

Advanced Metallurgical Thermodynamics
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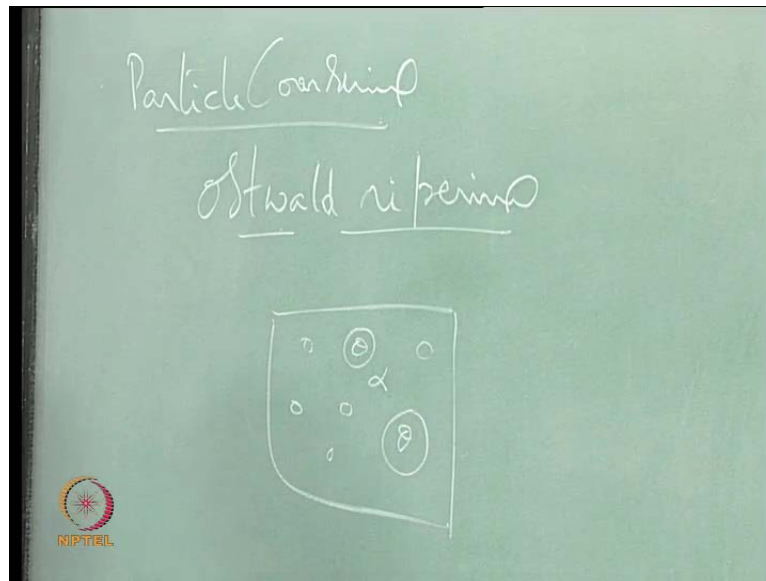
Module No. # 01

Lecture No. # 20

Precipitate coarsening, stability of a phase, spinodal decomposition

So, last class we were talking about precipitation, there is one concept in precipitation, which we have not yet covered.

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I thought today we will talk about it, that is Coarsening, particle coarsening let us say, people also call it as there is another name for this, anybody has heard of it, any precipitates, when you heat them to higher temperature take the alloy to higher temperature the precipitates coarsen. This phenomena there is a name generally used in hardening, what is it called

Phenomenon

A phenomenon, somebody said something no, it is called Ostwald ripening, ripen (O), so this is both are basically referred to the same concept. So, if you look at why should particles coarsen all of you know, yes whenever the temperature is high diffusion is there, so there is a growth. But, at the same time, if you look at if all the particles are of the same size; if you assume that there are number of particles inside the material all precipitates, and all of them are of the same the size, then you would never see any particle coarsening.

Particle coarsening happens only, when there are particles of different sizes and in fact, some particles dissolve decrease in size and some particle increase in size, this is the basic phenomena of coarsening. And we will understand that, if you understand again the same free energy concepts; if you look at a material, let us say this is one grain and you have particles of different sizes, something like this (Refer Slide Time: 02:16).

You may ask me sir, how do you get particle of different sizes, when do you get particle all of them are of the same size, can you tell me?

(O)

If there is a homogeneous nucleation at some time t equal to 0, and there is no further nucleation after that. Nucleation is a transient phenomenon and I told you that; there are different hierarchy of sites where nucleation can happen. For example, nucleation can happen on the surface first, and then we talk about grain boundaries, is it not, then you talk about stacking faults, dislocations and vacancies. So, there are varieties of places where nucleation can take place, and once certain nucleation sites are occupied, then you start seeing the other nucleation sites, start becoming active.

The nucleation sites with the highest energy, once they are all occupied, then the nucleation sites with the lower energy, lower with respect to highest energy will start working. For example, if the surface is there is for some reason, it is not possible to nucleate on the surface or if the surface is fully covered with nuclei, then as a function of time the nuclei which have formed on the surface will start growing.

And at the same time, further new nuclei you will start seeing them either at the triple junctions or at the grain boundaries; and if once they are covered, then you may see that as they start growing you may see further nucleation taking place, may be at the stacking

faults or at the dislocations. So, you will see that nucleation is not a kind of phenomena, where everywhere it happens at time t equal to 0, and all of them start growing at same rate; if that happens, then you would see a situation this is what we call it as site saturation.

When all the sites are saturated at the same time, at time t equal to some t whatever time it is, and then all this precipitates start growing at the same rate, then you can assume that all the precipitates are of the same size, which is a very **very very** ideal situation, it never happens that way. So, you will see that as the precipitate which is nucleated at some sites start growing, there will be further precipitation at some other sites; and as a result you will always see a distribution of particle sizes.

Whenever, you see precipitate particle size distribution, if you try to measure you will always see a distribution, there will be smaller particles, there will be bigger particles, and you can talk about what is the average particle size; that is why we always talk about average particle size. Because, we know pretty well, that they are all of not the same size. Once you talk about this kind of a distribution, and then you are heating this to a higher temperature, let us say all this kind of precipitation has taken place at some temperature.

Let us say during natural ageing or artificial ageing, and in service this material is being exposed to a higher temperature now. If it is being exposed to a higher temperature, this kind of a micro structure how does it grow, we know pretty well that at higher temperature you are providing sufficient thermal energy, and thermal activation for the diffusion to occur. So, there is a possibility that all particles can grow, but do you see all the particles grow or not.

So, that is where, if you try to understand this precipitate which is in equilibrium with matrix, and this precipitates which is also in equilibrium with matrix; if you look at the matrix composition, which is in equilibrium with this precipitate and this precipitate it is never the same. How does it come out, I would repeat that **the matrix composition**, the composition of the matrix which is alpha in our case, and let us say this is you call it as theta, whatever precipitates it is.

The composition of alpha in equilibrium with this precipitates, it is the same theta, this is also the same theta, the composition of alpha in equilibrium with this theta is different from the composition of alpha in equilibrium with this theta, why does this happen?

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Why?

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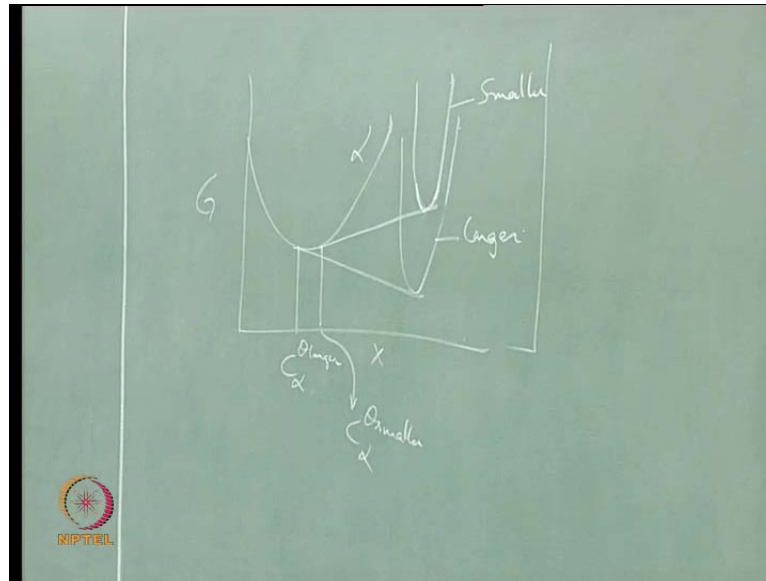
It has nothing to do with diffusion

(O)

This is the curvature effect, because of the curvature effect you would see actually the free energy of that two particles is different. You always see whenever, we are talking of a free energy diagram, we always talk about volume free energy only, we do not bring in the surface free energy term, that is why, if you look at all the free energy composition diagram that you draw, you assume that the precipitate size is infinite.

Actually precipitate size is not infinite, and different **different** precipitates will have different **different** free energies, though they all have the same structure, same composition. Because, the surface energy has to be added to the volume free energy, so that you actually talk about the free energy; so a smaller particle always will have a higher free energy, when compared to a larger particle.

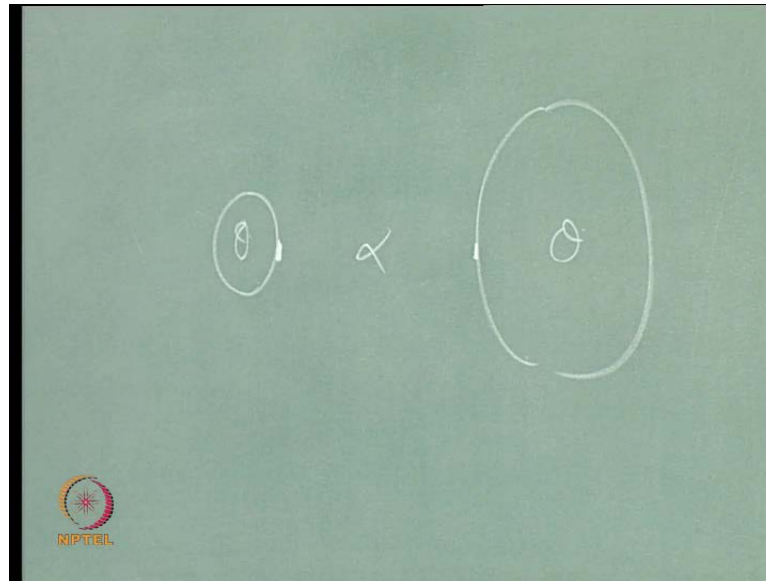
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And if that is the case, if you draw that G h diagram, let us say this is the free energy composition diagram, this is of alpha, and this is let us say theta phase with a larger particles and theta phase with a smaller particle. This is you can call it as a smaller particle, this is a larger particle. So, a smaller particle will always have a higher free energy, when compared to the larger particles.

And if that is the case, then if I draw now a common tangent, you would see that this concept which I just now said, that the composition of alpha in equilibrium, with a larger particle is different from the composition of alpha in equilibrium with a smaller particle. So, this is the composition of alpha in equilibrium with theta, which is let us say larger and similarly, this is the composition of alpha in equilibrium with theta which is smaller.

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The moment that is the case, then if I now simply look a smaller segment of where you have one small particle, one large particle, and there is alpha in the middle, the composition of alpha which is just in front of this particle, the composition of alpha which is just in front of this particle is different.

And which is higher

The smaller

The smaller is the higher, so if I now draw what is called the compositional profile, how would the compositional profile look like, the theta phase the theta phase, what is the composition of theta phase, in aluminum copper?

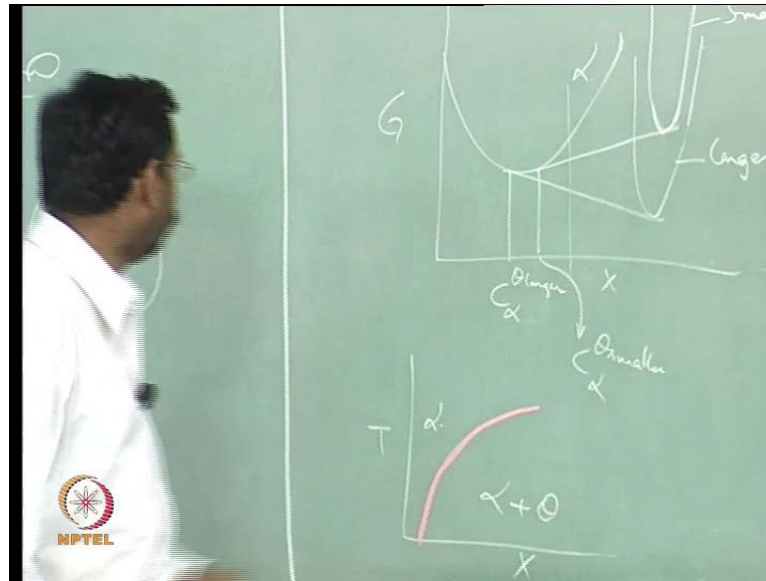
(O)

C a l 2 C u or C u a l 2, am I write and what is the composition of alpha

(O)

That is **that is** of composition with which you have started.

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And we are talking about the starting composition alloy composition is somewhere here, that is the alloy composition with which you have started, which will be a two phase mixture and what we are talking about is a equilibrium composition of alpha. That means, if you look at the phase diagram, this is let us say alpha plus theta here, and this is alpha.

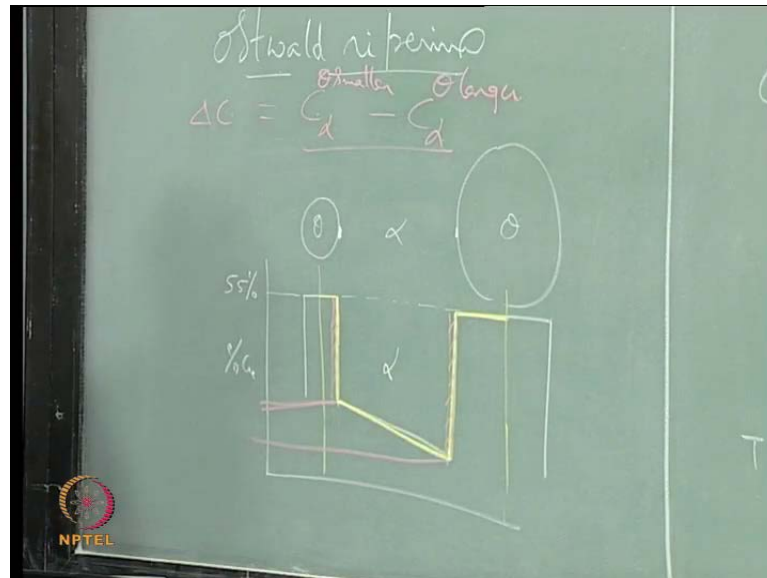
So, we are talking at any given temperature this composition, this composition that you are looking at of course, this is a temperature versus composition diagram or T X diagram, if you want to call it because, we called G X diagram; this line what is this line called solvus line. This solvus line is always assuming that, the theta has an infinite size, any phase diagram, any solvus line that you see, the assumption is that the second phase and the first parent phase; both parent phases is anyway matrix.

So, you cannot talk about the size of it, and there also in principle if the parent phase is also, a nano grained alpha let us say, it would definitely have a different free energy. So, there also, we always assume that the grain size of alpha is infinite, and also that the precipitate is also almost an infinite size.

The moment you bring in size effects, this is what we call it as size effects, then you will start seeing that the free energies start shifting, the alpha also instead of a an alpha of a very large grain size, if I now start looking at nano grained alpha, trying to precipitate out of the theta, then the alpha free energy curve also will shift. So, nano grained alpha

will have a definitely higher free energy with respect to an alpha of a much larger grain size, so all those things are what we call them as size effects. So, this solvus is principle for an infinite, and the moment I assume that the theta has a smaller particle size, you would see **that particle** that composition will be different.

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And that if I try to draw, you would see that if I draw composition, so let us imagine that this precipitate has certain **certain** composition, this is the composition in terms of percentage copper, if plot this is some value, let us call it whatever a 1 2 C u composition is, in terms of a weight percent it is approximately let us say 55 percent.

Now, this is the composition of alpha somewhere here, which is usually just for the sake of understanding, let us again take this the composition here also, this composition again this precipitate, inside the precipitate it is the same composition, it is the same theta, this whole thing is theta. So, the composition of the theta is this value, so inside the theta the composition is this (Refer Slide Time: 13:04). And then, if you look at this is alpha, the alpha composition here and the alpha composition here will be different.

So, there is a gradient here, inside this, so if I look at the concentration of profile it looks like this, if I start from the center of the particle to the center of the particle, let us not bother about the other sides; because on this side there may be another particle, on this side there may be another particle, we will not bother (Refer Slide Time: 13:43). So, we will simply look at from the center of this particle to the center of this particle is you

simply look at the composition profile, this is how we will see. Inside the alpha there is a gradient here, the smaller particle the alpha which is in equilibrium with smaller particle will have a higher composition, the alpha in equilibrium with the larger particle will have a smaller composition.

And once you have a gradient, you always have diffusion, you are always have a flux, at any given temperature, because a flux is j equal to

$(-D)$

Correct minus d into $d c$ by $d x$, and that $d c$ by $d x$ you can see here, the X is nothing but the inter particle distance, once you know the inter particle distance, you can talk about what is the $d c$ by $d x$ and at any given temperature d can be known. So, you can actually see and how does what is the result of this diffusion, you see that copper atoms which are here, want to diffuse towards this.

But, you need a constant supply of copper atoms for the copper atoms to go down the drain, down this particular decreasing concentration gradient, where are the copper atoms coming from, the copper atoms come from this particular particle (Refer Slide Time: 15:15). The smaller particle provides the reservoir of copper copper atoms, so that the copper atoms start moving to this direction, because the theta has a higher copper content.

So, this theta rejects some copper atoms by dissolving by a small amount, a small amount, a small delta x of this theta if this dissolves let us say, what happens some copper atoms are released. And those copper atoms will moved do down this concentration gradient, and come to this region and once that they reach that region, this particular theta needs copper atoms for it to grow.

So, it provides copper atoms, once the copper atoms come towards this, they join this particular theta and theta grows by a small delta x , depending on how many copper atoms have come and joined (Refer Slide Time: 16:04). So, this gradient will more or less remain the same, accepting that the concentration values this value and this value, what do these two values depend on, radius.

So, as the radius of these two change, in principle these two values also will change, as this particle becomes smaller and smaller as it shrinks what happens, so you can see as this particle shrinks this free energy goes up. If this free energy goes up the common tangent starts touching it, at a composition which is farther, which is higher in copper content, so that means, you would see this value keeps going up.

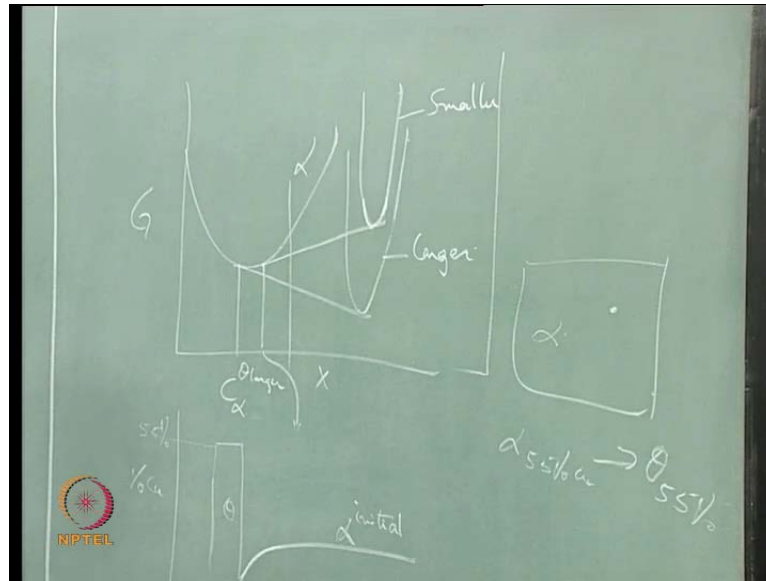
And what happens to this, as this starts becoming larger and larger this value, free energy comes down and that means, the common tangent again, the copper content of alpha comes down, that means, you actually see that the gradient is increasing. Because, the dC/dx which is nothing but, the composition of alpha in equilibrium with **large** smaller particle smaller theta, theta smaller minus composition of alpha in equilibrium with theta that is larger.

This delta starts increasing as the smaller particles start becoming smaller, the larger particle start becoming larger. So, in the process what happens is a slowly smaller particle will dissolve, at the expense of the smaller particle, the larger particle start growing; it is like you see that in a typical life, the bigger one try to grab the smaller ones. So, exactly the same thing is happening here, the bigger particle is just growing at the expense of smaller particle; and the whole thing the whole driving force for such a thing is coming because of this, free energy.

Once you understand this free energy, that the free energy of different particle sizes will be different, and you can easily understand, why this happening is. And this gradient starts increasing and of course, the distance you may say, what is going to happen to the dC/dx , dC/dx when you say dC/dx this theta is growing and this is decreasing. So, in principle they may remain the same or can change by to some extent, but we do not know, what is the rate at which this decreases, what is the rate at which this increases.

So, there may be a small change in the dC/dx also, but dC/dx you can see a significantly a large dC/dx , and because of which more and more, so as the time proceeds at that temperature; you will see the flux, the rate at which the atoms move is going to be higher and higher. This is usually against the normal case of precipitation, in a normal precipitation **how do** how does a precipitation happen?

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If you look at, the precipitation concentration gradient in precipitation, so the moment the alpha, if you take alpha inside alpha the moment a small nucleus precipitates, a small theta precipitates, how does the further growth happen there, the further growth happens again, because of the gradient, where is this gradient coming from. So, the alpha that you have is the starting alpha is this alpha, **am I right** that is 4 percent copper, the moment theta is precipitated, inside the alpha, the alpha which can be in equilibrium with that theta is not this alpha.

This 4 percent alpha cannot be in equilibrium with theta why, because if I take the forget about the smaller particle, let us look at the larger particle as equilibrium particle or you can choose any of them. So, in principle if you look at this particle, this particle it cannot be in equilibrium with this because, you cannot draw a common tangent between this point, alpha of that composition with the theta.

The only equilibrium that you can have is with the theta with some other alpha, and that is what we call it as composition of alpha in equilibrium with the theta; and that composition is different from this theta **with this** with this starting alpha. And as a result, if I now draw again a concentration profile, so if I take a small theta, this is let us say theta, whose composition, if I plot percentage copper whose composition is again the 55 percent **let us say** has nucleated.

And now, the composition of alpha just in equilibrium with theta that means, the alpha composition which is adjacent to the theta has a different composition, than the alpha composition which is far away from the theta. The composition of alpha which is far away from the theta is this composition, the starting composition; the composition of alpha which is adjacent to theta is of different composition.

Which is lower, which is higher?

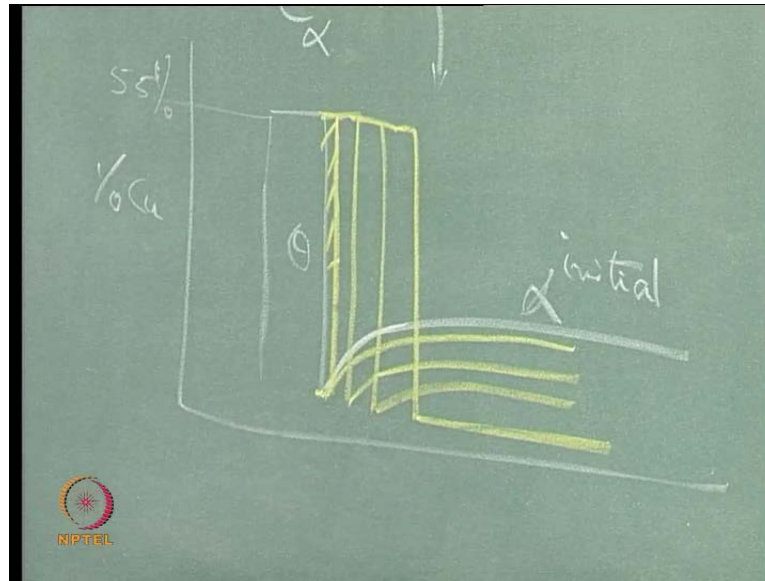
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Yes, adjacent to theta is a lower copper content, because of which you will see, I mean I have really exaggerated it will not be like that, because this is 55 and this is actually 4 percent something like this (Refer Slide Time: 22:05). This is the percentage of copper, this is the alpha of the initial alpha, the alpha with which you have started, you have taken an alloy of 4 percent copper made it into an (O) condition and then, quenched it and from there, the actual precipitation has started.

And that particular alpha is that 4 percent, but the alpha which is in touch with the theta is actually smaller and because it is smaller, now you see there is a gradient here. And because of the gradient what happens is, this copper which is there in alpha starts moving towards the interface, and once it starts moving towards the interface, there are some copper atoms get accumulated at this and once the amount of the copper atom is sufficient for the theta, because theta is 55 percent.

So, as the copper atoms keep coming towards theta, once in a small region the copper atoms become reach 55 percent, that small region gets converted. Now, it is like, almost like alpha of 55 percent copper gets converted to theta of 55 percent copper, it is like almost like a polymorphous transformation, allotropic transformation kind of. So, once the copper atoms reach that concentration level, it is only a structural transformation now; (O) structure changes to a theta structure. So, as the copper atoms get accumulated in that small region, that small region gets changed to the theta.

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And as a result, now the theta grows by a small distance, but in the whole process, because the whole precipitation is happening at a fixed temperature, this value will never change, because this value is coming from the free energy diagram. And in the free energy diagram, the free energy diagrams are always drawn at a fixed temperature, at a fixed temperature, the composition of alpha in equilibrium with theta is fixed.

Provided the theta size has not changed to such a significant extend, that its value can change, if the theta size changes, we can expect that **the** this value also can change otherwise, you can say this value is fixed. Once this value is fixed, what is **that** that is changing as a function of time, in this whole process, you have atoms of copper coming from this region, towards this and then theta is growing, and this is fixed.

And then what is, what changes

(O)

The composition of alpha in the matrix what happens to it

(O)

It decreases, because the copper atoms are being released from here and coming here, so the alpha concentration decreases and once it decreases, what happens to the gradient, gradient decreases; and as a result the process becomes slower. The reason why, I had to

tell you is that is which is reverse of this, so as a result you can see as a function of time you will see.

(O)

I am **I am** not talking about that situation, **you know** this is we are talking of one particular theta with respect to its alpha, how does this grow? There is the another nucleation somewhere else, at that region also similar thing will happen, as this theta wants to grow, the theta can grow only when copper atoms come and join to theta otherwise, theta cannot grow, because theta needs 55 percent of copper atoms. So, unless they are supplied to that **that** interfaces of the alpha theta interface, the theta cannot grow.

And where do these copper atoms come from, they cannot come from the thin air, they have to come from the alpha only. And as the alpha supplies more and more theta copper atoms alpha gets depleted in copper no, this is we are talking of a small region, very **very** small region and there can be some other region, where see this whole thing is happening in a region of few 100 nano meters. And in a alloy the grain size itself is very large 100 microns or so, in some other corner of the grain you can have another nucleation event can happen.

So, we are talking of that particular, because the theta in the beginning is about 10, 20 nanometers and that particular theta how is it growing, that is what we are looking at. So, as a result after sometime the whole thing would become like this, that theta would have grown to a certain extent and then alpha composition comes to that of the equilibrium composition (Refer Slide Time: 27:04). That means, there is no more excess copper left out in alpha to be supplied to the theta, so now, the growth stops.

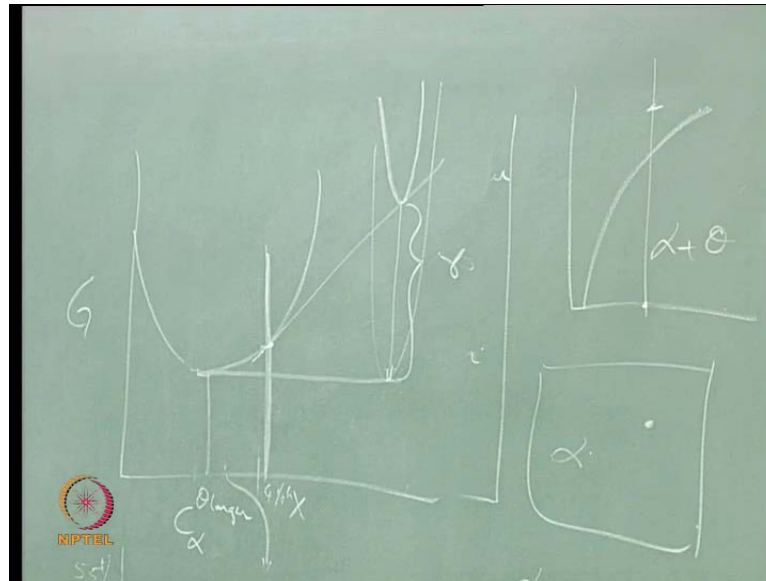
Once this happens the gradient is 0, once the gradient is 0 then there is no flux, and if there is no flux there is no growth. So, this is how the actual precipitation takes place, this (O) the next topic we are going to cover what is called Spinodal, you will see there is lot of difference between this and the spinodal we will talk about it in a minute.

So, is this clear now, so how do precipitates grow, **yes**

(O)

Why this is lower compared to this, **am I right**.

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So, so the point is, if I look at let us not talk about all this, imagine I have started with an alpha of certain composition, this is a 4 percent copper, I started with this alloy and I am holding this alloy at some temperature. I am holding this alloy which is solutionized brought to this temperature quenched, and I am holding at that temperature, at that temperature is alpha stable, it is not stable.

So, alpha as a single phase, it is not stable be very **very** specific when you say alpha is still stable, you still have the under in the equilibrium phase diagram, you have alpha plus theta; we cannot say alpha is not stable, alpha as a single phase it is not stable. Alpha can coexist with theta for that particular composition, for that temperature, and now if it is not stable as a single phase, it wants to precipitate.

How do you understand this precipitation, simply draw a tangent, if I draw a tangent at that composition, then what are all the phases, whose free energy is below that tangent all those phases can in principle nucleate. Let us not now consider about all the various phases that are possible, just look at only one phase, call it as theta phase, and that theta phase the moment I look at this, this particular theta at that temperature has a certain free energy, and the moment there is a driving force, this theta will nucleate.

The moment the theta nucleates inside the alpha somewhere, either grain boundary or where ever it is, the moment it nucleates this alpha this theta cannot be in equilibrium with this alpha, it is impossible that you can have a common tangent between the two.

So, then what happens is, you will see that this theta will find out some composition of alpha with which it can be in equilibrium, and as a result the alpha which is adjacent to the theta, will have a different composition. In fact, this can be even **you know** physically understood, see when of you think of a theta being nucleate inside an alpha, theta having a higher copper content, what happens is copper atoms get accumulated in small region, and that region gets converted to theta, that is what if you want to call it as a nucleation event.

Then they are getting accumulated from alpha, so the region adjacent to that obviously, is depleted, that is what this depleted region is and this depleted region is having a different composition. So, the alpha which is in equilibrium with theta is having a composition which is lower, and the alpha which is far away from this nucleation site is actually having a starting composition. The starting composition is this, and the composition in equilibrium is this, this is what we are talking of the gradient; if this difference was not there, there is no gradient **clear** (Refer Slide Time: 31:03).

(O)

Yes

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In principle **you are right, very right**, so in principle if I consider, that the theta is very **very** small, you can actually draw the free energy curve of theta, which is much higher and see that the common tangent with that particular theta, can be almost like, if this is the theta, theta have at the nucleation site stage, you can actually draw a common tangent between that theta and the alpha starting alpha itself, this is assuming **that** that particular small amount (Refer Slide Time: 31:43).

But, this is only at the nucleations event, but when you want to talk about what is the overall driving force for the nucleation, overall driving force you should always consider the theta after it has grown. In the after the whole precipitation process is over, when you are looking at the micro structure, what is the theta, and that particular theta with if you can compare, that theta which is what we calculate only from the bulk free energy point of view where surface energy is not considered, that is turns out to be this.

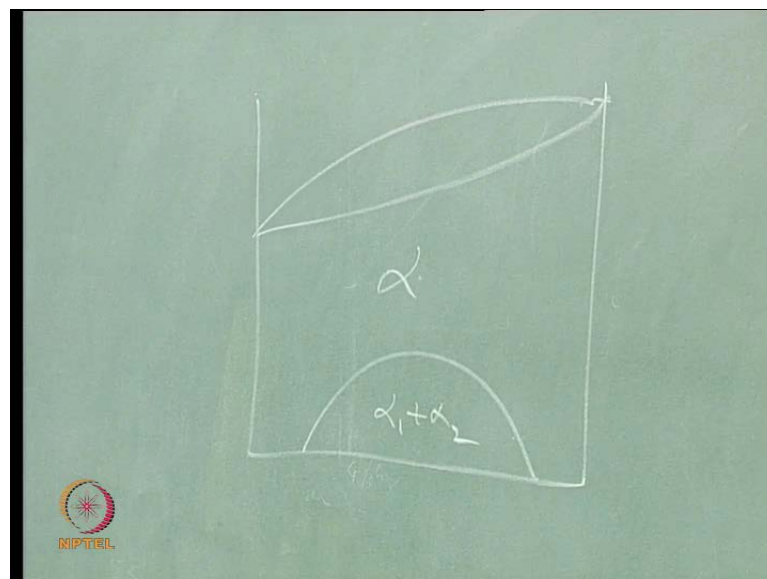
This is only the volume free energy, this plus the surface energy, so this whole thing is you can say ΔG surface or you can call it as γ , if you want to call it corresponding to that particle size of whatever is the initial particle size. So, the free energy gets lifted, because of the surface energy and at that particular moment, you can say yes it is in equilibrium, but the moment it grows to even a smaller extent, it cannot be in equilibrium with that.

So, we are now looking at only that is the reason why, you have to see that most of the free energy composition diagrams are always drawn only considering the volume free energy; capillarity effects or the surface effects are not considered. And once you start considering, this kind of concepts come into picture.

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Correct that is that is because, there is a size distribution if there was no size distribution, we would not have considered size effect. Because, there is a size distribution you wanted to know which one will grow, this will grow or this will grow, so only if you understand that, you will understand this (Refer Slide Time: 33:45). Otherwise, at when you are looking at one individual particle, you need not have to consider its size effect.

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Now, let us come to the next concept, which is similar to a precipitation, which is what we call it as spinodal, spinodal decomposition, let us understand try to understand what

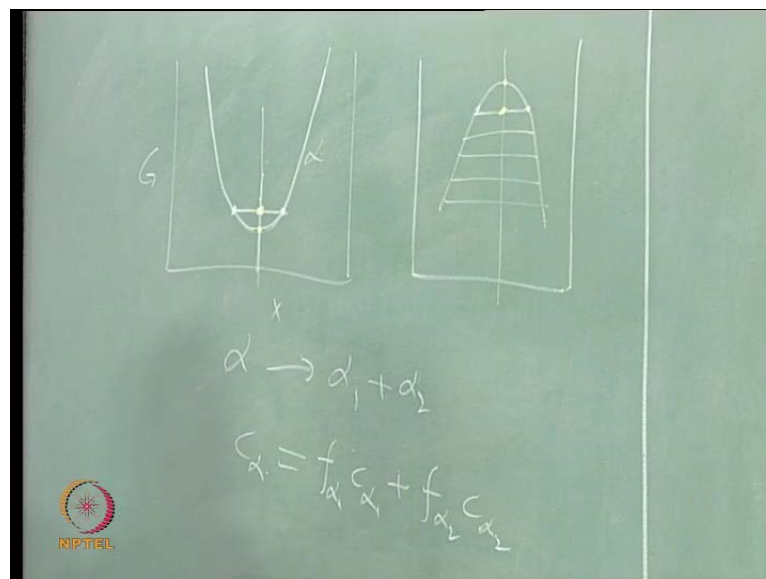
are the free energy concepts involved in this. As you can see this, we call it decomposition, we do not call it as precipitation; there is the difference between a precipitation and decomposition. What is the difference? When you say decompose, what does it English term mean?

(O)

Something is splitting into two, that is what we call it as decomposition, when you say precipitation basically, something is precipitating out of something else. So, there is a matrix from which some precipitate is coming out, here when I say decomposition a matrix is splitting into two, that is the meaning of decomposition. Let us try to understand that, and you will see that spinodal decomposition always occurs, when the phase diagram shows some miscibility gap, when there is no miscibility gap in the phase diagram, you will never see spinodal decomposition.

So, let us try to consider a phase diagram with a miscibility gap, something like this alpha splitting into alpha 1 plus alpha 2 and whenever, you talk about a spinodal decomposition, you need to consider one aspect of stability, what is this stability? (Refer Slide Time: 35:37)

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Whenever a free energy diagram, **correct** free energy curve looks like this, this phase is called a stable phase, why because if I take an alloy of this composition, if this alloy

wants to decompose into two different compositions of the same structure, that is what is the decomposition means that means, alpha giving you alpha 1 plus alpha 2. If this alpha, if we call this as free energy of alpha G versus x, if it splits into two, one with a lower composition, another with a higher composition. So, that the overall composition remains the same that means, if I do the volume fraction of alpha 1 multiplied by the composition of alpha 1 plus volume fraction of alpha 2 multiplied by the composition of alpha 2 should be equivalent to what, the composition of alpha with which I have started, this is what is the mass balance.

As long as the mass balance is maintained, some **the** alpha splits into some part of alpha 1, some part of alpha 2, for such a process to happen, what is the overall free energy of such a mixture, the overall free energy of such a mixture, if this is the free energy of alpha 1, this the free energy of alpha 2; then the mixture will always have a free energy which is decided by the line joining those two.

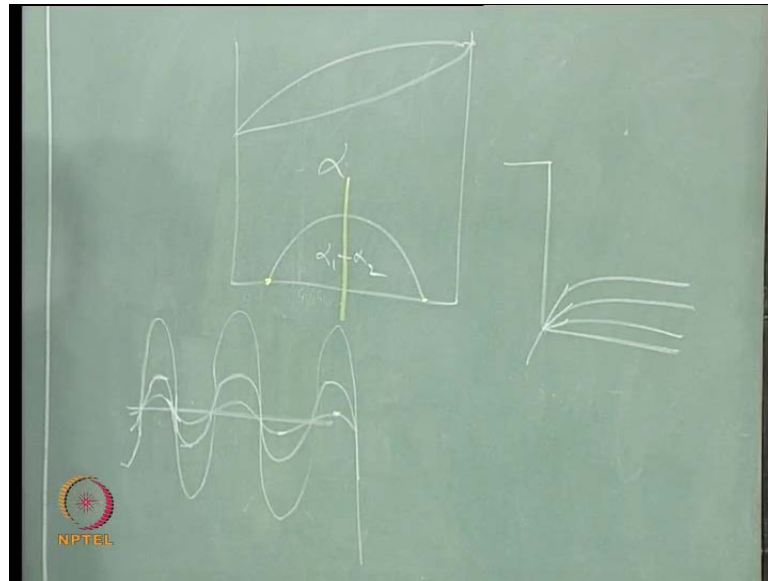
Any **any** two free energy any two phases having two different free energies, if you want to know the free energy of the mixture, you simply draw a line joining the two, and for the composition that of interest to you if I choose this alloy composition having this two phases, the free energy of such a mixture is this. This is the two phase free energy that is what we have been showing in all the phase, there even earlier case also precipitation also whenever, an alpha phase splits into alpha plus theta. So, the alpha theta common tangent that we consider and that particular point on the common tangent gives you the two phase free energy.

And the single phase free energy, if it is higher than the two phase free energy, then only precipitation will take place, we have seen that. So, this is the free energy of this fixture, and this is higher than the free energy of a single phase, as a result such decomposition to two is not usually observed; because there is no driving force such a thing to happen. So, for a single phase alpha to split into two phases in this kind of a situation, does not happen.

Because, there is no driving force, because of such decomposition, the free energy is actually increasing rather than decreasing, we know that every process where there is a decrease in free energy that is favorable, and increase in free energy is not favorable, is it not. But, if your free energy curve is like this, then this alpha can split into two phases of

alpha 1 and alpha 2 and which have a free energy of this (Refer Slide Time: 39:24). So, from here to here, and it can split and it can not only split like that, it can keep on splitting more and more that means, the alpha 1 and alpha 2 composition will keep on deviating more and more from the alpha; and this causes further decrease in the free energy.

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That means, if I start with a an alpha having a uniform composition in such, and if this alpha is having a free energy curve something like this, at certain temperature, then what happens is suddenly this alpha is not stable, because its free energy curve is like that. So, what happens is there will be a small fluctuation, even small thermal fluctuations, temperature whenever you say this particular alloy is at 500 degree centigrade, when you say this 500 degree centigrade is the bulk temperature, that you are talking about.

In a small region of a nano region, you can always have a small changes and this can cause a compositional fluctuations, in such a way that there can be a small region, where the composition can decrease, and another region where the composition can increase. Though I have drawn it with such a scale, this can happen in a less than a nanometer scale, so in less than a nanometer scale, if you see a small region where the atoms, because there are always atoms moving at any given temperature, unless you are at absolute 0.

Because of this, atomic fluctuations you can see a region where the composition goes slightly below the nominal composition in some region and obviously, those atoms have to move somewhere else. So, they go to some other region where the atoms are more than the nominal composition. Once this happens, this kind of a fluctuation is a stable fluctuation in this, because the moment such a change happens, then suddenly this region with a lower copper content, this region with a higher copper content (Refer Slide Time: 41:53).

Let us say will be a stable couple because, that has the resulted in a decrease in the free energy, but if that happens in this alloy it will not be stable, what happens is the atoms will come back the atoms which have the excess atoms here, will come back and join the alpha, so that again the alpha will have the same composition. Where as in this kind of a situation the atoms, once they come to this situation they will not go back, because that is a stable situation.

And now, what happens is this particular thing starts growing, why it grows, because by further growing you will have a further decrease in free energy. So, this fluctuation starts with the same wave length, the wave length gets fixed which may be of the order of few nano meters, and within the wave length the amplitude starts changing (Refer Slide Time: 42:38). So, that means, this region becomes more rich in copper, this region becomes less in rich in copper, but the overall composition satisfies this, the overall composition of the alloy is the same.

But, you will see that this composition start increasing and decreasing, and to an extent that finally, if I take that alloy and if I am holding at room temperature this alloy, and it will keep on growing until the extent that alpha 1 achieves this composition, alpha 2 achieves this composition. And these is what you call it as, let us say alpha 2 this is what you call it as alpha 1, the lower is alpha 1, let us say the higher is alpha 2.

So, this this wave or this compositional wave will keep on changing its amplitude to such an extent that finally, you reach this value and this is what happens whenever, you have this and I have directly co related this to this, we will see in a minute, why I should co relate that to this, at the moment this and this are not really co related. So, you will see that whenever I take a phase of this kind of a free energy diagram, you will actually see this kind of a free energy diagram, in this miscibility gap, we will see it within a minute.

So, but if that happens you can see this will keep on increasing, this in comparison to the precipitation, in a precipitation the composition of the precipitate is always fixed; you start with certain fixed composition. And that during the whole precipitation process as a function of time, that precipitate composition is not changing, only that is changing is your the alpha composition will keep of changing.

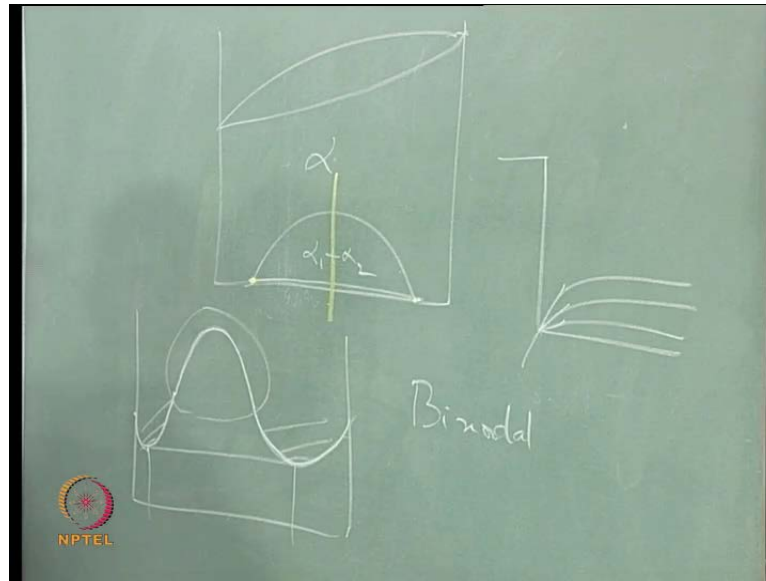
Whereas here, **the** if you want to call these as precipitates, they are actually not precipitates, but these are composition only, when the whole growth has completed. Then you we will see that this would be a different composition, this would be a different composition and this happens homogeneously throughout the sample (Refer Slide Time: 44:53). Whereas, a precipitation does not happen homogeneously, it happens heterogeneously, in some heterogeneous nucleating sites; whereas, here this happens throughout, why it happens throughout because, throughout wherever it can happen this is stable.

So, you can see a homogeneous nucleus can happen in this kind of a situation, and that keeps on growing, and this is a in contrast to the what I have shown you in precipitation, where the gradient will keep on decreasing as a function of time, here the gradient is actually increasing as a function of time. If you look at **at at** the interface, this is the if you want to call this as one phase, this as another phase at the interface, if you look at the gradient the gradient is actually keeps on increasing (Refer Slide Time: 45:41).

Whereas, in the precipitation, normal precipitation at the interface between the theta phase and the alpha, if you draw a gradient and that gradient will slowly decrease, because if you remember, this is the one this slowly becomes like this finally, it is like this (Refer Slide Time: 46:01). So, this gradient keeps on decreasing whereas, here the **gradient initially is 0** gradient is initially 0, there is no compositional difference and the slowly the gradient starts building.

And that is why some people want to call it as uphill diffusion, because the gradient is actually increasing, and this how do I understand from the free energy point of view.

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Let us now try to draw, the free energy curve at this temperature for this, if I draw the free energy curve, the free energy curve actually looks like this, **am I right** because when do you get a miscibility gap, when the Δh is positive. Whenever, the Δh is positive and that is higher than the $T \Delta S$ mixing term, then you will see the free energy curve will have this kind of a shape.

And that if that is the case, if I draw a common tangent you get these two points and what are these two points, these are these two points, we call them as the binodal points; they are usually called the binodal points, they **they** are nothing but, the equilibrium composition of α_1 and α_2 at that temperature. Now, if you look at this **this** particular free energy curve appears to be a mixture of two types of free energy curve; one which is a curve like this, again a curve like this and other another curve which is like this (Refer Slide Time: 47:46).

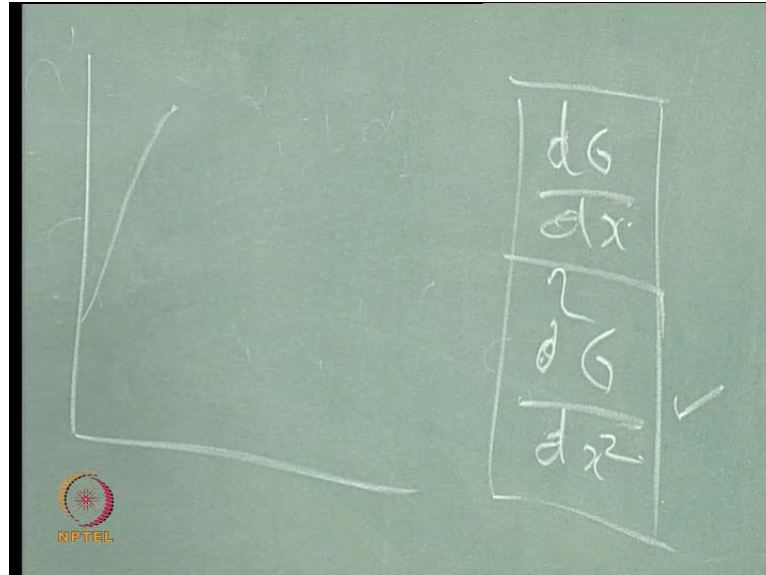
If you look at these two curves, concave upwards and concave downwards, so you have two parts here, which are if similar in nature, which are related to stable phase condition, and there is one region here in the middle, and that is the region, where there is a change that takes place of slope. If you look at the slope of this free energy curve, as a function of composition, the slope here is what is it, **at the two** at the pure metal end it is minus infinity.

So, this minus infinity slowly starts increasing and when you reach this value, what is the

(0)

It is not 0, it is low, it need not be, it will be 0 only when the tangent is horizontal, tangent need not be horizontal.

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So if it reaches a value, higher value, so from minus infinity if I now plot in fact, it would be nice if I plot it on this itself, so anyway. So, from the minus infinity it keeps on increasing, and then again you see the free energy curve, what is here **it is positive** it is positive and then it keeps on increasing and at some point of time, this slope is changing **am I right.**

So, can you draw this slopes, next class when we come, I want you to see how this free energy take any such curve, which has an inflection inside, draw the dG by dx and then also draw d^2G by dx^2 . Then you will see something interesting happening. Next class, when we start we will start with that, and by the time I want you to draw and see what happens.

You will see there is something which happens, when you look at this part and that is actually 0 at these two positions; we will try to see that. So, please draw a free energy curve and for that free energy curve just below that draw this, for the same scale and below that you draw this for the same scale and see how this changes, we will stop with that .