Introduction to Polymer Physics
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Lecture-30
Solutions Thermodynamics-IV

Welcome in the last couple of lectures we have discussed about the mixing and phase separation behaviour of liquid solution. We started talking about the Gibbs energy to begin with, but then we said we can write the Gibbs energy in terms of Helmholtz free energy density f of (ϕ,T) and then later on we said that how that single function basically characterises first the mixing and phase separation behaviour then we can also write osmotic pressure and the chemical potential in terms of that function of f of (ϕ,T). So we have not really said how we will get that particular function, we already know what that function form should for having a mixing behaviour or a phase separation behaviour.

So I want to take it further and talk about the phase equilibrium which you must have done in mass transfer or another courses. We talk about phase equilibrium in terms of equality of chemical potentials of components. So how does our description in terms f of (ϕ,T) for liquid solutions will adapt for the case of phase equilibrium.

So just to briefly recall what do you mean by a phase separation, so you can start with a certain volume fraction ϕ and a volume V in a beaker and this thing will phase separate into two layers ϕ_a,, V_a and ϕ_b, V_b provided that the final free energy ends up becoming lower than the initial free energy before phase separation which means-

$$V_a f(\phi_a) + V_b f(\phi_b) < V f(\phi)$$

But now once it is phase separated that in that case if I want to know the volume fractions ϕ_a and ϕ_b we can use the idea that for any component the chemical potential in the two phases must be equal that is given again by thermodynamics but at equilibrium. So at thermodynamic equilibrium we know that the chemical potential

$$\mu_s(\phi_a)=\mu_s(\phi_b)$$

The other way to think about it is let us say the chemical potentials are not equal in the two phases if they are not equal then the solute molecules will go from higher chemical potential to lower chemical potential whatever that direction is and this will continue to happen until the chemical potential becomes equal.

So only when the gradient of chemical potential ceases that you get the equilibrium conditions. The same thing I can do for the solute and now since we said that the osmotic pressure also characterizes the mixing behaviour.

$$\mu_p(\phi_a)=\mu_p(\phi_b)$$

So if one layer or 1 phase is at higher osmotic pressure then solute particles will move from there to solute or solvent particles will move from that layers with different layer and so this will continue until equilibrium where the osmotic pressure also becomes equal.

In fact we can think of both the chemical potential and osmotic pressure as some kind of a driving force for diffusion μ_s as μ_p and Ⅲ all driving forces for diffusion, and in fact all can be written in terms of f of (ϕ,T)

So we will do this derivation now and try to see like how these expression becomes in terms of the f of (ϕ) that you have discussed. So let us first look at the solute chemical potential-

$$\mu_p(\phi)=v_p\left[P+f(\phi)+(1-\phi)f'(\phi)\right]$$

$$\mu_p(\phi_a)=\mu_p(\phi_b)$$

$$v_p\left[P+f(\phi_a)+(1-\phi_a)f'(\phi_a)\right]=v_p\left[P+f(\phi_b)+(1-\phi_b)f'(\phi_b)\right]$$

After certain cancellations we get-

$$f(\phi_a)-f(\phi_b)=(1-\phi_b)f'(\phi_b)-(1-\phi_a)f'(\phi_a)\ldots\ldots\ldots\ldots eqation\,1$$

We can also write the same thing for equality of solvent chemical potential, but let us first write for the osmotic pressure, so you know the osmotic pressure is the following-

$$\pi=-f(\phi)+pf'(\phi)+f(0)$$

$$\pi(\phi_a)=\pi(\phi_b)$$

$$-f(\phi_a)+\phi_a f'(\phi_a)+f(0)=-f(\phi_b)+\phi_b f^{'(\phi_b)}+f(0)$$

$$f(\phi_a)-f(\phi_b)=\phi_a f'(\phi_a)-\phi_b f'(\phi_b)\ldots\ldots.. equation\,2$$

Comparing equation 1 and 2 we get-

$$(1-\phi_b)f'(\phi_b)-(1-\phi_a)f'(\phi_a)=\phi_a f'(\phi_a)-\phi_b f'(\phi_b)$$

$$so\,,finally\,we\,get-f^{'(\phi_a)}=f'(\phi_b)\ldots\ldots\ldots\ldots equation\,3$$

So now what we get is that to attain the phase equilibrium the derivative of the Helmholtz free energy density is at the two point must be equal. Now we can put equation 3 in equation 1 and we get-

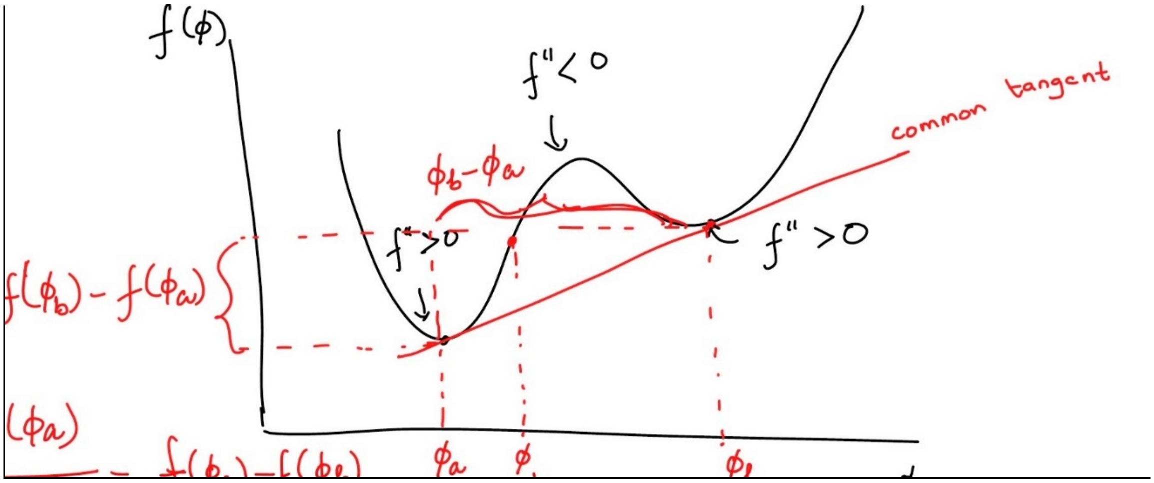
$$f(\phi_a)-f(\phi_b)=f'(\phi_b)\left[(1-\phi_b)-(1-\phi_a)\right]$$

Therefore,

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

So this tells me the concentrations that will occur at phase equilibrium in the two phases. Now let us see all exactly we can also interpret in a graphical way it is called a common tangent construction that will really help us talk about phase equilibrium in a way that we can intuitively feel from a graph.

So let us see show that the function has certain form like this, there is a particular reason why we have drawn in this way that will be clear to you in a moment and we want to know that what should be the concentration of the two phases in the case of phase separation. The first thing is that whether we will have a phase separation here or not, we of course have because there is clearly a convex part here for which a f'' is lower than 0. We do not know about the entire plot for the entire product course it has both concave regions and convex regions. So it is very difficult to say on the graph but of course since has a negative f'' somewhere in the graph, the system should phase separate depending on what is the concentration I begin with. So if it does phase separate then in that case we have derived.



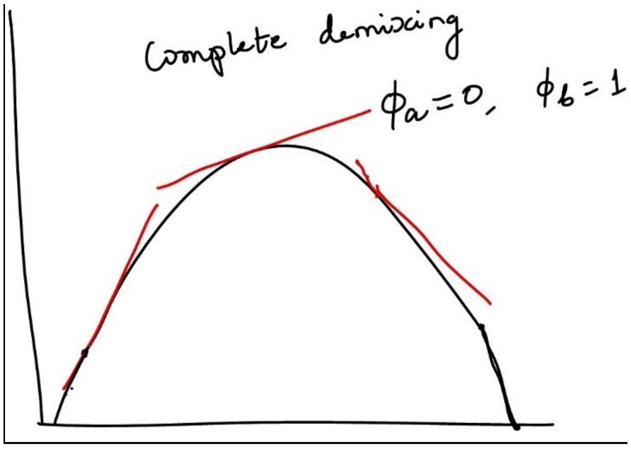
$$f'(\phi_a)=f'(\phi_b)=\frac{f(\phi_a)-f(\phi_b)}{\phi_a-\phi_b}$$

So now we can see that f' here characterizes the tangent to the graph and the tangent should be equal at two points. The tangent should be equal at 2 points that is one condition and the second condition is that the tangent value should be equal to the slope of the tangent should be able to this particular thing. It turns out it is only true if tangent that is common between the two points in this particular way and this is called common tangent, so let us say if I start with some ϕ here the only condition here is for that value of ϕ f'' must be less than 0, for that the system will phase separate into ϕ_a and ϕ_b or the other way round and you can say like how we recover a particular relation because we can do a construction here for this particular triangle.

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

So there are two things to get from here, the first thing is we can write the phase equilibrium in terms of a function f that we have discussed earlier and that and the second thing is that the equilibrium compositions will cause of the two phases will correspond to the common tangent and of course the system will phase separate only when if I start with value of ϕ the second derivative of f must be less than 0 that is the condition for the phase separate.

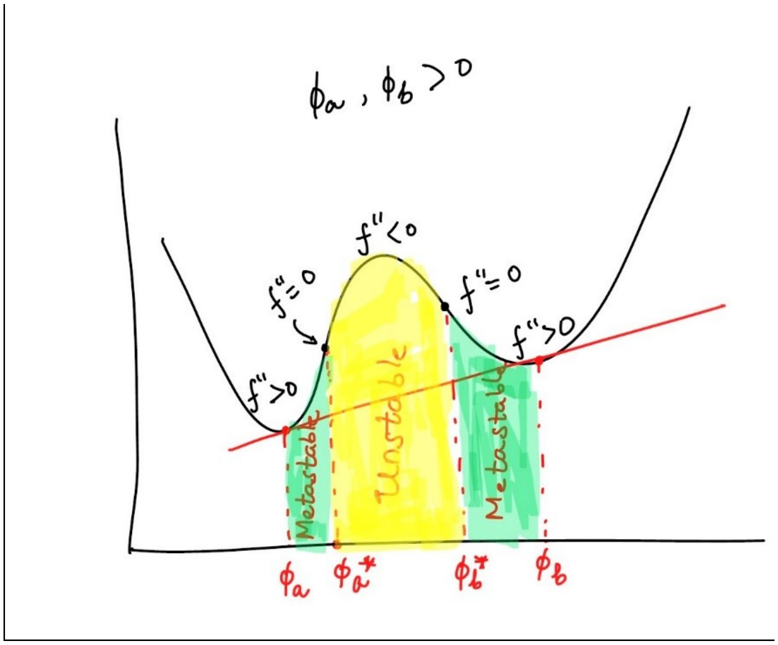
So now let us look more detail that why we have drawn this particular graph as opposed to a completely convex graph, what will happen in the case when the graph is fully convex and then we will discuss in more detail that what happens in other portions of this graph. So let us say if the graph was unlike what we had earlier and let us say the graph was like this-



So one thing is clearly see from here that is a graph was like this we can no longer draw a common tangent that passes through two points in the graph let us see if I draw a common tangent here, if I draw a tangent I cannot draw a tangent that passes through two points. I can draw tangents at different points but they do not really touch any other point on the graph, what essentially it means that in this particular case we do not really have a circumstance when we will have 2 concentrations which are different and they are in equilibrium and in this case the system will have a tendency to phase separate completely there will be like a complete di mixing- one of them will have a volume fraction of 0 the other one will have a volume fraction of 1 and we will not really have any kind of a coexistence of two different compositions which means-

$\phi_a = 0 \wedge \phi_b = 1$

So now let us see like what happens on the other part of the graph, let me again draw common tangent in this case. So if I look at the middle and it goes from a convex shape to a concave shapes to write here if f'' is higher than 0 write here f'' is less than 0, there must be a point in between that should be like an inflection point at which f'' will be is equal to 0. Similarly we may have inflection point here that f'' equal to 0 because again have f'' just becoming higher that one. So if I look at these two particular points and let me call that something like ɸa* and ɸb*, then if I am in between the ɸa* and ɸb* that in that case and f'' is less than 0 and then we always have a phase separation. But what happens when we are in the other who does seems that is it let me highlight here, this is a middle regime will assume that is when we have f'' is higher than 0, but you also have 2 other regions one here and one there for which f'' is actually a higher than 0 right. So this part in the middle is known as unstable regions and these 2 parts are known as metastable regions.



So the system is unstable when $\phi_a^* < \phi_a < \phi_b^*$ and Meta stable when the system is $\phi_a < \phi < \phi_a^*$ and $\phi_b^* < \phi < \phi_b$.

What really happens in these two regions is in the unstable region if I start with homogenous system and if I make any small perturbation to the system, the system will immediately phase separate. On the other metastable if we have the metastable region the system will not phase separate for small disturbances, this is what refer to stability, the one way to think about it is you are on a top of a cliff as soon as you get a small push you will actually fall down that will be an unstable case. In the metastable case you may not be at the minimum the global minimum of free energy but you are in some sort of a local minimum. The small disturbances will not lead to phase separation even if the final energy is lower than the energy of the state that you are in and you will require larger disturbances for the system to be phase separated into 2.

So I can then use these ideas in the next class to talk about what is known as the binodal spinodal and critical points of a system and then we will be all set to talk about the polymer solutions will start talking about how do we derive the function f, will talk about what is known as lattice model of polymer solutions and then finally you will apply in the context that we have discussed here and characterize different regions in the phase diagram of polymer solutions based on the function value that we get from the lattice model that will discuss.

So with that I will stop here, thank you.