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Phase field modeling; the materials science, mathematics and computational aspects

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Module No.3
Lecture No.14
Thermodynamic property: composition dependence

Welcome in the last session we defined the spinodal line the spinodal line was defined as the point where the second derivative of the free energy with respect to composition becomes zero, that is the curvature of the free energy versus composition curve wherever it becomes zero for that temperature you will note those points down in the phase diagram and if you keep doing it at all temperatures then you get this spinodal line.

So we also said that the physical significance of the spinodal line is that it separates regions which are meta stable from regions which are unstable. So we are going to make this little bit more quantitative we are going to derive and show that the region where things become unstable is the spinodal region, okay so that is what we are going to try and do today, so for doing that let me start with some thermodynamic property we will later say that that the thermodynamic property is actually the Gibbs free energy.

But that let us do it later, so for now let us take a generic thermodynamic property which is represented by the symbol X as a function of composition, let us say that it has some very complicated relationship, okay.

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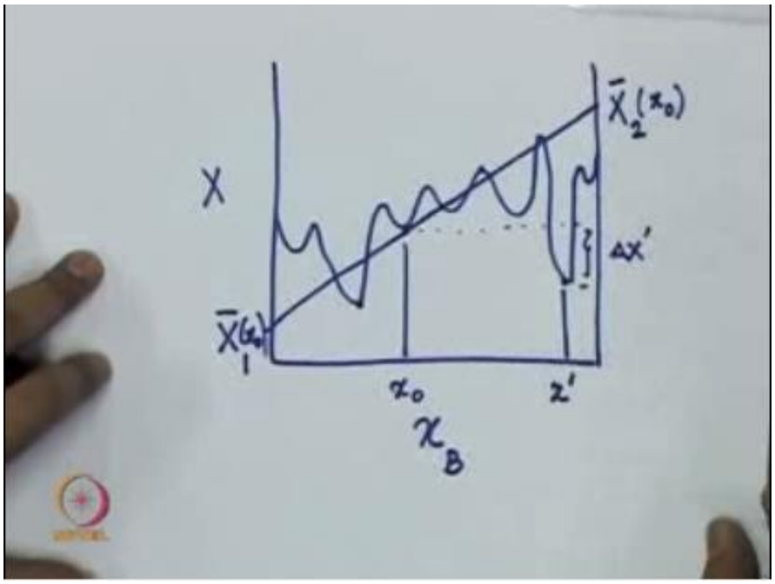

So the property versus composition diagram, so this is composition and this is the property, so let us say that it has some complex expression, something like this okay. So now I am going to choose a particular composition let me call it as x_0 and I am going to choose another composition let us say that that is some composition here for example or some compositions here for example okay, so let us consider this and let us call this composition as x′ for example, okay. So this derivation is again from the article of Hilliard, so we are going to start from this point okay, so I take a solution which is at the overall composition x_0 and let me produce some x′ from that composition.

If I ask you what is the change in the property x when you make this x′from x_0 and let us assume that the amount of x′that you are producing is so small and x_0 is solution is so large that solution composition remains at x_0, then one would think that the Nibelung the free energy difference will be given by this quantity, okay and let us say that say that is some $\Delta x'$, okay. But in a system like this, this is not actually the change in the property x because you are producing composition x' from x0 this will be if the system is open that is if you can take material from outside and produce then that is when this will be true.

But we are dealing with a closed system, right in such systems you have to account for the fact that you are dealing with a composition x_0 and when you add or remove A and B atoms from this composition then you are going to have changes in the property which are known as partial molar properties. If this was free energy that partial molar property would have been the chemical potential.

But we are talking about a generic property so there is a partial molar property which is given as we know by drawing a tangent to that point and the partial molar property for this composition x_1 is here, so let me denote the partial molar property by putting a line over that and similarly $\bar{x}_2$ of x_0 will be the partial molar property for this composition x0 because this is where it is cutting the y axis for the component 2, so these are A and B so this would be $\bar{x}_A$ and this is $\bar{x}_B$ for example.

So we are dealing with a binary system, so this partial molar property has to be accounted for when we are trying to see what is the change in the property x, because we are trying to form a small portion of x' composition from x_0 composition, x_0 is the solution. If you want to do that then we can calculate that quantity, so let us try and calculate that quantity that quantity is calculated as follows. So first we want to write the Δx.

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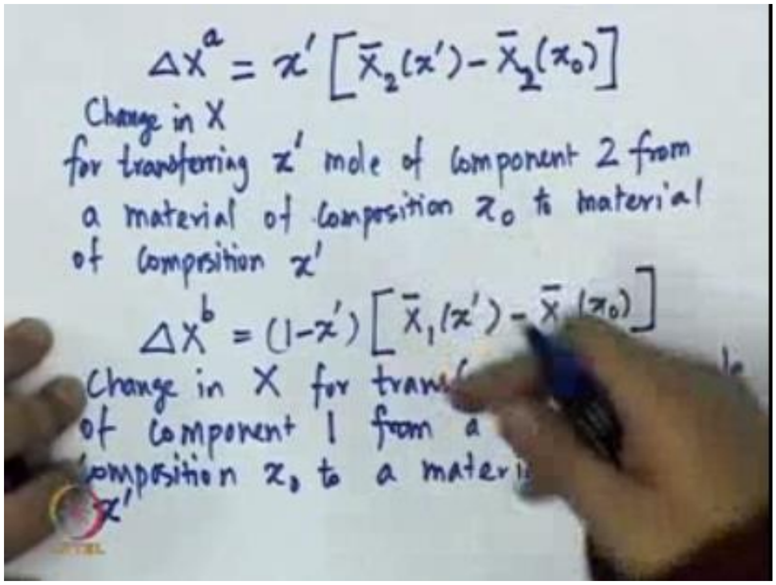

The change in property that is for transferring, so let me call this as ΔX^a so ΔX^a is given by $x[\bar{x}_2(x')-\bar{x}_2(x_0)]$ okay, so what does this represent, this represents the change in X for transferring x' mole of component 2 from a material of composition x_0 to materials of composition x' right, so this is what we mean by the partial molar properties when I am trying to take x' mole from a material of composition x_0 and if I added to a material of composite in x' the free energy changes associated the with this per atom changes associated in transferring the B atom is actually given by this quantity.

So the difference multiplied by the total number of atoms that you are transferring so that will be the free energy change associated with it. In a similar fashion let me call ΔX^b that will be given by $1-x'$ because remember this is a binary alloy so if it is x' this is $1-x'$ then $[\bar{x}_1(x')-\bar{x}_1(x_0)]$ this will be the change in the property for transferring, now we are transferring $1-x'$ mole of component 1 from a material of composition x_0 to a material of composition x'.

So the total change in the property associated the width of producing material of composition x' from a solution of composition x_0 is basically the addition of these two, okay.

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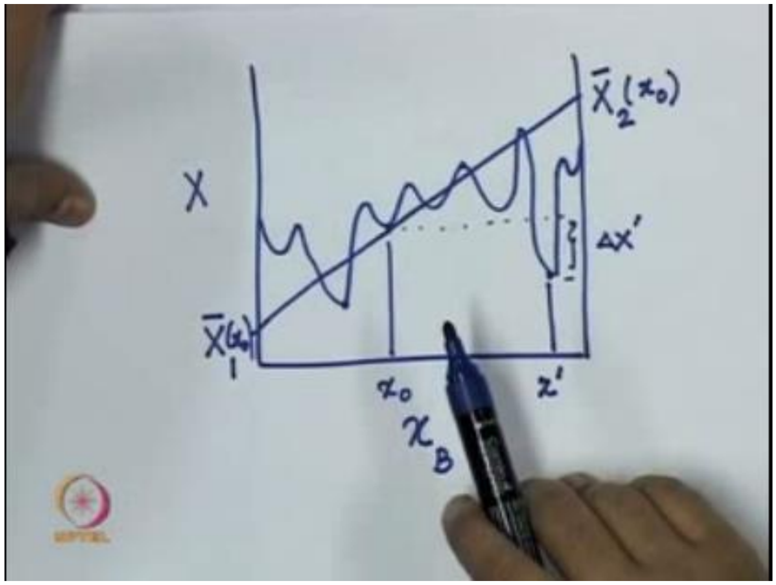

So if we then write the total change in the property, so that looks like this so that the total change in property ΔX is nothing but the ΔX^a that we wrote and the ΔX^b that we wrote that is nothing but $x[\bar{x}_2(x')-\bar{x}_2(x_0)]+(1-x')\ [\bar{x}_1(x')-\bar{x}_1(x_0)]$,okay. So again to go back to the initial picture we had so I am trying to take a solution of composition x_0 I am trying to produce some quantity of material of composition x' from here the amount that I am producing is so small that this overall composition remains the same.

If it is an open system the difference in the property X because of this will be just given by this difference, but we are in a closed system which means if you take or put A or B atoms at this composition the change in free energy is given by the intercepts along the y axis, for the tangent that is drawn at this point. Similarly, for this point you have to draw a tangent and where it cuts that will determine the changes in the property per atom that you add so that has to be accounted for when we are trying to calculate this change in the property X when you are trying to do this and so if you take the definition of partial molar quantities we find that you can write that expression.

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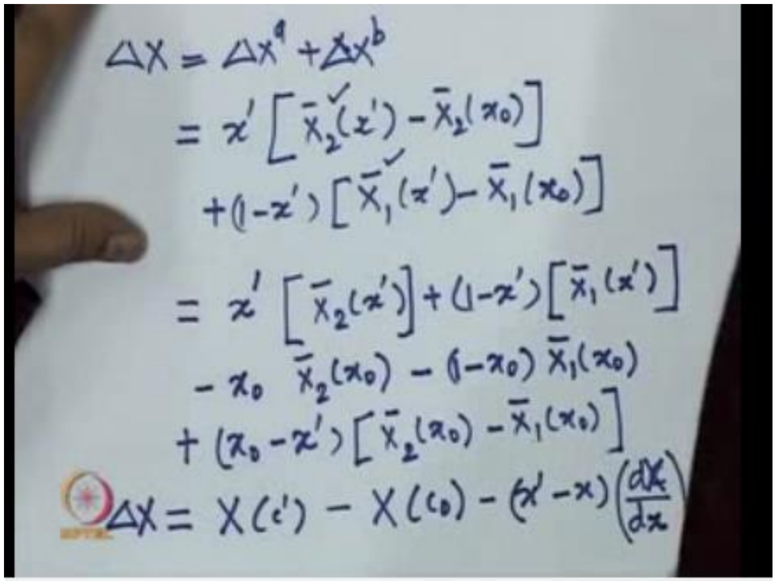

And that expression looks something like this, okay so it consists of two parts one is for taking the component to from a composition of x_0 and putting it to some composition x' and that is x' amount and $1-x'$ amount of component 1, if you take from a composition of x_0 and put it into x' so this is the quantity. So there is a little bit of algebra here, so let me simplify this and write this expression, so this expression can be simplified as follows. So let me take x' and let me take $\bar{x}_2(x')+$ so this is the term that I took and then this term.

So this $1-x'$ $[\bar{x}1(x')]$, okay so I multiplied this that is the first term I multiplied this, this is the second term. Now for the next term I am also going to write this so $-x_0$ x_0 $[\bar{x}_2(x_0)-(1-x_0)$ terms $\bar{x}_1(x_0)$, okay. So what did I do instead of multiplying $\bar{x}$ and $1-\bar{x}$ I have instead put x_0 and $1-x_0$ which means there is some more terms that we need to add to make sure that this goes back to that expression what is that $x_0-x'[\bar{x}_2(x_0)-\bar{x}_1(x_0)]$, okay.

So this $\bar{x}$ and that multiplied that term and this $1-\bar{x}$ when it multiplies those terms so they are all going to come here, so we are going to get this expression, okay. so why are we writing it like this to simplify the expression what does the expression simplify to you can see that this ΔX is nothing but what is this quantity this is nothing but the property X at the composition c', right what is this, this is nothing but the property X at the composition c_0 and what is this, this is nothing but x'-x_0 because remember $\bar{x}_2$-$\bar{x}_1$ what is this quantity, so you are taking at the two Y points and the difference and the composition access goes from 0 to 1.

So this part can be written as dc/dx at so sorry, DX/dx at composition x_0, right so this is nothing but the slope at x_0 if you take that will tell you the $\bar{x}_2$ $x'$is basically where the line cuts the y-axis for the component 2, this is nothing but where the line cuts of the y-axis at the pure A where x=0, so if you take the common tangent, the tangent at the position x_0 where it cuts the two lines.

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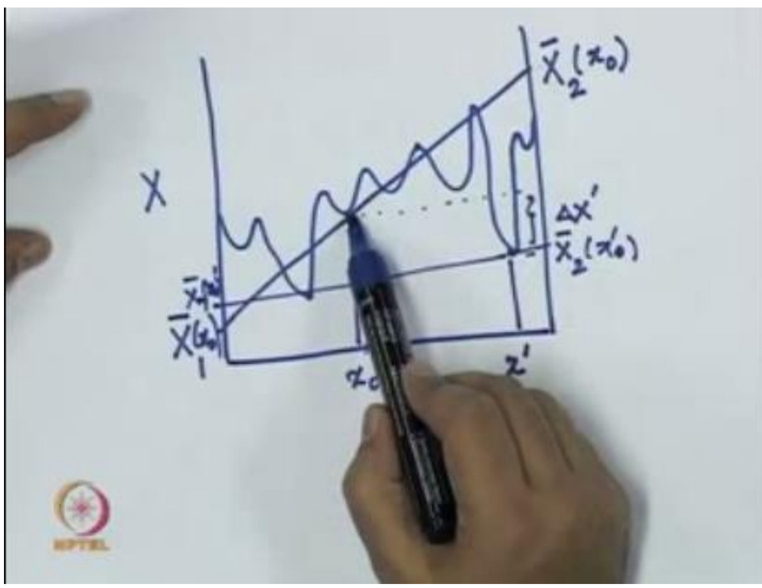

So let me go back here, so if I draw a tangent here so this will be $\bar{x}_2(x_0)$ and this will be $\bar{x}_1(x_0)$, right sorry so this will be x', I already have $\bar{x}_1(x_0)$ $\bar{x}_2(x_0)$ here, so if I take for x_0 the tangent where it cuts is $\bar{x}_2$ where it cuts is $\bar{x}_1$ so if I take this difference and divide by this because this goes from 0 to 1 so basically it is the slope of this curve at this point so that is what so we have done.

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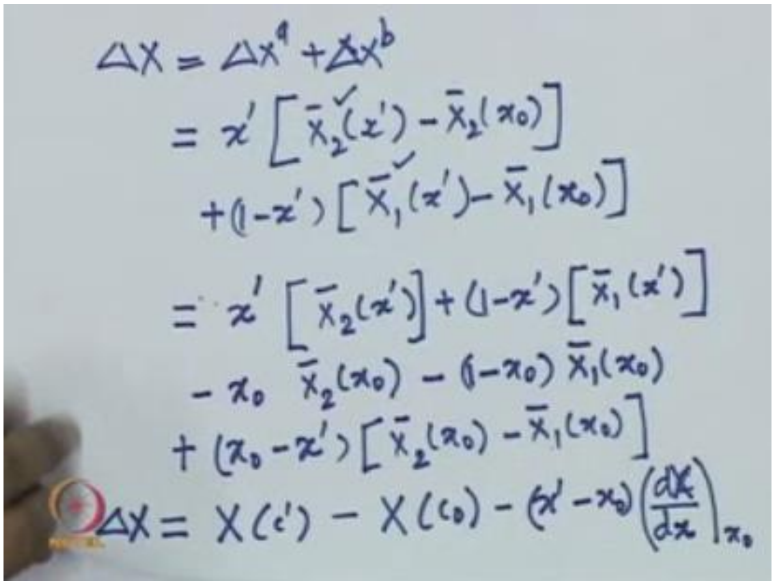

So $\bar{x}_2(x_0)$- $\bar{x}_1(x_0)$ is nothing but dX/dx at the point x_0 so I have switched the signs $\bar{x}_0$-x′ I have made it x′ - x_0 so there is a minus sign, okay. So this is the ΔX okay, now what does this correspond to as you can see from this figure.

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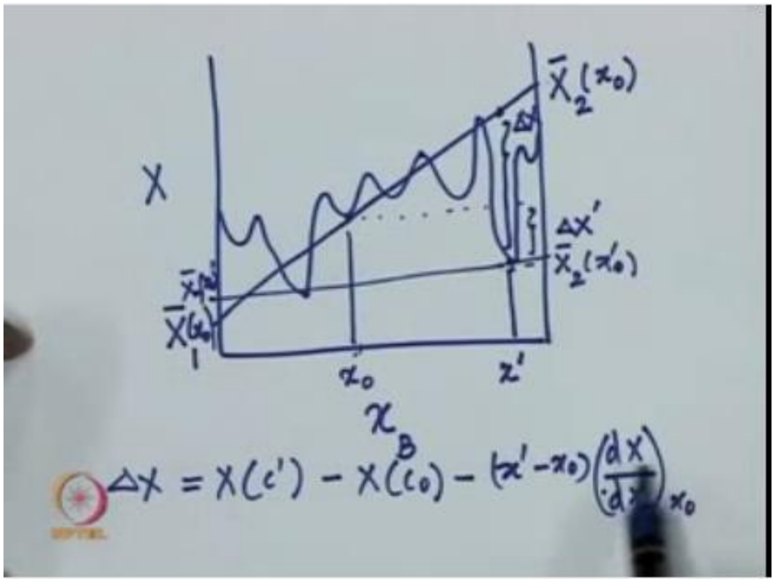

The quantity that we have derived that ΔX that we have derived let me write that expression ΔX=X(c′)-X(c_0) okay, so that is this difference –(x′-x_0)dX/dx at x_0. In other words this quantity that we are having is nothing but this point where you are trying to calculate x′this distance that is the ΔX okay, so that is why I marked it as ΔX′ so when you take from a solution of composition x_0 some material and make a composition of x′the change in the property X is given by basically you draw a tangent and from the tangent point to the composition that you are making at that point you find out how much is a property difference that is ΔX.

So that is what this quantity is, right so this will be the expression which is the difference between the two property values will be just for a open system and for a closed system this is what it is going to be, so this is the geometrical interpretation for the quantity that we have calculated, okay we have derived that this should be the quantity okay. So in the next part next segment of this lecture we will see what this means okay, so we will do a simple Taylor series expansion and we will try to understand what this means, thank you.

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