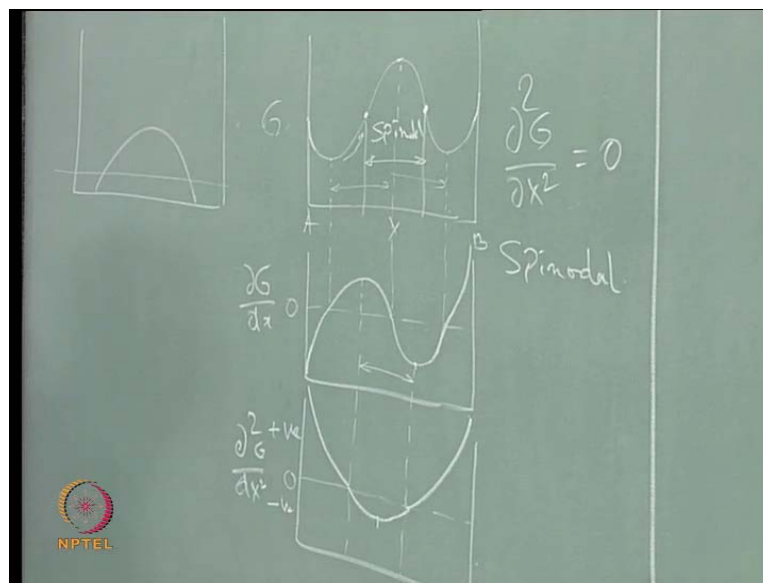


Advanced Metallurgical Thermodynamics
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Module #01
Lecture #21
Spinodal decomposition

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Last class we started talking about Spinodal decomposition, we will continue there. We said, you will see a Spinodal decomposition whenever, you have a miscibility gap in the phase diagram- this is what we have said. If there is miscibility gap in a phase diagram, something like this, it will be reflected in the free energy composition diagram something like this. Am I right? At any given temperature within that.

So, if you draw at a particular temperature, you will see a free energy diagram which looks like this. We always know that, towards the two pure metal ends, the slope of free energy verses composition is minus infinity. Right? So, this actually, in principle, is minus infinity, and this also, is minus infinity. This is minus infinity if you are looking from this side, if you take this as a solvent and A as a solute, then it will be minus infinity, but if you are looking it from this angle, it is plus infinity.

So now, if you look at this, we will understand the Spinodal decomposition better, if we try to see, what is the first and second derivatives of this free energy. Let us try to see the first derivative. Last class we just started talking about it. So if you try to look at the first derivative, of this free energy curve, basically what we are looking at is, what is the slope of this curve, as a function of composition. So try to see, how the slope is changing, as a function of composition. Start from one end, and start looking at how the slope is changing. If you look at it, when you start at pure A, it is minus infinity.

And as you increase the concentration, slowly, the slope is increasing or decreasing? Slope is increasing. And increases and reaches around 0 here. Isn't it? And then, it continues to increase, in the positive direction, up to here it is in the negative direction, it is increasing. So if I put somewhere some 0, here, I start from a negative, minus infinity, and then if I draw a line, so this up to here, it goes and then here, it becomes 0. And then it continues to increase, on the positive side. And the only difference is the slope of this increase; the rate of this increase, changes at some point. So, you can see that, the slope of this is higher and higher as you go, and at some stage, again it starts becoming lower and lower.

The slope is positive, but the only thing is, the rate of change of that particular slope, is going to be different. So, as a result you will see that, as you go along, the slope is increasing and at a particular point the slope reaches a peak, and then again starts decreasing and again reaches 0, somewhere here. So if I take a point here, it actually goes up, and then comes down. The slope of this is increasing, up to a certain point and then, from there, it starts decreasing and reaches back to 0. And that particular point, where it reaches a peak, is a point of interest to us. we will see it what is that point means.

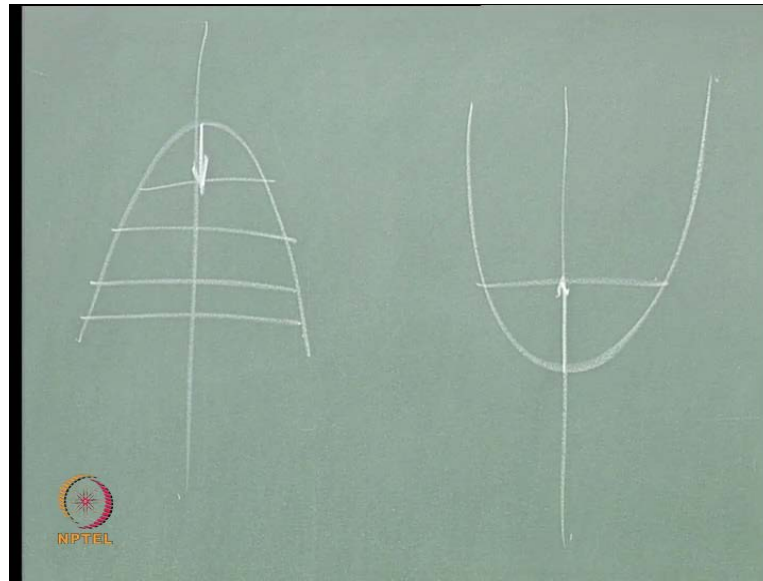
And, in the second direction again, you will see the slope now starts decreasing, the slope is negative now, from here onwards, it is negative and again up to certain extent, the slope keeps on increasing, beyond a particular point, the slope again starts decreasing and then, comes back to 0 somewhere here. This, if you look at it, goes to 0 and then, again, this is positive and it is positive and goes to something like infinity. It will be on plus infinity if you are looking at it from this angle.

So, you can see that basically, in this domain, and in this domain, there is a change in the slope. In this domain, the slope is always one sign only, slope is always positive, but, that positive is reaching a peak, and then, coming back to 0. Here, the slope is always negative, but the negative is reaching a peak, or you can call it as a trough, instead of a peak, and it is reaching a trough and again going up. Now, this particular thing, if we call this as $\frac{dG}{dX}$ and then, now, look at the second derivative of free energy, second derivative of free energy is nothing but the slope of this. Now look at the slope of this: how does this slope of this change. And you can see this is positive slope, and this positive slope keeps on decreasing: initially it is plus infinity, slope of this, because this was minus infinity, the slope of this will be almost like plus infinity. And from plus infinity it keeps on decreasing and reaches around 0 here. Am I right? So, the slope of this is 0.

So, if I now look at it, if I draw and then again draw this point, you will see that from plus infinity, it keeps on, somewhere I will put again 0 for you, so, somewhere call this as 0. So, it is plus infinity, and then slowly comes to 0. And then, this particular portion, this whole portion, the slope is negative, am I right? Slope is negative. Again here, the slope is positive. So, somewhere here, again this is a 0 slope. And then it becomes positive, so that means, is something like this. But in this period alone, in this composition range alone, it is negative slope. And the negative slope again, is in such a way that, at this point the negative slope changes its curvature, okay, in such a way that, you see that negative slope, reaches a kind of a trough here.

So, the slope is actually, increasing up to here, and then, it is again decreasing. So, you can see the slope in the absolute trough, is actually increasing and then again the slope is decreasing, in such a way that it again, comes to 0. So, this is in the negative, this whole domain is negative. This is negative; this is positive. So you can see that in this particular domain of composition, the second derivative of the free energy, $\frac{d^2G}{dX^2}$, is negative. And that, basically, boils down to two points somewhere here, where, the actual, we say these are the two points, where, the $\frac{d^2G}{dX^2}$ is 0.

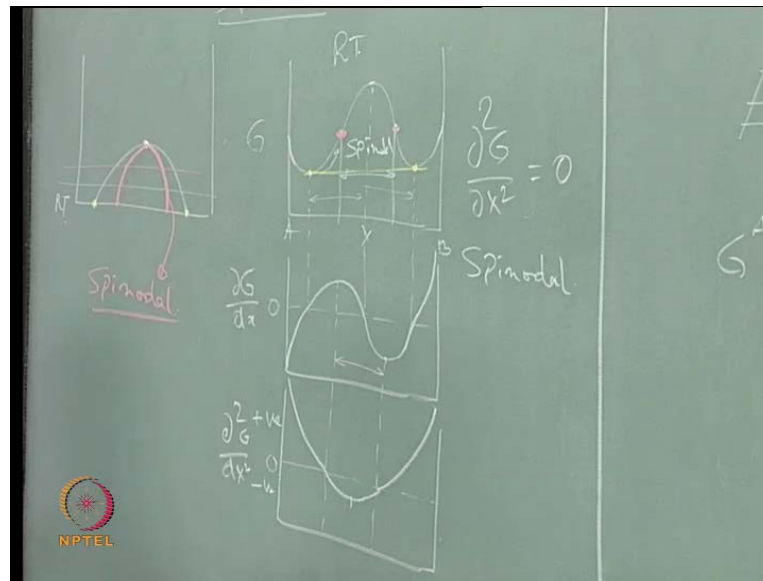
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Because, those are the two 0 points. And those two points where it is 0, indicates the points, which we call them as Spinodal points. And why are they significant? Because, within those, in the composition range, characterized by these two Spinodal points, within that, the free energy curve is, like this. Beyond those two points, the free energy curve is like this. Am I right? So, to the left of this point, to the right of that point, this free energy curve is of this shape. And the moment you have a free energy curve of this shape, yesterday we have seen, in the last class, that, this is a stable state; this is an unstable state. The moment you take any composition, the composition would like to split into two phases, of two different compositions. Whereas if you are here, it would not like to split, because by splitting, it is increasing the free energy. Here, by splitting, it is decreasing the free energy.

So the points which differentiate these two phenomena: one with a stable state, of a single phase being stable and the other region where the single phase is not stable, are those points which we call as Spinodal points. And to understand where these points are, you need to come to the second derivative, and see, where the second derivative is 0 and between those two compositions, the second derivative is always negative. That is why we say, Spinodal decomposition occurs, when the second derivative of the free energy is negative.

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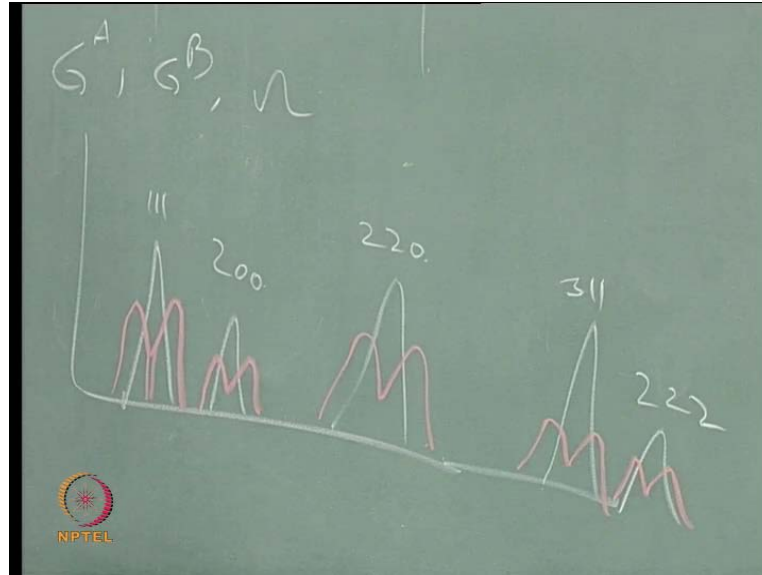
So, all those compositions, where the second differential to the free energy verses composition is negative, that whole region, is called Spinodal region. How do I, now, identify this on the phase diagram? So the moment, I draw a particular temperature, let us say at room temperature, let us assume that, this free energy composition diagram is drawn at room temperature; at room temperature, we know these two points. What are these two points? We call them as binodal points. And where are those two points? Those two points are nothing, but these two points. If I draw a common tangent, these two points, correspond to these two points.

Now, between these two points, you have two compositions, which are the, so called Spinodal compositions, and those points, are these two points. And obviously, the Spinodal points have to lie within the binodal points. They cannot be outside the binodal points, because from the nature of the curve itself, free energy curve, you can see, that the two Spinodal points are always, within the two binodal points.

If that is the case, somewhere here, you will see two binodal points, or two Spinodal points. And if I draw the same free energy curve, at different-different temperatures, at each temperature, you will get two binodal points, and two Spinodal points until, you reach a temperature, where, the two binodal points actually merge into one single binodal point. And obviously, when the two binodals themselves merge into one single binodal,

then obviously, you will see that the Spinodal points also merge, and that is, this temperature, where the miscibility gap vanishes.

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And that means, at various temperatures, I would get different-different compositions if I draw and finally, if I join all of them, I get a curve like this. This is what we call as, Spinodal curve. One can easily calculate this, by simply knowing, what do you need to know, to draw this free energy curve? Okay. Yes you are right; you need G^A G^B . What else? Ω . Once you know these three, provided, there is an assumption there when I say I need to know Ω , what is assumption? Of course. Ω is greater than 0, fine. Anything beyond that? The moment I say I need Ω , I am assuming something. It is a regular solution model. Somebody has said that! That, the system is following a regular solution model.

If the system is not following a regular solution model, one Ω is not sufficient for you. You need to consider, if it is sub regular, so Ω^A , Ω^B and so on. So, if I assume that it is regular solution model, then simply, once I need know these three, at any given temperature, I can simply calculate the whole free energy curve. Once I calculate the free energy curve, simply I ask the same software to even calculate what is the double G by double G X square. Find out that composition where that is 0.

And once you do that, you will be able to get these two points. And once you do it as a function of temperature, at regular intervals of temperature, you will be able to easily generate this curve. And this is something, which you will never be able to get, if you simply do, let us say thermal analysis. Miscibility gap, you may be able to get, using thermal analysis, or to some extent, the more easier technique, rather than thermal analysis is what, if you want to see miscibility gap? X-ray. X-ray diffraction. Because one single phase, splits into two phases, how will you find out the through x-ray diffraction? Superlattice? There is no superlattice here. There is no ordered structure here.

What will you see? If I take a single solid solution, which is splitting into two solid solutions, when I do x ray diffraction, what will I see? One of you. Yes? Two sets of peaks you will get, of the same crystal structure. Because the crystal structure is not changing here. It is an alpha, of an FCC structure, splitting into two alphas, both having the FCC structure, then what is the difference Aneesha? What is the difference, between these two, phases that are coming out? It is the composition. Once the composition is different, then obviously the lattice parameter is different; if the lattice parameter is different, then the d spacing's are different; if the d spacing's are different, then the theta is different- $\lambda = 2d \sin \theta$. Isn't it?

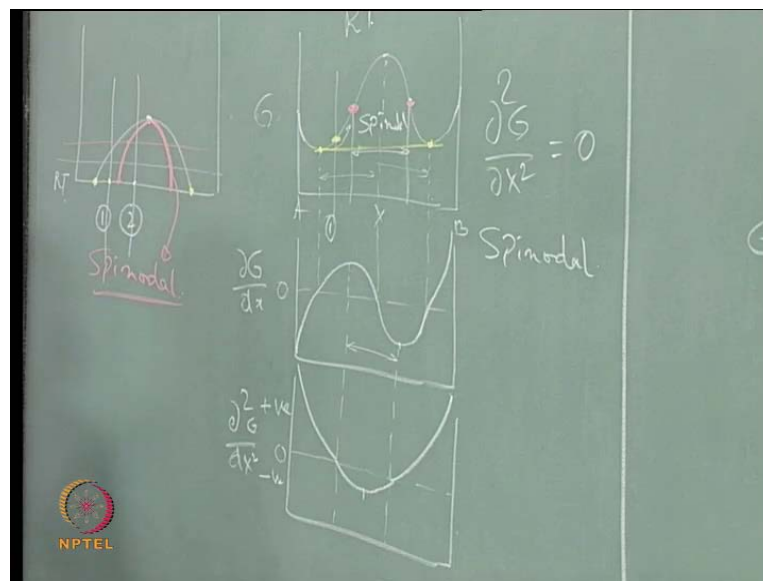
So, basically you would have got a set of peaks, whatever it is. If it is an FCC, you will get 2 1 2, that kind of a pattern. This is let us say, 1 1 peak, this is 2 0 0 peak, then 2 2 0 peak, what is the next one? How many have you done x ray course? 3 11. What is the next one? Yes. Perfect. 2 2 2. So, this is how, you get 2 1 2. I mean in fact, the moment you, anybody gives you an X ray diffraction pattern, and wants you to check whether it is really FCC or not, you will always see 2 peaks of them together, and one. And why does that happen? Because this is, $f^2 + k^2 + l^2$ is 3, 3, 4, 8, 11, 12.

So, 3 and 4 will be together, 8 will be separated; 11 and 12 will be together, and so on and so forth. You will have again, 16, 19, and 20, and so on. You will see always two-two peaks will be together, separated by one peak, this is a characteristic I say. Now if it is single alpha, now it is splitting into two alphas, then what you see is, here, this single alpha will be, if I put, you will see two peaks there. One with a lower lattice parameter, another with a higher lattice parameter. And similarly, this would also be, it may come as two individual peaks, or it could be over lapping, because most of the time there will be

overlapping, because there the lattice parameters are so close, that they actually will be overlapping.

And you actually need to do, what is called deconvolution, if anybody has done x ray diffraction they will know. So, you need to do deconvolution of the peaks, to be able to see them separately. Or even do a very slow scan, of x r d, to be able to see the two peaks separately. So you will be able to see every peak, will split into two peaks, and we will be able to clearly see, yes this is the two phase structure. And that is how you will be able to see that the Spinodal has taken place. Now let us come to, again, back to our Spinodal curve, and see what happens if I am inside the Spinodal, or outside the Spinodal. In a Spinodal, we always talk, whether you are inside the Spinodal, or you are outside the Spinodal.

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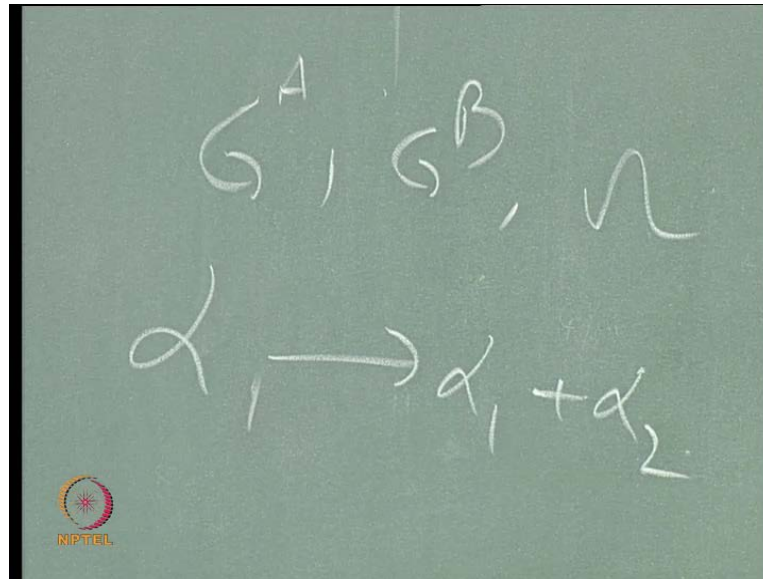


What does that mean? It means, that if I have 2 alloys, 1 alloy, I chose this composition, another alloy I chose this composition. And both of them are brought to this temperature. They are cooled to that temperature. What should happen, in both these alloys? First of all, in both these alloys, single phase alpha is not stable. Am I right? Because, both these alloys, are inside the miscibility gap. So that means, alpha has to split into, alpha 1 plus alpha 2. The only question is, how it splits, is the difference.

If I look at this alloy- alloy number one. Alloy number 1, if I look at it, where does this alloy number one lie, in the in the free energy diagram? Yes. It is between the binodal

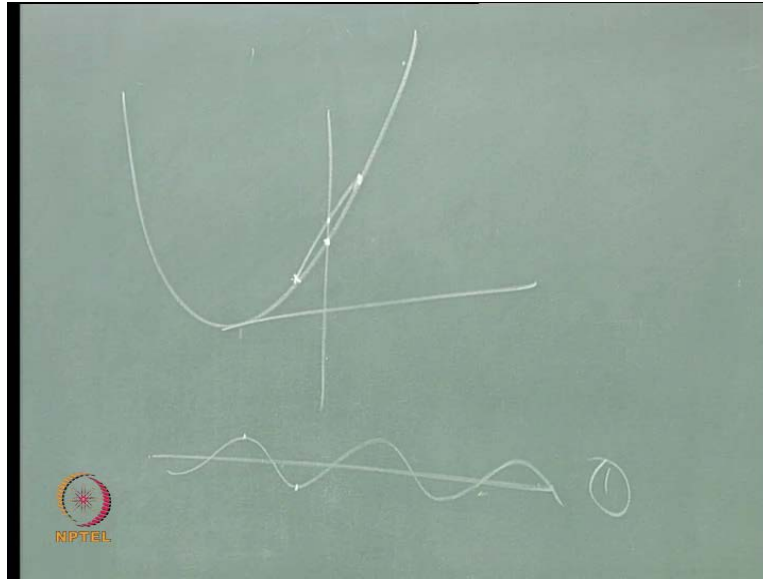
and Spinodal. Am I right? So, that means, if I chose this composition, that is call it as alloy 1; it is between the binodal and Spinodal. Now if I take this alloy, at this temperature, which is room temperature, the free energy of single phase alpha is this. Okay. Call, okay, let us chose this. So this is single phase alpha free energy. Obviously, you can see that, this is higher than a two phase free energy, which is this. Isn't it?

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If alpha splits into, alpha 1 plus alpha 2, if single phase alpha exists, at that temperature, it would have that free energy; if it splits into alpha 1 plus alpha 2, the free energy of that mixture will be this. So, it clearly tells you that there is a decrease in the free energy, when single phase splits into two phases.

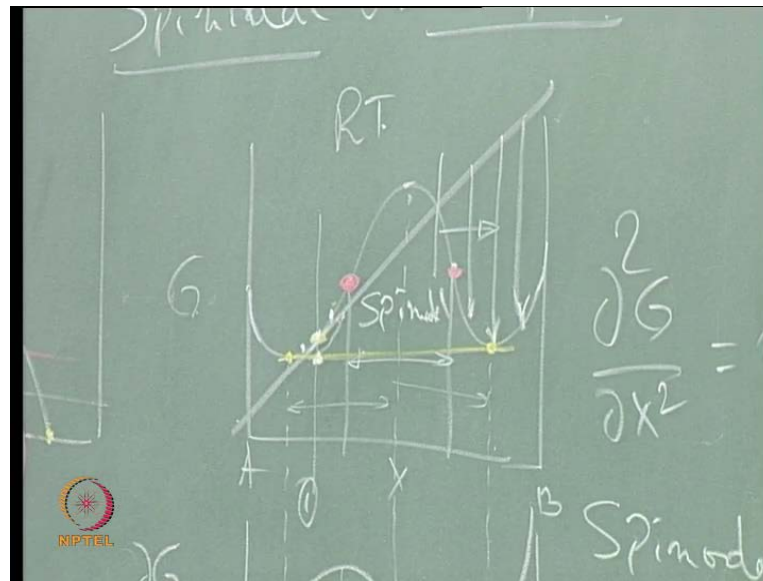
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So that means, this single phase alpha will not remain as single phase alpha, it would like to split. But how does this split take place? If you look at, so, let us assume the way we have seen in the last class, that if alpha is of a particular composition, we call it as alloy 1 composition, and if there is a small fluctuation in the composition that takes place, because of the thermal vibrations, if such a composition fluctuation takes place, what does it mean? In a small region, the composition it goes up, beyond the alloy composition nominal composition, in some other region it comes down.

That means, if I show that as a one composition which has decreased in terms of the B content, another composition which has increased in terms of the B content, if I look at those two compositions, **and then take,** now, if I treat this as alpha 1 and treat this as alpha 2, and take what is the free energy of the mixture of this alpha 1 plus alpha 2, that free energy mixture, will always be identified, by joining a line, between those two spots. If I enlarge this for you, so, let us say, let us enlarge this portion, I am talking of an alloy composition somewhere here. So this is the composition; it is splitting into two. Just for the sake of understanding, I drew it this way; actually it is a straight line. Assume it to be a straight line. So, this straight line which is joining these two spots: one is alpha 1 composition, another is alpha 2 composition. The free energy of such a mixture is this. So if alpha splits into two compositions, of alpha 1 and alpha 2, the free energy, there is an increase in the free energy. So obviously, this alpha will not give alpha 1 plus alpha 2, by this process of splitting.

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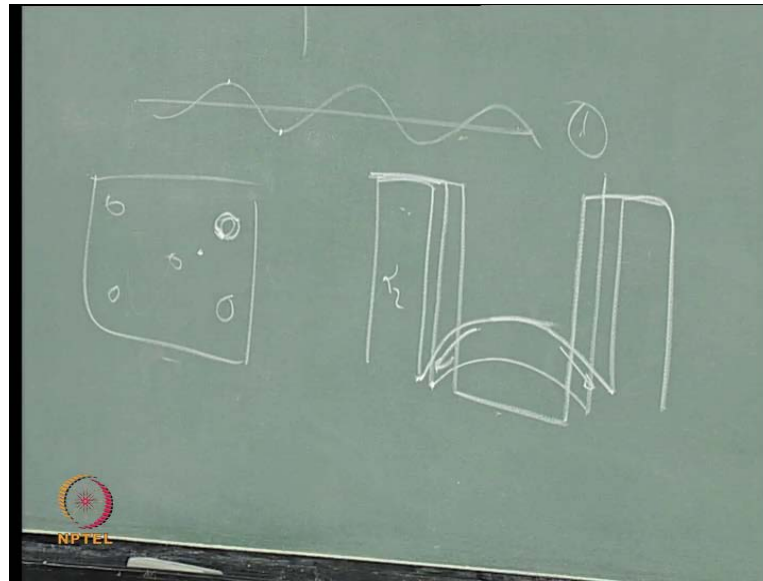


Then what is the way it can give you, it can finally give you, alpha one plus alpha 2? Because it cannot remain as alpha. Alpha is not stable at that temperature. So, alpha somehow wants to become, alpha 1 plus alpha 2. How does that happen? To understand that, what you have to do is, at this particular composition, if I draw a tangent: let us say I draw a tangent, for that alloy composition. Once I draw a tangent, I see that, the compositions that can nucleate from alpha, that can come out of alpha, which is stable, are only those compositions, which are beyond this point.

Once it is beyond that point, all the free energies are below the tangent. **That means, there is a driving force for such a, that means, the only composition that can, and** if you take any composition, which is near to that alloy composition: all the compositions near to the alloy composition are always above the tangent. That means, the only way the alpha can become a stable state is, that, it can precipitate something else, whose composition is far off from its original composition.

And if something is coming out which has a composition, far off from the original composition, that can only happen by a nucleation growth. So that means, this alpha 2, of different-different compositions, can actually nucleate. And then the question is, which one you will nucleate? Always the one, with the highest driving force will try to nucleate.

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So that means, inside the alpha, there will be compositional fluctuations taking place at a particular temperature. And in a small region, the B atoms come nearer, in such a way that, once their composition becomes that of this, suddenly, that particular region becomes alpha 2.

And that alpha 2, which gets nucleated here and there, now, it starts growing. Growing how? By the atoms, solute atoms, joining from the matrix to the precipitate. And this is exactly similar to our precipitation process, where we are talking of theta coming out or beta coming out from alpha. Exactly similarly, here, the only difference between this process, and what we talked about precipitation, is what? There, the second phase that is coming out, would possibly have a different composition, different structure. Theta, or some beta, coming out of alpha, is a different structure.

Here, the second phase that is coming out, will have the same structure as the first phase, so, there is not major problem, in terms of coherency problems. Okay? The only coherency problem comes is, only because, this lattice parameter is different. So, the strain will be different. Structure is the same; lattice parameter is different. So the strain is still involved. And, the interfacial energy problems will not be there much, because the structure is the same. So it is alpha nucleating inside another alpha. FCC nucleating inside another FCC. Excepting the strain energy, surface energy problem will not be

there for it. So, it will nucleate at some regions: could be grain boundaries, could be within the grain.

Usually, it occurs at the grain boundaries, because they are a high energy region. And that, when it nucleates, then, the moment it nucleates, you will see the situation is something like this. The moment alpha 2 nucleates, then the alpha which is adjacent to that alpha 2, can only have this composition. Because the moment alpha 2 nucleates inside, the alpha which is surrounding that alpha 2 has to be in equilibrium with alpha 2. That is why, that alpha will immediately change its composition. And this is also physically easy to understand, because, we said all the atoms, the solute atoms from a small region have come together, and become rich in the solute, and then alpha 2 has precipitated out.

So, surrounding that alpha 2 obviously, the solute atoms get depleted. And that is how, you see, that, this alpha 2, the moment it comes out, the alpha around it, will have a lower composition, in comparison to, the alpha which is far away from here. So, if this alpha 2 will have a lower composition, alpha here, will have the starting composition which is, we called it as alloy 1.

And this is exactly similar to precipitation that we have seen. The only difference being, that the structure of alpha 2, is same as that of this. And, in fact, if you look at the G-P zones, G-P zones situation is exactly like there. There also, the structure of the G-P zones is same as that as the matrix. There, the problem is, because the equilibrium phase is not able to come out, being a different structure so, G-P zones which are the transient phases that are coming out. Here the equilibrium phase itself comes out, but the equilibrium phase has a composition far away from the parent phase that you are starting with.

So, if you see one more precipitate somewhere here, you will see, this kind of a situation. You have one precipitate, another precipitate, between these two, the alpha will have a higher composition, similar to that of the alloy composition. But near the precipitate, the composition is small. And if this happens at time T equal to 0, as a function of time if you see, slowly the atoms, solute atoms start moving in this direction.

And, what would be the result? There are two results: one, alpha 2 size increases; second is, the composition of alpha, within the matrix will come down. So that means, you will see, slowly this would grow, and this composition would not change; this composition is

fixed for the temperature. And, only thing is, you would see, that this would decrease. And, slowly, after sometime, it could become something like this.

So the alpha 1, the alpha, with which you have started, has actually got converted to what is called alpha 1 now. Between the two alpha 2s, what would remain is what is called alpha 1, which was originally called alpha. So, this would have a lower composition, this would have a higher composition. You will have a matrix of alpha one, inside which, you will have precipitates of alpha 2. That is how the whole micro structure look like, after the whole process is finished.

This is for the alloy 1. Clear? If I now chose alloy 2; alloy 2, would undergo the same decomposition, in an entirely different fashion. The reason is simple. Now, I do not have the situation like this. I have, alloy 2 is falling within the Spinodal. Am I right? So, the composition that I am choosing, is between the 2 Spinodal points. Right? So, then I can say that this alloy is, within the Spinodal, whereas alloy 1 is, outside the Spinodal, for that particular temperature. So, if it is within the Spinodal, that means my alloy composition is somewhere here, wherever it is, somewhere between the 2 Spinodal.

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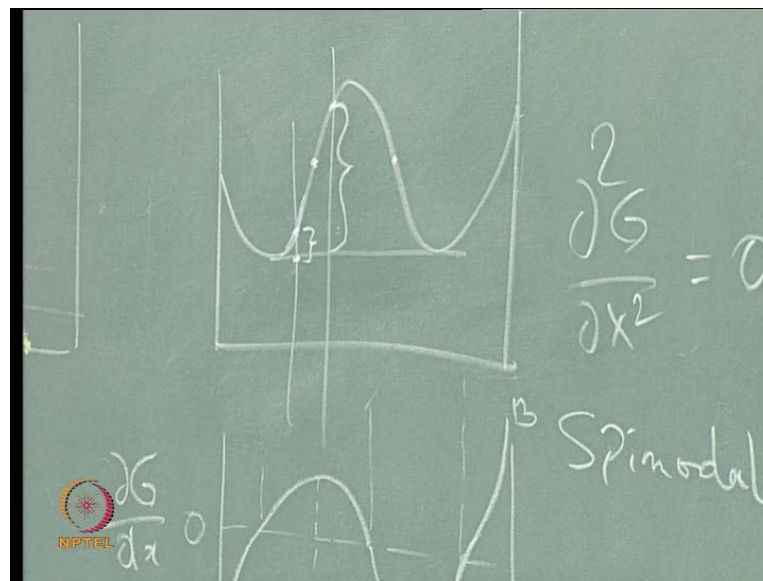


That means, my alloy composition, if these are the two Spinodal points, my alloy composition is somewhere here. If that is the case, in the free energy curve, then this one, for it to split into 2 phases, is very easy. That means, if I draw a tangent, at that composition, **if I draw a tangent at that composition**, the compositions which are adjacent

to that alloy composition, can nucleate, because there is a driving force. Any composition.

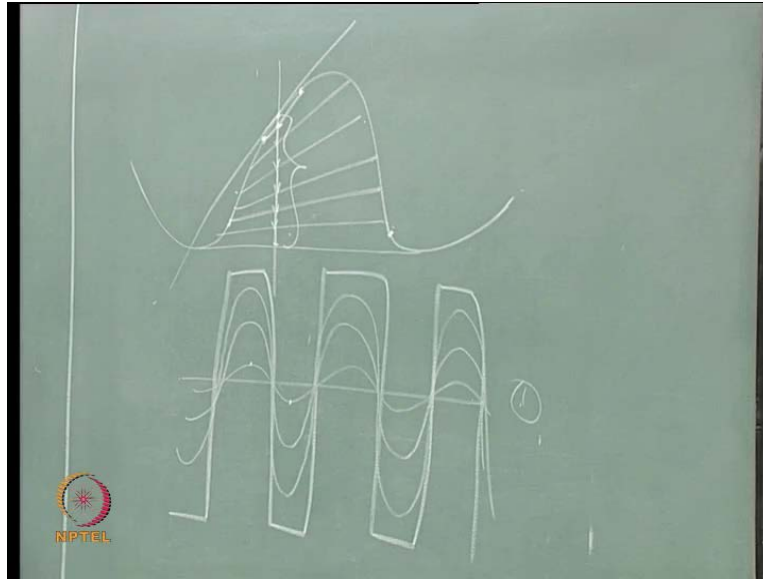
So if I draw a tangent here, to that alloy composition, any small deviation from this alloy composition, has a lower free energy, with respect to the tangent. And that is the reason why, a small fluctuation like this, with one region becoming depleted in solute, another region becoming enriched in solute, can be stable: because that would cause a decrease in the free energy, with respect to the alloy.

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But if you remember the overall driving force, if I again redraw this, for your sake. We have chosen one alloy which, these are the two Spinodal points; we have chosen one alloy, in which, we said the driving force is this. This is the driving force. In the other alloy, which we have chosen here, the driving force for decomposition is this. The overall driving force is very large. Not only that overall driving force is very large, but also, because the composition is falling within the Spinodal, a small fluctuation, in the composition, can be a stable.

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And then, this fluctuation will start growing further and further, until, the composition reaches that. So, it starts with a small fluctuation, and both the fluctuations start becoming bigger and bigger, at every stage there is a decrease in the free energy, and the final driving force is reached, as a function of time.

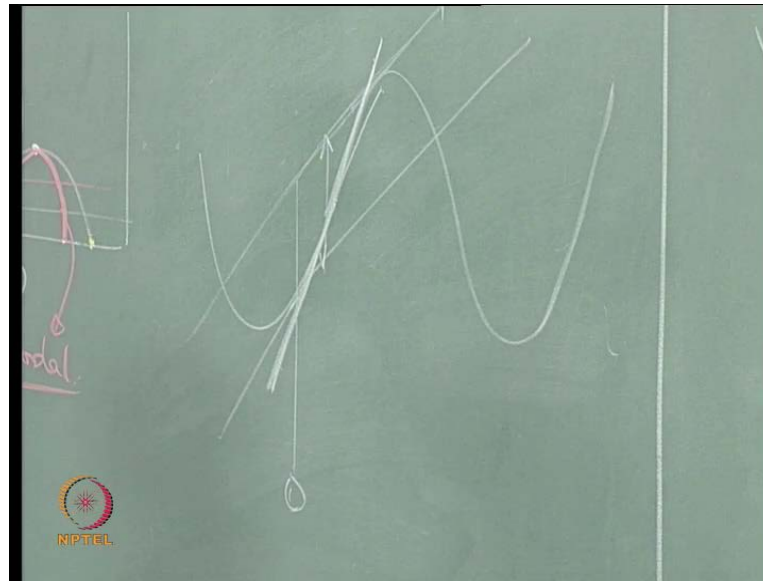
And, as a result, you can see, this fluctuation grows and grows. The wave length is, whatever is the initial wave length. **So, the composition** once there is some wave that is created, that wave depends on that diffusivity at that particular temperature. Once certain wave is created, certain fluctuation wave is created, that wave length gets fixed and **the** only the amplitude changes. Because the atomic gems, at any given temperature, are fixed. Depends on the structure, and also depends on the temperature.

So, once the atomic gems are fixed, then this wave length gets fixed. It depends on that particular temperature. And for the particular structure, whatever structure that we are talking about. And once that happens, you will see that this happens. And finally, you will see that this. If you compare this with the previous one, the final stage is the same in both the cases. The only difference is, the distance between the two precipitates in a normal case of alloy 1, could be much larger.

And this, the precipitate, I mean if I want to call them as precipitates, they are not really precipitate, the second phase that is nucleating out of it, can be precipitating: can be forming at the grain boundaries, or some high energy regions. Whereas here, everything

happens homogeneously, within a material. And, there is no activation barrier for that. That is why we say, in Spinodal decomposition there is no activation barrier. Because it is a small fluctuation, thermal fluctuations at any temperature, will take place, and as a result, there is no activation barrier for this. And in fact, there is way to calculate the activation barrier also, I mean measure the activation barrier, people do it regularly.

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For example, if I can show you that. One way to show the activation barrier is: if you have a region like this, if I take an alloy of this composition; draw a tangent, for this alloy, this alloy is, let us call it as alloy 1, which is outside the Spinodal. And, if you want to see, what is the activation barrier, for the nucleation for this alloy: activation barrier, usually people obtain, by drawing a parallel, to this tangent.

If you draw a parallel to this tangent, so that you get another tangent which is, touching one of the compositions, the distance between, the vertical distance between these two, would indicate the activation barrier. One can derive this, okay, let us not go into the greater details of it, but, that gives you an idea of what is activation barrier. And as you shift your composition, towards the Spinodal: if this is the Spinodal, at the Spinodal, if you draw a tangent, okay, again try to find out the parallel to that, you would see that the distance vanishes to 0; because, at this point, it is not inside, it will be outside. It will be something like that. Okay.

So, as a result, both the tangents will actually merge into each other. So, you would see that, this distance, as I go from here to here, it will keep on decreasing and finally it merges. That is one way to graphically show that. **But physically we can easily understand, that activation energy does not,** whatever activation energy that is there for diffusion, will still remain. Okay. Because diffusion has to take place. So, that activation energy will be there, but there is no activation energy for the nucleation of the phases, because there nothing nucleating. This is not a nucleation event, unlike the alloy 1 case, where, something has to nucleate. And, its composition is entirely different from this. So, all the atoms have to travel. So, there is a lot of diffusion that is involved, long range diffusion that is involved. Here it is all short range diffusion. And as a result, the activation energy for this is 0.

So, that is how, you see a Spinodal and, as a result, even in the micro structure also, would look entirely different. A Spinodal decomposed micro structure, if you carefully observe, it will be homogeneously distributed; different you know gray levels. One is slightly higher composition, as there is, if you really try to etch the surface let us say, with some etchant, and if this etchant is sensitive to the composition, you will be able to see the gray and darker regions, inside the thing on a very, very, very small scale, nano scale. Obviously, you do not have an optical microscope to show that, so, the only way we do is, we go to an electron microscope. In an electron microscope, how do I differentiate different regions of different? Of course, yeah, if you can use a CM, scanning electron microscope, luckily now we have SCMs that are available which can really go the nano meter levels, which are called **feggus** CMs. Otherwise the older generation SCMs, you would not be able to see, really a ten nano meter kind of a modulation inside, you will not be able to see. Whereas, in **feggus** CM it is possible.

But, if you want to go to a, transmission electron microscope, and try to see, how do you see? **Where does the, where does the contrast comes,** where does the contrast come from, in a transmission electron microscope? Anybody did any course on microscopy? No? Nobody knows? Why do you see some contrast in a in a TEM. Why some regions look black, why some regions look white? There are two types of scattering, in an electron microscope, in a TEM. One is called diffraction contrast, okay; another is called phase contrast, okay. Diffraction contrast comes, wherever you are the atomic plane, in that particular phase, is properly oriented with respect to the beam, such that the Bragg's law

is satisfied, it gives you a dark region, because it gets diffracted. Otherwise, there is another way to look at it, which is what is called the phase contrast, where you see the regions, which have a different composition. The moment you have a different composition, obviously, it also means, that it has different concentration of electrons.

For example, if you take an aluminum copper region. One is aluminum rich region, another is copper rich region. Copper has different valence electrons, aluminum has different valence electrons. So, as a result, the region where you have, copper rich regions, will have different electron concentration. If there is a different electron concentration, the electrons beam which is going through, gets scattered by the electrons present inside that. So, as a result, wherever you have more electrons, that region looks darker, wherever you have less electrons, that region looks brighter. So, you will be able to see that, on a very small scale.

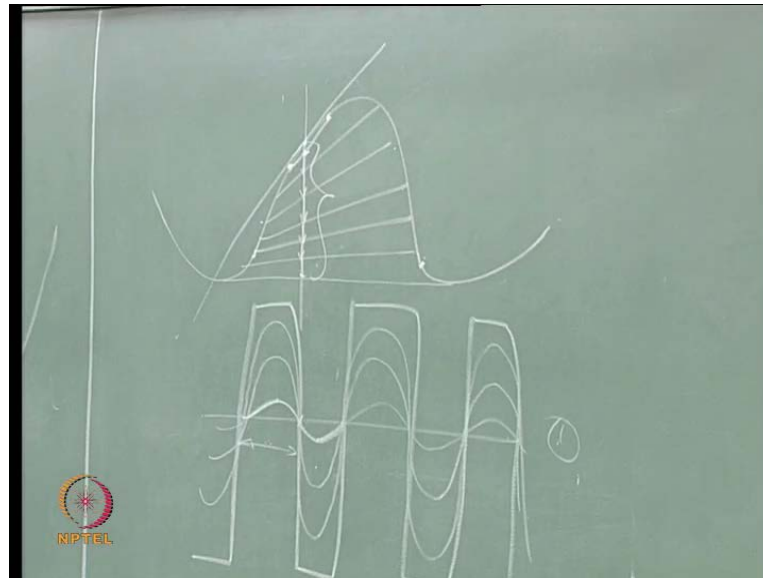
So, in TEM, one can easily observe such kind of modulations. Even at an early stage, you will be able to see, before the whole wave grows to the final stage. But once it goes to the final stage, it almost looks like a precipitates inside a matrix. But these precipitates, the only difference between the alloy 1 and alloy 2 is, they will be uniformly distributed, within the grain, within the grain. It is almost like, normal precipitation happening within the grain. Excepting that, a normal precipitation and this also are different. In which way they will be different?

A precipitation that we talked about it, where G-P zones first come, and then you have a theta double prime, theta prime and finally it becomes theta. If you look at that micro structure and a Spinodal micro structure, would you be able to see some difference? Shape, perfectly, yes. Most of the cases, this kind of Spinodal decomposition would be, more or less like, it is a, you would not be able to see the borders. The interphase is not very, very sharp. The interphase is sharp there, because there is a different structure that comes out.

So, will be able to see the differences very easily, because the interphases are not sharper, and the structures are same. You can easily do the diffraction from both the regions, and be able to see, that this is, both the phases have the exactly the same structure. Anyway, in case of actually, a normal precipitate, the moment G-P zones grow to theta double prime, immediately the structure changes. And, at the G-P zones stage,

you will not be able to see anything. The only way to see is, by the strain contrast. Because the strain, there is a lattice strain associated with that, and that is what we will see in a minute here also, there is a strain at that is associated.

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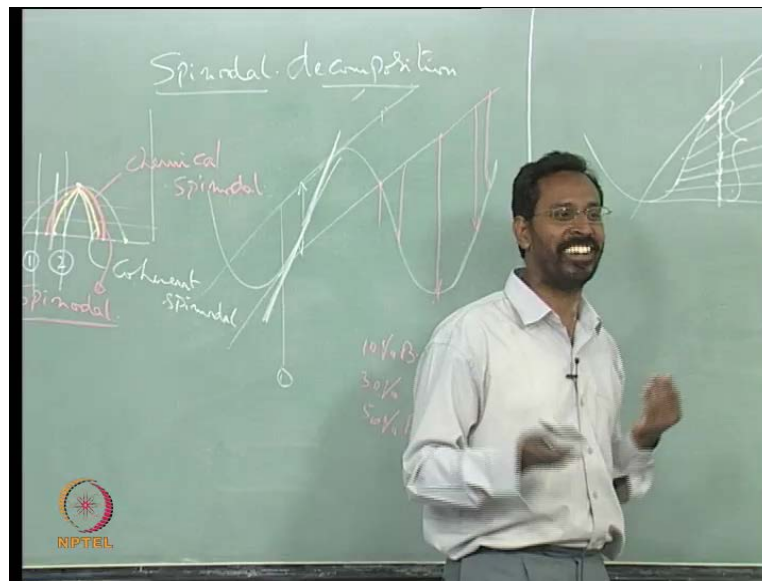
The moment you talk about a different composition, **the moment you talk about a different composition**, different composition means different lattice parameter. Am I right? So, that means, in a particular region: this region will have a different lattice parameter; in fact, this lattice parameter in this region also, is changing as a function of distance, because the composition is changing.

Similarly, in this also the composition is changing. So, as a result this region and this region, there will always be, at the interphase, some kind of strain. This is what we call it as coherency strains, similar to what we talk about coherency strains in precipitation. And because of this coherency strains, though you have a driving force, for the alpha to split into two, the coherency strains would be a barrier for this split. As a result, usually, just because I have brought an alloy, to within the Spinodal, does not mean that always this alloy will undergo Spinodal decomposition.

So, you need an extra energy. That means, you need a higher under cooling. If you provide sufficient under cooling then, you will have a sufficient driving force, for this alloy to split into two, by Spinodal decomposition. And as a result, you will always see that there is another curve, which we usually refer to as Coherent Spinodal curve. That

means, if I take this alloy 2, in principle, the moment I reach below this particular point, Spinodal decomposition should start. But just because I have reached this point, Spinodal decomposition does not start. Unless, you come to another point, here, where you have sufficient driving force, to be able to take care of the coherency strains.

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So, unless you come below this particular point, you will not be able to see the Spinodal decomposition taking place. So, there is a separate curve, a Spinodal curve, which takes into account the coherency strains and that particular Spinodal curve, is what we call it as a Coherent Spinodal curve. And, in contrast, this particular curve is what is called Chemical Spinodal. Because, there, you are only looking at composition, you are not considering any strains there. So, this Chemical Spinodal is something which comes simply from $\text{d}^2G/\text{d}X^2 = 0$.

So, that is the Chemical Spinodal, and there, if you add the strain energy contribution, then, you will see that the free energy expression itself you have to change now. The free energy curve actually, because of the strain goes up, and then you would see, this comes down. And, as a result, in principle, there may be cases for example, if now carefully chose an alloy like this let us say, somewhere between the Chemical Spinodal and Coherent Spinodal. **That alloy, if I bring it to room temperature, though I have brought it to room temperature, because it is between the two Spinodals, it may not undergo**

Spinodal decomposition, until, you bring it to a sub 0 temperature, so that, it crosses the Coherent Spinodal, and then only Spinodal decomposition will take place.

Then, what should happen to this alloy? This alloy also, would undergo a decomposition like alloy 1. Though, you are inside the Spinodal, it will not undergo a Spinodal decomposition, because of the strains that are involved. If the strains are very large, then it would prefer, rather than going through a Spinodal decomposition, it would prefer nucleating an alpha 2, which has a different composition and then growth of that alpha 2, rather than a Spinodal decomposition.

So, that is why we need to have an understanding of this Coherent Spinodal. And this Coherent Spinodal, basically, the extent of which, whether it is very close to the Chemical Spinodal or far off from the Chemical Spinodal? Because in some systems, the Coherent Spinodal can even, be something like this: far away from the Chemical Spinodal. Why? It depends on, how much is the strain energy. For each system, as the lattice parameter changes the strain changes. The rate of change of strain, with the lattice parameter, decides the position of the Coherent Spinodal.

In some systems, the **this** strain energy may be very small. In such a case Coherent Spinodal and Chemical Spinodal will be almost close to each other, you will not be able differentiate them. So, that is how, we need to have an understanding of the strain energy term, in a particular system and it depends on different-different crystal structures it will be different, and that gives you an idea of what is this Spinodal. So, and once you are within the Spinodal, the Spinodal decomposition takes place. Okay.

We will stop with this, and then continue later. Any doubts here? So far whatever we have said. You may ask me, what is the use of this Spinodal decomposition. In fact, people do not want Spinodal decomposition to take place. The reason is the moment you have Spinodal decomposition, the alloy splits into two compositions. So, people want to avoid Spinodal decomposition. So, they want to chose those systems, where there is no miscibility gap, or chose alloy compositions, which do not fall into this Spinodal decomposition. So that you can have a precipitation taking place, rather than, overall composition is splitting into two.

That means, in a small scale, you have composition, the properties are going to be different. So, you have an inhomogeneous property inside the material. It depends. Of

course, one it can be useful, but then strengthening mechanism, as a Spinodal decomposition may not be really a strengthening, because it is also a solid solution. It is not a, basically alpha is splitting into alpha 1 plus alpha 2, both are FCC. So, the alpha 2 that is coming out, is not a hard phase any way. It is a solid solution; does not give you an exceptional high strength.

So instead, you chose a particular system, where you have a precipitate with a different structure coming out, that can give you a higher strengthening. Yeah. How does it choose the composition? So, as I told you, when you draw a tangent, it can have all this composition possible. Out of these compositions, there are two problems. One is, it wants to choose, let us say, one with the highest driving force. Because, obviously, this is the highest. As you go to higher, you can see that this height keeps on decreasing. Here also the height is smaller. But there is a problem for this to come out. In principle, this alloy, this particular phase, a phase which is close to this composition, should come out, because, the amount of deviation from the alloy composition that is needed, for this phase to come is smaller, than the amount of deviation that is required for this. That means, if this, if you are starting from an alloy composition of let us say ten percent of B, if this is let us say thirty percent B, and if this is 50 percent B, let us say.

So that means, as the atoms accumulate in a small region, and only the moment 30 percent accumulate, in principle that is enough for the beta to nucleate, beta or alpha 2 to nucleate. Here, you need more accumulation to happen. That means atoms have to come together more, to be able to do that. But, this will always have the highest driving force, because the driving force is higher. And, thermal fluctuations always anyway take place. So, because the driving force is higher, if you remember, the nucleation kinetics, the ΔG^* , is inversely proportional to the driving force. Inversely proportional to the square of the driving force. So, as a result, you would see, that this would tend to form. Obviously, if you look from the point of view of only the thermal movement, the atomic vibration alone, this is true. Okay. Isn't it?

So, if you simply look at only from the atom view of atomic movement, it is fine. But if you look at, what is the R^* star, for this thirty percent; what is the R^* star, for the 50 percent? R^* star for the 50 percent will be smallest, because the ΔG is larger, R^* star is smaller. So, you need a bigger R^* star, if thirty percent has to nucleate. You need a smaller R^* star, if 50 percent has to nucleate. Though you know it is like a, you know kind

of managing, you need a greater deviation, but the extent of the greater deviation, a smaller is enough. So, the system would choose that one. So, it is a very, very interesting situation, if you look at it. I do not know how really system chooses, at least to understand it is really interesting. Okay, we will stop here.