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Phase field modelling: The materials science, Mathematics and Computational aspects

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Module No.3
Lecture No.15
Regions of stability

Welcome we were trying to quantitatively derive the change in some thermo dynamic quantity, when you are trying to produce two phase mixture, okay so let us look at this diagram,

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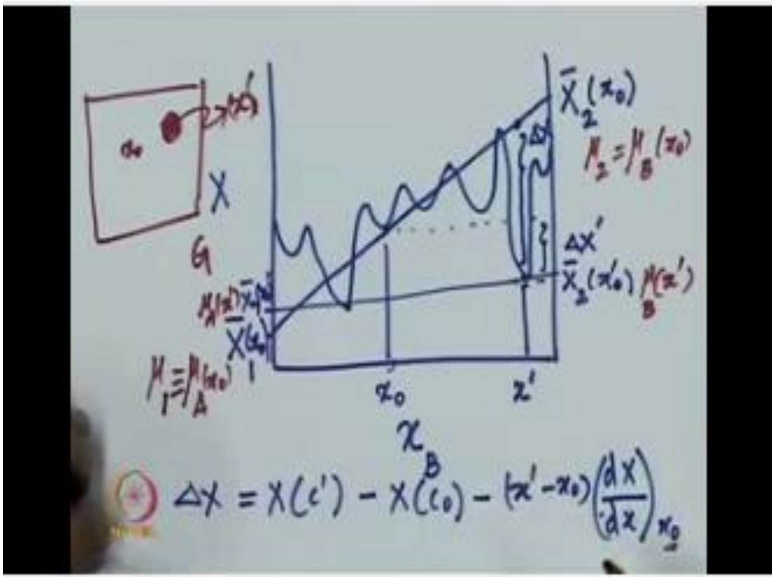

A which I drew earlier, so there was this property called X at some point we are going to say that this property is nothing but the free energy, and the partial molar property that is if you that the property curve and if you draw a tangent that at some particular composition then the partial molar property for that composition will be given by the Y intercept, so that is $\bar{X}_1$, $\bar{X}_2$, later if this X becomes G, then this becomes nothing but μ 1, or the same as μ A, the chemical potential and this is going to become μ 2, or μ B.

At this composition X_0 okay, so this is at composition X_0, if I draw another line at some other composition then that is μ at that composition, will be similarly become μ A at that composition XY, so what is that we are trying to do we are going to take a large amount of material, with the overall composition X_0, and then I am going to produces small region, which has the composition x`, okay.

So I am going to take a large amount of material with over all composition X_0, from there I am going to take some A atoms and B atoms and I am going to produce as a region which has the composition x`, what we showed in the previous section of this lecture, is that the change in the property associated with this exercise the Δ , is nothing but, X(c`) – x(C_0) , because from C_0 we are producing the C`-(x`-x_0) times, rate of change of property with respect to composition calculated for the overall composition which are trying to produce material, okay.

So dx/dx calculated at X_0, multiplying the difference in composition, that also has to be subtracted, wise this Δ x, not this but this, that is because we are dealing with the closed system and I am trying to take from a material of composition X_0 some A and B atoms, if I try to remove then the free energy change associated with that is related to this chemical potentials or the property changes associated with that will be given by this partial molar quantities.

So that I have accounted for and I have derived this, okay now let us proceed a little bit further and let us do a, different computation let us say that I have this property X,

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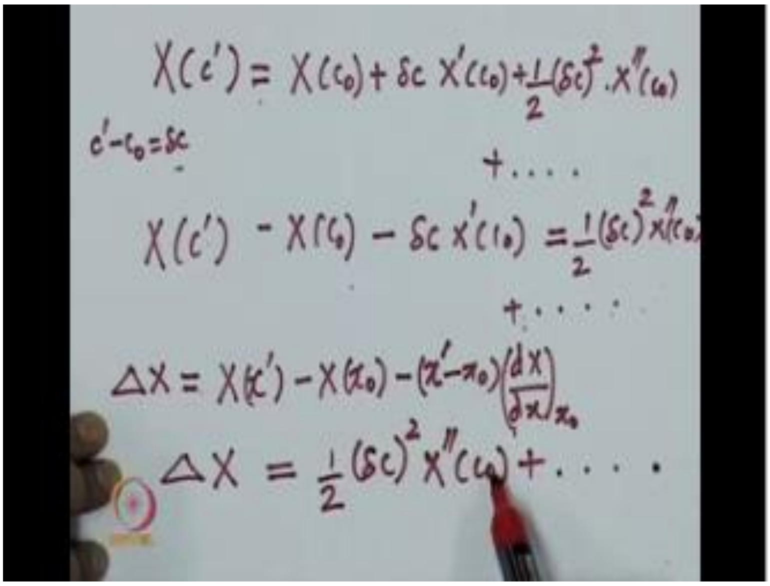

$$X(c') = X(c_0) + \delta c\, X'(c_0) + \frac{1}{2}(\delta c)^2 . X''(c_0)$$
$$+ \ldots .$$
$$c' - c_0 = \delta c$$
$$X(c') - X(c_0) - \delta c\, X'(c_0) = \frac{1}{2}(\delta c)^2 X''(c_0)$$
$$+ \ldots .$$
$$\Delta X = X(c') - X(x_0) - (x' - x_0)\left(\frac{dX}{dx}\right)_{x_0}$$
$$\Delta X = \frac{1}{2}(\delta c)^2 X''(c_0) + \ldots .$$

And I am trying to calculate this property at the composition C` okay, now if I assume that the difference between C` and C_0 right, is very small some Δ c, if I assume this then I know that I can do a Taylors series expansion, okay what does the Taylor series expansion give me? It will give me X (c_0) +Δ c times x`(c_0)+1/2! That is to Δ c^2 x``$c_{0+\ldots,}$ okay.

So what is this? So if I want to get the property x at some compositions c`, and if I assume that this property that I am trying to evaluate at a composition which is close to the initial composition that I started with, then I am allow to do this Taylors series expansion, okay from this Taylors series expansion, one can see that X (c`) –X(c_0) -δ c X`(c_0)=1/2 (δ $c^{2)}$X`` $C_{0+\ldots.,}$ now let us recall the expression that we derived, in the earlier case we said that the

Change in free energy associated with making some quantity with composition C` from a solution of composition $C_{0,}$ was nothing but X(c`)-X(c_0) –(x`-$x_{0)}$ okay (dx/dx) $_{X0,}$ okay.

So compare this to what is X_0 here C_0 here? So this was at $x_{0,}$x`,$x_0$ x`-$x_{0,}$ so whatever x` and $x_0$ i have called it as c` and c_0 and x`-$x_0$, that is nothing but Δ c okay, so if you compare these two expressions , you see that the change in the property associated with producing some quantity with composition x` from s solution of composition x_0, is nothing but ½ (δ c^2)X``($C_0$)+....., okay now if this δ c is very small that higher order terms can be neglected you can see that to first approximation, the change in property, is nothing but ½ (δ $c^2$$_{)X``(C0).}$What is that mean? That means the following, okay so I have this

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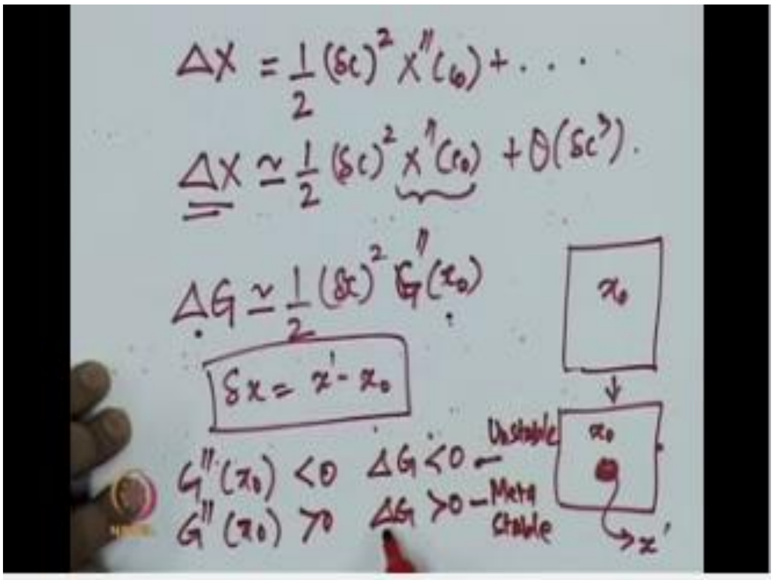

Quantity Δ X =1/2(δ c^2) so it doesn’t matter what the sign of δ c is, I choose the compositions so let us look at this diagram again, I choose this $x_{0,}$ and I choose the x to be right of this, which means when you take x`-$x_0$ it will be positive, I could have been chosen it on this side, okay for example some point here then x`-$x_0$will be negative, but weather it is to the left or to the right does not matter, because this quantity squared, so its sine is always going to be positive, and then I have x`` evaluated at $c_0$ + higher order terms, so if I take approximately, okay let me through away all the higher order terms this is nothing but δ $c^2$x``(C_0)+(δ c^3) right so there are higher order terms 1/3!(δ c^3) x```, x_0, and so on.

So let me not worry about this order of δ c^3, because i am going to choose δ c , so small the δ c^3 is negligible, δ c^2 is the only term, now you can see that the sine of x``(c_0) decides to what the sine of this Δ X is going to do, okay let me also now switch because this is any general thermo dynamic property let me say that I am looking at the free energy, then Δ G okay, the free energy change associated with producing from a solution of X_0 right? I am going to produce the solution of X_0.

But the small region which has the composition x`, right from a solution of $x_0$, I am going to produce something which is at $X_0$ and a small region with composition x`, if I try to do that, then this is nothing but ½, δ C^2, okay which is the change X_0-$x`^2$ and x``, so this case will become G``, evaluated at the composition $c_{0,}$ evaluate at the composition x_0, okay so this δ c also let me call it as Δ x, where Δ x is defined as x`-x_0.

So what is this mean? The change I free energy the sine is given by the second derivative of the free energy with respect to composition at that point which is the initial starting alloy, so if take this initial starting alloy if I find out in the free energy versus composition diagram, what is the curvature? Okay and that curvature evaluated at this for this system at composition x_0, its sine is going to decide where this the sign of the Δ G is going to do.

Suppose G``$X_0$ <0 $\Delta$ G <0, that means the system is unstable, because by producing this, the system can reduce its free energies so it is going to spontaneously do that, on the other hand if G`` x_0>0 Δ G>0, that means the system is going to be meta stable, because to produce something like this the system has to overcome this barrier, right so much of free energy increase, it has to account for so this is what we were discussing, using the mechanical analogy, what happened in the mechanical analogy we said that

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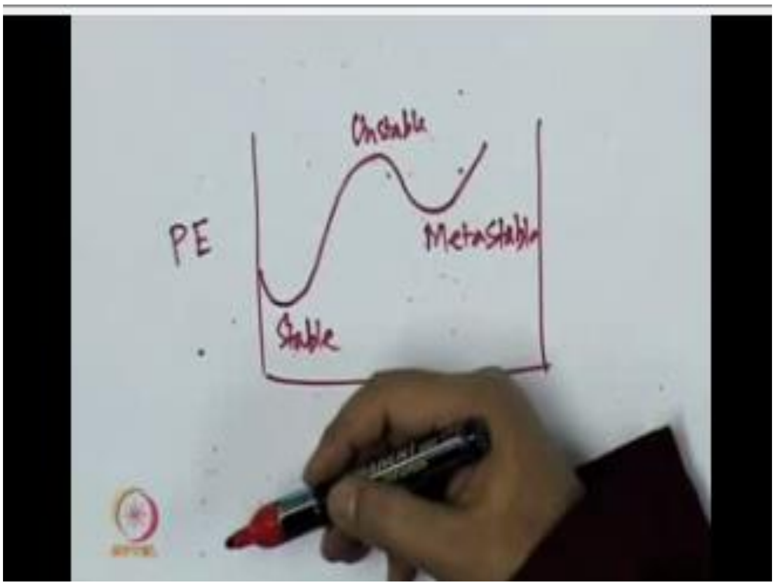

You know the potential energy curve for example, this was the mechanical energy so we were looking at the potential energy curve and we said that you know it can have regions like that, so we said that this is meta stable and this is unstable, and this stable, right this is meta stable, so for small changes the potential energy change is positive then it is meta stable.

For small changes the potential energy changes negative which means it is unstable, because spontaneously it will do that, so that it can reduce its potential energy, in a similar fashion when this quantity is positive the system has to overcome the barrier, right, from this meta stable state it is possible for it is possible for it to go to the stable state, for that it has to overcome this barrier.

Similarly in this case unless it overcomes this barrier the system is not going to be able to reduce its creativity, so then it will be meta stable state on the other hand when this is negative then the $\Delta G > 0$, so it is unstable, as you can see from the geocentric interpretation that we gave, so let’s go back to this curve

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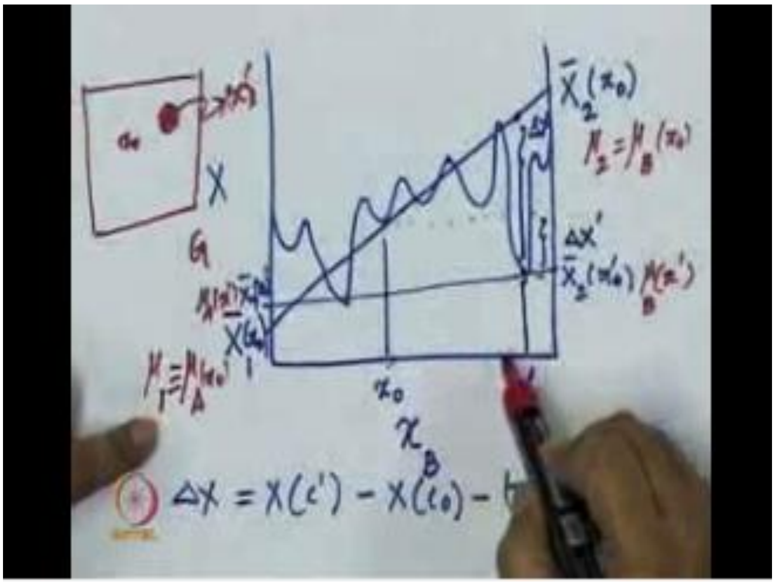

Which was the property versus composition curve, you can see that at any position if I draw a tangent for all the points which are lying below the tangent, this quantity is going to be negative, right? For all this points wherever right, this quantity is going to be for example here, right? Anywhere here, it’s going to be negative which means, the free energy change is going to be negative.

That means spontaneously the system will undergo, the transmission on the other hand for all the points which are above this line that we are drawn, the change because from here to here is going to be positive, that means the system is going to be meta stable with respect to those stage.

Okay so we are going to stop at this point so we have related the free energy change associated with infinite decimal fluctuations and we have derived it for a general case where we didn’t make an approximation, then we compared it with some infinite decimal fluctuations so that you can do a Taylor series expansion and you compare the two expressions and you see that the change in the property.

In this case the free energy associated with producing the two phase mixture from a solution of a given composition, where the second phase has a particular composition can be related to the second derivative of the free energy, with respective to composition and that quantity is known as curvature of the free energy versus composition curve.

So the curvature sine basically decides what is the free energy change, what happens when this curvature is 0 the free energy change associated with this is 0, okay so it doesn't have a tendency either to go this way or that way, so it will be struck there, that is the point that we drew as this denote the line in this diagram, that is why it is the line that it separates meta stable regions from stable region.

So its denote a line basically tells you that if you are inside this nodal energy, if you produce the two phase mixture that will spontaneously happen because the free energy reduces automatically, outside of it try to produces to phase mixture, then you have to come a barrier before you can produce a two phase mixture, so the system is meta stable, overcoming that barrier is through nucleation, so outside this nodal the mechanism of two phase formation is by nucleation followed by growth.

And growth is controlled by are described by the fix laws, right growth is described by the diffusion equation, on the other hand inside the free nodal region you have skipped this first step, it doesn't have to overcome any barriers, so there is no question of nucleation, everything is simply given by the diffusion equation.

Everything is like growth in the other case, so we are just looking at how this system is going to undergo this transformation from a single homogeneous phase to 2 phase mixture, the reason it happens spontaneously is because the free energy changes negative and that is what we have derived and shown, okay so in the next section of this lecture we will take a look at our regular solution free energy, and see what that means, thank you.

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