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

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Module No.3
Lecture No.16
Understanding spinodal region

Welcome so we are looking at the change in properties when you try to produce a second phase from a given phase of given composition and the second phase has a particular compilation, we have derived the change in the property in the thermodynamic property associated with this two phase that you are trying to make and we have shown geometrically that if you have some property.

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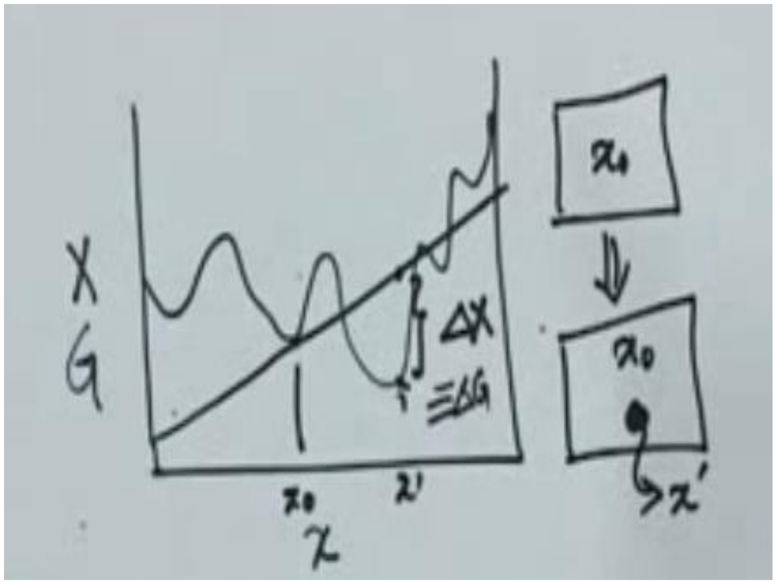

And if as a function of composition and then if you say that the property changes something like this and then if you say that this is my overall composition and this is the composition that I am trying to make then the way to calculate the change in this property ΔX is by drawing a tangent line and taking this composition so you find out what is the property value on the tangent at that composition and you take the value at that composition you take this.

This is what the ΔX property change associated with producing from this composition X_0 something with this composition X', so I initially have this X_0 composition everywhere in the system then I go to one where this X_0 composition gives rise to a small region with composition X' if I do that what is the change in free energy associated with that that change in property associated with that is given here.

And because this is property it could as well be free energy so in this case then that will be ΔG but we know that actual free energy assess or composition curves do not look like this, right I took a generally curve and try to do this derivation.

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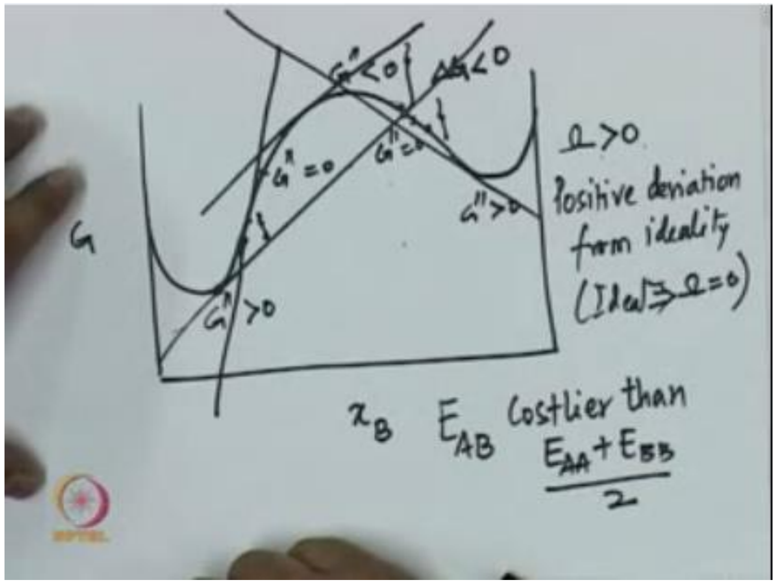

So let me take a proper free energy versus composition curve especially in the case, right. So this is a free energy versus composition curve and we said that this kind of free energy versus composition curve will be seen in regular solution models when $\omega > 0$ that is positive deviation from ideality, why? Because Ideal means $\omega = 0$, right so Ideal implies ω is 0 so $\omega > 0$ is positive deviation from this ideality, whenever you have positive deviation from ideality you will have free energy curves like this and when you have free energy curves like this you can see that $G'' > 0$ and here $G'' < 0$ and there is a point we identified on both sides where $G'' = 0$ so here also $G'' = 0$.

Okay now when the curve is like this between this $G'' = 0$ and this $G'' = 0$ where $G'' < 0$ so any tangent that you draw to the curve you can see that all the points of the free energy basically lie below this line and we said that the free energy change associated with producing something of this composition for example will be this which means that free energy is negative right because the all the all the points are lying below this line.

Which means all the free energy changes that we are going to be calculating will be less than zero, so anywhere in between this region because any tangent that you can draw is going to be above this entire curve the free energy is always going to be change is always going to be negative so spontaneously it will go into the phase separation, on the other hand when you have $G'' > 0$ and here also $G'' > 0$.

When you take some composition you will see that if you if you draw a line it will be like that so there will be some points let me take a proper composition somewhere like this, so if you if you draw a tangent you will have tangent going like this so there that means that there are points which are above this tangent line which means this is the barrier it has to overcome unless this system produces region of this composition.

The free energy change is not going to be negative so for anywhere here suppose you are at this composition and you try to produce a composition of this free energy change is positive, composition of this free energy change is positive, composition of this free energy change is positive, composition of this free energy change is positive, composition of this free energy changes lead to be 0, and below this anywhere here you try to produce then the fr4ee energy change is negative so that means that will happen.

So in other words from a composition here, you have to produce at least some compositions somewhere here before the free energy change becomes negative for anywhere else this free energy change is positive, that means this is the barrier that the system has to overcome.

In other words, whenever you are to the lefter $G''=0$ here or to the right $G''=0$ here and same story here, so I can draw a tangent and there will be regions which are above the tangent and then there will be big regions below the tangent, so at least that composition has to be produced before my free energy change becomes negative. So in other words, we have derived this and we have given the geometric interpretation namely that at the composition draw a tangent and find out the free energy curve whether it is lying below the tangent or above the tangent.

If it lies below that is unstable, if it lies above that is metastable and you can see from the regular solution free energy that this spinodal region is always associated with positive deviation from ideality because in that region all points on the free energy are going to lie below so it is unstable so that is why it is the spinodal region, and why is the spinodal region coming up because you had the curvature of this type, why did we get curvature of this type because we had positive deviation from ideality.

What does the positive derivation from ideality mean that means that E_{AB} is costlier than the average of E_{AA} and E_{BB} that means the system in this region would like to produce AA bonds and BB bonds AB bonds are costly that is the reason why you got this curvature in the first place, that is this deal positive is the reason why this is positive and if this is positive is when you get that curve and when you get that curve there are regions where the tangents will be drawn so that all the points will be below the tangent.

Which means all those regions will be unstable, that means that will be the spinodal region, so spinodal decomposition is related to positive deviation from ideality which means that in spinodal systems AA BB bonds are preferred over AB bonds, this is very important because we are going to come back to this point later and discuss and instead of taking a generic property verses composition curve I have taken the septic free energy verses composition curve and I had tried to show you that why we make this distinction between points which lie within this $G''=0$ and lie outside of this $G''=0$.

So wherever the curvature is negative is where the unstable regions are and this is the geometric explanation for the same based on the derivation that we made, okay so this explanation is coming from the derivation which we made earlier and explain so why spinodal region is like this and why positive deviation is associated with spinodal decmpoistion, okay so this brings us to the end of this part we will continue with this again later we will come back to this point and we will have more of a discussion on what it means to have this positive deviation and how to model this mathematically using diffusion equation and so on.

So to do that I need to go back to the diffusion equation that, I have derived earlier and try to look at type of solution in one dimension for the diffusion equation, which is what we will do in the next part of this lecture, thank you.

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