Introduction to Polymer Physics

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Lecture-28
Solutions Thermodynamics-II

Welcome all of you, so in the last class we have been discussing about the mixing and phase separation in the context of liquid solutions more specifically a binary liquid solution containing a solute and solvent. So today I will take it further first talk about some graphical interpretation of the same thing and then we will talk about how we can get the osmotic pressure and chemical potential also in terms of what we defined as the Helmholtz free energy density.

So what we have discussed so far is if we mix for example 2 solutions one containing a volume fraction ϕ_1 of solute and in a beaker of volume V_1 and another one containing some other volume V_2 content having volume fraction ϕ_2 of the solute. They would form homogenous mixture having some volume fraction ϕ and net volume V where V is a course V_1+V_2. If the free energy in the final state is lesser than the sum of free energy in the individual previous states. So we talked in terms of the Helmholtz free energy just to recall we said that the Gibbs free energy can be written as –

$$G=V\left[P+f\left(\phi,T\right)\right]$$

Here $f(\phi,T)$ is known as Helmholtz free energy.

So if we look at the individual states and multiply the volume with the function f at a constant temperature. So we do not care about the dependence on temperature just for simplicity notation we can also put a temperature dependence. So sum of these two states the free energies are-

$$V_1 f\left(\phi_1\right)+V_2 f\left(\phi_2\right)>Vf\left(\phi\right)$$

Then mixing will occur.

What we can also do is we can find the final volume fraction in terms of the initial one using the material balance over the solute-

$$\phi V = \phi_1 V_1 + \phi_2 V_2$$

So we have 2 equations to solve for ϕ_1 and ϕ_2 if you solve what you can get is the ϕ is-

$$\phi = \phi_1 x_1 + \phi_2 (1 - x_1)$$

$$Here, x_1 = \frac{V_1}{V_1 + V_2}$$

When I said that the reverse of this can happen that is we can start with a volume V containing a solute volume fraction ϕ and this can then phase separate into two layers a bottom layer with volume V_a and volume fraction ϕ_a and in a top layer volume fraction ϕ_b and volume V_b again

$$V = V_a + V_b.$$

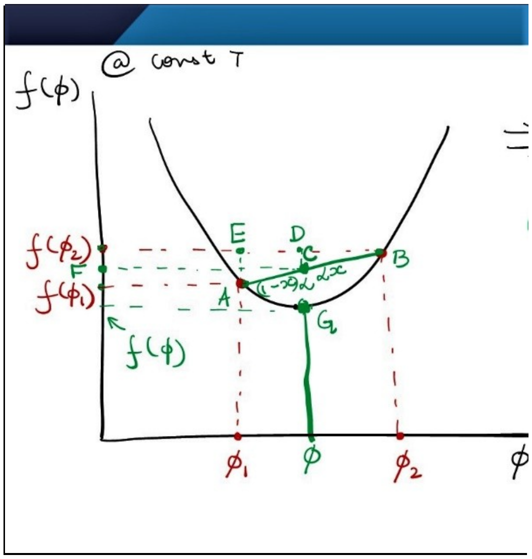
So this will happen the phase separation will happen again using the free energy criteria that is opposite of what we had earlier in the case of mixing that is the free energy in the final state free energy in the homogenous state is higher than the free energy summed in the phase separated state.

$$Vf(\phi) > V_a f(\phi_a) + V_b f(\phi_b)$$

So put it simply the mixing or a phase separation is given by a free energy criteria which ever direction will lead to a decrease in the free energy that would happen. So if the phase separation results in a lowering of free energy the system will phase separate. On the other hand if mixing leads to a lowering in free energy the mixing will occur.

So now until so far we have not really bothered about what that function f is like it can be any kind of function of course it will depend on the system under consideration it will depend on for example the interaction between solute and solvent and things like that but still if I know the particular form of function I can suggest whether the system has a tendency to mix or to phase separate.

So now you can look at and the graphical interpretation of the same thing without even knowing the function form f of ϕ just by looking at the graph we can already say whether we have the tendency to mix or to phase separate. So let us try to look into that, so what I claim is again I am doing for a constant T just to make a simpler representation, but the idea applied in general. See if I plot f of phi verses p and if the graph is same upper concave that is it has a minimum like this. So it is an upper concave graph I claim that the system will have a tendency to mix together and why is that? So let us say we mix 2 concentrations ϕ1 and ϕ2 on the graph then if I look at the corresponding value of the function they will be f of ϕ2 then f of ϕ1. If I connect these two points on the graph and look at any point intermediate on this particular lines. This corresponds to X multiplied by f ϕ1+1-x multiplied by f of ϕ2 and this we can justify in the following way. So let us say we look at this particular thing and let me say that this is my x and this is my 1-x, this would be like something multiplied by x something multiplied –x because the length of the line will not be 1, but that does not really matter. So we can think of like alpha multiplied by x for instance and alpha multiplied by 1-x for instance and let us say what we have here let us say I call this some f ok. Then by using the similar triangle relation we know that if I write segments as a, b, c then may call these points as they are, so I know that my similar triangle relation let me call the point d we know that BC/BA that is the length from here to here/the entire length of the line=CD/AE that I have just drawn here.



$$\frac{BC}{BA}=\frac{CD}{AE}$$

Now we can write this as-

$$\frac{\alpha x}{\alpha}=\frac{f(\phi_2)-F}{f(\phi_2)-f(\phi_1)}$$

Now α cancels out and we get-

$$x\left[f(\phi_2)-f(\phi_1)\right]=f(\phi_2)-F$$

$$Therefore, F=xf(\phi_1)+(1-x)f(\phi_2)$$

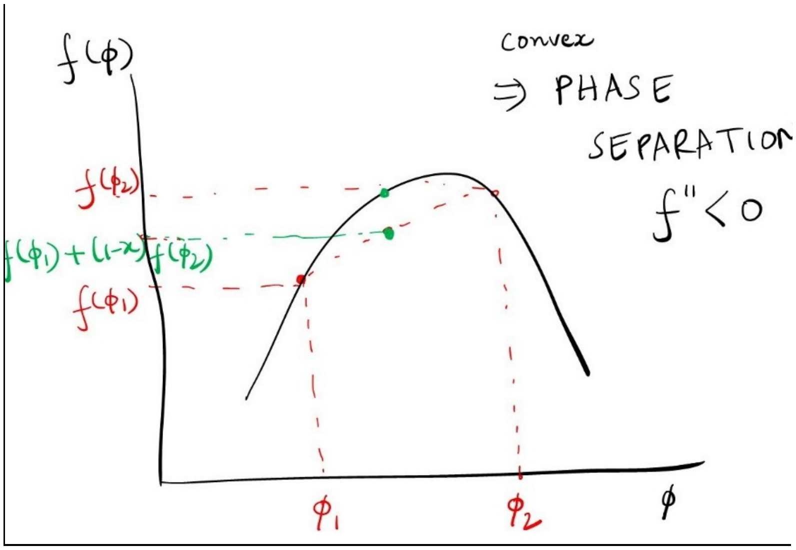
Now we have already discussed that for phase separation to occur-

$$f(\phi)<f(\phi_1)+(1-x)f(\phi_2)$$

So if the function value is less then the system has a tendency to mix together which is indeed the case because I think of any intermediate value between ɸ1 and ɸ 2 of course if I mix these two liquid at phi1 and phi2 the new mixture will have volume fraction intermediate between ɸ1 and ɸ2 so it will lies somewhere in between. So if graph has an upper concave shape we always have this particular relation that the function value is less than this. You can think of any particular value of x it does not really matter what x we choose we always have this thing that if I connect the two points by a line the function value will always be below that particular line ok as long as the graph is upper concave.

Let us see like what happens if the graph is opposite of this let us say we have convex graph that has a maxima as oppose to a minima. So now again if I think of two values ɸ1 and ɸ2 again I can do the same construction, now if I think of any value in between so this is my f of ɸ1, this is my f of ɸ2 and then this value becomes my x multiplied by f of ɸ1+1-x multiplied by f of ɸ2 that is my capital F now.

Now you can see the function value is always higher than this particular point that is always true in the case of a convex graph is just opposite of what we had for a concave graph ok. So, in this case we always have f of f ϕ higher than x of fϕ1+1-x of fϕ2, but this means is if the graph is upper concave we always have mixing as a graph is convex we always have phase separation.



Now we know from calculus that the concave graph must be for the cases where the second derivative of the function is higher than 0, so graph possess minima only when the second derivative is higher than 0. On the other hand the graph will be convex or possess maxima if the second derivative is less 0. So irrespective of the actual form of the function if we know the second derivative we can tell about the mixing and the phase separation behaviour and that is where this whole idea of the using the Helmholtz free energy density becomes useful. So this single function can tell you about whether the system is has a tendency to mix or to phase separate, we only have to look at the second derivative of the free energy.

So now I will take it further and try to discuss some 2 other concepts that we encountered in thermodynamics that is osmotic pressure and chemical potential using chemical potential we typically talk about phase equilibrium. So when I want to illustrate how these two concepts related to the definition of the f of ϕ that we have discussed it turns out that I can write the osmotic pressure and the chemical potential also in terms of this particular function and that really makes our job easy that if I know the function f of ϕ I can get all the thermodynamic quantities that I care about.

So let us first look at what the osmotic pressure is, the typical way the how osmotic pressure is defined in text is the following. So you have a chamber that contains a semipermeable membrane, on one side of chamber you have a solution containing solute particles so this is solution on the other side you have a pure solvent that contain no solute particle. We can think of the volume of the solution side to be V and if I think of the total volume as V_{tot} the volume of this side is V_{tot}-V and now what is typically said is that the semipermeable membrane first of all does not allow solute to pass through but allows solvent.

The best way to think of it is the RO setup that we have at homes. It allows the water to flow through but not the dirt particles ok, but in that case we apply an external pressure here what we discuss is slightly different idea but the membrane here in this case can really move across the chamber and can go to the left or to the right, but the solute particles cannot pass through the membrane and this is typically practically happening when for example the membrane is composed of a porous media that does not allow larger particles to pass through solute they are like larger molecules when compared to solvent this is typically an easier way to think about it.

So now to maintain the solution at a constant volume V we do need to apply an external pressure Ⅲ which we call as an osmotic pressure. Ok. This typical way we think about osmotic pressure that there is a membrane in between that does not allow the solute particles to pass through and the membrane can translate to the left or to the right and to maintain the solution at a constant volume we need to apply an external pressure and that pressure is my osmotic pressure.

Now there is a slightly different way to think about it and that is there is no membrane that say we have a room containing say a closed room and it is a smoke start coming in from one end of the room. We can also think of osmotic pressure by the fact that the smoke has a tendency to fill the entire room. So if I want to keep the smoke right there I need to apply of a pressure on the smoke such that it does not mix with the entire room. So the whole idea of semipermeable membrane the membrane is the whole idea of the semipermeable membrane is hypothetical. We do not need to think about it we can think of that I have some hypothetical line separating the solute phase and a solvent phase and that hypothetical line is pushed by the solution phase because of the presence of solute particles. So when the smoke is coming in smoke is pushing into the air and this pushing in is what is I referred to as osmotic pressure, so I have to have to apply an external pressure opposite to that that will basically prevent the smoke from filling the room.

So I want to call this chamber as a hypothetical membrane which can go this way or that way. So the only way we are differentiating the with what is normally given in books is we discard the idea of a membrane to think of a boundary separating the solution phase and the bulk and that boundary will move into the left or to the right or in 3D it can move in any direction and to prevent that movement we have to apply an external force so in that kind of a language osmotic pressure becomes a measure of the mixing tendency. If osmotic pressure is higher that means the system has a tendency to mix let us say smoke is coming in and pushing in with a large pressure that would mean a large osmotic pressure that means smoke has a tendency to mix in with the air present in the room. On the other hand if we if the smoke had a lower osmotic pressure then smoke will have lesser tendency to mix with what is present in the room. So in that kind of context we can think of high osmotic pressure ℿ as a higher tendency of mixing and now since f of ϕ that we have discussed earlier f of (ϕ,T) that we have discussed earlier Helmholtz free energy density already characterized the mixing behaviour that should also characterize the osmotic pressure. This is a qualitative way to look into this and now we will do a derivation of why it is indeed the case.

So let us now say that the total energy of system that I have just drawn say-

$$Total\,energy\,of\,system = F_{TOT}(V)$$

So if I am moving the membrane the hypothetical membrane by say a small volume dV the work done is my osmotic pressure multiplied by dV. So if we move again I am using the word hypothetical semipermeable membrane by dV to the right positive to the right, then we do the work –ⅢdV on the system just because they are in opposite direction.

If we think of work done by the system it is Ⅲ multiplied by dV, so then Ⅲ should be equal to-

$$\frac{\partial F_{tot}}{\partial V}$$

Because the change in the free energy is the work done. So now let us think of like f of TOT is?

So we have two sites of chamber one side has volume fraction of ϕ of a solute and a volume, the other side has a volume fraction 0 of solute its pure solvent and volume V_{TOT}-V. So using the idea that we have discussed earlier I think of the total Helmholtz free energy that is-

$$F_{TOT}(V)=Vf(\phi)+(V_{TOT}-V)f(0)$$

I am simply multiplying the volume with the Helmholtz free energy and adding up for the two sides and now of I use the definition of phi that is the number of solute particles multiplied by their specific volume/V i.e.-

$$\phi=\frac{N_p v_p}{V}$$

$$V=\frac{N_p v_p}{\phi}$$

$$F_{TOT}(V)=\frac{N_p v_p}{\phi}f(\phi)+\left(V_{TOT}-\frac{N_p v_p}{\phi}\right)f(0)$$

$$as\, we\, know\, \pi=\frac{-\partial F_{TOT}}{\partial V}=\frac{-\partial F_{TOT}}{\partial \phi}\frac{\partial \phi}{\partial V}$$

$$here,\frac{\partial \phi}{\partial V}=\frac{-N_p v_p}{V^2}=\frac{-N_p v_p}{\left(\frac{N_p v_p}{\phi}\right)^2}=\frac{-\phi^2}{N_p v_p}$$

$$So\ now, \frac{\partial F_{TOT}}{\partial \phi} = N_p v_p \left(\frac{(\phi f^{'}(\phi) - f(\phi))}{\phi^2} \right) + \frac{N_p v_p}{\phi^2} f(0)$$

$$\frac{\partial F_{TOT}}{\partial \phi} \frac{\partial \phi}{\partial V} = \phi^2 \left[\frac{\phi f^{'}(\phi) - f(\phi)}{\phi^2} + \frac{1}{\phi^2} f(0) \right]$$

After simplifying I get the following expression-

$$\pi = \phi f^{'}(\phi) - f(\phi) + f(0)$$

That tells me that if I know the function f of ϕ I can also get the osmotic pressure and the reason why it is happening because osmotic pressure in the end is something that characterises the mixing tendency anyway the higher osmotic pressure means higher mixing tendency and we can also look at mixing in terms f of ϕ. So both qualitatively and quantitatively we have shown that how we can write osmotic pressure again in terms of same variable. So if I know the function f of ϕ we still do not know it yet, but if I know the function f of ϕ I can also get the osmotic pressure.

In the next lecture I will also show that the same applies for the chemical potential and actually we can do the entire thermodynamics of solutions using a single function f of ϕ, so with that I will stop here.

Thank you.