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

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Module No.3
Lecture No.12
Spinodal decomposition

Welcome so in this module I want to define what is spinodal for doing that we will go back to the models that we were looking at and let us look at the free energy versus composition diagram in a system which a drill goes phase separation so the free energy verses composition diagram.

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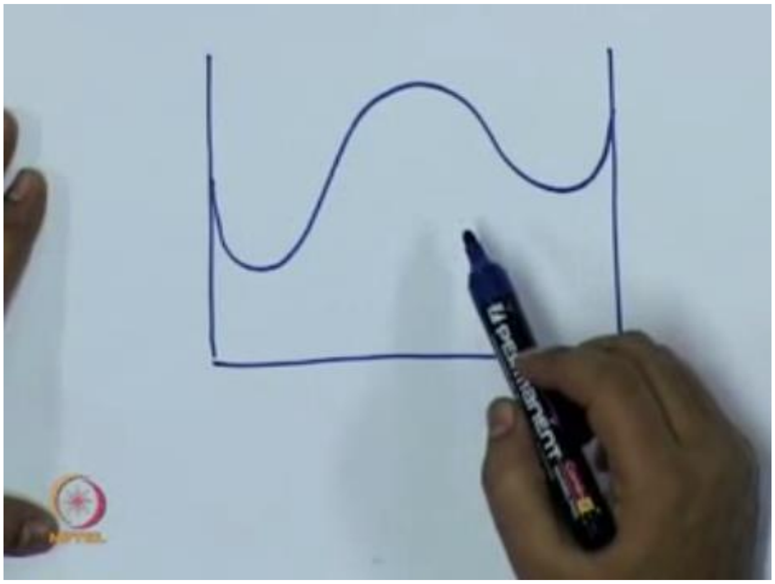

Looks something like this is what we have seen so there is a concave region and there is two wells and one maxima and if you just look at the free energy of mixing the models we had it was symmetric and the minimum where at the same level but when you add the end composition free energies GA for pure and GB for pure B then that is like a straight line so it shifts and so the two minima need not beat the same level and because we have drawn a continuous curve for the two end phases that we see it means that the phases of these two crystal structures for these two phases is basically the same okay.

If it is not so what will happen if the phases are not the same then we will have two different of free energy suppose if I have one α phase and one β phase.

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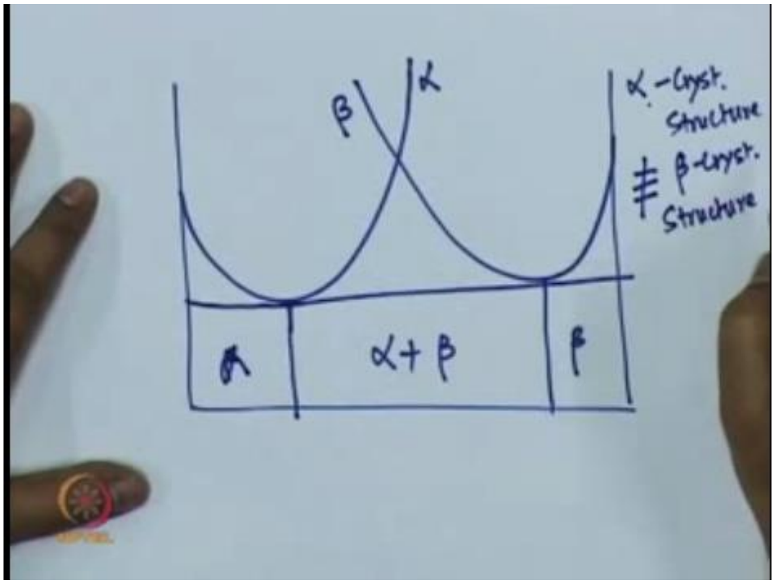

And that is what forms the two-phase structure then α phase is a different phase and β phase will be a different phase okay so this is for α this is for β so we can see that these two free energy curves are independent curves there is a region where you have some sort of concavity in the free energy curve so here also you have to draw a common tangent and the common tangent points will be the ones which will form the two phase equilibrium because the free energy curve has to be convexify which means so this will be α up to this and then α + β and then this is β after this so this is what will happen but this is by assuming that α and β crystal structures are not the same α crystal structure is not the same as β crystal structure okay however the kind of curve that I have drawn.

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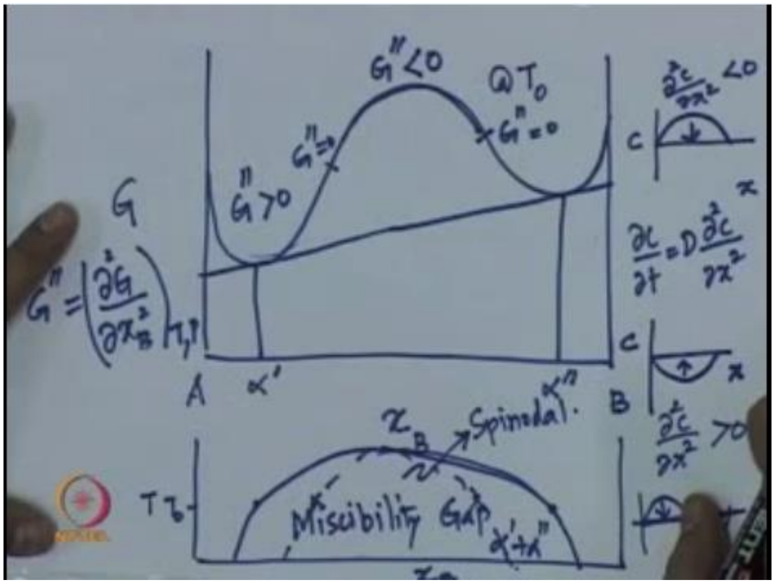

In which we are assuming that it is a continuous variation means that at the two phases are basically having the same crystal structure so sometimes they are noted as α´ and α´ ´ for example to indicate that it is the same crystal structure the only difference is the composition because remember this is free energy versus composition right so this is pure A and this is pure B so which means that when you draw a common tangent let us draw a common tangent then you get the two phases.

So you have let us call this as α´ and this is α´ ´ and α´ is rich in A because this is closer to the A point α´´ is richer in B so you have a system which phase separates because remember this is the concave region so that is not preferred thermodynamically so the convex regions are the ones that are preferred so the concave region is replaced by this convexify version which is a straight line which is the free energy of a mechanical mixture of α’ and α´´ depending on composition only the volume fractions of α´ and α´´ will be different but the end compositions of α´ and α´´ this will be the same composition anywhere in this region.

So we have convexify curve and we have these two phases one is rich in A and the other one is rich in B we are trying to look at what happens when this system undergoes a phase separation so we know that these are the points where it is going to undergo phase separation in terms of the phase diagram okay so what we have is that at this particular temperature remember this is drawn at some temperature T_0 so phase diagram is for temperature so we have the T_0 point versus composition right.

So composition versus temperature is basically the phase diagram so at this point so there will be this and at this point there will be this so at different temperatures then you will draw this kind of free energy of composition diagrams and then you will trace these points and that is what gives you a phase diagram so basically in this system the phase diagram will be something like that right so this is what the phase diagram will look like because this is a phase separating.

So this is basically the miscibility gap meaning that in this region there is no complete mixing of A and B atoms and it will phase separate into a mechanical mixture consisting of a rich regions and B regions so that is what is described by the miscibility gap now what is spinodal okay so we are going to describe spinodal and it has a physical significance and meaning so that is what we are going to discuss in the next model so let us define spinodal so how do I define spinodal so let us look at this free energy versus composition diagram once more let us look at this region.

So in the case of fixed law of physical meaning also we have discussed this so if you take for example composition as a function of position and if you see that the composition changes like that thus this means what the curvature is negative that is the reason why because the Fick's first law says to see by $\partial c / \partial t$ is equal to D $\partial^2 c / \partial x$ sorry Fick's second law says this B being constant and positive so this sign then decides how the composition is going to change with time so this is a region with negative curvature which means a composition is going to keep dropping similar we said that if you had composition with distance no I need to distinguish between x which is distance and X_B which is composition of B okay.

Probably it is bad notation but I hope you understand from the context what is what so if you have composition profile like that that means $\partial^2 c / \partial x^2$ is > 0 which means the composition is going to keep increasing at this point this is how we explain the saying that if you had the sinusoidal variation in composition this is going to come down this is going to go up so you are going to have a homogenized composition in other words we know that if you take the second derivative of the concentration with respect to position then that basically gives the curvature in a similar fashion.

If I have G versus X_B then this is basically given by the curvature of this expression so what is it so it is sometimes denoted as G´´ and this is > 0 and what is G ´´ is nothing but $\partial^2 G / \partial_{xB}{}^2$ keeping everything else a constant a temperature pressure everything I am keeping a constant and so partial derivative because free energy depends on everything so when you are taking the derivative you want to keep all the others are constant and then this curvature is positive by the same token if you look at the curvature in this region this is a region where G´ < because remember this curvature is looks exactly like this gap okay.

So this concave curvature region okay some part of the concave curvature region now concave curvature region is there everywhere but this part has the G´´ to be < 0 now if it is positive here and if it is negative here so some where it is going to cross at 0 so there are two points where G´´ = 0 in the phase diagram if I also mark these compositions and similarly at every temperature I do that you know at a different temperature if I draw a different free energy versus compositing curve that might have these G´´ = 0 points going towards the center of the composition or might be going away it depends on whether you are at higher temperature or lower temperature.

So in other words you will have a set of points which are described by these points what are these points these are points where $\partial^2 G / \partial_{xB}{}^2 = 0$ okay are G´´ = 0 the points where G ´´ = 0 are called the spinodal points and the plot of these points on the phase diagram basically gives you this spinodal region inside the miscibility gap okay so let me draw the free energy curve once again to make it clear as to how the phase diagram looks.

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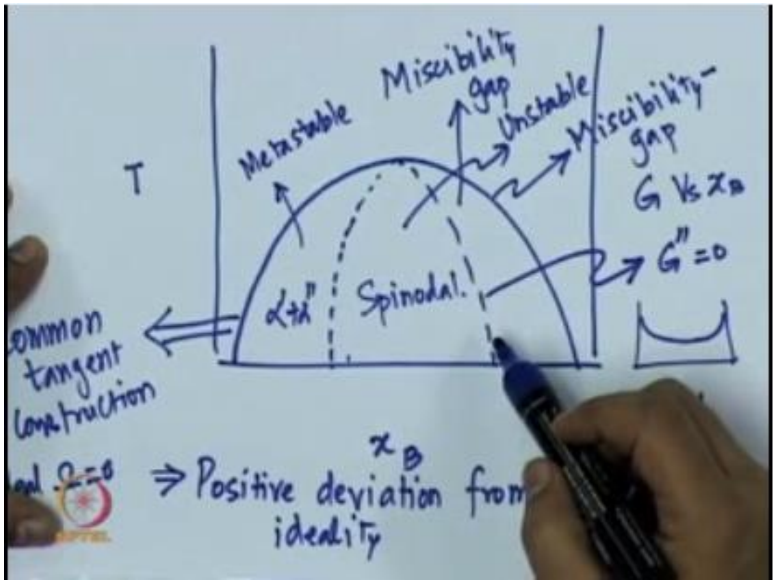

Okay so this is the T versus x_B so I have a miscibility region and inside the miscibility region I have another region and what do these curves represent these curves basically represent the points on the free energy versus composition curve where G´´ = 0 what do these points represent so this is spinodal region and this entire region right which includes this spinodal is basically the miscibility gap miscibility gap is the region where it is going to be a mechanical mixture of we said α´ +α´´ inside the miscibility gap there is a specific region which you can identify by looking at the free energy of this composition curve and looking at where the second derivative of the free energy with respect to composition becomes 0.

And that region when it is marked is known as the sphenoid already okay so this basically is the miscibility gap okay so this is miscibility gap is basically obtained by the common tangent construction right so where the miscibility gap points are or basically from the these are obtained from the common tangent construction we take the free energy we construct a common tangent and where the tangent touches the free energy versus composition curves are basically the points at that temperature and at every temperature we do this so we identify all the points we draw the line that gives us the miscibility gap.

Miscibility gap is the region where it will be a mechanical mixture of the two phases one is A rich other one is B rich and if you look at the free energy composition diagram and look at where the second derivative is becoming 0 that is known as the spinodal and you can mark a spinodal region inside the miscibility gap okay now as you can see because the miscibility gap is the basis and the miscibility gap and spinodal actually require that your free energy versus composition diagram has a concave curvature and using your regular solution model you know that such concave curvatures will develop only when $\Omega > 0$ in other words this kind of phase diagram implies this is very important this kind of phase diagram implies using a regular solution model that we have a positive deviation from ideality remember we have defined an ideal solution as one which has so ideal meant Ω equal to 0 right > 0 it will undergo phase separation.

So that is what will lead to spinodal also spinodal is also defined by the region's inside this concave region where the G'' becomes 0 right so if you had a free energy versus composition curve which is like this you will not be able to identify this point so this kind of spinodal region is always associated with this type phase diagram which by our discussion on regular solution model indicates that there is a positive deviation from ideality what does a positive deviation mean.

It means that the system does not like A,B kind of bonds unlike bonds it does not like it wants to have all the AAA bonds or all BB bonds that is the reason why it phase separates in the first place so yet it is show regions are there and B rich regions of it okay the system would prefer to have as many A atoms surrounding A atoms and as many B atoms surrounding B atoms.

So that is the reason why it phase separates so this is something that we know so this kind of free energy versus composition diagram implies positive deviation from idea right okay now what is the physical significance of this spinodal region okay now this spinodal region implies or indicates the separation between what is known as metastable and unstable right what is the spinodal line spinodal line separates the meta stable from the unstable what is the meaning of metastable what is the meaning of unstable okay.

So it is a our definition spinodal is obtained by looking at $G'' = 0$ you take the free energy composition diagram you take the second derivative you look at wherever the curvature becomes 0 and you plot all those points on the phase diagram at different temperatures you find out where this curvature is becoming 0 that basically gives you the spinodal line the physical significance of the spinodal line is that it is the boundary between the meta stable and unstable regions inside the miscibility gap.

Inside the two-phase region you have a two-phase region and the two-phase region has some metastable regions and some unstable regions spinodal line is basically the one that is distinguishing the metastable from the unstable and wherever the curvature is < 0 that is the unstable region wherever the curvature is > 0 that is the meta stable region, so what is the meaning of meta stable and unstable we will use the mechanical analogy that is given by Khan and we will try to understand what it means so that is what we will do in the next model thank you.

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