Material Science

Professor S. K. Gupta
Department of Applied Mechanics
Indian Institute of Technology Delhi

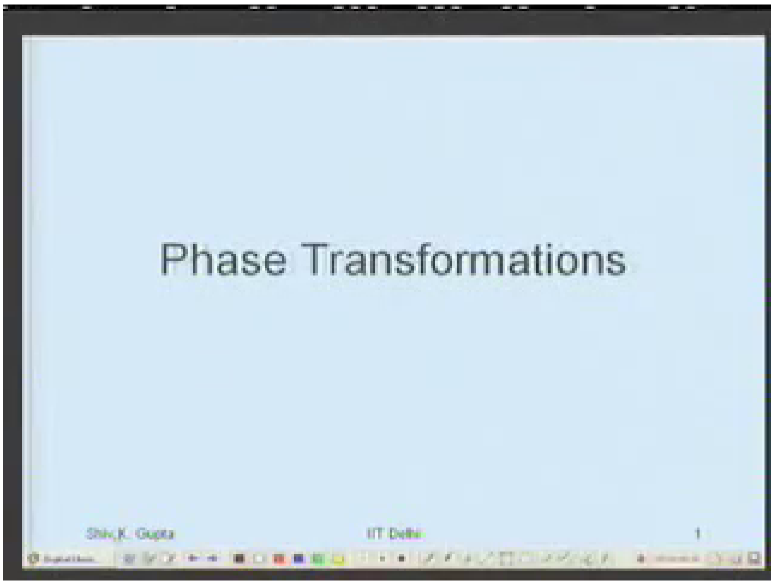
Lecture No 22

Phase Transformations

Well so far we have looked at the equilibrium in systems with 1 phase, 2 phase, 3 phase and so on so forth and binary systems. And then we have seen when we cool how the microstructure changes and we understood that it requires certain movement and migration of atoms, we saw the diffusion in solids, and we are talking about the thermodynamic equilibrium so far but only when talking about the jumping of atoms diffusion process we started talking about sometime element of required for diffusion process.

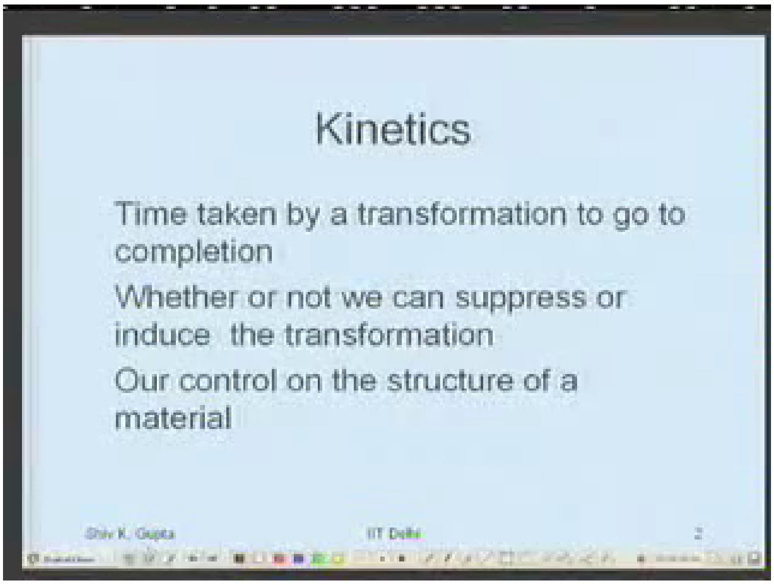
This movement of atoms whereby they change their neighbors is certainly time dependent. Likewise this allows the transformation to go one and therefore time is an element, what we call the kinetic of the process. We want to look at the time element and that is what we referred to as the phase transformations.

(Refer Slide Time: 1:58)



Phase Transformations

Shiv K. Gupta IIT Delhi 1



Kinetics

Time taken by a transformation to go to completion

Whether or not we can suppress or induce the transformation

Our control on the structure of a material

Shiv K. Gupta IIT Delhi 2

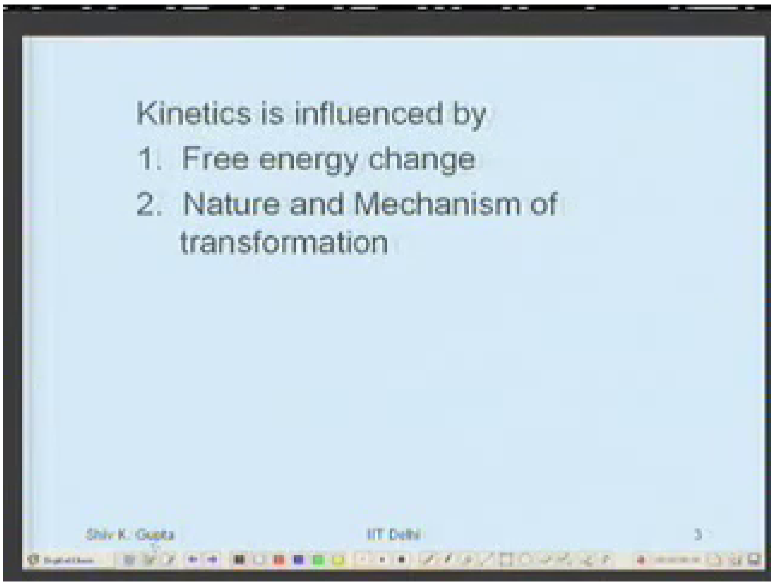
In phase transformation we are trying to understand the kinetics after having understood the equilibrium. We are going to look at the time taken by a transformation to go to completion. Rather it is going to be in years, it is going to be in months, it is going to be in weeks, it is going to be in days, in hours, in minutes, in seconds, milliseconds, microseconds, it could be a range, it could be from a small time, fraction of a microsecond to a very large time which could be in many years.

After having understood this time taken by the process, we have to see whether or not it is possible for us to accelerate a process if it is slow, like it is taking many-many years can I do it in few hours? Can I do it in few minutes? And if it is a very fast process like it is taking place in a millisecond can I suppress it. Can I? That means I am trying to control the transformation process.

So I have not only understand the time taken by the process, I have to understand how the process is taking place, what step of the process I can control. Why? And that shall give us an idea whether or not we are in a position to control structure of the material. After we have understood this we will talk about how the… What are the properties of the material, how they relate it to the structure.

And then you would understand, it is a control of the structure in my hand. I can inculcate the properties but I require in a material. But we have to first understand whether we can do that or we cannot do that, some places we may be going to do it, other places we may not be able to do it.

(Refer Slide Time: 4:16)



Kinetics is influenced by

1. Free energy change
2. Nature and Mechanism of transformation

Shiv K. Gupta

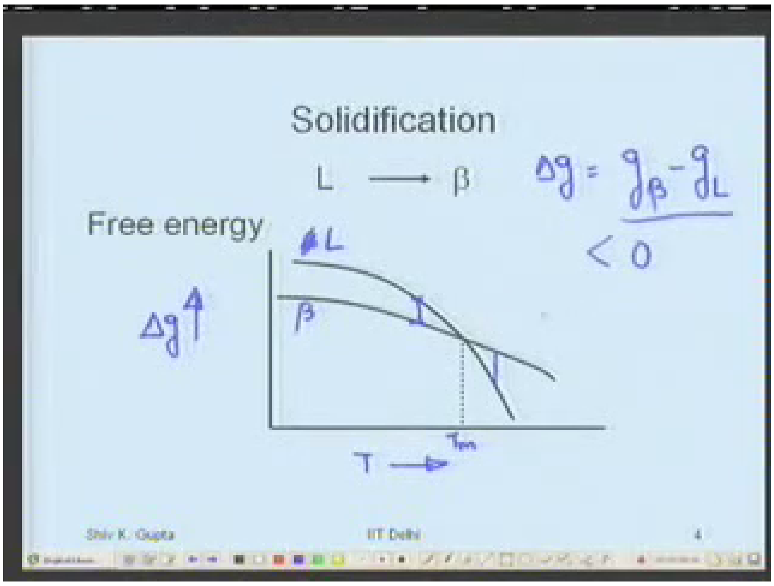
IIT Delhi

The kinetics of a process or the time taken in a process is dependent on a free energy change. The free energy change of the process is of course a process is to take place the free energy is low and then decrease in free energy is very large than obviously we would notice the process would be faster. Decrease in free energy would be less the process would be slower, right?

Then comes the nature and mechanism of transformation that we will dwell sometime, devote sometime to understand the nature and mechanism of transformation. Let me just give you some idea, whether the process is going to involve migration of atoms or diffusion of atoms 5, 10 atomic distances or is going to involve millions and billions of atomic distances. So short range or is it a long range, okay.

Obviously if it is a long range diffusion time is much more, short range diffusion time is much less. Okay. That is the kind of you can think of mechanism and the nature, the transformation, whether it is a solid state or is the liquid to solid, or process is taking place, homogenously all over the volume or they are taking place preferentially at some places not so at other places. That means it is a process which is not taking place homogenously and things like that. That is what we shall try to look at.

(Refer Slide Time: 6:07)



Solidification

$L \longrightarrow \beta$

$\Delta g = g_\beta - g_L < 0$

Shiv K. Gupta IIT Delhi 4

Here I am going to take one example. Try to understand the whole process with one example is it solidification. Liquid on cooling goes to become a solid beta, and here I show you the free energy change of the process. This axis I have temperature let us say, and on this axis I have the free energy if you write the free energy for this process, it will be free energy of beta minus free energy of liquid.

Final state minus initial state that is how we define the delta and the process is to take place it must be less than 0. Let us look at the temperature which are less than this, this is the melting point, the melting point of course, this is going to be for the solid. I am sorry, this is going to be liquid and that is solid. At temperature which are greater than the melting point, the free energy of the liquid is lower and the free energy of solid is higher therefore this is greater than 0.

Solidification cannot take place above the melting point. Only at the melting point if the free energy 2 are equal and this is equal to 0. I do not know whether solidification take place there or not but definitely there I know at lower temperature which is lower the melting point free energy of the solid is less than that of the liquid and that is a negative number, less than 0. Transformation can take place here.

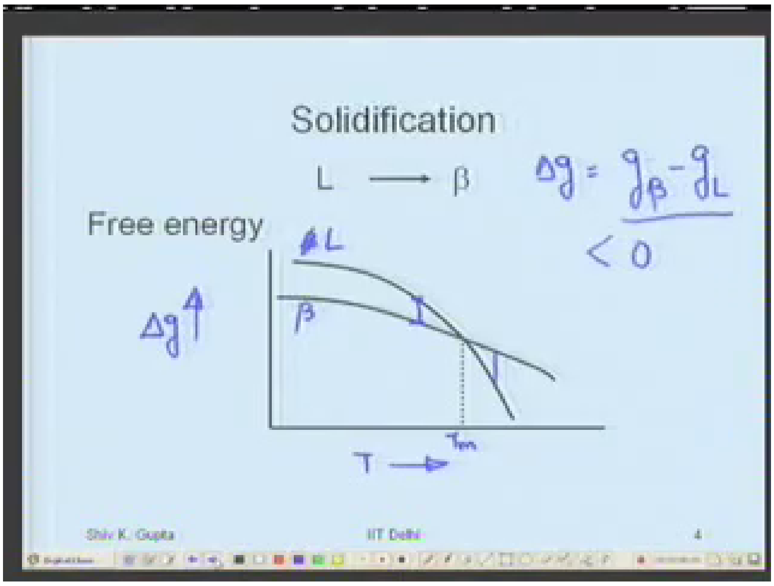
Before we proceed further I am using small g, earlier I talked about the Gibbs free energy capital G. There is convention associated with use of the later capital G in thermodynamics. All thermodynamic properties whether we use capital letters of small letters, the convention is whenever the property is expressed per unit volume of the solid or the material it is used as small letter. If it is expressed per mole or per kilogram we use a capital letter.

So here I am going to use per unit volume. So that is what it is. So transformation can take place at temperature which are less than the melting point but not the temperatures above the melting point. Why I am considering the transformation liquid going to solid, not solid going to liquid, one thing would become very clear to you… When I heat a process which means I am heating a solid material, the process is absorbing heat of thermal energy from the surrounding.

And more the thermal energy available to you faster will be the movement or diffusion of atoms, your control is not going to be enough because thermal energy is playing the role. But when we are doing from high temperature to low temperature phase that is like the cooling or solidification process maybe at lower temperature thermal energy is not so much, I am probably able to control something that is why we are considering solidification process liquid going to solid that is going from high temperature phase to a low temperature phase. Another you noticed that this delta G is not same at all temperatures below the melting point.

At the melting point this delta G is 0 and below the melting point this negative but less greater than 0, you can say less than 0 and becomes more and more in magnitude as the temperature is lowered. So when I said the free energy can play a role in controlling the time or the rate of the process, in this solidification is done right in the melting point, it may be a very slow process we will show you that but as you lower or increase the degree of under-cooling or super cool the liquid the process of solidification may become fast. Right?

(Refer Slide Time: 10:50)



Solidification

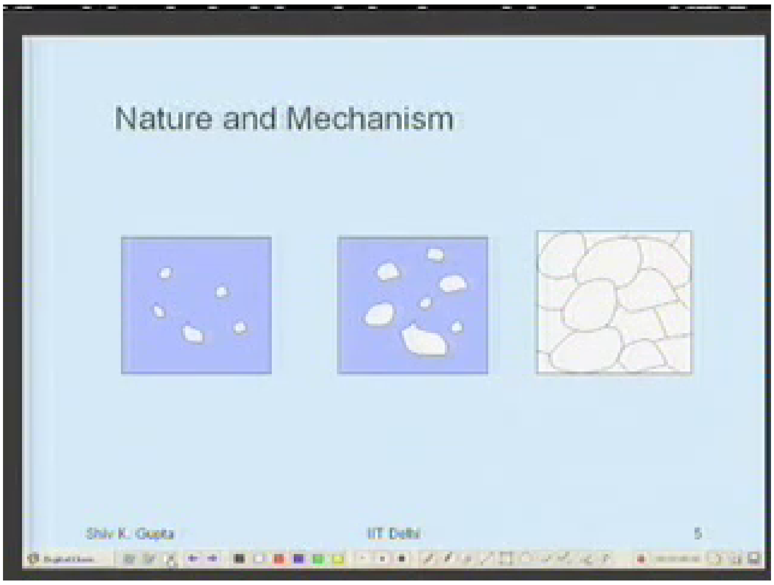
$L \longrightarrow \beta$

$$\Delta g = g_\beta - g_L < 0$$

Shiv K. Gupta IIT Delhi 4

Let us next look at the nature of the transformation; the transformation we call is a homogeneous.

(Refer Slide Time: 11:17)



Nature and Mechanism

Shiv K. Gupta IIT Delhi 5

Alright, I think this is the figure which has missed out first. Now when we look at the nature and mechanism of transformation it seems very unlikely that the entire volume of the solid, let us I take a very small quantity in the laboratory like a centimeter cube, in a centimeter cube of the liquid I may have 10 to the power 23 atoms. If I have taken a element from first long period that is the kind of number of atoms I shall have. It looks very unlikely that all the 10 to the power 23 atoms fall in line to become a crystalline structure in one go.

When I ask 50 of you to stand in a line makes ruckus, same thing is about atoms. But if few atoms, not 50, 4, 5, 6, they can come together and form a crystalline arrangement and then one by one more of them can join and the process can began.

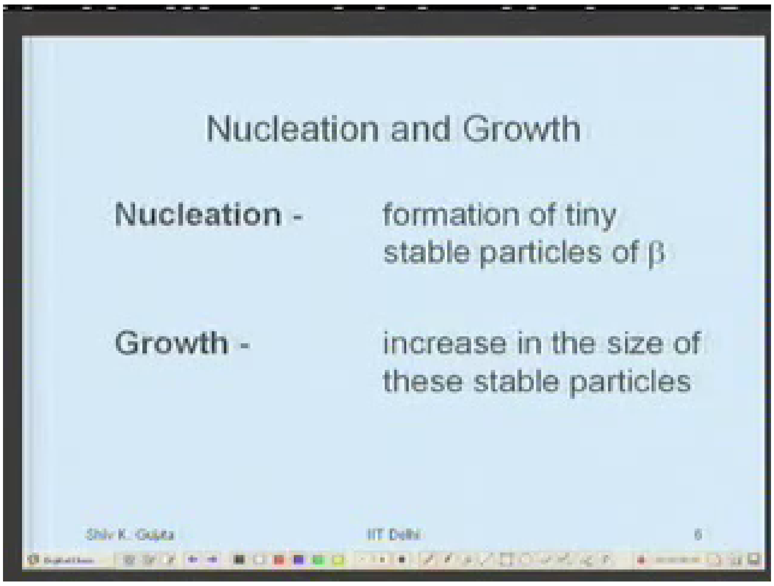
So let us say a particular formed where few atoms come together like here form a crystalline solid, some of them come together here and form a crystalline solid. Like that, like this and like this and then slowly once they become their more and more atoms from the liquid jump the interface, join the solid and they become bigger and bigger and some more form at the same time. While they are growing some more are forming and this whole process keeps on going till we get a complete solid but it is a polycrystalline solid.

This is one grain, next grain, next grain like that there are number of grains here. It is a polycrystalline because each one started on its own. At its orientation of the atoms here, 100 axes maybe let us say parallel to the x axis here. Here 100 may be at 45 degree, here 100 maybe at 135 degrees and so on so forth. So there may be a different orientations. If there are different orientations they cannot be a one single crystalline arrangement, there may be different crystalline arrangement what we call grains. These kinds of structure we have already seen in the polycrystalline copper hat grain boundaries are formed like this. This is more likely.

Instead of 10 to the power 23 atoms which are randomly placed in the volume suddenly become orderly arrangement, the change in entropy required will be prohibited. But now when few of them come together change in entropy is going to be small of this small volume and it is possible and more more atoms can join and similarly the whole thing can become orderly crystalline arrangement but will add up with polycrystalline solid, not with a single crystal.

For getting a single crystal you must have only one particle forming and only that particle is allowed to grow, others are not, right? So that, we shall come to that but then now here it is clear that the process occur starting with the few small smaller particles forming what I call nucleation process. Once this particles becomes stable then they can grow to become bigger and bigger by absorbing atoms from the (())(14:46) matrix or the liquid in this case.

(Refer Slide Time: 14:54)



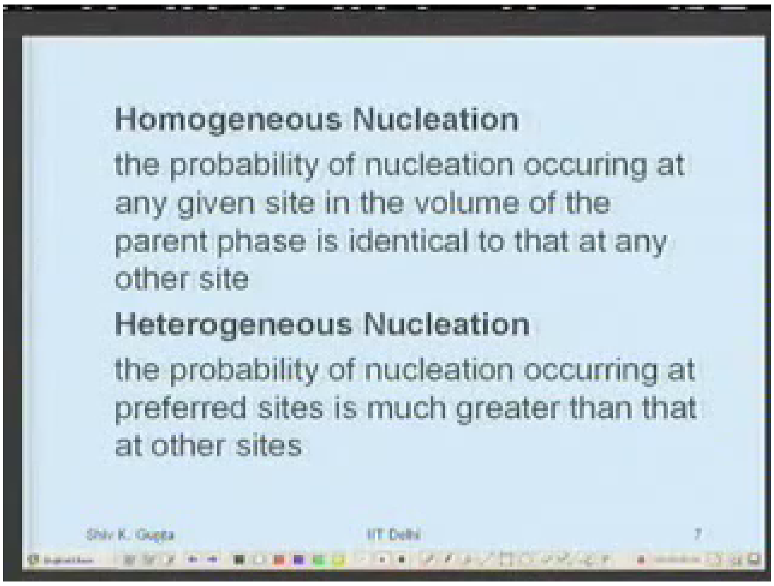
Nucleation and Growth

Nucleation -	formation of tiny stable particles of β
Growth -	increase in the size of these stable particles

The nucleation and growth is the mechanism by which the transformation occurs. Nucleation is the formation of tiny stable particles of this solid beta. Why I am emphasizing here, stable particles will become clear to you when I start working out with some numbers. Another way when I am trying to increase a certain size of the particle would be stable and the size smaller than that may not be stable. That is what I am trying to comment and we will talk about it.

Growth… Once the particle is the stable particle then only it has to grow in size. More and more atoms from the liquid come and joint this and it grows in size and that operation I called growth. Till the particle become stable I call it nucleation process, once this become a stable particle more and more atoms joint to grow it in size and then it is only called growth. The two are slightly different, I will see the difference between them when I talk about that mechanism.

(Refer Slide Time: 16:18)



Homogeneous Nucleation

the probability of nucleation occuring at any given site in the volume of the parent phase is identical to that at any other site

Heterogeneous Nucleation

the probability of nucleation occurring at preferred sites is much greater than that at other sites

Shiv K. Gupta IIT Delhi

Now the nucleation process can be divided, can be also called taking place every way in the volume, anywhere the nucleation can take place with the equal probability and with the equal preference and we call it homogeneous nucleation. Let us say 1 centimeter cube I have talked about, 10 to the power 23 atoms, or near about any atom, if the nucleation can place it is a homogeneous nucleation. If it can take place only of 10 to the power 5 atoms instead of 10 to the power 23, around there then it is a heterogeneous nucleation, it is not homogeneous nucleation.

That is the probability of nucleation at all atomic locations and atomic sites is not same, it is more on preferred sites, it is not on the other sites and therefore it is a heterogeneous nucleation.

Student: Sir, can we expect bigger grains in the heterogeneous equation there only at some places grain (())(17:27) occur and those (())(17:28) there only?

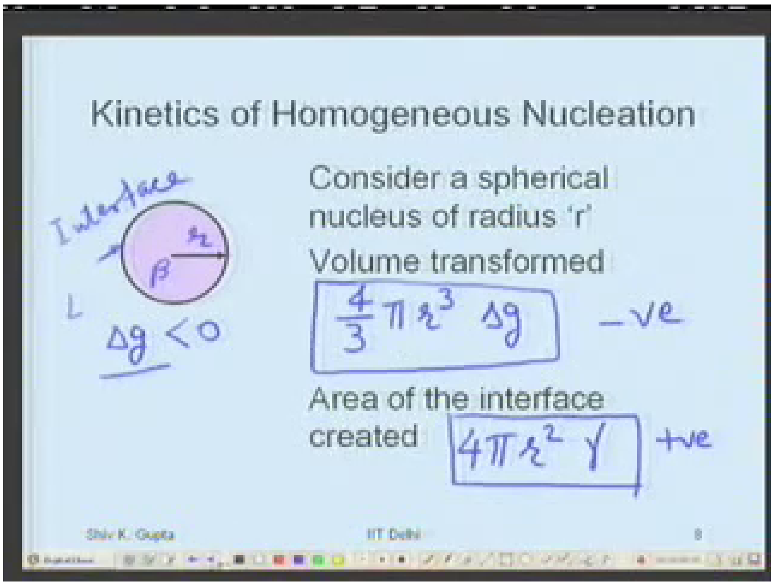
Professor: You can, you can think about that but we shall look into the process, okay? What you are trying to hint at is a very good concept is talking about, if the nucleation is taking place only at a few places grains which are going to grow will ultimately be big enough in size, will be bigger size. That is a good thing but he has thought of, right? And that is how it happens and some time we have to control that.

The examples of heterogeneous nucleation are more found in real life rather than homogeneous nucleation. When they, let us say I have a small crucible where we have some liquid matter which is solidifying, the wall of the crucible is at a lower temp when I pour the liquid in it, at room temperature rather so that can provide the nucleation side because it is a lower temperature, it can take out the heat immediately. So nucleation occurs along the wall, that is a preferred cycle, more preferred than inside the volume of the melt.

Like the transformation is taking place you take the transformation austenite, the austenite is going to form ferrite and cementite, I told you this happens at the grain boundaries of austenite, not in the middle so once it happens in the grain boundaries cemetite particle forms, carbon atoms diffuse to the form the cementite particles happening in the grain boundaries not in the volume. It is heterogonous nucleation side.

Similarly I talked about super saturate solid solution. If it cools it becomes, second phase comes out and it starts to form at the grain junctions, it doesn't form in the middle of the solid usually, it form the grain junction and then spills over the grain boundary. Like what happens when austenite is cool and ferrite proeutectioid ferrite begins to form and it starts with the grain junction and fills the grain boundary. That is what I already said about, these are all heterogeneous nucleation processes and they are found more. But it is easy to understand with homogenous process we shall first take up a homogenous nucleation process.

(Refer Slide Time: 20:14)



Kinetics of Homogeneous Nucleation

Consider a spherical nucleus of radius 'r'

Volume transformed

$\boxed{\frac{4}{3}\pi r^3 \Delta g}$ –ve

Area of the interface created $\boxed{4\pi r^2 \gamma}$ +ve

Shiv K. Gupta IIT Delhi 8

Let us consider its spherical nucleus of radius r. This is not an atom. This is a nucleus of radius r means it contains, it is the particle of the beta phase and it contains large number of atoms. I don't know maybe 10 or 50, 20, depending upon what is the size of this nucleus. And also surrounding area is the liquid in that this is formed somewhere the volume of the material which is transformed or the liquid which is transformed can be written as, this is the radius of this spherical particle. And not necessarily the particles which formed are spherical in nature.

I consider this spherical for simplicity and then I am creating, when this volume is transferred to the solid it form the beta particle outside is liquid, I create an interface between liquid and beta that is an interface. And area of the interface that I create is 4 pi r square. Now I can see that when this is the volume of the liquid which is transformed and become a solid beta per unit volume free energy is delta g. Delta g multiplied by this will be the change in the free energy.

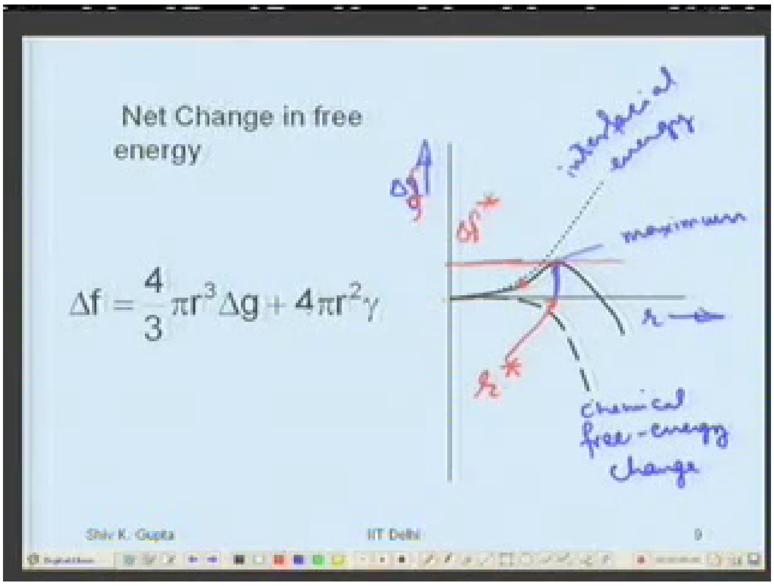
This number is positive or this number is negative.

Student: Negative.

Professor: Why delta g is less than 0? So this is a negative number. And interfacial energy what has specific value of the energy is gamma. So many joules per square meter then energy which I have created and never existed before in this matter or the liquid matter, 4 pi r square gamma let us say positive number. What is interface? What should it be? Interfacial energy, this is pacific interfacial energy. Interfacial energy I told you earlier what you had called in chemistry the surface tension is the energy here, surface energy.

So this is the specific surface interfacial energy interface between liquid and beta and this interface did not exist before the beta particle formed. Only when the beta particle formed this came into being and therefore that energy is added and the volume which is transformed decreases this energy and this interface which is created increases that energy, right? You are going to see some interesting things.

(Refer Slide Time: 23:52)



Net Change in free energy

$$\Delta f = \frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \gamma$$

Shiv K. Gupta IIT Delhi 9

So I can say the net change in free energy is like delta f total change in free energy, 4 upon 3 pi r cube delta g plus 4 pi r square gamma, that is the interfacial energy, this is the Gibbs free energy or the volume free energy change. This plot I make the energy, let us write delta g doesn’t matter and this we write here r on the x axis. First term which is q of r and is negative, 4 upon 3 pi is a constant delta g is a constant but whatever temperature the (()) (24:41) change take place per unit volume it is a constant.

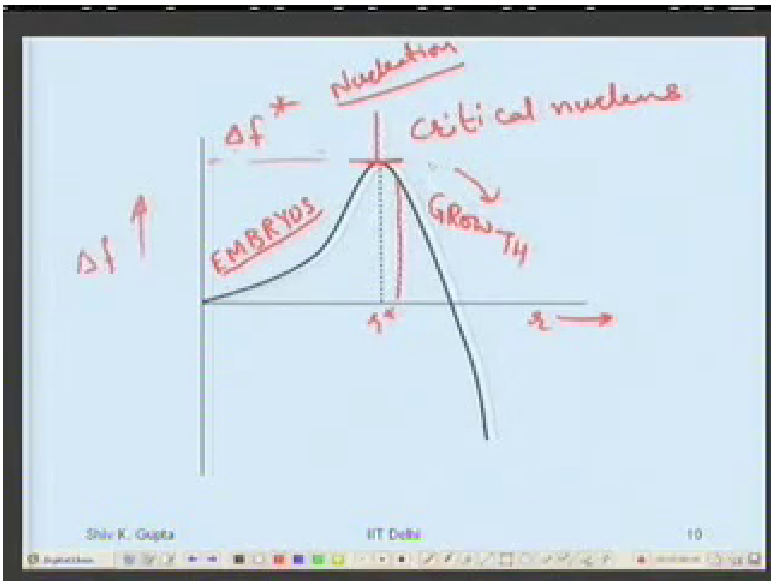
So this term goes as r cube like this and that is a negative number. So this is the chemical free energy or change. And this term which goes as r square this is that parabolic function here, it interfacial energy. Now you know that for the smaller values of r it is r square which is more than r cube and it is for larger values of r it is r cube which is larger than r cube. When I sum these two functions therefore initially I have a positive value and then when r cube becomes more it becomes negative so it goes through a maximum somewhere it goes through a maximum.

Is clear that r cube for small values of r is going to be small than r square, that you can see if we take number like 0.5 its cube is 0.125 and if you take its square it is only 0.25, 025 is greater than 0.125. But if you take 2 then the cube is 8 and the square is only 4, right? So, therefore we find that this is going to dominate after the r becomes large and when the r is small this is the one which is dominating so energy initially increases, now you can try to see when the nucleation is taking place beta particle is forming starting with 4 – 5 atoms more and more joining it, a nucleus is forming, energy is increasing.

See it is interesting to see that energy is increasing and it increases to this value, maximum at which I call this Delta F star. Instead of G let us call it F because these are the components of F, one is G and other is gamma. So they are all components of F, let us call it delta f star. So and corresponding to that the R value let us call it R star. If you have a particle form let us say of size less than R star, right, it can learn its free energy by dissolving back and becoming the liquid again. I am here.

I can load my free energy by dissolving back with to 0 size, but if I grow in size I have to increase my energy. This increase in energy is to be provided by the thermal energy only, nobody can help it otherwise from outside. So that is why we have to look at the maximum first and then we can see what is happening in the maximum.

(Refer Slide Time: 28:43)



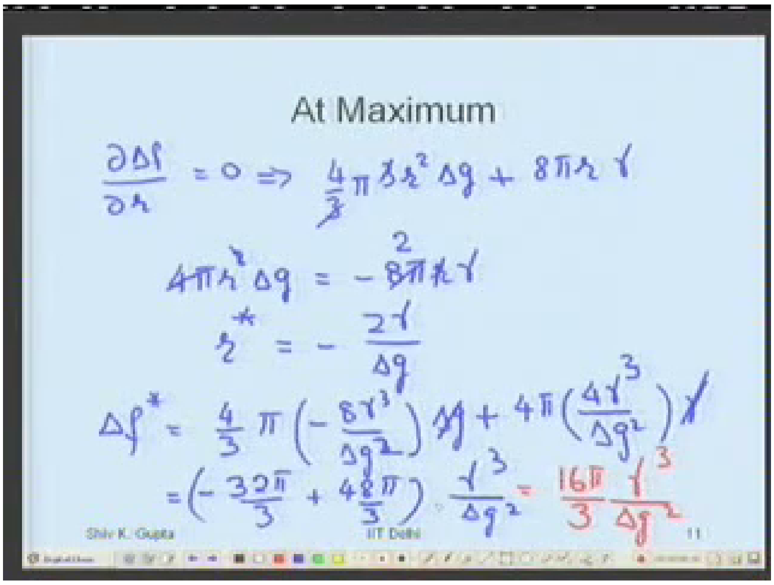
Alright, this is what it is. I have this here, delta F, this is R and I am looking at this R star and this value here. Delta F star that is what I am trying to find out because if the particles in the right hand side of delta F star, right is somewhere here, it can lower its energy by growing its size. If it decreases it size its energy would increase. So this is what is say the particle of this Delta F star is the critical nucleus. And the moment I add one atom to the critical nucleus it become super critical, it comes to the right hand side and then nit can grow. So growth occurs here.

But particles smaller than the critical nucleus it can lower its free energy by dissolving back, these are not called nuclei, these are called Embryos because these embryos can dissolve back. Only the process of nucleation is that we have the critical size particle and make it super critical, that operation of nucleation is over and then this is only the growth which is going to take place. So we have to now get the value of the maximum, what is delta f star, what is R star and from there try to work out how many particles I can have, and what is the rate of transformation that can be there.

Student: In the process with (())(30:47).

Professor: These are all particles forming to aid the nucleation but the actual nucleation process is having the critical nucleus and making it super critical there because critical nucleus also can lose one atom and become under critical or become Embryo and then dissolve back, but in the critical nucleus I add one more atom, it become super critical, then it can grow in size and lower its free energy. Right?

(Refer Slide Time: 31:25)



At Maximum

$$\frac{\partial \Delta f}{\partial r} = 0 \Rightarrow \frac{4}{\cancel{3}}\pi \cancel{3} r^2 \Delta g + 8\pi r \gamma$$

$$4\pi r^{\cancel{2}} \Delta g = -\overset{2}{\cancel{8}}\pi \cancel{r} \gamma$$

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

$$\Delta f^* = \frac{4}{3}\pi\left(-\frac{8\gamma^3}{\Delta g^{\cancel{3}2}}\right)\cancel{\Delta g} + 4\pi\left(\frac{4\gamma^{\cancel{2}3}}{\Delta g^2}\right)\cancel{\gamma}$$

$$= \left(-\frac{32\pi}{3} + \frac{48\pi}{3}\right)\frac{\gamma^3}{\Delta g^2} = \frac{16\pi}{3}\frac{\gamma^3}{\Delta g^2}$$

Shiv K. Gupta

IIT Delhi

11

So write down at maximum now I can say that delta f, delta r is going to be 0 and when I differentiate this look at the first term if 4 upon 3 pi R cube, and I get 4 upon 3 pi, r cube gives me three r square and delta g. Second term if 4 pi R square gamma, that gives me 8 pi R gamma and that is equal to 0. So when we go that let us say these 3 cancels here, I am left with this 4 pi R square, delta g is equal to minus 8 pi R gamma. So 4 pi if I take out both sides this is left with 2 here and R also I will take out because R is not 0.

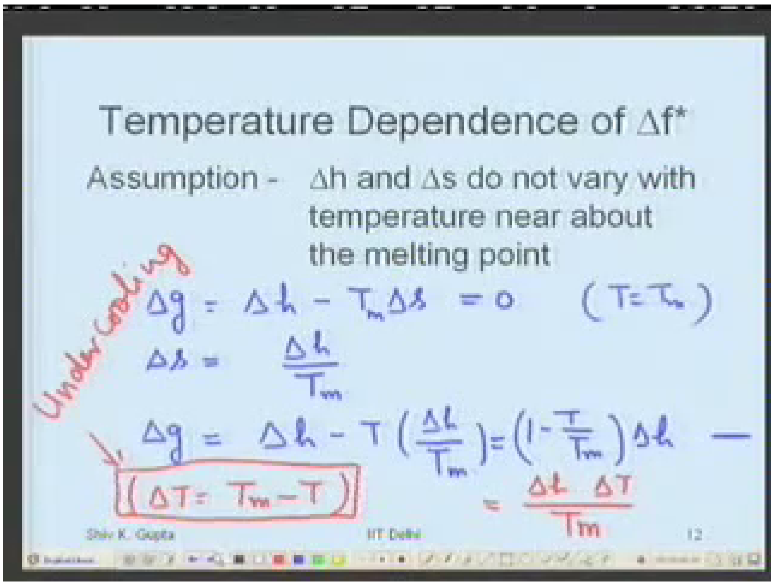
Let us say for maximum which can be… I can take this out, I get from here R which is going to be at the maximum if I call it R star equal to minus 2 gamma by delta G. So is R star negative, cause Delta g is negative, R star is a positive number, gamma is a positive number.

For substitute this R star back into this expression of Delta F, so I get delta f at maximum, corresponding to R star will be 4 upon 3 pi R cube, R cube is this minus 8 gamma cube by delta G cube into delta G plus 4 pi R square, 4 pi R star square that is square minus would become plus so it becomes 4 gamma square by delta G square into gamma.

We can simplify this, delta g cancels here becomes the denominator delta g square and this becomes then gamma cube, you take this gamma out, so gamma cube by delta g square is in both the terms and rest is all constant. This is 4 into 8, 32 pi by 3, this is 4 into 4, 16 pi, 16 pi is 48 pi by 3, right. So I can write it as minus 32 pi by 3 plus 48 pi by 3 into gamma cube by delta g square. Now 48 by 3 minus 32 by 3 becomes 16 pi by 3, so I can write this as delta f start is 16 pi by 3 gamma cube by delta g square.

So once I have a critical nucleus its free energy would 16 pi by 3, gamma cube by delta g square. It is not 0, it is not negative, it is more. It is positive number and the particle which are smaller than R star are in a position to dissolve back, only when it is R star and one more atom is added because there also chances are that one atom goes out but one more atom can also add, there is equal chance. One more atom is added and it becomes super critical. Now it can lower its free energy only by growing that we shall next as the growth.

(Refer Slide Time: 36:10)



Temperature Dependence of Δf^*

Assumption - Δh and Δs do not vary with temperature near about the melting point

Undercooling

$\Delta g = \Delta h - T_m \Delta s = 0 \quad (T = T_m)$

$\Delta s = \frac{\Delta h}{T_m}$

$\Delta g = \Delta h - T\left(\frac{\Delta h}{T_m}\right) = \left(1 - \frac{T}{T_m}\right)\Delta h$

$\boxed{(\Delta T = T_m - T)}$

$= \frac{\Delta h \; \Delta T}{T_m}$

Shiv K. Gupta

IIT Delhi

12

Now we shall look at the, before I proceed further just a nucleation itself temperature dependence of delta f star is what I am interested in. Near about the melting point I can always assume that the (())(36:30) fusion is not varying very strong with temperature, a few degrees here and there. Similarly delta S is not so much temperature dependence and I am talking about a few degrees near the melting point. So therefore I can write at the melting point delta g is equal to delta h minus t delta S and that is equal to 0 when t is equal to Tm. So from here I can find out delta S is equal to delta h upon Tm.

So when I write now at any other temperature a few degrees around the melting point delta g can be written as delta h minus T times delta h divided by Tm that any temperature other than Tm, slightly few degrees below. This can be simplified as, if I take delta h out it becomes 1 minus t upon Tm which can be written as, here delta T is melting point minus the temperature at which you are considering this. And since T is less than Tm, delta T is positive. This is called the degree of under cooling or degree of super cooling. So delta t is under cooling or super cooling and under cooling is positive.

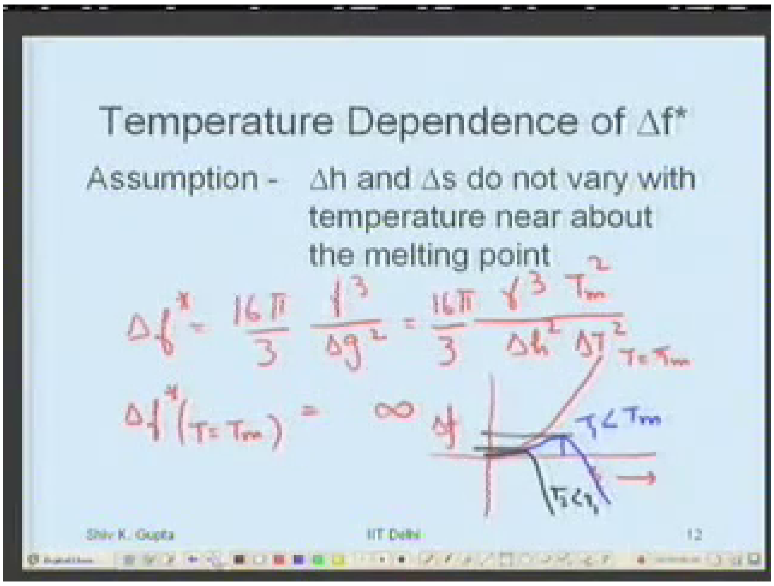
Student: It can be negative or positive, delta T?

Professor: Delta T is always positive, only if above the melting point it will become negative; below the melting point it is always positive. If delta g is negative what term is going to be negative here.

Student: Delta T.

Professor: Delta H, when your liquid is solidified or becomes solid (())(39:38) the fusion is given out, solid has a lesser heat content so delta H is the one which is negative. Friends make this mistake, that is why I emphasize this delta H is the one which is negative in this case because you are considering solidification, right? Alright. SO now with this knowledge of delta g we can see how the temperature depends on delta f star is.

(Refer Slide Time: 41:03)



Temperature Dependence of Δf*

Assumption - Δh and Δs do not vary with temperature near about the melting point

$$\Delta f^* = \frac{16\pi}{3}\frac{\gamma^3}{\Delta g^2} = \frac{16\pi}{3}\frac{\gamma^3 T_m^2}{\Delta h^2 \Delta T^2}$$

$$\Delta f^*(T=T_m) = \infty$$

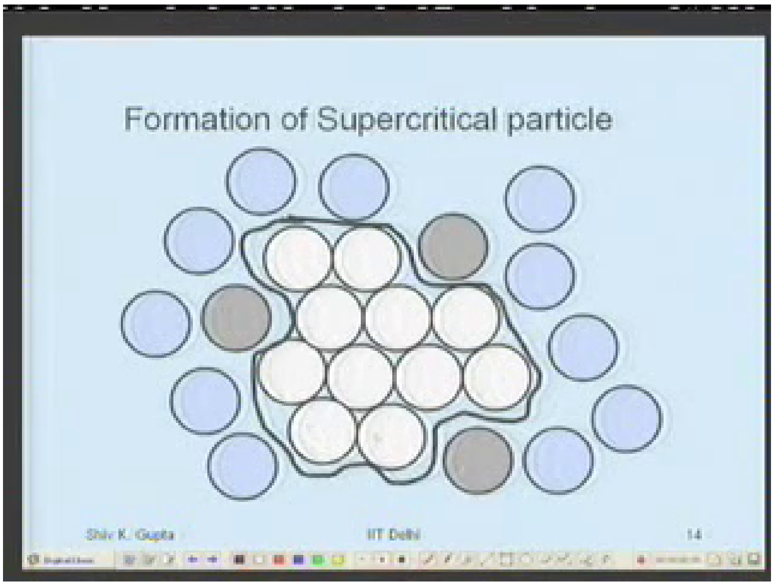
Shiv K. Gupta IIT Delhi 12

So delta f star, we have written already, 16 pi by 3, gamma cube by delta g square, let us write down whatever we have worked out for delta g. Gamma is not such a strong function of temperature so that remains there but delta g is a function of temperature of now, delta h square, delta T square, Tm square. Now notice here that delta f star goes inversely with delta T square, for a given solidification process given material delta H is going to be constant, melting point is going to be constant, gamma is not a function of temperature, so delta f star inversely proportional to delta t square.

More the under cooling lesser will be the value of delta f star and it decreases very rapidly. What shall be delta f star at the melting point? At melting point delta t is here, so therefore delta f star is infinity and as the temperature is lower delta f star becomes finite and becomes smaller and smaller as the delta t becomes more and more after few degrees, maybe 10 degrees or so it may become very small value, right?

So another word if you look at delta f as a function of R at melting point it goes like this but below the melting point at some under cooling it will go like this, so T less than Tm that is T1. And then at some other lower temperature it will simply be like this, this is T2 is still less than T1, so delta f star can become a small value, it would be decreasing like this, if the temperature is decreasing delta f star and r star both will be decreasing like this.

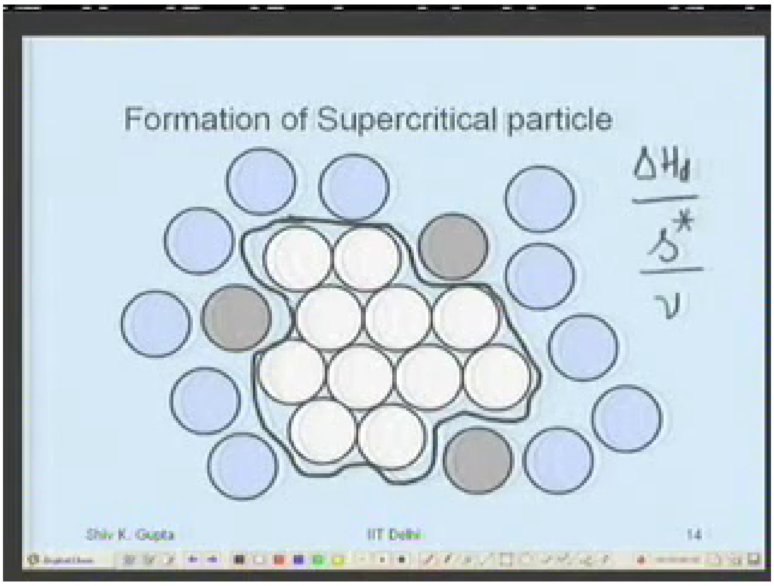
(Refer Slide Time: 45:37)


Formation of Supercritical particle

Now I will look at the process of nucleation, homogenous nucleation cell, number of critical size particles other ones which have acquired the energy delta f star or becomes size R star, what I do here to find out all those particles which have got the energy or how many atoms could have the energy greater than delta f star, they are the ones which can become critical size. So number of critical size particles I can write then Nt is the total number of locations, the total number of atoms multiplied by exponential of minus delta f star by kt, that is the probability that Boltzmann statistic gives us.

Natural Boltzmann statistic tells us the fraction of particles which have (())(44:58) energy greater than delta f star is exponential of minus delta f star by kt is the total number of locations and particles where the particles can form. This becomes a number of critical size particles which we have. Okay. And then what I want to know is once this particle is there, there is a chance that it can lose that atom and become and embryo or it can add an atom and become a stable particle. The process I am looking for forming a stable particle, right.

(Refer Slide Time: 45:41)

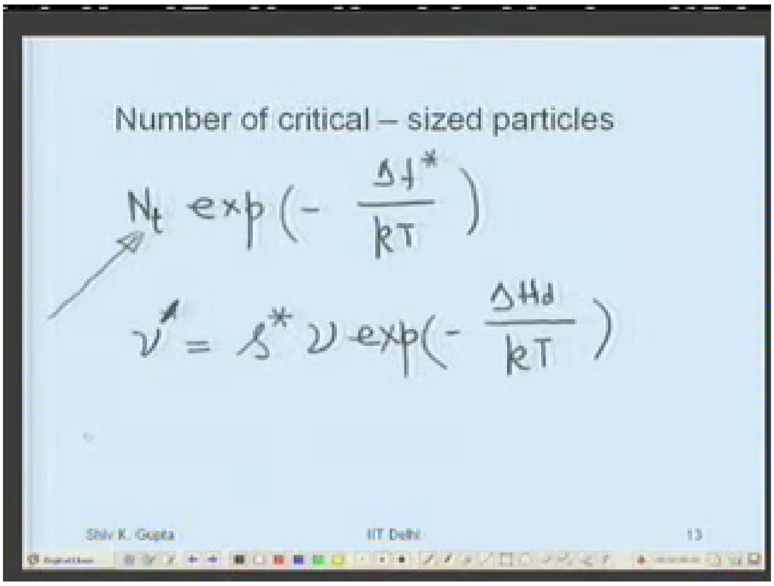

Formation of Supercritical particle

Now forming of a stable particle, let us look at the process before I come that number. Look at this, these are the atoms or the beta which have formed the beta crystalline arrangement and rest is all liquid around and that is the interface which is drawn the black line and these are three atoms in the liquid which are very close to the interface and they can try to jump to form the crystalline arrangement, it can jump here and become the crystalline arrangement, this can jump here and become the crystalline arrangement, this can jump there to take this position.

Others are far off. These are the ones which are nearest and can jump, a few atoms which are facing this, right. And they are all oscillating with the lattice vibration frequency (())(45:41). So it is going to cross this, jump this, provided it has enough energy to cross the interface, where on the other side when it goes chemical free energy will be lower so it can jump provided it can diffuse through the interface, activation energy for that, let us call it delta Hd.

And let us say these are the number atoms which are just facing the interface, let us call it s star and they are vibrating with the lattice vibration frequency and in that if they are vibrating towards the interface and can't cross the interface they will jump to become the part of the crystalline particle or they would join this crystalline arrangement.

(Refer Slide Time: 47:26)



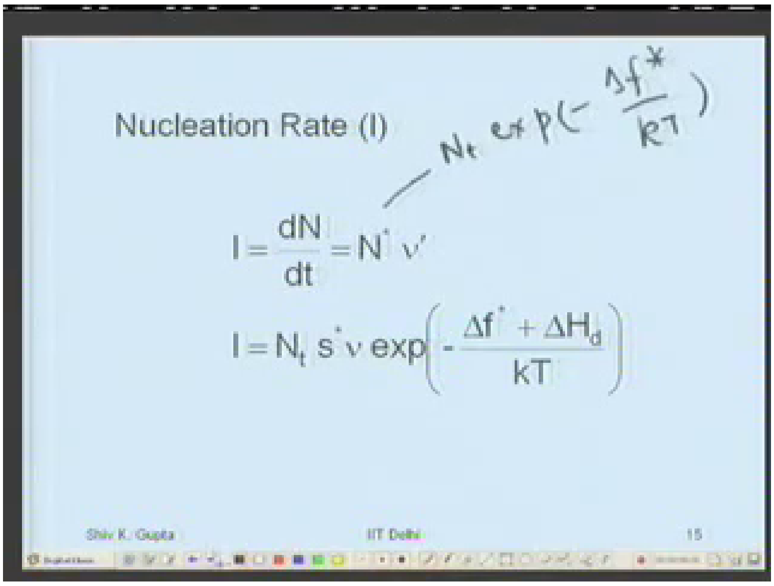
Number of critical – sized particles

$$N_t \exp\left(-\frac{\Delta f^*}{kT}\right)$$

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

So I can write that the rate at which this particles can become super critical, let us call Nu prime is equal to the number of atoms which can't jump into it, the rate at which they are oscillating towards the interface and probably they can cross the interface is that they can acquire the energy greater than or equal to delta Hd. So these many particles I have which can be critical sized and this the rate at which they can become super critical, so now I can write the rate of nucleation as…

(Refer Slide Time: 48:16)



Nucleation Rate (I)

$$N_t \exp\left(-\frac{\Delta f^*}{kT}\right)$$

$$I = \frac{dN}{dt} = N^* \nu'$$

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

As dn by dt, as N star times Nu prime and star we have found out is Nt, you can call that, I wrote that Nt exponential of minus delta f star by kt. Nu prime I wrote S star Nu exponential of minus delta Hd by kt. This exponential minus delta f star by kt and minus delta Hd by kt have been added together to form exponential of minus delta f star plus delta Hd by kt. These two have been multiplied together like that.

Student: What is S star?

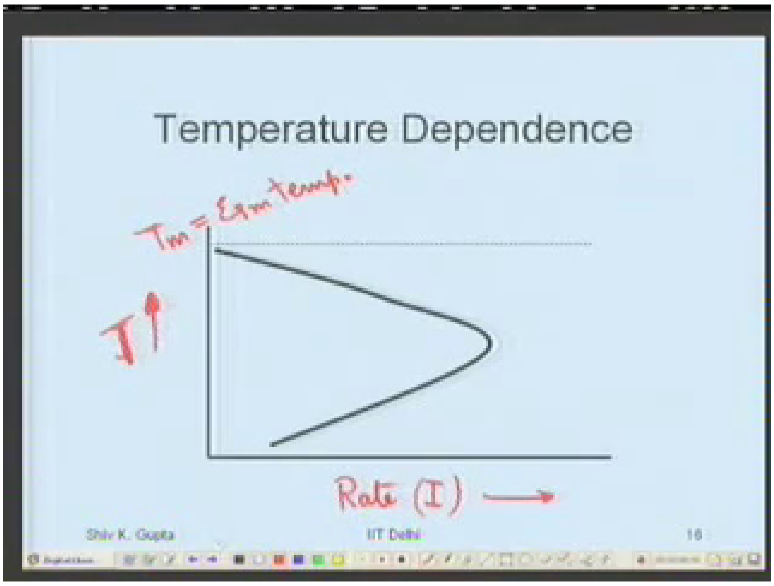
Professor: I just showed you number of atoms which are facing the interface and can become the part of the (())(49:06). All other cannot, they are far off, they are few, this number is around 10 or less for the critical nucleus size so they can. Only one of them has to make it super critical, I am not worried about others whether all of them can jump into, only one should is good enough, so I am finding out at what rate they can jump to become the crystalline part, right? So that is the rate of nucleation is this. That is the rate of nucleation for rather homogenous talked about the homogenous nucleation.

Usually, usual temperature range is delta f star, delta Hd we know the dependence of the delta f star, delta Hd is a diffusion cross interface and is not dependent on temperature but delta f star is a function of temperature, at melting point delta f star is infinite so nucleation rate would be zero, at melting point nucleation rate would be 0, no particle can nucleate so can you get a solid form at the melting point, no it is not possible.

But as the temperature is lower delta f star becomes smaller than infinity, it becomes finite and more and more under cooling delta f star becomes smaller and smaller so what shall happen to the nucleation rate, it should become more and more and more, right. So at the melting point the nucleation rate is 0, as the temperature is lower nucleation rate become more and more and more, but the temperature would be reached after few degrees then delta f star has become almost 0 or negligible as compared to the value of delta Hd.

When it becomes much-much less than delta Hd, let us say it becomes one 10th or one 50th of that it can be treated as negligible, after that any further cooling it is only delta Gd by kt and delta Hd is not a function of temperature then the temperature takes over, what shall happen then? When the temperature is lower the nucleation rate would decrease because it will increase only with increasing temperature so that is constant. So in other words nucleation rate passes through a maximum intermediate temperature. By the time we reach 0 (())(51:52) then the nucleation rate will again be 0. So how the nucleation rate changes with temperature is shown here.

(Refer Slide Time: 52:00)



Temperature Dependence

Shiv K. Gupta

IIT Delhi

16

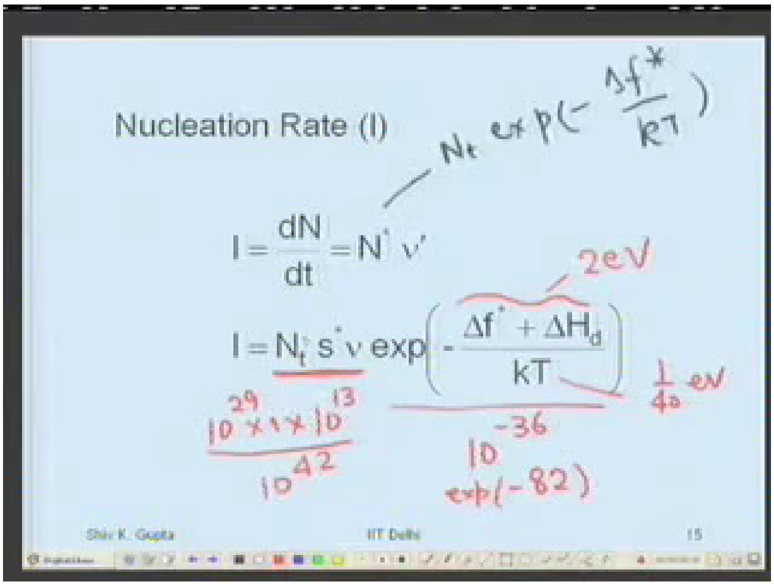
Here I have nucleation rate, sorry this is the temperature, I am sorry. Y axis I am already putting temperature whether it is phase diagram or it is the phase transformation and this is the rate, nucleation rate I and this is the melting point. This melting point you can also call the equilibrium temperature. At this point the rate is 0 and as rate increases as the temperature is lowered passes through the maximum and again decreases.

Well the reasonable rate of transformation is what you can observe in the laboratory if it is around million nucleation per second per cubic meter, in other words in a cubic centimeter you have one nucleation per second, cubic centimeter is more comfortable to work in the laboratory and there is a one nucleation per second is experimentally observable, those are the ranges in which it is taking place. So if we look at the numbers which are involved…

Student: Is delta Hd experimentally determine?

Professor: Yes, you can determine experimentally, yes. All diffusion processes you can do that, activation energy you can work out.

(Refer Slide Time: 53:59)



Nucleation Rate (I)

$N_t \exp\left(-\frac{\Delta f^*}{kT}\right)$

$$I = \frac{dN}{dt} = N^* \nu'$$

$$I = \underline{N_t s^* \nu} \exp\left(-\frac{\overbrace{\Delta f^* + \Delta H_d}^{2eV}}{\underline{kT}}\right) \quad \frac{1}{40} eV$$

$$\frac{10^{29} \times 1 \times 10^{13}}{10^{42}} \qquad \frac{10^{-36}}{\exp(-82)}$$

Shiv K. Gupta

IIT Delhi

15

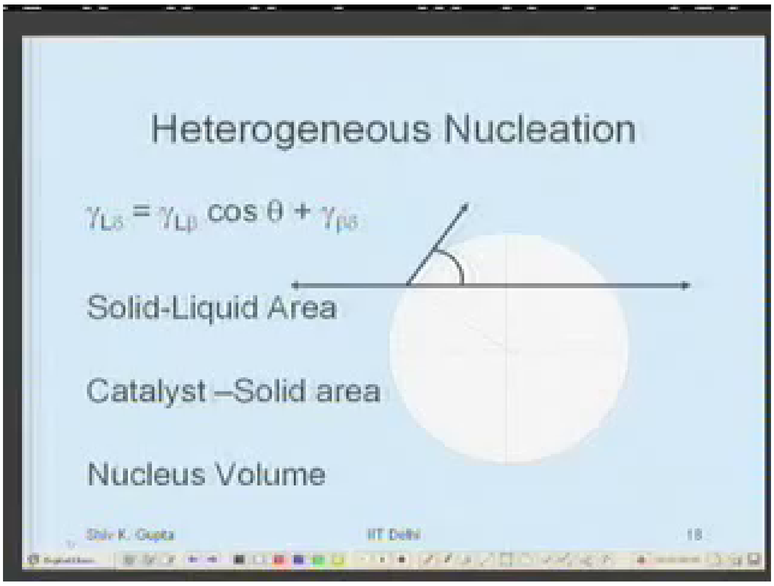
Now let us look at these numbers which are involved here to give you a feeling for the numbers. This number Nt is of the order let us say 10 to the power 29 per cubic meter, we talk about per unit volume so per cubic meter we take. S star let us take an order of magnitude because that I am taking care of, because 4 or 5 atoms together can form a particle and that I am taking 4 or 5 are there, right and facing the interface.

Nu is of the order 10 to the power 30, so this product is of the order of 10 to the power 42, if this is observable, 10 to the power 6 per cubic meter per second, this number exponential term here should be of the order of 10 to the power minus 36, if you look at the exponential term this should be exponential of 2.3 times this, it should be, let us say the order of 82.

Kt at room temperature is of the order of 1 upon 40 electron volt so this number can be of the order of 2 electron volt. That is reasonable that is what we know, delta Hd is going to be in the range of one electron volt, all activation energies are round there could varied from 0.6 to maybe 1.3 and delta f star is also the same order of magnitude when it is observable.

So that is how these numbers look like in homogenous nucleation that this number is, this product is 10 to the power 42, it is pretty large but then because of this delta f star which is there, which is high like to the order of 1 into (())(56:38) this number is not becoming more, right. Alright that is about the numbers which are involved and that is the temperature dependence of the nucleation rate.

(Refer Slide Time: 57:00)



Heterogeneous Nucleation

$\gamma_{L\delta} = \gamma_{L\beta} \cos \theta + \gamma_{\beta\delta}$

Solid-Liquid Area

Catalyst –Solid area

Nucleus Volume

Shiv K. Gupta IIT Delhi 18

I think I will stop here and talk this heterogeneous nucleation in the next class.