Introduction to Polymer Physics
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Lecture-29
Solutions Thermodynamics-III

Welcome, so in the last class we have discussed how the osmotic pressure relates to the function that we have discussed earlier the Helmholtz free energy density before that what we said was that function f of ϕ characterizes completely the mixing and phase separation behaviour. We only have to look at the second derivative of the function second derivative is higher than 0 or the function is upper concave we will have the mixing behaviour. If the second derivative is less than 0 or the function is convex we do have a phase separation behaviour.

So now I will take further and then there is one more thing we discuss in thermodynamics very often that is chemical potential so today I will discuss the how the chemical potential also can be written in terms of the function that we have discussed the f of ϕT and Helmholtz free energy density and after that we will talk about what is thermodynamic origin of mixing, so we have been talking about the fact that the function characterizes the mixing behaviour or the phase separation behaviour, but then we talk in general about diffusion and try to see let call how all these things fall into place and how does this relate to our ideas of mass transfer that you may have discussed in the mass transfer course.

So let us talk about chemical potential, just to recall chemical potential essentially referred to the change in energy if I add a molecule of a species into the system that is my chemical potential. We talk in terms of the partial Gibbs energy that is a derivative of the Gibbs energy in respect to the number of moles, but more general sense it is simply a change in energy that we get if I add a molecule to the system and the chemical potential is very useful if I want to think of the phase equilibrium up to 2 phases when the system has a tendency to phase separate. So the way we define, so again going back to the example we have where we have a solute + solvent it's a binary system, so I can talk about 2 chemical potentials here, one of solute that is how much with energy change if I add a molecule of solute into the system. So N_p characterises the number of solute molecules and of course while doing that the number of solvent the temperature and a pressure must be held constant.

$$\frac{\partial G}{\partial N_p}]$$

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$$\mu_p=¿$$

Similarly I can define the chemical potential of the solvent which is simply the derivative of Gibbs energy with respect to the number of solvent molecules that is Ns while picking the number of solute molecules fixed and the temperature and pressure are fixed.

$$\mu_s=\left.\frac{\partial G}{\partial N_s}\right]_{N_p,T,P}$$

Now the Gibbs free energy is-

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

This is the function is the Helmholtz free energy density. Now as we know-

$$V=N_p v_p+N_s v_s$$

Therefore,

$$G=(N_p v_p+N_s v_s)\left[P+f(\phi,T)\right]$$

So now,

$$\mu_p=\frac{\partial G}{\partial N_p}=v_p\left[P+f(\phi)\right]+(N_p v_p+N_s v_s)\frac{\partial f}{\partial N_p}$$

Since we know,

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

So we can write-

$$\frac{\partial f}{\partial N_p}=\frac{\partial f}{\partial \phi}\cdot\frac{\partial \phi}{\partial N_p}$$

So now

$$\phi=\frac{N_p v_p}{V}=\frac{N_p v_p}{N_p v_p+N_s v_s}$$

$$\frac{\partial \phi}{\partial N_p}=\frac{\left(N_p v_p+N_s v_s\right)v_p-N_p v_p\cdot v_p}{\left(N_p v_p+N_s v_s\right)^2}$$

After cancellations we get:

$$\frac{\partial \phi}{\partial N_p}=\frac{N_s v_s v_p}{\left(N_p v_p+N_s v_s\right)^2}$$

Now,

$$\mu_p=v_p\left[P+f(\phi)\right]+\left(N_p v_p+N_s v_s\right)f^{'}(\phi)\frac{N_s v_s}{\left(N_p v_p+N_s v_s\right)^2}$$

After Cancellations we get-

$$\mu_p=v_p\left[P+f(\phi)\right]+f^{'}(\phi)\left[\frac{\left(N_s v_s\right)v_p}{N_p v_p+N_s v_s}\right]$$

If I now look at this particular term it is simply the volume of solvent/the total volume. So it is simply the solvent volume fraction which is 1-solute volume fraction and so we can write-

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

So again just like we did for the case of osmotic pressure we can also write the chemical potential also in terms of the function f that we have discussed earlier that is Helmholtz free energy density. In fact we can put a temperature back in here because no where we have assumed anything to do with constant temperature, same thing I can do for the chemical potential of solvent and if I do the derivations what I will get is-

$$\mu_s(\phi)=v_s\left[P+f(\phi,T)-\phi f^{'}(\phi,T)\right]$$

$$\mu_p(\phi)=v_p[P+f(\phi,T)+(1-\phi)f'(\phi,T)]$$

So if recall before from the last class we have the found expression for osmotic pressure as,

$$\pi(\phi)=\phi f'(\phi,T)-f(\phi,T)+f(\phi,T)$$

And now you can see the chemical potential can also be written in terms of osmotic pressure, because you can see this particular term that we see here is common in the previous expressions that we have derived just a - of that. So in fact we can write the solvent chemical potential as-

$$\mu_s(\phi)=v_s[P-\pi(\phi,T)]+\mu^\circ(T)$$

Here $\mu^\circ(T)$ is standard chemical potential.

So what it gives me is the chemical potential apart from the constant V_s can be thought of the difference between the bulk pressure and the osmotic pressure that is present. So going back to the smoke example smoke will exert some osmotic pressure, but ultimately it depends on the existing pressure in the room, let us say the room is a very low pressure then in that case the osmotic pressure will of course win and we will have a high mixing on the other hand the room pressure is also high then in that case the pushing in will have little effect so ultimately we can think of the mixing behaviour in terms of not really the osmotic pressure but the difference between the bulk pressure and the osmotic pressure.

But none the less the key idea that a single function f describes all that we care about thermodynamically speaking is really true because we can write the Gibbs energy in terms of ϕ we can write the chemical potential and terms of this we can write osmotic pressure in terms of this and now as I will demonstrate we can also talk about phase equilibrium in terms of the function f of phi and that way you without knowing the function even without even talking about what the function is we can always talk about that what forms of functions will give what kinds of behaviour.

So now I want to take up the ideas that we have discussed in the mass transfer or in treatments of diffusion. So you may have learnt that things go from higher concentration to a lower concentrations that is how we characterize mass transfer to be more accurate things go from a higher chemical potential to lower chemical potential that in turn depends on the concentration gradient. So how does that idea of diffusion relates to the function f that we have discussed and how does that fit into the scheme that we have been developing in solution thermodynamics.

So let us think of the thermodynamic origin of diffusion. So what do we care about you care about a gradient in the chemical potential things move from a high chemical potential to low chemical potential. So we are interested in terms like $\frac{\frac{\partial \mu_p}{\partial \phi} \wedge \partial \mu_s}{\partial \phi}$ how does the chemical potential changes with the change in ϕ. So now-

$$\mu_p = v_p\left[P + f(\phi,T) + (1-\phi) f'(\phi,T)\right]$$

$$\frac{\partial \mu_p}{\partial \phi} = v_p\left[f'(\phi,T) + (1-\phi) f''(\phi,T) - f'(\phi,T)\right]$$

$$\text{¿} v_p (1-\phi) f''(\phi,T)$$

$$\mu_s = v_s\left[P + f(\phi,T) - \phi f'(\phi,T)\right]$$

$$\frac{\partial \mu_s}{\partial \phi} = v_s\left[f'(\phi,T) - \phi f''(\phi,T) - f'(\phi,T)\right]$$

$$\text{¿} - v_s \phi f''(\phi,T)$$

So now let us go back to the original idea that for mixing f “is higher than 0 that came from the concave nature of f. So f’’ is higher than 0 we can see from here that $\frac{\partial \mu_p}{\partial \phi} > 0$ and $\frac{\partial \mu_s}{\partial \phi} < 0$.

Now since things go from a higher chemical potential to a lower chemical potential and what we see here is μ_p is increasing with increasing ϕ and μ_s is decreasing with increasing ϕ.

The chemical potential will decrease when the ϕ decreases that means going back to the chamber analogy, so if you think membrane again for the solute particles if they move to the right that results in a decrease in the volume fraction of solute this must be favoured because this is a process going from a high chemical potential to lower chemical potential. On the other hand for the solvent particles as the volume fraction increases we will have a lowering of the solvent chemical potential so solvent will try to mix with solute because when it mix this is with the solute the volume fraction increases and that results in an lowering of the chemical potential. On the other hand when we have mixing of solute with solvent the solute chemical potential decreases because it starts with higher ϕ due to mixing that results in lowering of ϕ so in both ways this is actually characterizing a mixing behaviour.

So if the analogy is somewhat confusing to you let us start with say a concentrated solute solution that has a very high value of volume fraction ϕ and let us say I mix in into a pure solvent. So when I mix in then the volume fraction of the solute decreases when compared to the initial concentrated solution of solute and this is a favoured process because the chemical potential of solute is decreasing, it is going from a high to a low chemical potential. In the same problem if I am now look at the solvent phase, solvent phase also goes to a lower chemical potential when the solute is added into it. So the motion of the solvent and solute are actually opposite of each other that is what results in the mixing behaviour.

If on the other hand if we have a phase separation then f'' is less than 0 that is when $\frac{\partial \mu_p}{\partial \phi} < \frac{0 \wedge \partial \mu_s}{\partial \phi} > 0$. It means that μ_p decreases with increasing ϕ, so if μ_p is decreasing with increasing ϕ then the concentrated solution will prefer remaining concentrated it will not like to be dilute. On the other hand the μ_s is actually increasing with increasing ϕ so the pure solvent will prefer remaining pure solvent because when it mixes with the solute the volume fraction increases and the chemical potential also increases.

If I mix with dilute solution and concentrated solution, so ultimately for them to mix together solute molecules will go in the dilute phase if the chemical potential is decreasing in that direction and that will only happen when f'' is higher than 0. Similarly solvent molecule will go in the in the bottom phase only when f'' is higher than 0 because that results in the lowering of chemical potential of solute. So the mixing only happens when we have a positive value of the second derivative of f.

So now you can see that this whole idea of the mixing and phase separation that we started with basically explains or relates the concepts of osmotic pressure and chemical potential that we have discussed in thermodynamics classes. And now I want to take it further and talk about the phase equilibrium that is when the things phase separate and let us say the system prefers to remain phase separated as oppose to mix that will be the case when f'' is less than 0, but when it is phase separated then we can talk about a phase equilibrium that is given by the equality of chemical potential. So how can we use the idea of f of (ϕ,T) that Helmholtz free energy density to characterize the phase equilibrium.

So again the whole motivation of the exercise is to simplify our analysis of thermodynamics to a single function in the case of a liquid solution and then we will go on talk about polymers and we tried to argue what that functions should be based on some simplistic models that we will discuss.

Ok, so with this I conclude this lecture, thank you.