Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Lecture - 24
Common Tangent Construction, Definition of Binodal, Spinodal and Critical Point

Hello all of you. So, in the last lecture we have been discussing what should be the mathematical form of the Helmholtz free energy density f of Φ to define the mixing behaviour and to define the phase separation behaviour. So, today I will take this further and discuss what is known as the binodal and spinodal lines and the critical points and then finally I will try to argue that I can also find the osmotic pressures and chemical potentials as a function of f of Φ and therefore, if I know this function, we pretty much know everything about the equilibrium behaviour of a liquid solid.

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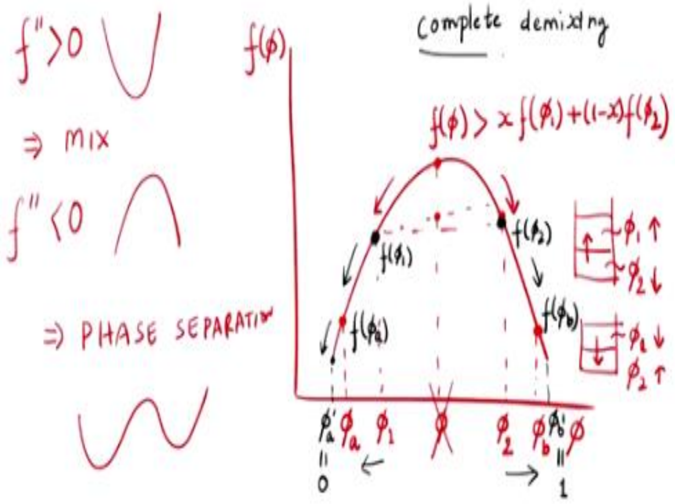


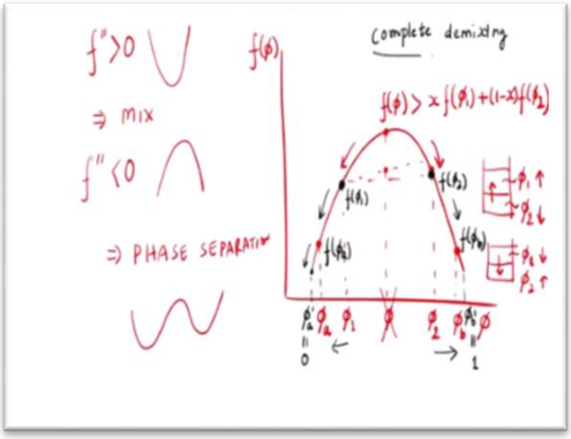
So, what we had started with is that I have to look at the function form of f of Φ and if that is more than 0 that is my function looks like that or it is upper concave. In that case, we will have mixing. On the other hand, if f double prime is less than 0 or the function looks like convex then in that case, we will have a phase separation. And finally, I was saying that we may not, have a single minima or a single maxima we can have a situation like that and in that case, we have to identify the function value in the range of volume fractions and reconsiderations and using that I can find whether we will have mixing or phase separation behaviour.

So, I want to take that further today. But before I do that, let us first look at the phase separation case where I also need to evaluate what should be the volume fraction in the phases that form. So, let us say first of all, we take the case when we had a convex function and I was saying that I will start with some Φ1 and Φ2 values. And clearly, we have figured out that for them to form a homogeneous solution, whatever, the free energy density that come out comes out to be it happens to be higher than what we got from here, that is x f (Φ1) + 1 - x f (Φ1) x (Φ2) and therefore, the system is not going to mix.

So, they are clearly this is not a possibility at equilibrium. So, they will form 2 phases coexisting which will have volume fractions Φa and Φb. Now the question is what is that Φa and Φb how will I find that so if you look at it as we are going on the two sides of this the free energy density is decreasing. So, let us say for example, if the new phase have the volume fraction Φa and Φb. So, 1 of them is slightly less than Φ1 and other 1 is slightly more than Φ2, now this is possible. Because let say if I start with a solution having volume fractions Φ1 and Φ2 in the 2 phases. Now this may increase at the expense of decrease in Φ2, as solute will go from 1 phase to the other. So let us say solute moves in this particular way then the top phase is getting and higher volume fraction and the bottom phase is getting a lower volume fraction.

If the opposite happens let us say solute is going in this particular way then in that case, the Φ1 is going to decrease and Φ2 is going to increase. So, only for the mixing case the final volume fraction has to be between Φ1 and Φ2. For the case of phase separation, the opposite happens one of them may decrease and the other one can increase and this is what the phase separation is. And therefore I said that the Φa and Φb need not be same as Φ1 and Φ2, generally it is not same as Φ1 Φ2.

So, now if I compare these two situations, you can clearly see that the energy in the Φa and Φb case in the picture that I have drawn here is less than the Φ1 and Φ2 case. So, this was my f of Φ1, this is my f of Φ2, this is my f of Φa, this is my f of Φb. Since the Helmholtz free energy density of both these phases have decreased by going from Φ1 to Φa and Φ2 to Φb. You can clearly see, even without doing the full math that the energy will decrease as I go from this state to this state and simultaneously from this state to that state. But the same is true if I go further down there that means if for example, I think of a new state Φa’ here and Φb’ here that will have an even lower energy in comparison to Φa and Φb.



This will keep on happening until we reach this equal to 0 and this equal to 1 because there is a single maxima in the curve so pretty much 1 of the volume fractions are going to decrease and the other volume fraction is going to increase until the system is fully phase separated because once that happens then Φ cannot further decrease or increase because we have reached the limiting cases of 0 and 1 that means you will have a pure solute phase in equilibrium with a pure solvent phase and that is a condition of complete de-mixing close to that we see in an oil water solution the system wants to completely de-mix. So you will have a most pure oil on top and pure water at bottom and it is for those cases, the function curve should look like this because it has to be like this so that the system wants to completely phase separate.

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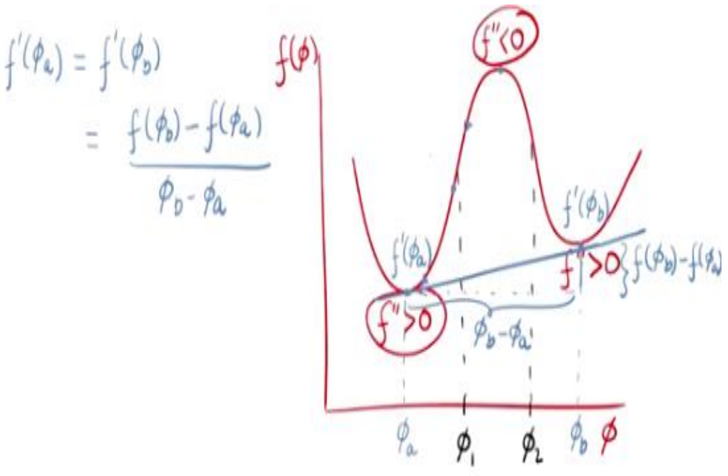
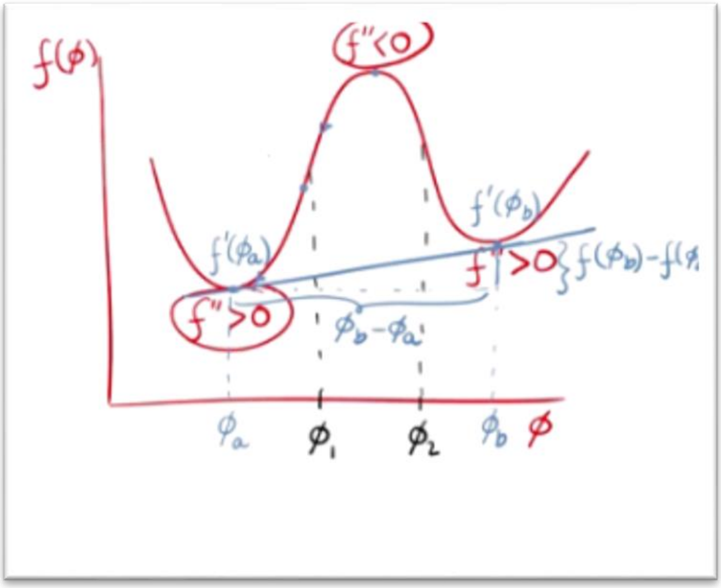


$$f'(\phi_a) = f'(\phi_b) = \frac{f(\phi_b) - f(\phi_a)}{\phi_b - \phi_a}$$

So, let us look at the other extreme that we had discussed where the function looks something like that-



And now in this case we have two regions in the graph in one of the regions the f’’ is less than 0 and in other part the f’’ is higher than 0 and now the question is where do we lie on this particular curve to decide whether we have a mixing behaviour or phase separation behaviour.

So, if we have the phase separation or if the tendency is for the phase separation then we are lying in this particular part of the curve somewhere over here or we are lying somewhere over here or the other branch of the curve. So, now if I start from say 2 concentrations. Let us say Φ1 and Φ2 which are lying in the reason were f’’ is less than 0 we will have a phase separation there.

So, the first question is what is going to be the concentration of the 2 coexisting phases? And the answer to that is that will lie along a common tangent. That we can draw like this in the graph that is basically a tangent to the 2 minimum points in the curve. And these points let me refer them as Φa and Φb will be the volume fraction of the 2 coexisting phases. And to find that particular thing what we can notice is that the slope of the function f’ at Φa, should be equal to the slope f ‘ at Φb that is, f ‘ (Φa), = f ‘ (Φb) and we can find the magnitude of this slope by a simple geometry. So, we can note that we can draw a triangle like this and the slope is given by basically this divided by that. So, the y axis is f Φb - f Φa, and the x axis is Φb - Φa. And therefore the slope is given as-

$$slope = \frac{f(\phi_b) - f(\phi_a)}{\phi_b - \phi_a}$$

Now there is something interesting here if for example, I now start from this maxima point on the curve and let us say if I go towards any of the two minima let us say for example, if I go in this particular direction towards this minima right here. So, while doing that the f double prime is going from a negative value to a positive value. So, you can expect that there would be a point on the curve where the f ‘’ = 0.

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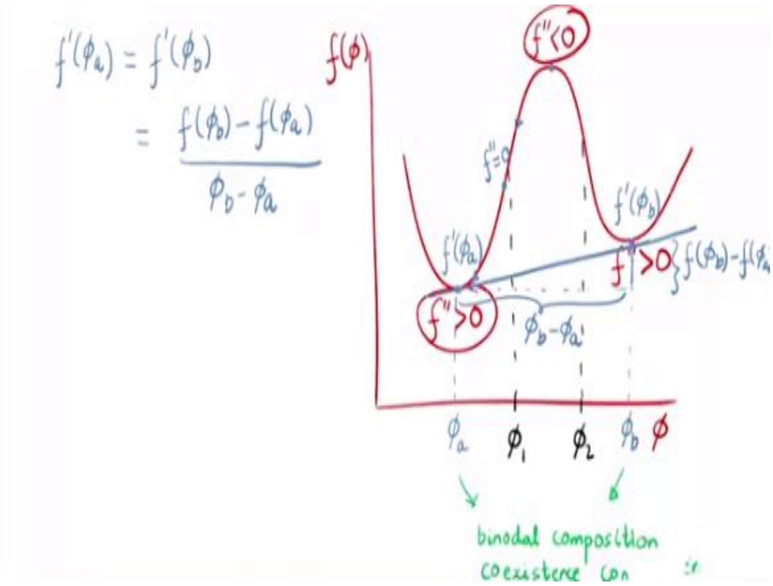
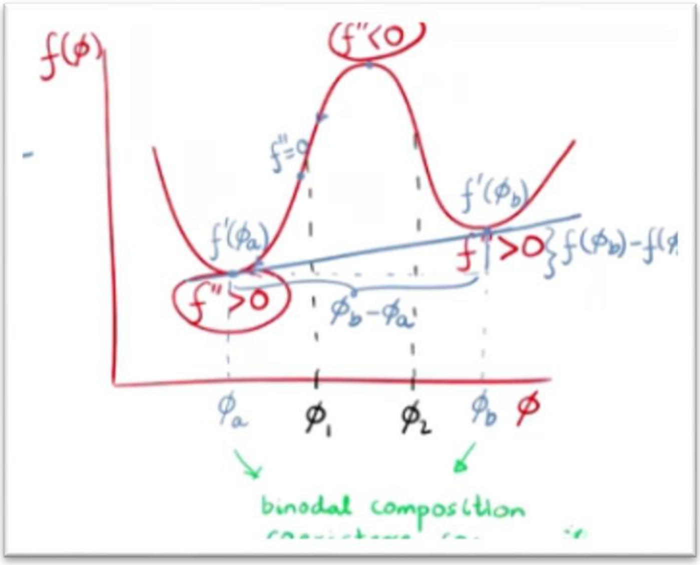


Let us look at this particular point in more detail. So, I am starting from the maxima and going towards the minima and we are going to have a point on the diagram where f ‘’ is equal to 0 that is some sort of an inflection point. The same is true on the other side as well. We will have some sort of an inflection point somewhere in between these 2 points. Now, let us say for example, my Φ1 happens to be here and Φ2 happens to be here.



So, using the construction that I have done earlier the net Φ will be somewhere around here and clearly for that net Φ the condition for mixing is not being met because clearly for this value of Φ what we have is $f(\Phi) > x\, f(\Phi1) + (1 - x)\, f(\Phi2)$.

So even if that is true at both of these points, the f ‘’is actually higher than 0 because we are passed the point where f ‘’ = 0. If the, point laid between this regime that I will draw now. If the points slide in this regime where f ‘’ is higher than 0. Then clearly say that system has a tendency to face separate but if for example it laid in the, remaining part of that. Let say for example, the points lie somewhere here, so even though for these points the green guys here my f ‘’ is for this has to be less than 0 because we are in the; convex regime and for this f ‘’ is higher than 0. So, if we are in the yellow regime, we can clearly say that we have a phase separation because not only f ‘’ is less than 0 but also we are finding that for the Φ value that we will get for mixing condition, the condition that we had for mixing will not be satisfied because Φ happens to be higher than $x\, f(\Phi1) + 1 - x\, f(\Phi2)$.

If on the other hand if I lie in this green regime, then it becomes a tricky situation. So, on one hand if I find the net phi value for these 2 cases I will still have this condition not this condition being met so using this condition I can say that system has a tendency to face separate. However, f ‘’ is higher than 0 that means system has a tendency to mix. So, these two regimes of the phase diagram are referred as unstable and stable regions.

Now what really means is that let us say my Φ1 and Φ2 are in the stable regime then in that case, even when the equilibrium state is a state which is phase separated system does not have a tendency to go there. Why? Because f ‘’ is higher than 0. On the other hand, if I am in the unstable regime if I pick volume fractions in that regime, I will always have a tendency to goes towards phase separated state. So, keep in mind that f ‘’ is telling me the tendency but f‘’ is not telling me whether we will have energy minima in that state or we are having energy minima in some other state that is phase separated.

So, if I am in the stable part of this graph what we are going to have is that we know that the energy minima is still in the regime when we have phase separation but there is no tendency to get there because f ‘’ is higher than 0 and this is something with the physical meaning. We can have a state that remains far from the global minima for very long time because f ‘’ is higher than 0 and there is not a tendency to get there.

In other words, we can say if I give a small fluctuation because ultimately to go from a state of a higher energy to a lower energy will require some kick. So, if I give it a lower fluctuation, then those stable regimes will remain as it is but if I give large fluctuations then they have to get to the energy minimized state. On the other hand, if I am in the unstable regime then any fluctuation will drive me to a state of phase separation. So, this is state is actually referred as a meta stable state that means the state remains mixed as long as the fluctuations are small.

If the fluctuations are large then the system will go towards a phase separated state because anyway, that is the state where energy is being minimized. In the unstable regime, even if we give a very small fluctuation that is enough to drive the system to a state of energy minimum and that is the state of phase separation.

So, therefore, we have these two regimes and beyond that clearly if I am in say for example, here and here then in that case we are very clear that we will have a mixing behaviour. So, only in the middle part of the phase diagram we need to be concerned about the phase separation behaviour. And in that two there is an unstable regime only in which f ‘’ remains throughout negative. In the remaining regime, when f double prime is higher than 0 we can be in a state that is metastable that will remain in a state of a higher energy in comparison to the equilibrium energy that is the state of phase separation as long as the fluctuations are not large enough.

So, this particular point where f ‘’ is equal to 0 is called spinodal point. So, these 2 volume fractions define what is known as the binodal composition or the coexistence composition. So, we know that we have a binodal that is giving me 2 values of volume fractions which are for the state of phase separation, but then we need to be between these 2 spinodal so as to speak for any small fluctuation to drive it to a phase separation if we are not in that regime then in that case we can be in a metastable state for very long time.

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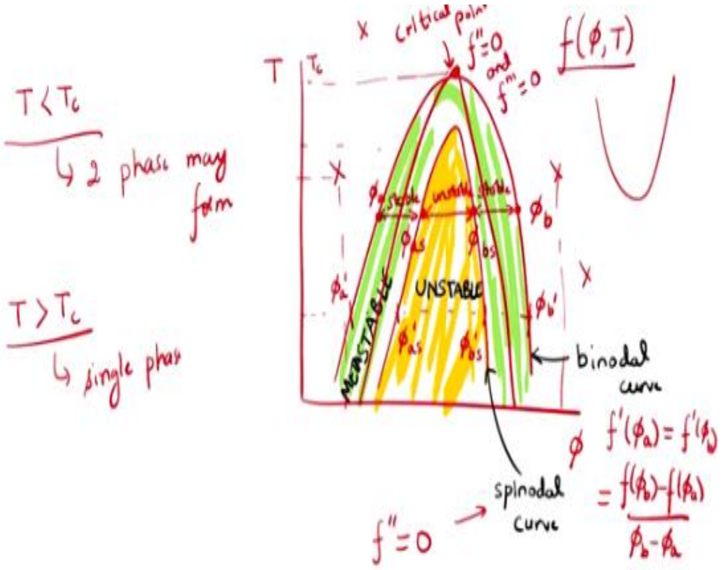
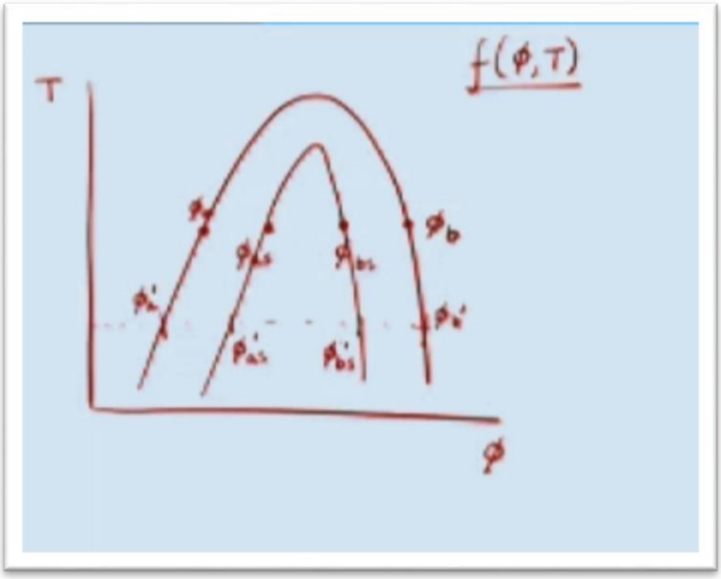


So, with this particular idea, I now want to include the effect of temperature. So, since I have been working at a particular temperature value If I now want to put that plot in temperature versus volume fraction diagram then for a given temperature value, we had a Φa value and a Φb value and between these two we had 2 spinodal points, which I will refer as Φas and Φbs.

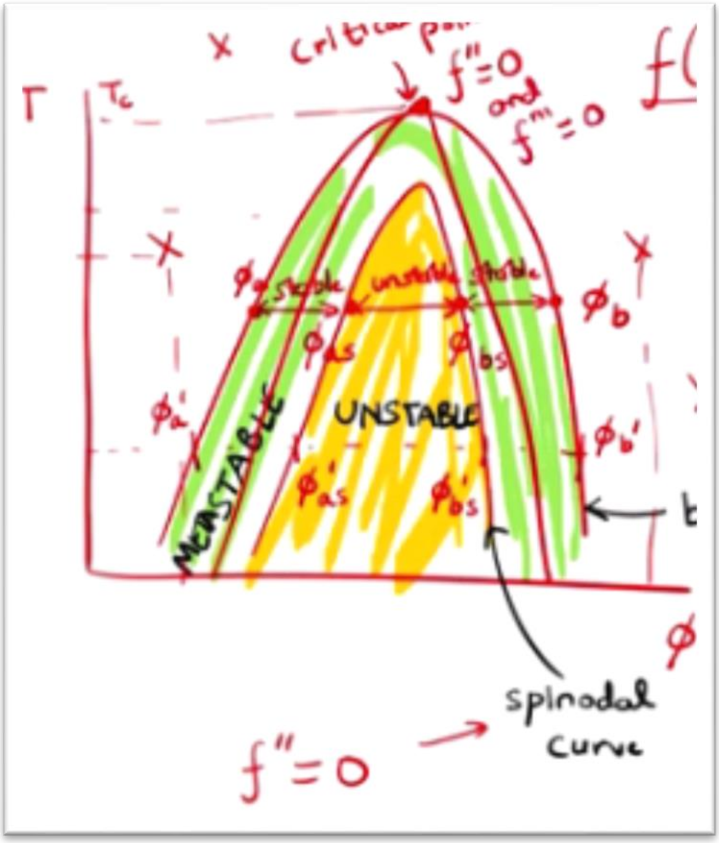
Now, I may imagine that as I vary temperature since the function value f is a function of temperature. So, ultimately, we started with a function f of Φt. Until, so far we have been working at a given value of temperature but now if I want to see what temperature variations will do to that then clearly this f is going to change. So, if I connect those points for different temperature values what essentially we have is something like that-



So, for any given temperature I can locate the 2 binodal compositions, let us say Φa’ and Φb’ here and I can locate 2 spinodal Φas’ and Φbs’ and this is of course changing as the temperature is increased.

So, even though I have drawn the curve in this particular way, it need not always look like this it may look as something different but nonetheless as long as we have a regime were phase separation is happening we should be able to define the binodal and spinodal. A phase separation is not happening then binodal and spinodal clearly does not have any meaning. So, though using that logic since we were unstable between Φas and Φbs and stable in the remaining part for the temperature under consideration.

Now if I look in the entire temperature space what we can say is we have a regime in the phase diagram that is unstable and another regime in the phase diagram that is stable.



So, depending on where we lie. So, if we are in the orange regime, then we are in the unstable part of the phase diagram. If we are in the green regime, then we are in the metastable part of the phase diagram these curves have a name, so this one is called a binodal curve. It connects all the binodal compositions. This is referred as spinodal curve and now you may notice that as this temperature increase we have at the peak of this a condition where both binodal and spinodal curve match and that particular point is referred as the critical point. So, when temperature becomes at the critical point Tc, then we have first of all a single volume fraction and secondly at that single volume fraction value the binodal and spinodal both are matching.

In other words the regime between spinodal compositions decreases as we increase temperature or the unstable regime decreases as we as we increase temperature but stable regime also decreases as we increase temperature and at the critical point both these curves match the binodal spinal at the critical point and this is actually a definition of the critical point and the reason why it is important is because if I am working for temperature less than Tc, then only we can see 2 phases forming, provided that other conditions are being met. Let us say if we are in the proper regime in the diagram then two phases may form.

On the other hand if temperature is higher than Tc, we will not see that happening. So, we will have always a single phase because anything outside this orange and green regimes, here are where we have a single phase. Let us say if I look at a point here or somewhere else we are going to have a single phase in those points. So, for all this temperature values and volume fraction values we are going to have a single phase. So, beyond the critical point, we are going to have a single phase regime and below the critical point we are we may have a two phase regime.

So, just to think of an example of that let us say if I look at water below the critical point, so let us say if I am looking at water because the critical point then if I start with liquid water, and if I start heating it, I go to a vapour state right. At the boiling point of water, we have both liquid and vapour phases coexisting and that is what is referred as the binodal composition for the liquid water and the vapour.

On the other hand, beyond the critical point we will not have such a point. We will never have a condition where the liquid water and vapour will coexist. The other word to think about it is that we will go continuously from a liquid phase to a vapour phase. And what we have is what is referred as a second order phase transition as we have earlier discussed. When we were doing the phase diagram of water so the second order phase transition, we will not have a jump in properties.

And the reason actually for that is because we do not have a coexistence right so once we have a distance imagine that you will have a liquid water and the vapour and their compositions of the liquid and vapour will vary. The amounts will vary for a pure component and this is what is giving rise to the jump in the properties such as density. If I am beyond the critical point then no such coexistence happens.

And when no such coexistence happen then in that case, we can say that we are in the regime of a second order phase transition where we remain the single phase regime and still we are going from a liquid phase to a vapour phase, so in common language we say that we will not be able to differentiate between a liquid and a gas once we are beyond the critical point. And the reason is that we are always in the single phase.

We are going from the liquid part of the phase diagram to the gas part but there is no such point in between where you see both of them coexisting. There is pretty much no distinction. In the in the properties when going from a liquid state to a gas state and this is what is a definition of a critical point. And clearly critical point is going to vary depending on the material under consideration.

In most cases in thermodynamics, we are dealing with conditions below the critical point, but there are circumstances when we are super critical that is beyond the critical point condition yes, So, if I want to get the expression of the binodal and spinodal, we already know what should be, so curve is given as-

$$f'(\phi_a) = f'(\phi_b) = \frac{f(\phi_b) - f(\phi_a)}{\phi_b - \phi_a}$$

The critical point is given as f ‘’ is equal to 0 and f ‘’’ is also going to 0 that is the mathematical definition of the critical point because in some sense it is the maxima of f‘’ curve and that has to be the derivative of that particular curve and that is why we get a f ‘’’.

So, what I have been able to establish in this discussion is that, we have found this magic function f of phi t for which if the function looks like this then it should be mixed. If the function looks like that then it should be separated we only need to know this particular function. We have not yet said how we like derived that function but we know what that function is.

In the next class I will show you that if I know this function, we can also find the properties that you are more used to hearing such that osmotic pressure and chemical potential right. So, typically, the driving force of the mixing is characterized in terms of the chemical potential or osmotic pressure.

And are what I will show you is that both of them are also related to f of phi. So if I know f of phi I can find the osmotic pressure and I can find the chemical potential. And therefore in principle all we need to know is this particular function f to get the entire physics of the mixing and phase separation. So, coming from the statistical mechanics background that we have been doing this should not be a great news because we already know that the energy function dictates the behaviour.

But coming from an undergrad thermodynamics perspective, this may be somewhat big news because we had too many definitions of different terms like chemical potential, osmotic pressure and all that. And what we will be able to show is all these definitions are actually linked together and we can characterize the tendency of mixing and phase separation using either of that not one of that right.

I can use osmotic pressure, I can use chemical potential or I can use f of Φ whichever is convenient to our problem, but nonetheless if I know one of them, I can find the other variables that we are interested in.

So, with that, I want to conclude here. Thank you.