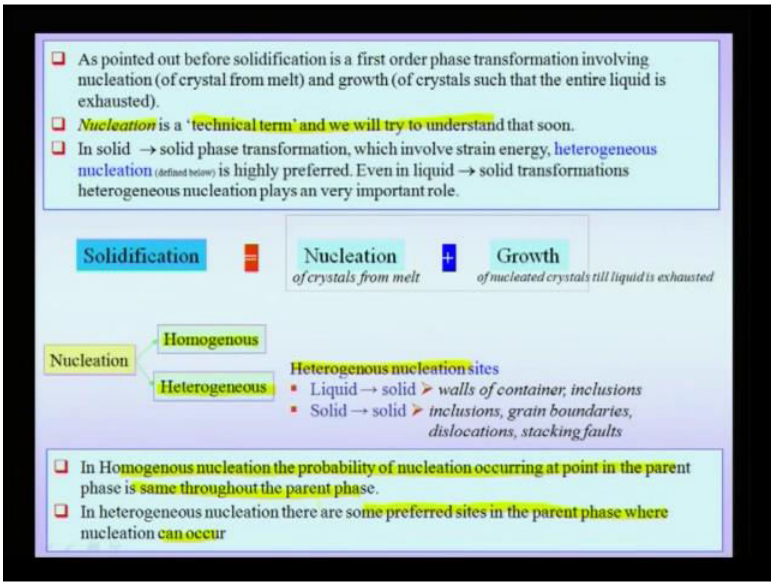

- ☐ As pointed out before solidification is a first order phase transformation involving nucleation (of crystal from melt) and growth (of crystals such that the entire liquid is exhausted).
- ☐ *Nucleation* is a 'technical term' and we will try to understand that soon.
- ☐ In solid → solid phase transformation, which involve strain energy, heterogeneous nucleation (defined below) is highly preferred. Even in liquid → solid transformations heterogeneous nucleation plays an very important role.

Solidification = Nucleation *of crystals from melt* + Growth *of nucleated crystals till liquid is exhausted*

Nucleation
- Homogenous
- Heterogeneous

Heterogenous nucleation sites
- Liquid → solid ➢ *walls of container, inclusions*
- Solid → solid ➢ *inclusions, grain boundaries, dislocations, stacking faults*

- ☐ In Homogenous nucleation the probability of nucleation occurring at point in the parent phase is same throughout the parent phase.
- ☐ In heterogeneous nucleation there are some preferred sites in the parent phase where nucleation can occur

Now, we will try to understand this term nucleation in lot more detail because, it is a technical term and we have to understand the full meaning of this. An important point in this context is that, that nucleation itself comes in two forms, the homogeneous nucleation and the heterogeneous nucleation. At the beginning of this chapter, we had done the experiment and in which we have taken a aerated drink and we had opened the bottle and poured the aerated drink into the glass.

Anybody who had done this experiment, had would have noticed that, the bubbles tend to form at the glass walls or at the interface between the straw and the aerated drink. And further we are done in that experiment, that we had taken the some salt and put it into the into the aerated drink and we founded lot of vigorous fizzing that means, lot of evolution of gas takes place. Now, in that case, why is this kind of a nucleation where, there is a mold wall or a straw or some kind of a solid we are putting into the liquid, these are all called heterogeneous nucleation sites.

That means, there is some second phase involved or a second kind of a entity involved and that kind of a nucleation, there is some preferred sites where, the parent phase, the nucleation of the product phase can take place preferentially so, that is what is called heterogeneous nucleation. On the other hand, homogeneous nucleation, the probability of the nucleation occurring in the parent phase is throughout the same that means, that there is no preferred site.

If I take a liquid melt for instance, held in say zero gravity conditions and suppose, it forms a spherical ball that means, any point in this liquid of course, the surface could be preferred. But, any side any point inside the liquid would have a equal probability of forming a nucleation site. On the other hand suppose, I take about a molten melt in a container.

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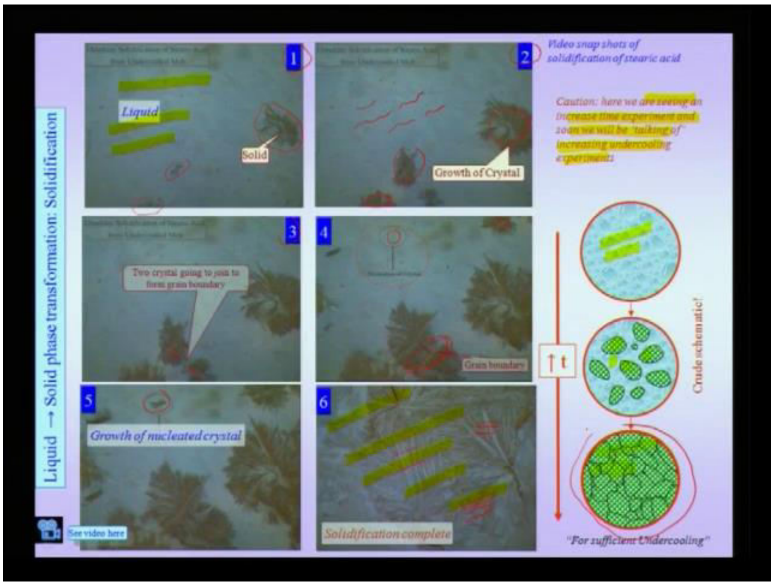

Liquid → Solid phase transformation: Solidification

Video snap shots of solidification of stearic acid

Caution: here we are seeing an increase time experiment and soon we will be 'talking of' increasing undercooling experiment!

Or for instance, in this example we saw before that, I am actually solidifying this stearic acid between two glass plates. Therefore, the molt melt glass interface could be a preferential site, there could also be some impurity.

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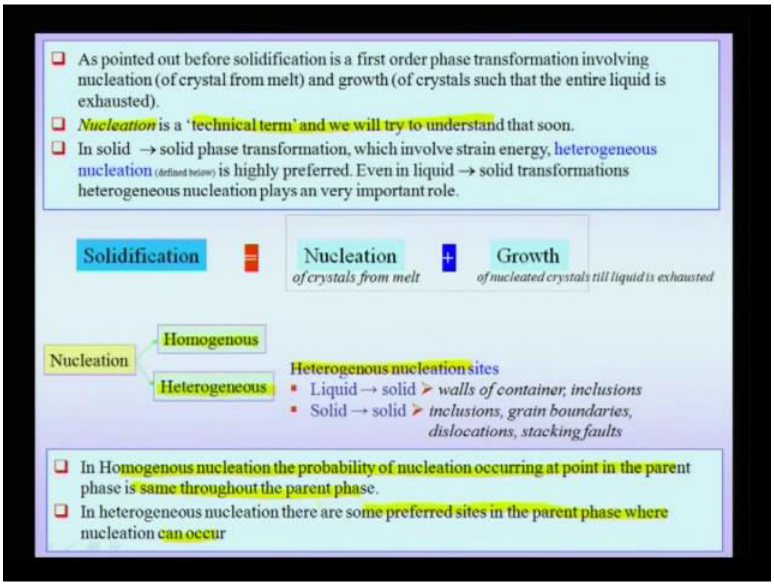

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Solidification = Nucleation + Growth

Nucleation: *of crystals from melt*

Growth: *of nucleated crystals till liquid is exhausted*

Nucleation
- Homogenous
- Heterogeneous

Heterogenous nucleation sites
- Liquid → solid ➢ *walls of container, inclusions*
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Or some kind of a small particles within this to melt, which also act can act like preferential sites and the presence of such preferential sites, we call this as heterogeneous nucleation. In liquid to solid phase transformations, the wall of the container, inclusions in the melt, etcetera can be preferential nucleation sites or heterogeneous nucleation sites.

And if you are talking about a solid to solid phase transformation then, very many types of heterogeneous nucleation sites can occur, these include inclusions, green boundaries, dislocations, stacking faults, etcetera so, all these can play the role of an heterogeneous nucleating agent.

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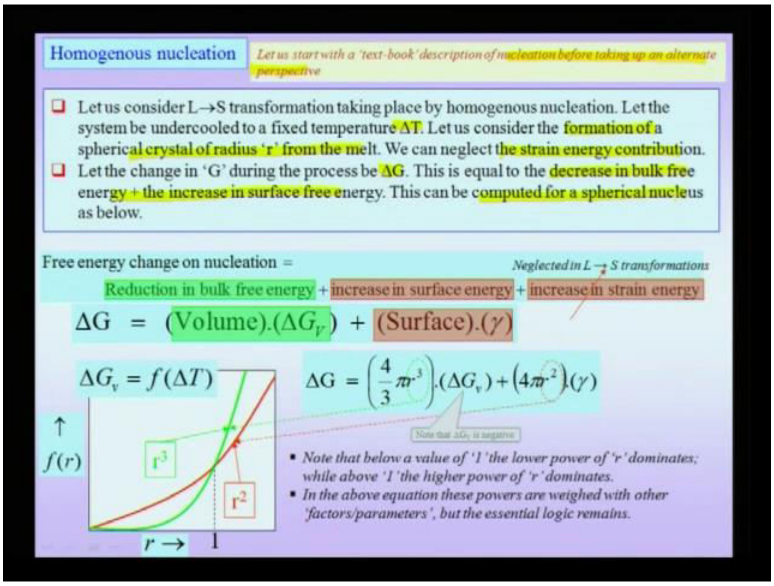

Homogenous nucleation

Let us start with a 'text-book' description of nucleation before taking up an alternate perspective

- ☐ Let us consider L→S transformation taking place by homogenous nucleation. Let the system be undercooled to a fixed temperature ΔT. Let us consider the formation of a spherical crystal of radius 'r' from the melt. We can neglect the strain energy contribution.
- ☐ Let the change in 'G' during the process be ΔG. This is equal to the decrease in bulk free energy + the increase in surface free energy. This can be computed for a spherical nucleus as below.

Free energy change on nucleation = Reduction in bulk free energy + increase in surface energy + increase in strain energy

Neglected in L → S transformations

$$\Delta G = (\text{Volume}).(\Delta G_V) + (\text{Surface}).(\gamma)$$

$$\Delta G_v = f(\Delta T)$$

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

Note that ΔG_v is negative

- *Note that below a value of '1' the lower power of 'r' dominates; while above '1' the higher power of 'r' dominates.*
- *In the above equation these powers are weighed with other 'factors/parameters', but the essential logic remains.*

So, let us start with this phenomena called homogeneous nucleation and first we will give a text book description of nucleation, before taking up an alternate perspective as to, how I can understand this mystery of under cooling and the definition of melting point. So, assuming that, I am at a fixed under cooling delta T that means, I am not slowly cooling the melt, I am at a fixed under cooling or a fixed temperature below the melting point.

And let me consider the formation of a spherical crystal of radius r from the melt and we are also neglecting the strain energy contribution to the overall change in Gibbs free energy. And the free energy change let us consider is to be delta G, this is now equal to the decrease in the bulk free energy plus the Gibbs free energy plus an increase in the surface free energy. And these values can be computed for a spherical nucleus because, now we are considering a spherical nucleus r, which is forming from the melt. So, let me draw this on the bold so, I am at a fixed under cooling delta T.

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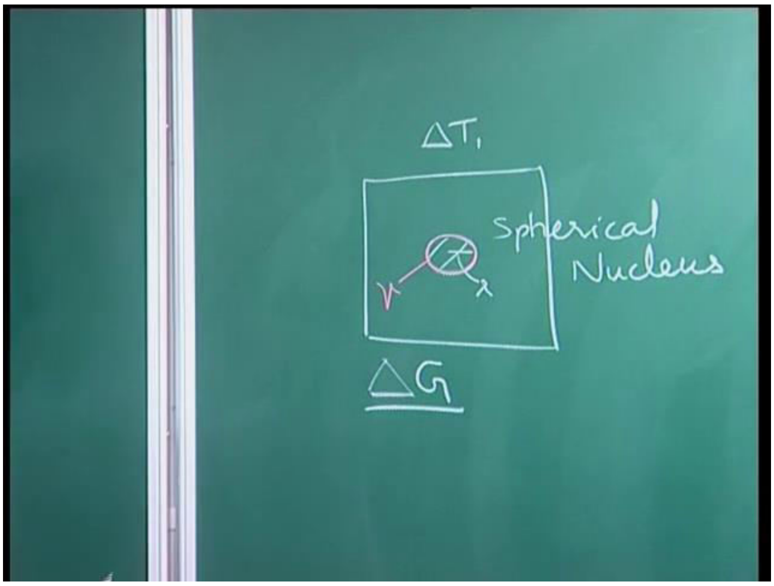

And under these conditions, I am assuming that a nucleus of radius r forms, assume that a spherical nucleus of radius r forms and therefore, there are two terms energy terms involved for computing the overall delta G for this whole process.

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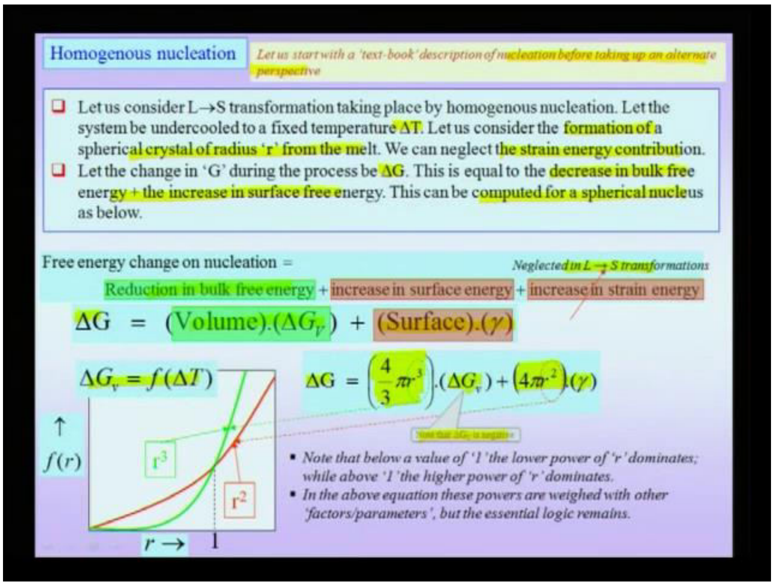

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So, for this spherical nucleus, I can consider the reduction in overall bulk free energy is delta G v into the volume of this spherical nucleus. The increase in interface energy gamma is the surface area multiplied by the gamma term since we are already neglecting for this liquid to solid phase transformation, the strain energy term. So, delta G can be written as the green term, which is supporting my cold phase transformation process. The term in red box, which is opposing my phase transformation or the solidification process and therefore, delta G can be written as 4 by 3 pi r cube into delta G v.

Because, this as now, spherical nucleus and the volume of this nucleus is 4 by 3 pi r cube and 4 pi r square, which is the surface area of this spherical nucleus multiplied by the surface free energy term, which is gamma. Now, of course, delta G v is negative that means, it is helping the process, gamma is a, this second term is positive that means, it is opposing the process. This delta g v needless to say, as you have noted before, is a function of the under cooling that means, it is not a constant term, it depends in this.

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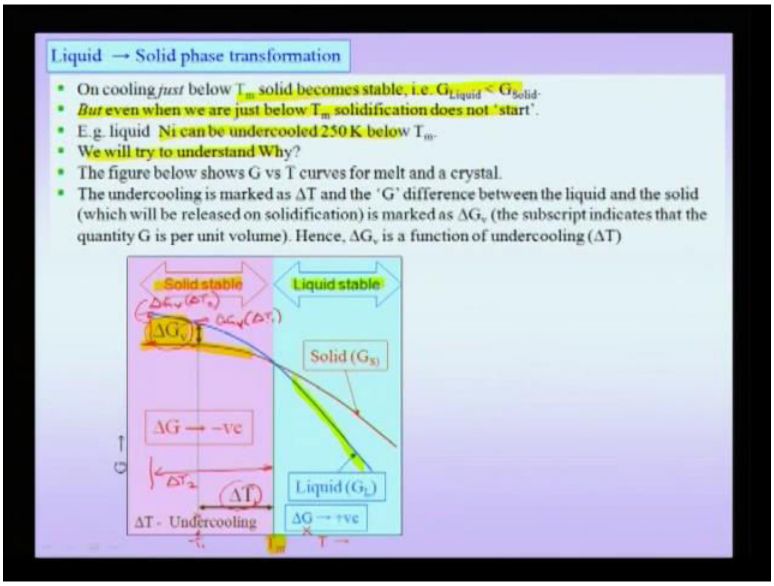

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As we noted in this graph before thus, delta G suppose, I go to a further under cooling here so, to under cooling not delta T 1 but, I go to under cooling delta T 2. Now, my Gibbs free energy benefit at this temperature happens to be this term, which is here so, this becomes my new change. So, this becomes delta G v at an under cooling delta T 2 so, this delta G v is at delta G v as a function, which is now at delta T 1. So, this delta G v term is obviously, a function of the under cooling.

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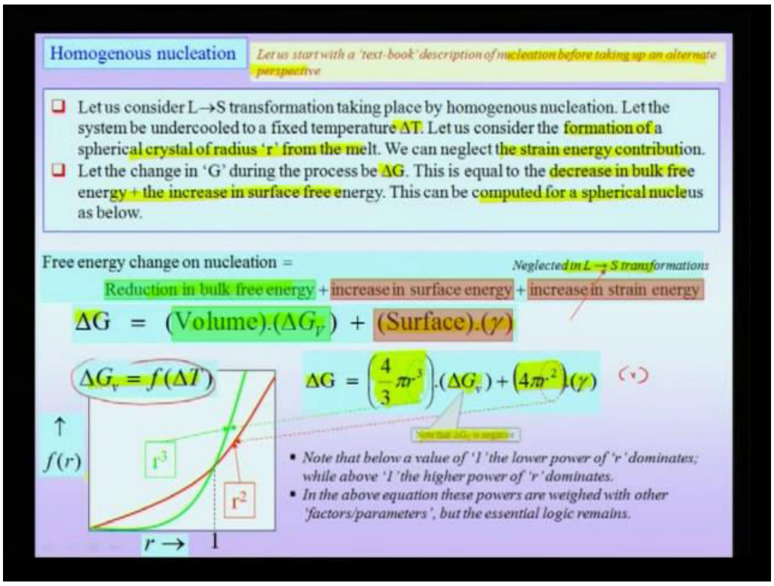

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And that is what, we have stated here as delta G v is a function of the under cooling, since we are working at a fixed under cooling and for a fixed under cooling, I can write an equation as the equation 1 here, which is the equation in green shade. Now, one important point is that that means, there is one negative term, there is one positive term, both of them depend on the radius, both are polynomial functions of the radius. One of these functions differs in the other by an one order of magnitude that means, one is an r cube term, one is an r square term.

Now suppose, I plot an r cube and r square functions so, this is f of r now, which could be r cube or r square, the polynomial and I call it as function of r. We known that, the smaller power dominates for values of r below 1, if you take a value below 1, it is a smaller power, which is r square term which dominates. For a power larger than 1, it is actually the higher power, which dominates and here we already know that, the r cube term is a negative term.

Because, that is what is supporting here, as in this case and the r square term is the positive term in the coefficient is to these terms as shown here are positive and negative respectively. That implies, that when I am subtracting this one, r cube term from the other term, minus r cube plus r square, I would expect such a function to be a not monotonic in r. And we would notice that, if you plot this function, this function actually goes through a maxima so, let us consider this in a little more detail because...

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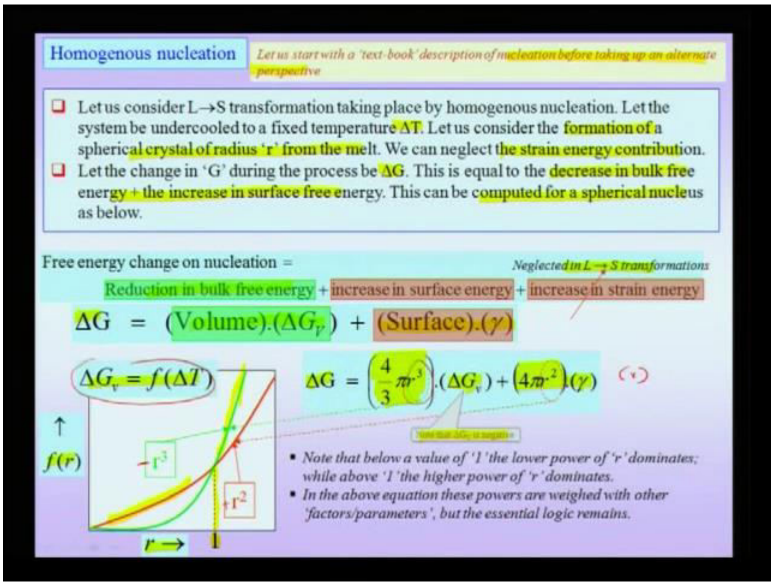

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- *Note that below a value of '1' the lower power of 'r' dominates; while above '1' the higher power of 'r' dominates.*
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So, what we are saying here is that, the delta G term for the whole phase transformation at a constant under cooling delta T is a function of two terms, one which depends as r cube, the other depends as r square. And we have noted that, the r cube term would dominate after a value of 1 and r square below value of 1. But, in this case of course, there are other factors, which are multiplied with this r cube so therefore, there is a scaling factor.

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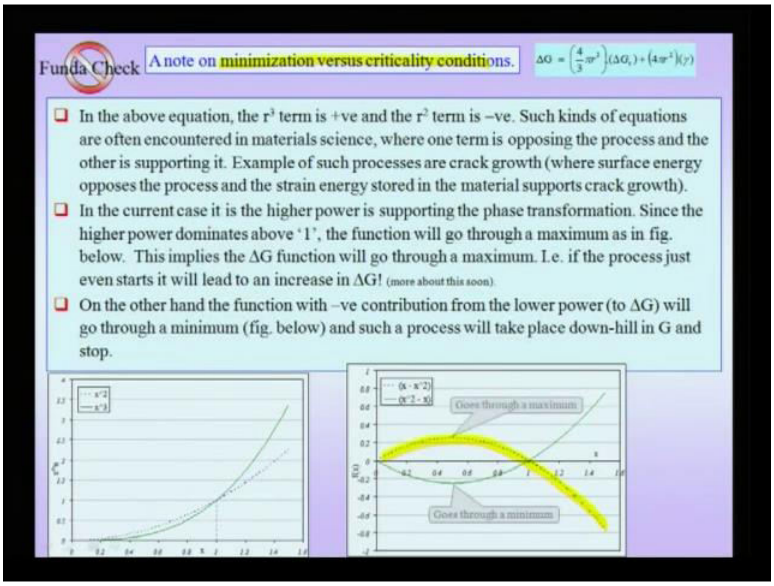

Funda Check

A note on minimization versus criticality conditions.

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

- ❑ In the above equation, the r^3 term is +ve and the r^2 term is –ve. Such kinds of equations are often encountered in materials science, where one term is opposing the process and the other is supporting it. Example of such processes are crack growth (where surface energy opposes the process and the strain energy stored in the material supports crack growth).
- ❑ In the current case it is the higher power is supporting the phase transformation. Since the higher power dominates above '1', the function will go through a maximum as in fig. below. This implies the ΔG function will go through a maximum. I.e. if the process just even starts it will lead to an increase in ΔG! (more about this soon)
- ❑ On the other hand the function with –ve contribution from the lower power (to ΔG) will go through a minimum (fig. below) and such a process will take place down-hill in G and stop.

And the important point you note is that, that such functions are found in many many circumstances and but, the important thing is that, depending on which term is positive and which term is negative. This function would either go through this kind of functions like suppose, you could have a term like wherein, one term opposes you like could be positive or negative.

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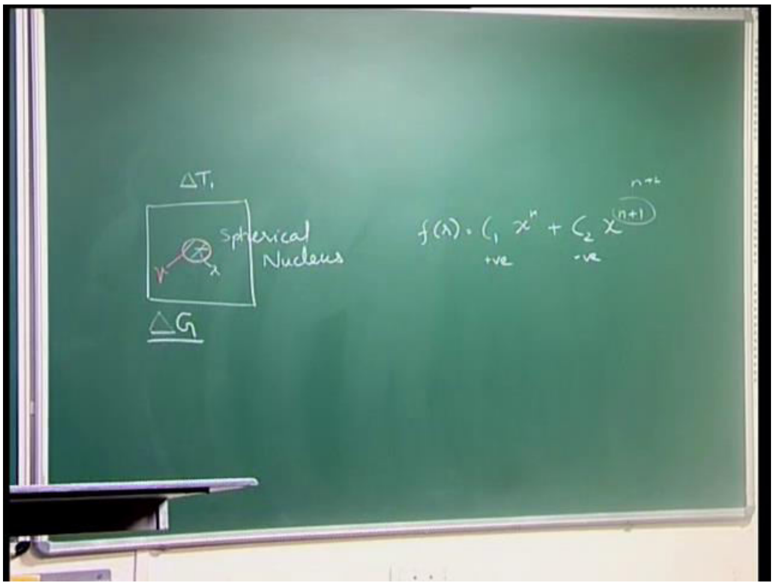

And therefore, this is say, this function of r can be 1 power of n and multiplied by this coefficient C 1, there is another power of n multiplied by coefficients say, n plus 1 or even it could be n plus 2 for instance, this could also be n plus 2. So, there are two differing powers say, one of them is C 1 could be positive, other one could be negative or other way above. But, the important point is that, when you have two such functions, the sum of these two functions can undergo either a maxima or a minima so, this is an important point to note because, now one is positive, other is negative.

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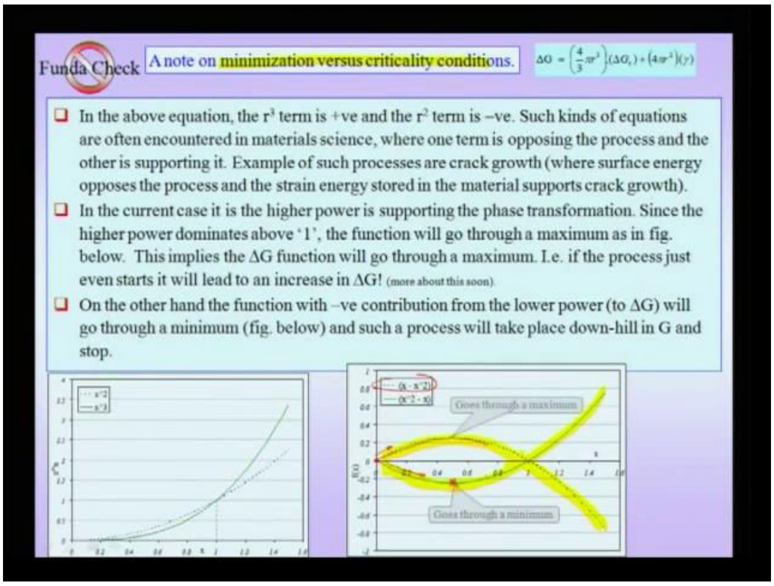

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- ☐ On the other hand the function with –ve contribution from the lower power (to ΔG) will go through a minimum (fig. below) and such a process will take place down-hill in G and stop.

And in the present case, if I note, if I am writing the term like for instance, suppose I write down a function of x minus x square, which is the dotted line here, this x minus x square goes through a maximum. If I other way, talk about another function x square minus x is opposite function, this will go through a minimum. Now, how is this physically very very important, it is spherically very very important because, if we had a function like delta G, which is going to tell me what is going to be the stable state and I am seeing a function, which goes through a minima.

That means, the system if suppose, this is the starting point of the system with a certain r equal to 0, such a system will go down hill in Gibbs free energy, come to the minima and there the system will tend to be at it is stable state. But suppose, I am talking about a function like in the current case, which is now a negative r cube term with a positive r square term then, such functions which is similar to now, for the r minus r square kind of term will go through a maxima.

That implies, now suppose, this is not function of x, I am actually plotting the Gibbs free energy, such a function the momment any change in r takes place, increase in r takes place, the system is going uphill in Gibbs free energy. So, this is the important point and we will return to it in the coming slides in the context of this solidification. But, to summarize this slide, what you are saying here is that, if the functions go through a minima then, there is no confusion, such a system will evolve in r and finally, settle down in the minima.

But suppose, the system goes through a maxima then, things are not that obvious and we will have to consider that, how such a transformation will take place, in which the very first step in the transformation formation of say, small r, we will actually take you above in Gibbs free energy.

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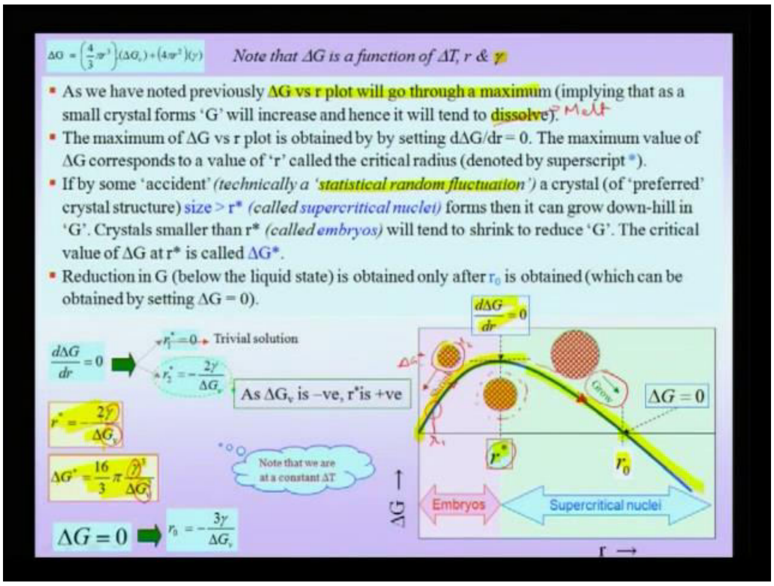

$\Delta G = \left(\frac{4}{3}\pi r^3\right)(\Delta G_v) + (4\pi r^2)(\gamma)$ *Note that ΔG is a function of ΔT, r & γ*

- As we have noted previously ΔG vs r plot will go through a maximum (implying that as a small crystal forms 'G' will increase and hence it will tend to dissolve). Melt
- The maximum of ΔG vs r plot is obtained by by setting dΔG/dr = 0. The maximum value of ΔG corresponds to a value of 'r' called the critical radius (denoted by superscript *).
- If by some 'accident' *(technically a 'statistical random fluctuation')* a crystal (of 'preferred' crystal structure) size > r* *(called supercritical nuclei)* forms then it can grow down-hill in 'G'. Crystals smaller than r* *(called embryos)* will tend to shrink to reduce 'G'. The critical value of ΔG at r* is called ΔG*.
- Reduction in G (below the liquid state) is obtained only after r_0 is obtained (which can be obtained by setting ΔG = 0).

$\frac{d\Delta G}{dr} = 0 \Rightarrow r_1^* = 0$ Trivial solution

$r_2^* = -\frac{2\gamma}{\Delta G_v}$

As ΔG_v is –ve, r^* is +ve

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

$$\Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G_v^2}$$

$$\Delta G = 0 \Rightarrow r_0 = -\frac{3\gamma}{\Delta G_v}$$

Note that we are at a constant ΔT

So, this is the thick question we are asking and we will try to answer this in this question, in this slide. Now that means, the delta G versus r plot will go through a maximum, given the fact that, gamma is a positive term and the delta G v term is the negative term. Now, this implies suppose, I form suddenly a small crystallite of say for instance, this is my small crystallite forming of a sudden radius say or whatever a small radius here.

Now, this crystallite of this very small size here has taken my system uphill in Gibbs free energy, the Gibbs free energy is increasing, as you can see along the blue curve and then, decreasing later, of course. But, the point is that, now the system is growing to increase in Gibbs free energy, what will be the tendency now of such an small crystallite. The crystallite will tend to shrink and dissolve because, now dissolve implying, it will tend to remelt back, the term should have been remelt but, I am used a term dissolve.

But, what exactly it means here is that, the tendency would be to melt, now if the small r 1 crystallite is going to melt back that means, that there is no chance that transformation can take place. Because now; obviously if a small crystallite has to form, it cannot be as large crystallite, which can form immediately. But, a smallest piece in the whole melt, which will be forming a crystalline and this solid crystal would dissolve away. And therefore, you can see that automatically that, there is some kind of a barrier to this crystallization process.

That means, the formation of a small crystallite is not preferred in Gibbs free energy, now let us carry for the mathematical accepts of this, before we understand the physical aspects. I have see that, this curve actually goes through a maxima and then, goes through a point where it becomes 0. So, there are two 0's, one trivially at in the molten state that there are no crystallites, one where the crystallite size is r 0, which I labeled as r 0.

So, I can find these two values, the maxima corresponds to dou delta G by dou r equal to 0 and by setting dou delta G by dou r is equal to 0, I can find that, there is a radius r star, at which the maxima takes place. And that r star can be computed to be minus 2 gamma by delta G v and the Gibbs free energy corresponding to this value of r star is delta G star, which can be found to be 16 by 3 pi gamma cube by delta G v square, in other words both r star and delta G star are functions of gamma and delta G v.

So, the maxima of this plot can be computed using d delta G by d r is equal to 0 and the maxima corresponds to a value of r star delta G star and these two values can be computed by setting d delta G by d dou r equal to 0. Now, the important point is that, suppose now, let me consider somehow a crystallite, which is of the size r star forms. So, this is my crystallite of r star which forms, which is bigger than the crystallite size shown here for instance, this size. So, they suppose, this is r 2, it is bigger than r 1, it is bigger than r 2 but, it is of the size of r star.

Now suppose, a crystallite of r star size forms somehow then, it can actually then reduce the Gibbs free energy by growing downhill in this plot. So, it can actually decrease the Gibbs free energy by going down in a plot, though the formation of r star itself has taken place uphill in Gibbs free energy but, further after it is reach the top of the hill, it can actually go downhill. Of course, there are two options it can also melt back but, there is one option here, in which case it can go downhill in Gibbs free energy by growing.

So, there is a possibility of growth if I somehow assemble a crystallite of size r star, we can ask this question, how does this assemblage take place. And technically, this is called, these are referred to as statistical random fluctuations, which lead to such kind of nucleus. That means, what we are implying is that, the solid is actually exploring many configuration, the liquid state is exploring many configurations. And some of these configurations resemble the crystalline state, we will have a little more to talk about that later on.

But, for now, we will assume that, somehow an r star has formed and it can grow downhill in Gibbs free energy. Now, sizes of crystallites smaller than r star are called embryos that means, these are embryos which are smaller than r star, the r star is called a critical size nuclei, sizes greater than r star are called super critical nuclei. So, embryos will tend to remelt back into the liquid state, super critical nuclei will tend to grow and cause further solidification.

That means, they will become bigger and bigger and therefore, single super critical nuclei can itself grow and cause the entire liquid to become crystalline solid state. Now, actual reduction if you we observe in the Gibbs free energy, takes place only after we cross a size which is r 0 and we can find r 0 by setting delta G is equal to 0. And we said delta G equal to 0, we find that the value of r 0 turns out to be minus 3 gamma by delta G v. While r star is minus 2 gamma by delta G v, r 0 is minus 3 gamma by delta G v.

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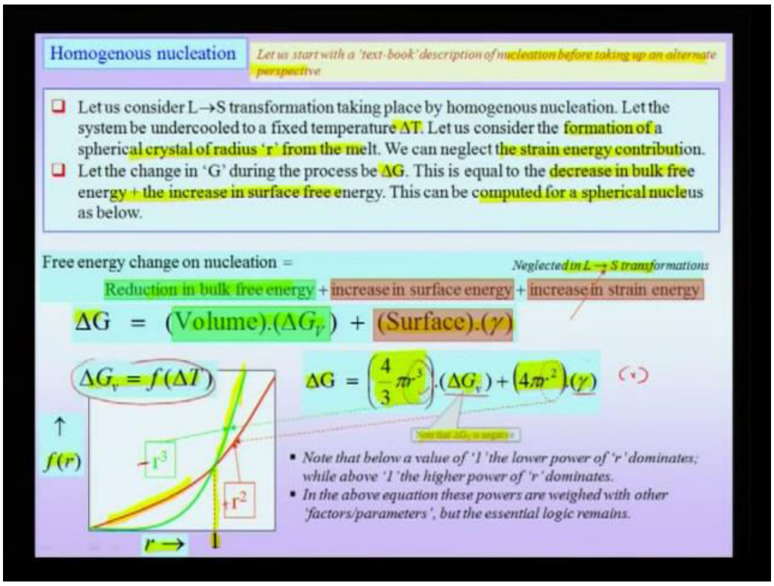

Homogenous nucleation

Let us start with a 'text-book' description of nucleation before taking up an alternate perspective

- ❑ Let us consider L→S transformation taking place by homogenous nucleation. Let the system be undercooled to a fixed temperature ΔT. Let us consider the formation of a spherical crystal of radius 'r' from the melt. We can neglect the strain energy contribution.
- ❑ Let the change in 'G' during the process be ΔG. This is equal to the decrease in bulk free energy + the increase in surface free energy. This can be computed for a spherical nucleus as below.

Free energy change on nucleation = Reduction in bulk free energy + increase in surface energy + increase in strain energy

Neglected in L → S transformations

$$\Delta G = (\text{Volume}).(\Delta G_v) + (\text{Surface}).(\gamma)$$

$$\Delta G_v = f(\Delta T)$$

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

Note that ΔG_v is negative

- *Note that below a value of '1' the lower power of 'r' dominates; while above '1' the higher power of 'r' dominates.*
- *In the above equation these powers are weighed with other 'factors/parameters', but the essential logic remains.*

So, to summarize this slide, we are not talking about a delta G v function, delta G function for the process which has two terms, the term which is just supposing us, the gamma term. And when you plot, one of them depends on r cube here and the other term depends on r square.

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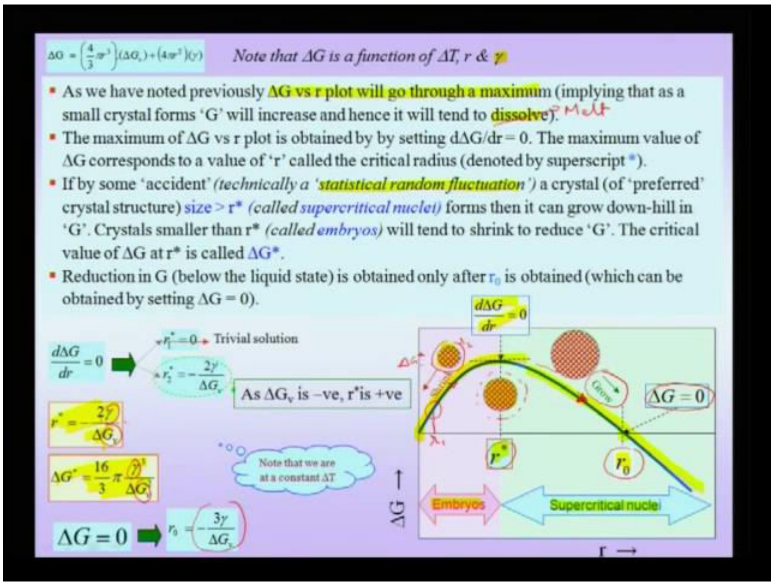

$$\Delta G = \left(\frac{4}{3}\pi r^3\right)(\Delta G_v) + \left(4\pi r^2\right)(\gamma)$$

Note that ΔG is a function of ΔT, r & γ

- As we have noted previously ΔG vs r plot will go through a maximum (implying that as a small crystal forms 'G' will increase and hence it will tend to dissolve). ? Melt
- The maximum of ΔG vs r plot is obtained by by setting dΔG/dr = 0. The maximum value of ΔG corresponds to a value of 'r' called the critical radius (denoted by superscript *).
- If by some 'accident' *(technically a 'statistical random fluctuation')* a crystal (of 'preferred' crystal structure) size > r* *(called supercritical nuclei)* forms then it can grow down-hill in 'G'. Crystals smaller than r* *(called embryos)* will tend to shrink to reduce 'G'. The critical value of ΔG at r* is called ΔG*.
- Reduction in G (below the liquid state) is obtained only after r_0 is obtained (which can be obtained by setting ΔG = 0).

$$\frac{d\Delta G}{dr} = 0 \Rightarrow r_1^* = 0 \rightarrow \text{Trivial solution}$$

$$\frac{d\Delta G}{dr} = 0 \Rightarrow r_2^* = -\frac{2\gamma}{\Delta G_v}$$

As ΔG_v is –ve, r^* is +ve

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

$$\Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G_v^2}$$

$$\Delta G = 0 \Rightarrow r_0 = -\frac{3\gamma}{\Delta G_v}$$

Note that we are at a constant ΔT

When you plot this function, this function goes through a maxima, we can find the maxima by setting delta G by d r equal to 0. And we find that, that maxima corresponds to a r star labeled r star, which is minus 2 gamma by delta G v, this corresponds to a

Gibbs free energy increase, the important term is increase, of 16 pi by 3 gamma cube by delta G v square. Now, by somehow if I form a nuclei of r star then, this can grow and become super critical and cause solidification to take place.

Clearly this implies that, the process of nucleation is uphill in Gibbs free energy and the process of growth is downhill in Gibbs free energy so now, we have a clearcut definition of nucleation and growth. Nucleation is this process taking place starting from 0 to r star, which is uphill in Gibbs free energy and any process taking place, which takes a critical nuclei to super critical nuclei is called growth, which is happening downhill in Gibbs free energy.

So, we now understand what is the terms of nucleation and growth and in this context, there is another term which will come, perhaps important is a term called coarsening but, we will not consider that term here in more detail.

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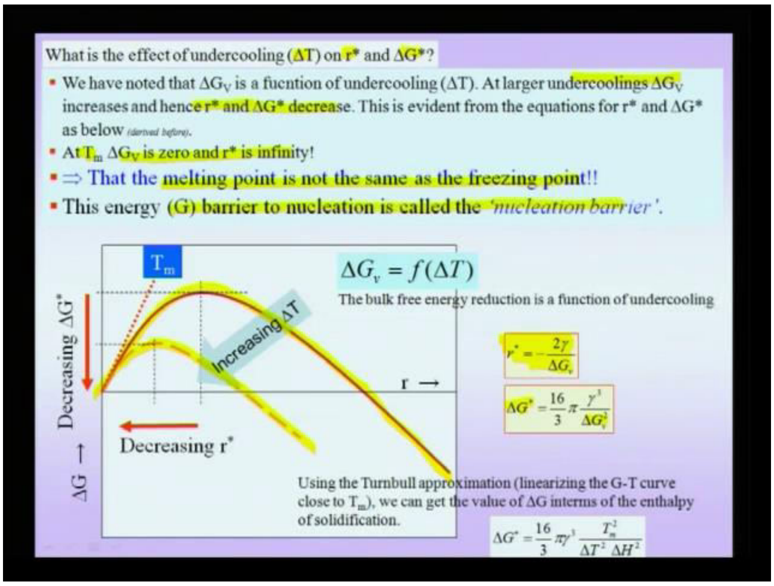

What is the effect of undercooling (ΔT) on r^* and ΔG^*?

- We have noted that ΔG_V is a fucntion of undercooling (ΔT). At larger undercoolings ΔG_V increases and hence r^* and ΔG^* decrease. This is evident from the equations for r^* and ΔG^* as below (derived before).
- At T_m ΔG_V is zero and r^* is infinity!
- ⇒ That the melting point is not the same as the freezing point!!
- This energy (G) barrier to nucleation is called the *'nucleation barrier'*.

$$\Delta G_v = f(\Delta T)$$

The bulk free energy reduction is a function of undercooling

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

$$\Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G_v^2}$$

Using the Turnbull approximation (linearizing the G-T curve close to T_m), we can get the value of ΔG interms of the enthalpy of solidification.

$$\Delta G^* = \frac{16}{3}\pi\gamma^3\frac{T_m^2}{\Delta T^2\,\Delta H^2}$$

Now, we have to ask ourselves, what is the effect of under cooling, we have said that because, delta G v is already a function of under cooling so, what is the effect of under cooling delta T on r star and delta G star. So, we have noted that, at larger under cooling, delta G v increases and this implies, r star and delta G star decrease. So, suppose, I am at an under cooling, which originally shown by this red curve here, this is for a particular under cooling.

Now suppose, I increase my delta G v that means, I go to larger under cooling's like in the curve before, I am not at this one, this temperature T 1 but, I am at a lower temperature T 2, which corresponds to delta T 2. Now, at such a larger under cooling, we would note that, that r star would decrease, delta G star would decrease because, the delta G in both cases is situated in the denominator that means, my curve would tend to become this curve for larger under coolings.

And needless to say, suppose at the melting point T m, delta G v is 0 and that implies, r star is infinity. Because, at the melting point, there is no propensity for formation of solid and this implies that, my r star goes to infinity. And this implies, solidification cannot take place, which also is makes it very clear that, the melting point is not the same as the freezing point. That means, for freezing to take place, we have to under cool the system and this G barrier to nucleation is often referred to as the nucleation barrier.

This maxima is referred to as the nucleation barrier and more and more under cool, the r star keeps on decreasing and because of this function, that minus 2 gamma by delta G v and this implies at larger and large under coolings, there is a better chance of solidification. Now, why is the better chance because now, the way the r star appears, the solid of a certain size appears, is by a statistical random fluctuations. And such kind of fluctuations, it is easier to assemble an r star which is smaller than a r star which is larger.

So, this is an important point to note here that, now we introduce the concept of nucleation, we have introduced the concept of a nucleation barrier. And we have seen that, at larger under cooling, there is a better chance of a nucleus of r star forming because now, here r star value decreases and that also means that, solidification would become easier at larger under coolings.

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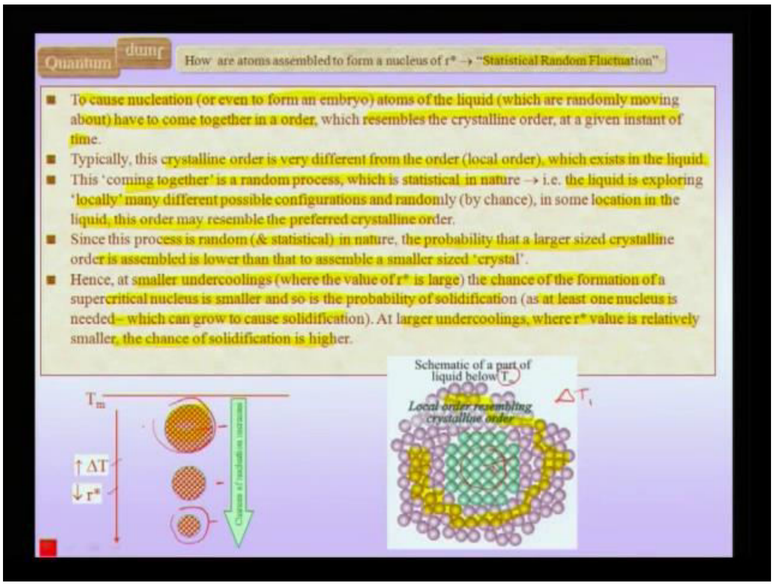

How are atoms assembled to form a nucleus of r^* → "Statistical Random Fluctuation"

- To cause nucleation (or even to form an embryo) atoms of the liquid (which are randomly moving about) have to come together in a order, which resembles the crystalline order, at a given instant of time.
- Typically, this crystalline order is very different from the order (local order), which exists in the liquid.
- This 'coming together' is a random process, which is statistical in nature → i.e. the liquid is exploring 'locally' many different possible configurations and randomly (by chance), in some location in the liquid, this order may resemble the preferred crystalline order.
- Since this process is random (& statistical) in nature, the probability that a larger sized crystalline order is assembled is lower than that to assemble a smaller sized 'crystal'.
- Hence, at smaller undercoolings (where the value of r^* is large) the chance of the formation of a supercritical nucleus is smaller and so is the probability of solidification (as at least one nucleus is needed– which can grow to cause solidification). At larger undercoolings, where r^* value is relatively smaller, the chance of solidification is higher.

Now, we have used a term called statistical random fluctuation, let us try to get a physical picture of what is happening, in other words how does this r star come about. To cause nucleation or an even an embryo, atoms of the liquid which are randomly moving about, have to come together in an order, which resembles the crystalline order at a given instance of time. So, I have a liquid here right in the schematic below, in which atoms are randomly arranged here as in the picture.

But, at some instant of time, I expect that one of the configurations being explored or being found in some region of the liquid is like the one, which is shown in green. And this is like the crystalline order and this is occurred randomly and if this or which I am drawing here, is below the r star then, such a random order would melt away, such an ordered region would melt away. But then, the liquid will try to explore some other region, though the we are assuming that, we though T m and we are at it say for instance, the fixed under cooling delta T 1.

Now, there will be certain other region, again this kind of crystalline order may appear and if this crystalline order becomes larger than the that means, which is r star then, such a crystalline order can grow. Now, this crystalline order is very different from the local order which exists in the liquid, it is obvious because, the liquid perhaps is highly disorder and this crystalline order is very very different. It is coming together to form this order, which is statistical in nature that means, that the liquid is exploring locally many different possible configurations and that too randomly.

And in some location in the liquid, this order may resemble the preferred crystalline order. Since the process is random and statistical in nature, the probability that a larger site crystallite is assembled is lower than that a smaller site crystallite of a preferred order is assembled so, this is the important thing, which we were talking about. So, hence at small under coolings where, the value r star is large, the chance of formation of a super critical nucleus is small and so, the probability of solidification. As at least one nucleus need is needed, which can further grow to cause solidification of the entire melt.

At larger under coolings where, r star is relatively smaller, the chance of solidification is higher, this is what we see schematically here. Suppose, I am plotting r star for different under coolings say suppose, I am at under cooling 1 here and this is my r star which I need to assemble, at a larger under cooling this r star decreases. And even larger under cooling so, delta T is increasing down and r star is decreasing down. And therefore, it is easier for me to assemble this kind of an r star, rather than this kind of an r star at a higher under cooling.

Therefore, I observe that, probability of solidification is higher because, at least I need to form one nucleus, which can become super critical and cause the solidification of the entire melt. So, at the heart of all this process is this kind of fluctuations, which is taking place in the liquid state and some of those fluctuations is giving rise to a green region shown in this graph, which is like a crystalline order and which can further grow to cause solidification of the melt.

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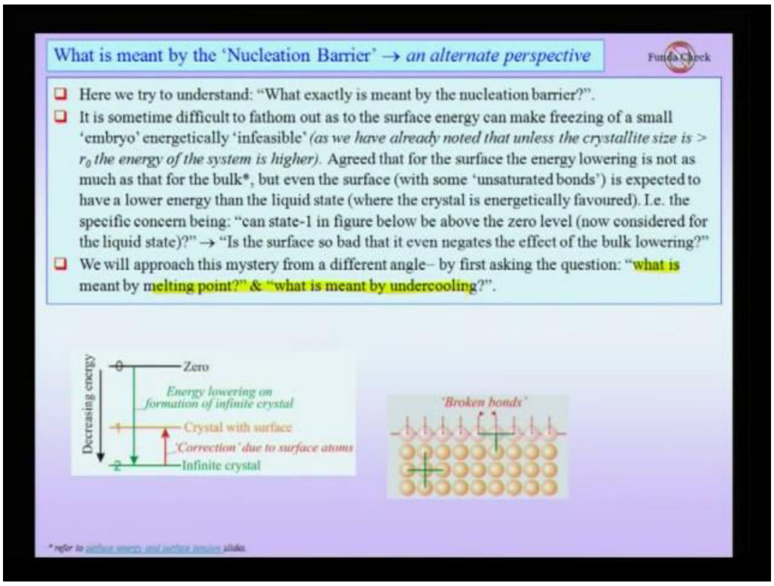

What is meant by the 'Nucleation Barrier' → *an alternate perspective*

- Here we try to understand: "What exactly is meant by the nucleation barrier?".
- It is sometime difficult to fathom out as to the surface energy can make freezing of a small 'embryo' energetically 'infeasible' *(as we have already noted that unless the crystallite size is > r_0 the energy of the system is higher)*. Agreed that for the surface the energy lowering is not as much as that for the bulk*, but even the surface (with some 'unsaturated bonds') is expected to have a lower energy than the liquid state (where the crystal is energetically favoured). I.e. the specific concern being: "can state-1 in figure below be above the zero level (now considered for the liquid state)?" → "Is the surface so bad that it even negates the effect of the bulk lowering?"
- We will approach this mystery from a different angle– by first asking the question: "what is meant by melting point?" & "what is meant by undercooling?".

* refer to surface energy and surface tension slides

Now, let us consider an alternate perspective of, what is meant by this nucleation barrier.

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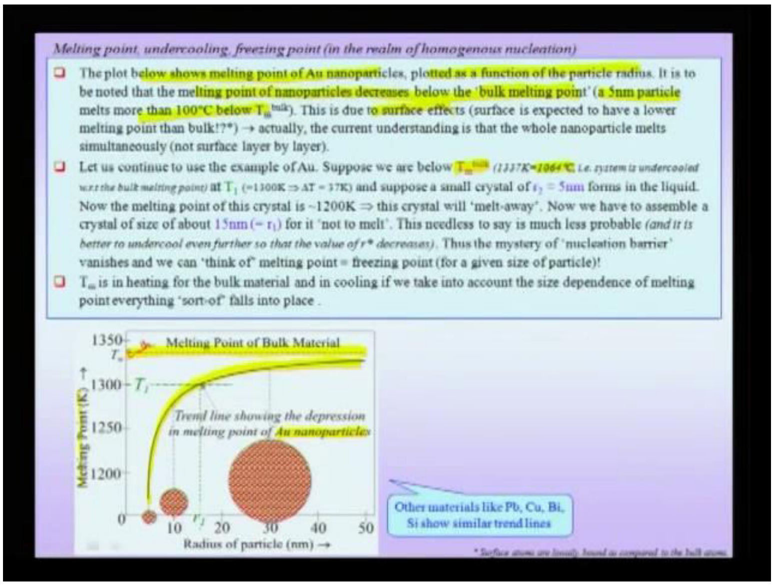

Melting point, undercooling, freezing point (in the realm of homogenous nucleation)

- The plot below shows melting point of Au nanoparticles, plotted as a function of the particle radius. It is to be noted that the melting point of nanoparticles decreases below the 'bulk melting point' (a 5nm particle melts more than 100°C below T_m^{bulk}). This is due to surface effects (surface is expected to have a lower melting point than bulk!?*) → actually, the current understanding is that the whole nanoparticle melts simultaneously (not surface layer by layer).
- Let us continue to use the example of Au. Suppose we are below T_m^{bulk} *(1337K=1064°C i.e. system is undercooled w.r.t the bulk melting point)* at T_1 (~1300K ⇒ ΔT ~ 37K) and suppose a small crystal of r_2 = 5nm forms in the liquid. Now the melting point of this crystal is ~1200K ⇒ this crystal will 'melt-away'. Now we have to assemble a crystal of size of about 15nm (= r_1) for it 'not to melt'. This needless to say is much less probable *(and it is better to undercool even further so that the value of r* decreases)*. Thus the mystery of 'nucleation barrier' vanishes and we can 'think of' melting point = freezing point (for a given size of particle)!
- T_m is in heating for the bulk material and in cooling if we take into account the size dependence of melting point everything 'sort-of' falls into place .

Other materials like Pb, Cu, Bi, Si show similar trend lines

* Surface atoms are loosely bound as compared to the bulk atoms

And we will see that, in some sense that this perspective will sort of help us, sort of get read of mystery of, why this nucleation barrier should exist or how we can alternately understand that, there is actually at different way of understanding why melting or solidification becomes easier at larger under cooling. To understand this question so, we will ask ourselves the question, what is meant by melting point and what is meant by under cooling so, these are two important questions.

Now suppose, I take the example of say, for instance, gold nano particles and here, I got gold nano particles of various sizes and I am plotting the melting point of these gold nano particles with size. So, the plot below shows melting point of gold nano particles, plotted as a function of the particle radius. Now, it is we noted that, the melting point of nano particles decrease below the bulk melting point. So, the bulk melting point of large poly crystalline pieces say suppose, I take a big chunk of gold and try to see it is melting point is somewhere around 1064 degrees Celsius thus, the melting point of the bulk.

So, this is T m bulk, is a bulk melting point now, with respect to this bulk melting point, if I track the melting point of all these nano crystals, I would notice that, nano crystal of smaller and smaller sizes, melt at lower and lower temperatures. And that means, that the melting point is lower than the bulk melting point for example, 5 nano meter particle melt more than 100 degrees below the bulk melting point, this is due to surface effects. And we have already noted that, surface region where, the bonds are unsaturated that means, that the surface region atoms are not as well bonded.

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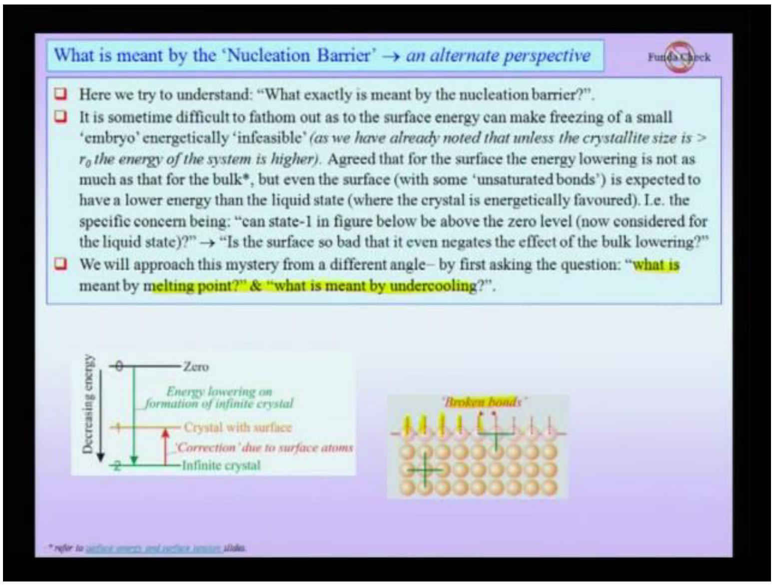

What is meant by the 'Nucleation Barrier' → *an alternate perspective*

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- ☐ It is sometime difficult to fathom out as to the surface energy can make freezing of a small 'embryo' energetically 'infeasible' *(as we have already noted that unless the crystallite size is > r_0 the energy of the system is higher)*. Agreed that for the surface the energy lowering is not as much as that for the bulk*, but even the surface (with some 'unsaturated bonds') is expected to have a lower energy than the liquid state (where the crystal is energetically favoured). I.e. the specific concern being: "can state-1 in figure below be above the zero level (now considered for the liquid state)?" → "Is the surface so bad that it even negates the effect of the bulk lowering?"
- ☐ We will approach this mystery from a different angle– by first asking the question: "what is meant by melting point?" & "what is meant by undercooling?".

* refer to surface energy and surface tension slides.

And we already explored, what is called the broken bound model where, we see that the surface atoms. There are some bonds, which are unsatisfied and this atoms perhaps have a, what we call have a freedom to move more than the bulk atoms.

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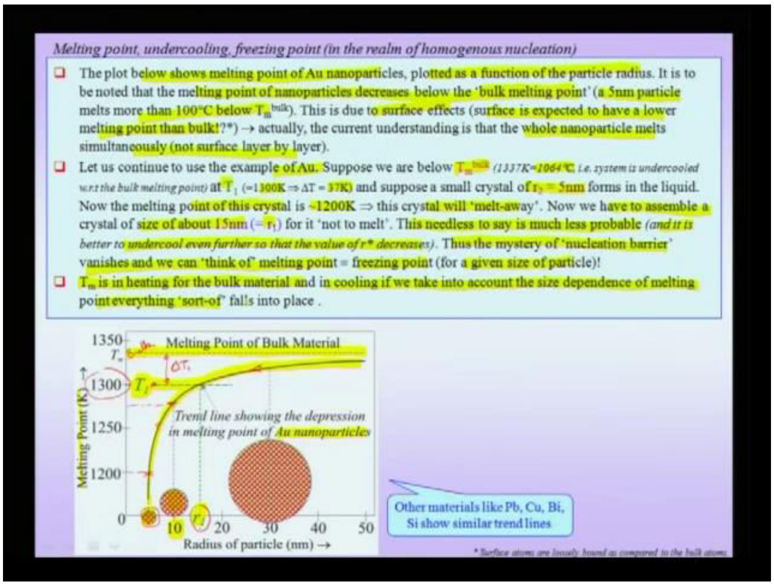

Melting point, undercooling, freezing point (in the realm of homogenous nucleation)

- ☐ The plot below shows melting point of Au nanoparticles, plotted as a function of the particle radius. It is to be noted that the melting point of nanoparticles decreases below the 'bulk melting point' (a 5nm particle melts more than 100°C below T_m^{bulk}). This is due to surface effects (surface is expected to have a lower melting point than bulk!?*) → actually, the current understanding is that the whole nanoparticle melts simultaneously (not surface layer by layer).
- ☐ Let us continue to use the example of Au. Suppose we are below T_m^{bulk} *(1337K=1064°C i.e. system is undercooled w.r.t the bulk melting point)* at T_1 (~1300K ⇒ ΔT ~ 37K) and suppose a small crystal of r_2 = 5nm forms in the liquid. Now the melting point of this crystal is ~1200K ⇒ this crystal will 'melt-away'. Now we have to assemble a crystal of size of about 15nm (= r_1) for it 'not to melt'. This needless to say is much less probable *(and it is better to undercool even further so that the value of r* decreases)*. Thus the mystery of 'nucleation barrier' vanishes and we can 'think of' melting point = freezing point (for a given size of particle)!
- ☐ T_m is in heating for the bulk material and in cooling if we take into account the size dependence of melting point everything 'sort-of' fal!s into place .

Other materials like Pb, Cu, Bi, Si show similar trend lines

* Surface atoms are loosely bound as compared to the bulk atoms

So, because of this surface effects, we do expect crudely speaking and we will have few most things to say about this very soon. The surface is expected to, may have a lower melting point on the bulk where, the atom are free and therefore, give temperature there is a chance that, atom would actually breaks free and cause that means go random, do not sit in the crystalline order and therefore, we can think of it as having being molded.

An important point of course, notice that, though we except the surface to melt at lower temperature, as per as current experimentations go and current understanding goes, it is seems that whole nano particle melts simultaneously at the same temperature and not layer by layer. Therefore, for now will assume that, there is something called a melting point, which is the bulk melting point, there is a melting point for a nano particle of different sizes.

And as we decrease the size of the particle, the melting point decreases as shown in the curve below that means, that you have melting point, there is a depression in the melting point as we make the particle size smaller. Now, using this example of gold suppose, that we are below the melting point at say, a temperature T 1 now, this is my temperature T 1. That means, that now at these temperature for instance, which could be about 1300 Kelvin, we are under cool to about 37 Kelvin, we are about 37 Kelvin below the bulk melting point.

And suppose, a small crystallite of size r 2 equal to 5 nano meter forms in the liquid so now, we note that, the melting point of this crystal is 1200 Kelvin. So, if you have take 5 nano meter particle which is sitting here, the melting point of this crystal is somewhere here and which is 1200 Kelvin, which is also below the melting point of the bulk. Now, this crystal will melt away, it is not going to sustain because, for this small crystal which is 5 nano meter because, we note that, we are at this delta T that means, we are at a temperature T 1, let us note that once more.

We are at under cooling, which is given by this temperature difference here so, we are this under cooling which I call delta T 1. And at this under cooling delta T 1 suppose, I form a crystallite which is 5 nano meter in size, which is shown here. It is melting point will be closed about 1200 Kelvin and such a crystallite obviously, for such a crystallite I am above the melting point now because, I am at T 1 which is here. And therefore, such a crystallite will tend to melt away now, if I have to assemble crystalline of about 15 nano meter which is r 1 here.

If that crystal has not to melt that mean suppose, I make a crystal which is anything smaller like for instance, 10 nano meter crystalline or 5 nano crystalline, such crystalline will melt away. Because, I am sitting T 1, which is above the melting point of such kind of nano crystals and needless to say that, assembling a r 1 size crystal which is same 15 nano meter approximately, is going to be a more difficult than assembling a 10 nano meter crystal or even more easier to be 5 nano meter crystal.

Therefore, this needless to say, is much less probable and it is better to under cool even further so that, the value of r star decreases. And thus, the mystery of the nucleation barrier varnish and we can thing of melting point is equal to the freezing point for given size of the particle. So, this is an alternate analysis and the settle point in this analysis to be noted is that, now we are not only talking about a bulk melting point, we are talking about a melting point which is now size dependent.

That means, I talking about particle r 1, it is going to melt at temperature T 1, if I am talking about 10 nano meter particle, is going to melt at a alternate temperature which I can mark in this graph as here. So, this is going to meet somewhere between 12 15 1300 suppose, I am at even smaller particle then, that will melt say 5 nano meter particle, melt approximately at 1200. Therefore, then, below my melting point and I assemble a small particle, this small particle will tend to melt away say, 5 nano meter particle will melt at a temperature T 1.

And therefore, I will have no growth or no crystallization suppose, I may assemble a nano particle, which is 10 nano meter and I am sitting again at 39 degree Celsius, such a nano particle will also melt away. Therefore, I have to assemble a particle which is say, about 15 nano meter, which is close to r 1 and r 1 size crystallite so that, I can have solidification at temperature T 1. So, in an alternate perspective we are seeing that, the very fact that, if I under cool more my r star decreases or the melting point decreases.

Though therefore, if I am sitting a T 1, the chances that I will have actually solidification is small because, I have to assemble this large crystallite but, if I go to and if I assemble any small crystallite, it will melt away. Therefore, I have go to lower preferable that, I under cool system more so that, I can form at least the crystallite which is say, 5 nano meter or 10 nano meter, which is easier to assemble. And if such a crystallite form then, I can have solidification of the melt and therefore, we have understand that, T m is the heating of the bulk material.

And in cooling if we take into account, size depends on melting point and if we do that, everything sort of falls into place. That means, now I understand that, melting point is not a fixed number, that melting point which I call melting point is actually for the bulk and their under cooling, I am defining with respect to bulk. But suppose, I take size depending melting points then, I know 5 nano meter particle has a different melting point than the 10 nano meter particle. And therefore, sort of the mystery of the nucleation barrier vanishes.

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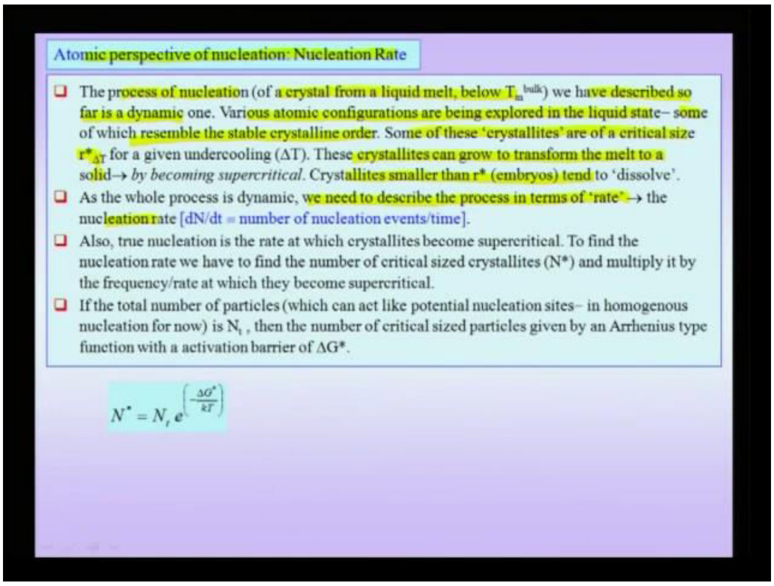

Atomic perspective of nucleation: Nucleation Rate

- ☐ The process of nucleation (of a crystal from a liquid melt, below T_m^{bulk}) we have described so far is a dynamic one. Various atomic configurations are being explored in the liquid state– some of which resemble the stable crystalline order. Some of these 'crystallites' are of a critical size $r^*_{\Delta T}$ for a given undercooling (ΔT). These crystallites can grow to transform the melt to a solid→ *by becoming supercritical*. Crystallites smaller than r* (embryos) tend to 'dissolve'.
- ☐ As the whole process is dynamic, we need to describe the process in terms of 'rate'→ the nucleation rate [dN/dt = number of nucleation events/time].
- ☐ Also, true nucleation is the rate at which crystallites become supercritical. To find the nucleation rate we have to find the number of critical sized crystallites (N*) and multiply it by the frequency/rate at which they become supercritical.
- ☐ If the total number of particles (which can act like potential nucleation sites– in homogenous nucleation for now) is N_t , then the number of critical sized particles given by an Arrhenius type function with a activation barrier of ΔG^*.

$$N^* = N_t e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

But, nevertheless since literature uses this terminology, we will stick to such a terminology to understand the process of solidification or any phase transformation, in which we have this process wherein, nucleation growth is involved. So, let us talk about the atomic perspective of nucleation and talk about the nucleation rate. The process of nucleation of a crystal from a liquid melt below the melting point obviously, the bulk melting point, we have described so far is a dynamic one.

Various atomic configurations have been explored in the liquid state, some of which resemble their stable crystalline order and some of these crystallites are of critical size r star for a given delta T. And these crystallites can grow to transform the melt to a solid by becoming supercritical, crystallites smaller than r star which are called embryos tend to dissolve or tend to melt, dissolve into the melt or just vanish into the melt. As the whole process is a dynamic one, we need to describe the process in terms of rate, the nucleation rate.

So, we have a dynamic process wherein, various atomic configurations are being explored. Some of these atomic configuration resemble their crystalline state and these some of the nucleus are forming.

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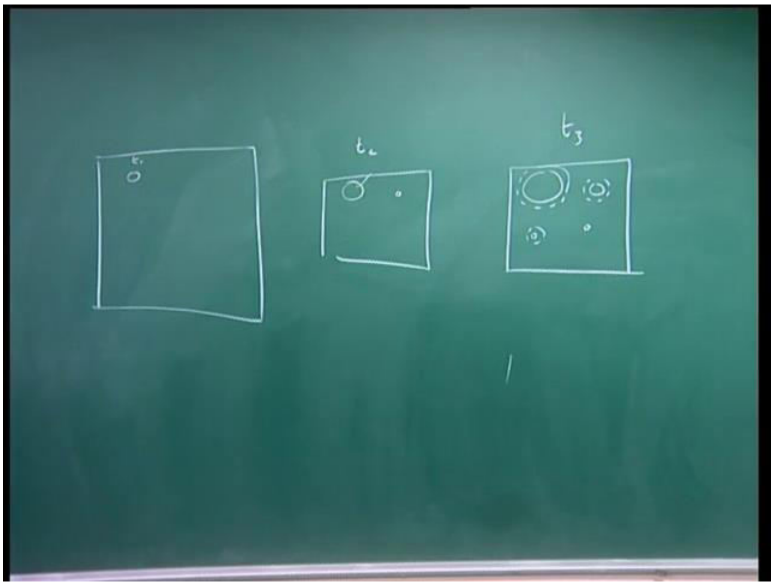

So, suppose that, I have a melt here so, some point of time, I may have a small critical nucleus forming r star here then, later on in a different point of time so, this at time T 1, this is T 1. Suppose, I go to a later time T 2 so, this is T 2 by this time, this r star particle would have grown and you may have one more nucleus r star forming here. At a later time T 3, this particle would grown even bigger, this particle would grown a little larger, may be have one nucleus forming here.

And even at a large time T 4, you will find that this would have grown to a large size, this would grown to a large size, this would have grown, may be one more nucleus occurred here. So, this whole process a dynamic process and I need to describe this process of solidification in terms of a nucleation rate and what I might call a growth rate.

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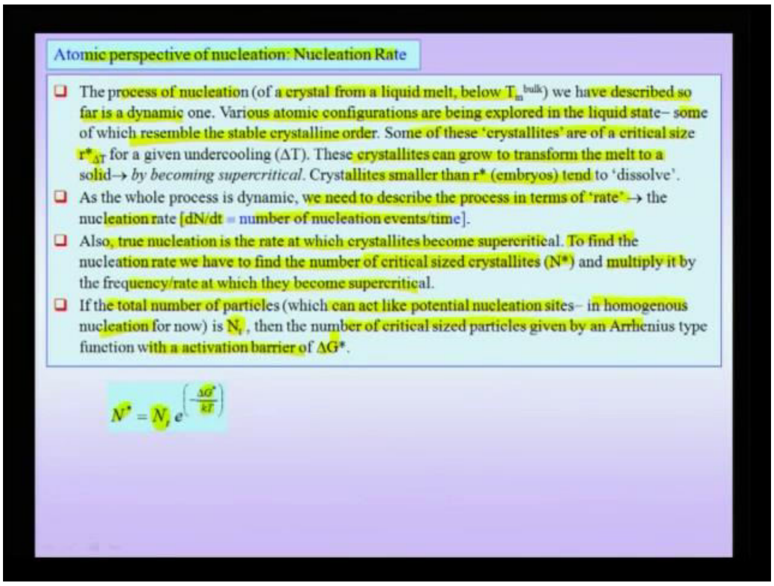

Atomic perspective of nucleation: Nucleation Rate

- ☐ The process of nucleation (of a crystal from a liquid melt, below T_m^{bulk}) we have described so far is a dynamic one. Various atomic configurations are being explored in the liquid state– some of which resemble the stable crystalline order. Some of these 'crystallites' are of a critical size $r^*_{\Delta T}$ for a given undercooling (ΔT). These crystallites can grow to transform the melt to a solid→ *by becoming supercritical*. Crystallites smaller than r* (embryos) tend to 'dissolve'.
- ☐ As the whole process is dynamic, we need to describe the process in terms of 'rate' → the nucleation rate [dN/dt = number of nucleation events/time].
- ☐ Also, true nucleation is the rate at which crystallites become supercritical. To find the nucleation rate we have to find the number of critical sized crystallites (N*) and multiply it by the frequency/rate at which they become supercritical.
- ☐ If the total number of particles (which can act like potential nucleation sites– in homogenous nucleation for now) is N_t, then the number of critical sized particles given by an Arrhenius type function with a activation barrier of ΔG^*.

$$N^* = N_t\, e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

So, this nucleation rate which is written as d N by d t is a number of nucleation events per unit time. So, I take an interval of time and I see number nucleation events, I can calculate the nucleation rate. Also, true nucleation rate is the rate, at which crystallites becomes supercritical, to find the nucleation rate we have to find the number of critical size crystallites nuclei. That means, N star which is a number of critical size nuclei and multiplied by the frequency, at which they become super critical.

So, at any instant of time, I need to locate how many of these nuclei are critical and then, multiplied by the frequency, at which becomes supercritical and this I can think of as the nucleation rate. If the total number of particles and of course, I am talking about particles mean, this crystalline ordered regions of r star, which can act like potential nucleus insides in the homogeneous and we are considering homogeneous nucleation for now, is N t then, the number of critical size particles given by the Arrhenius type function with the activation barrier delta G star.

So, here I have N t is total number of, what you might call potential nucleation sites and given the fact that, these potential nucleation sites is connected to the number of N star, what is the number of critical size nuclei by the activation barrier given by the Arrhenius functions. So, I can write N star equal to N t exponential minus delta G star by k T that means, larger the activation barrier then, smaller will be the number of these potential nucleation size, which act like actual critical size nuclei.

So, in this slide, I am trying to define in a nucleation rate which is number of nucleation events per unit time. And I need to do so because, the whole process of solidification or phase transformation is a dynamic one, in which at any point of time, there are some nucleation events taking place, some perform nuclei are growing with time. And at the later instant of time, whatever the supercritical nuclei, they have also grown and therefore, I need to track this kind of a dynamic event. And to track that, I need to define what I might call the nucleation rate of course, followed by a growth rate.

And the truly, the nucleation rate is the rate at which a critical size nuclei becomes supercritical that means, I have to find the rate at which the number of critical size nuclei and also multiply by the rate at which or the frequency, with which they becomes supercritical. And to do so, I take the total number of potential nucleation sites and then, use an Arrhenius type of function e power minus delta G star by k T. So therefore, function of temperature to arrive at the potential or the number of critical size nuclei.

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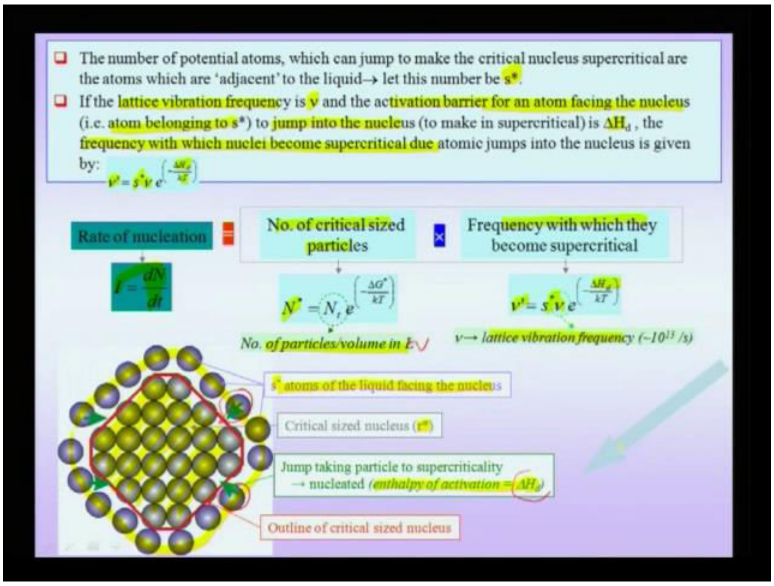

- ❑ The number of potential atoms, which can jump to make the critical nucleus supercritical are the atoms which are 'adjacent' to the liquid→ let this number be s*.
- ❑ If the lattice vibration frequency is ν and the activation barrier for an atom facing the nucleus (i.e. atom belonging to s*) to jump into the nucleus (to make in supercritical) is ΔH_d, the frequency with which nuclei become supercritical due atomic jumps into the nucleus is given by: $\nu' = s^* \nu \, e^{\left(-\frac{\Delta H_d}{kT}\right)}$

Rate of nucleation = No. of critical sized particles × Frequency with which they become supercritical

$I = \frac{dN}{dt}$

$N^* = N_t \, e^{\left(-\frac{\Delta G^*}{kT}\right)}$

No. of particles/volume in L

$\nu' = s^* \nu \, e^{\left(-\frac{\Delta H_d}{kT}\right)}$

ν → lattice vibration frequency (~10^{13} /s)

s* atoms of the liquid facing the nucleus

Critical sized nucleus (r*)

Jump taking particle to supercriticality → nucleated (enthalpy of activation = ΔH_d)

Outline of critical sized nucleus

Now, how does an critical size nuclei r star becomes supercritical, a critical size nuclei can become supercritical by the jump of an atom, which is around this critical size nuclei. Suppose, I consider the figure below, there are atoms which I shaded in grey, which I call say, for this is approximately a critical size nucleus. This of course, crude schematic then, if any one of the atoms say, in the liquid medium surrounding, which is colored in a purple color or a violet color. So, one of these atom jumps into the for instance, into this critical size nucleus then, it would become supercritical.

So, the potential number of atoms which can take this critical size nuclei to super criticality is the number of atoms facing this nucleus, which is this number denoted by s star. So, s star is the number of atoms facing in the liquid, which is facing the nucleus which can actually potentially jump into this critical size nucleus and therefore, taking into super criticality.

So, I have a critical size nucleus r star, s star is a number of atoms which surrounded and if the lattice vibration frequency is new that means, if all these atom are vibrating with the frequency new and the activation barrier for an atom facing the nucleus. That means, an atom belonging into s star to jump to the nucleus to make it supercritical is delta H d therefore, this is delta H d is the enthalpy of activation barrier, which can take that means, that this atoms sitting here around the critical nucleus r star.

For instance suppose, I take this atom or in any alternate atom here, this atom has to overcome a barrier, whose site is delta H d so that, it becomes part of the critical size nucleus. And when it becomes part of the critical size nucleus, the nucleus would have become super critical. Therefore, using this activation barrier delta H d, I can find the frequency at which nucleus become supercritical due to atomic jumps, writing that as new prime s star into mu into minus delta H d by k T.

So, I have two term now to contribute to the nucleation rate, the first term being to locate the number of critical size particles, which we are done before, which is N star and this number of critical sizes particles are in volume L or volume V, we can call it better cell. So, in a volume V, I can locate all the number of critical size particle and the frequency with which, such kind of crystallites become supercritical and that frequency new prime depends on the lattice vibration frequency.

New, depends on the number of atoms which are potentially can be vibrated into this state and the activation barrier which again depends on Arrhenius kind of function, which is on a exponential minus delta H d by k T. Therefore now, I can find out multiplying this two functions, the rate at which my nucleation takes place.

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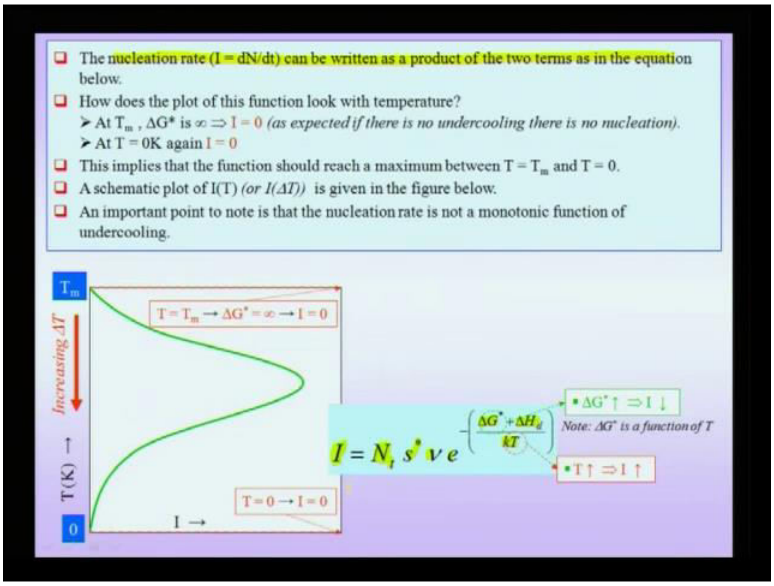

- ☐ The nucleation rate (I = dN/dt) can be written as a product of the two terms as in the equation below.
- ☐ How does the plot of this function look with temperature?
  - ➢ At T_m , ΔG^* is $\infty \Rightarrow I = 0$ *(as expected if there is no undercooling there is no nucleation).*
  - ➢ At T = 0K again I = 0
- ☐ This implies that the function should reach a maximum between $T = T_m$ and T = 0.
- ☐ A schematic plot of I(T) *(or I(ΔT))* is given in the figure below.
- ☐ An important point to note is that the nucleation rate is not a monotonic function of undercooling.

$$I = N_t\, s^* \nu\, e^{-\left(\frac{\Delta G^* + \Delta H_d}{kT}\right)}$$

- $\Delta G^* \uparrow \Rightarrow I \downarrow$

Note: ΔG^* is a function of T

- $T \uparrow \Rightarrow I \uparrow$

Therefore, I can write by nucleation rate as a product of two terms and as in the equation here so, nucleation rate I can be write as N t s star new exponential minus delta G star plus or minus delta H d by k T. Now, this is therefore, we have arrived at a function, which describes the nucleation rate and the important thing is to see that, how this function behaves with progressive under cooling. And this will tell us that, how we can monitor the nucleation rate with progressive under cooling.

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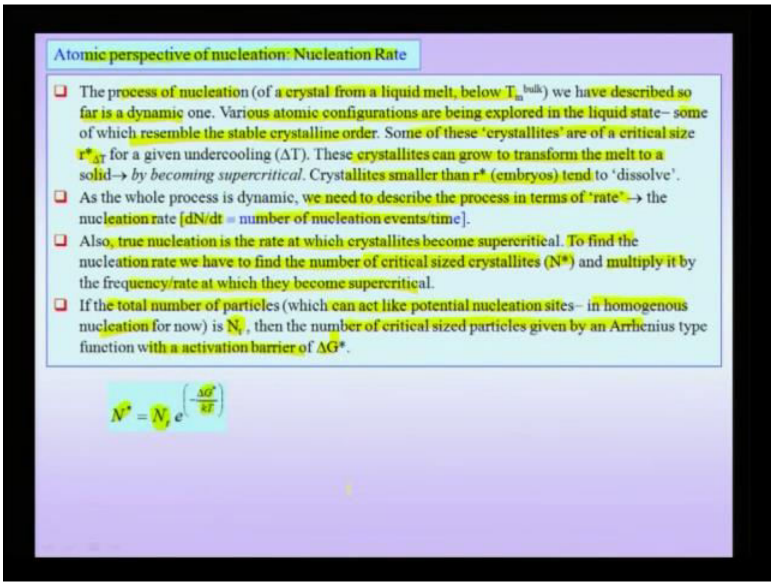

Atomic perspective of nucleation: Nucleation Rate

- ☐ The process of nucleation (of a crystal from a liquid melt, below T_m^{bulk}) we have described so far is a dynamic one. Various atomic configurations are being explored in the liquid state– some of which resemble the stable crystalline order. Some of these 'crystallites' are of a critical size $r^*_{\Delta T}$ for a given undercooling (ΔT). These crystallites can grow to transform the melt to a solid→ *by becoming supercritical*. Crystallites smaller than r* (embryos) tend to 'dissolve'.
- ☐ As the whole process is dynamic, we need to describe the process in terms of 'rate'→ the nucleation rate [dN/dt = number of nucleation events/time].
- ☐ Also, true nucleation is the rate at which crystallites become supercritical. To find the nucleation rate we have to find the number of critical sized crystallites (N*) and multiply it by the frequency/rate at which they become supercritical.
- ☐ If the total number of particles (which can act like potential nucleation sites– in homogenous nucleation for now) is N_t , then the number of critical sized particles given by an Arrhenius type function with a activation barrier of ΔG*.

$$N^* = N_t\, e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

So, before we going that, let us summaries the previous slide or the previous two slide wherein, we are trying to understand nucleation rate for an atomic perspective. We found that, the nucleation rate is a important term because, we cannot just work with numbers because, we are talking about a dynamic process which is changing in time.

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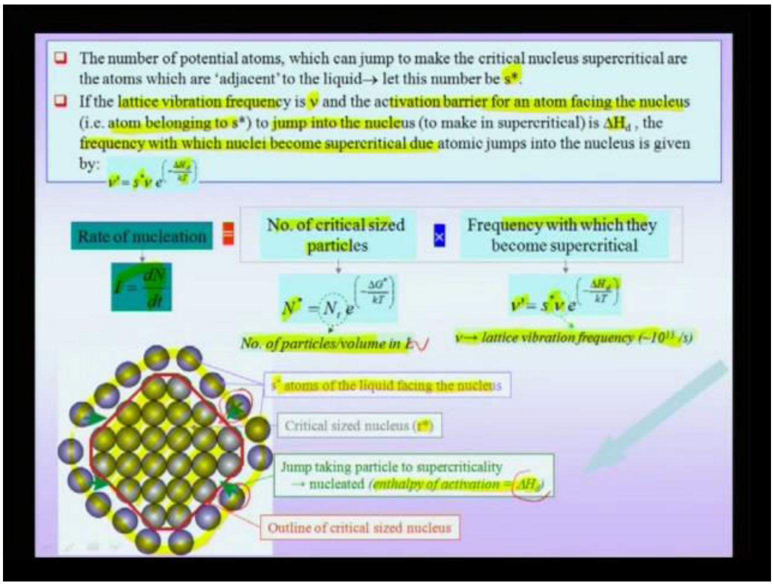

- The number of potential atoms, which can jump to make the critical nucleus supercritical are the atoms which are 'adjacent' to the liquid→ let this number be s^*.
- If the lattice vibration frequency is ν and the activation barrier for an atom facing the nucleus (i.e. atom belonging to s^*) to jump into the nucleus (to make in supercritical) is ΔH_d , the frequency with which nuclei become supercritical due atomic jumps into the nucleus is given by: $\nu' = s^* \nu \, e^{\left(-\frac{\Delta H_d}{kT}\right)}$

Rate of nucleation = No. of critical sized particles × Frequency with which they become supercritical

$I = \frac{dN}{dt}$

$N^* = N_t \, e^{\left(-\frac{\Delta G^*}{kT}\right)}$

No. of particles/volume in L ✓

$\nu' = s^* \nu \, e^{\left(-\frac{\Delta H_d}{kT}\right)}$

$\nu \rightarrow$ lattice vibration frequency ($\sim 10^{13}$ /s)

And therefore, I have to talk about a process which is the nucleation rate and we are seeing thus, nucleation rate depends on two things, number of potential critical nuclei and the rate at which this nuclei become supercritical by atomic jumps from the phase around to the product phase. And this atomic jump depends on the lattice vibration frequency, the frequency with these atoms in a star are vibration and of course, they have to cross the activation barrier to join the product phase, the grey phase.

And this implies that, such a process is an activated process and this implies that, there is Arrhenius kind of exponential function, which would dictate the rate at which such a process going to take place. And since the first term is only numbers per unit volume, the second term brings in the time quantity and it is important note that, this lattice vibration frequency is very large about 10 power 13 per second. So, multiplying these two, I get my nucleation rate. And the next thing I need to do is of course, track this nucleation rate as a function of the under cooling.