Introduction to Polymer Physics
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Lecture-34
Phase Behavior of Liquid Solutions

Welcome in the last class we have derived the expression for the Helmholtz free energy density for a liquid solution and we will take from that expression today and go on to describe the different phase behavior of a liquid solution and then we can extend that to a polymer solution. So, just to recall what we have derived using the lattice model of liquid solutions that contains essentially two species- a solute and a solvent. Both are assumed to have the same volume same as the lattice cell volume and they are essentially occupying positions on a lattice rather than moving on a 3 dimensional volume. So, for this case we have derived that the Helmholtz free energy is given as-

$$f(\phi,T)=\frac{k_B T}{v_c}\left[\phi\ln\phi+(1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)\right]$$

We can identify some terms here and assign some meaning to them and those meanings will then make some sense and using those meanings we will develop the model for polymer solutions. So, although when I am assigning this particular meaning to these terms it is not very rigorous because it is anyway is mean field approximation and we cannot really decouple terms the way I am proposing it to but it really helps us understand that what kind of contributions come in to the free energy of solute solvent system in general.

So, the first term ($\phi\ln\phi$) we can associate to some entropy of solute because ϕ is its volume fraction if you go back in the derivation we had a logarithmic of the number of microstates and from there we have got this particular term in this expression. The second term $(1-\phi)\ln(1-\phi)$ for the same reason is the entropy of solvent and the last term $\chi\phi(1-\phi)$ is the interaction that is apart from entropy between solute and solvent. I will use the word effective interaction here just to recall you that χ came from an effective energy $\Delta\epsilon$ and $\Delta\epsilon$ was something like ϵ_{pp} + ϵ_{ss} - 2 ϵ_{ps} that is it depends on not only the solute-solute interactions but also solute solvent, solvent-solvent interaction. So, it is like an effective interaction between the solute and solvent.

So, with this what we have also discussed is this function happens to be symmetric around $\phi = \frac{1}{2}$ and of course this is what should happen for a phase separation for no phase separation we should have a behavior like this in terms of χ, if χ is higher than χ_c some critical value we will have phase separation then when χ is less than the critical value we will have a homogeneous result. So, the larger value of χ refer to the poor solvent conditions the solvent larger value of χ means poor solvent lower values particularly negative values would mean a good solvent that will tend to form a homogeneous solution of solute and solvent.

So now let us work on this expression you also said that the advantage of symmetric f is we can draw a common tangent and solve f' = 0 for the binodal rather than solving a more complicated equation. So, let us go ahead and look at how the derivatives of this look like and then we can find the binodal, spinodal and critical point for this system.

So, I will reproduce my function here-

$$f(\phi, T) = \frac{k_B T}{v_c}\left[\phi \ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right]$$

So if I take the first derivative now it becomes-

$$f' = \frac{\partial f}{\partial \phi} = \frac{k_B T}{v_c}\left[1 + \ln\phi - 1 - \ln(1-\phi) + \chi\phi(1-2\phi)\right]$$

Here so the in the first - 1 comes because we take 1 - ϕ multiplied by the derivative of ln that is 1 by 1 - ϕ with a negative sign, so that is how we got a minus there. And the second term is simply we keep ln of 1 - ϕ and take a derivative of 1 - ϕ that is also – 1.

So for binodal line or the coexistence curve in this particular case what we have is-

$$\frac{\partial f}{\partial \phi}=0\, therefore\, , \chi_b(1-2\phi)+\ln\frac{\phi}{1-\phi}=0$$

$$so\, , \chi_b=\left(\frac{-1}{1-2\phi}\right)\ln\left(\frac{\phi}{1-\phi}\right)$$

Now we can go ahead and find the spinodal by simply looking at the second derivative of f. So, we already have found the first derivative

$$f'=\frac{k_B T}{v_c}\left[\ln\frac{\phi}{1-\phi}+\chi(1-2\phi)\right]$$

$$f''=\frac{\partial^2 f}{\partial \phi^2}=\frac{k_B T}{v_c}\left[\frac{1}{\phi}+\frac{1}{1-\phi}-2\chi\right]$$

Now if I want to get the expression for the spinodal line and it has to be given by f'' = 0, which give me the expression if I represent χ_s as the function value of solvent quality for spinodal line that has to be-

$$Spinodal\, line\, f''=0\, is\, \chi_s=\frac{1}{2}\left(\frac{1}{\phi}+\frac{1}{1-\phi}\right)$$

If I want to find the value of the critical point I have to find the third derivative. So, let us go ahead and try to find the third derivative. So, this has to be-

$$f'''=\frac{\partial^3 f}{\partial \phi^3}=\frac{k_B T}{v_c}\left[\frac{-1}{\phi^2}+\frac{1}{(1-\phi)^2}\right]=0\, at\, crtical\, point$$

If, I solve the equation for the third derivative what I will have is-

$$\frac{1}{\phi^2}=\frac{1}{(1-\phi_c)^2}=\frac{1-\phi_c}{\phi_c}=\pm 1$$

$$So\, , 1-\phi_c=\phi_c\, therefore\, \phi_c=\frac{1}{2}$$

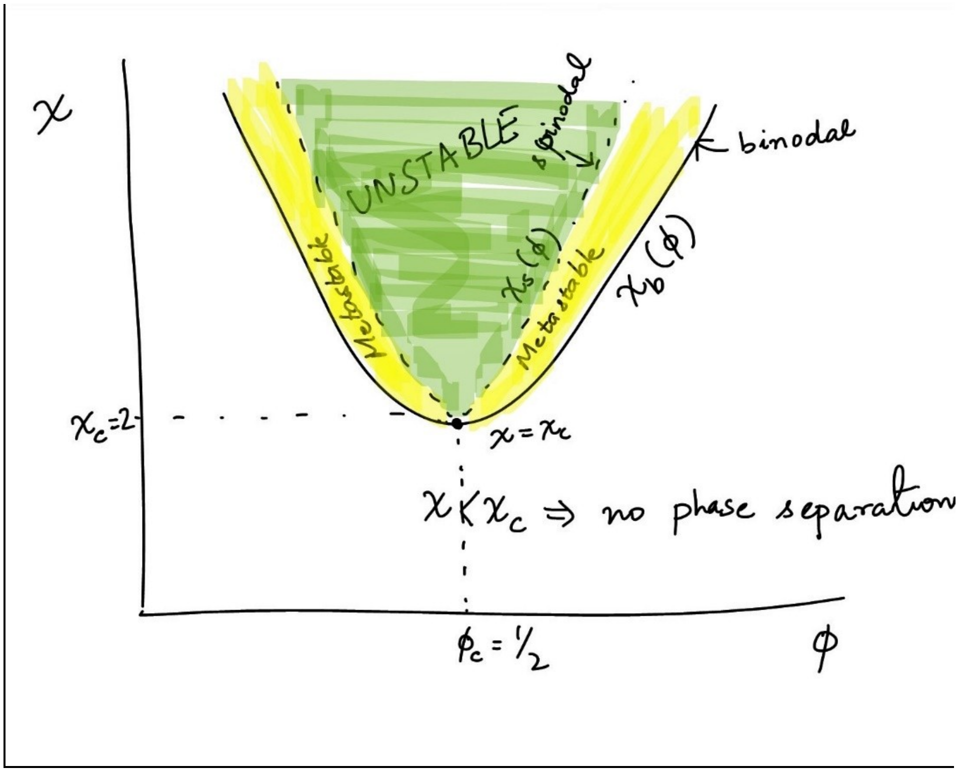
Here ϕ_c is a value of the volume fraction at critical point.

If I want to know the value of χ at the critical point I can put this value of ϕ in the expression for spinodal or in the expression for binodal because both binodal and spinodal do merge at the critical point. So, let us say I am computing-

$$\chi_c = \chi_s(\phi_c) = \frac{1}{2}[2+2] = 2$$

You can try plugging in also in the earlier equation and you should essentially get the same value but the problem here is that in this particular case you get a 0 by 0 kind of a term so you have to take a limit and use lapels rule if you are going by the bimodal. But essentially both of you should give you the same result that the solvent quality at critical point is equal to 1 by 2.

So, putting all these ideas together what we then have is the following phase diagram that I will draw here so we have χ, versus ϕ. So, of course for χ less than χ_c there is no phase separation. Phase separation only occurs beyond $\chi = \chi_c$ this point by the way is ϕ_c = ½ and this is χ_c = 2 this curve is my co-existence curve this I get by solving the equation for the binodal inside this we will have a curve for the spinodal χ_s ϕ and both of them of course will merge further at the critical point. So, just the way we have defined the metastable and unstable regions earlier we can define here as well sides are metastable region and the middle region is unstable reason and of course outside the envelope we do not have any phase separation occurring.



So, this we have discussed for liquid solution. Now I will tell you like how can we extend these ideas to a polymer solution. So, a more rigorous way of doing it is to try to get the actual number of a polymer configuration on the lattice but it turns out to be somewhat complicated in maths. So, we will first describe purely into intuitive approach and try to see like how does it captures the behavior of polymer solution it turns out that even by doing a more rigorous mathematics will give you the same result.

So, I want to start with the f that we have derived,

$$f=\frac{k_B T}{v_c}\left[\phi\ln\phi+(1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)\right]$$

and now recall in this particular case of liquid solutions we have identified these three terms as my solute entropy, solvent entropy and the solute solvent interaction and now we note that if I now want to put a polymer chain there the first approximation that goes wrong is the approximation that the solute and solvent are of the same volume of course the approximation was not very correct even for a simple liquid solution but at least they were of a similar size or similar order of magnitude of size but if we have a polymer chain present in say water then of course the size of a polymer chain is nowhere comparable to the size of a water molecule it is of course the polymers chain is much larger compared to the water molecule.

Now the other thing that we have to keep in mind is the solute molecules can then go anywhere in the lattice with relative ease. In the case of a polymer molecule now they have to move together so when all the ingredients or all the beads all the segments of a polymer chain are moving together compared to the case when the solvent solute molecules the small ones are moving separately inside a lattice what you can note is that the entropy of a connected polymer chain where it is formed by connecting this individual segments or beads should be much smaller compared to the entropy of small molecules.

So, other way to think about it is and I will build on this representation in the next lecture is if for example you have solute molecules on the lattice and remaining positions are occupied by the by the solvent molecules they will have much larger entropy compared to the case when these solute molecules represent a bead or a segment of a polymer chain. So, in that case now these molecules let us say you had five molecules as here now they have to move together so the number of configurations is much, much lesser than the number of configurations that we had in the case of a liquid solution because now the segments of a polymer chain cannot move anywhere the reason why we have chosen segments as the unit is because we can imagine the segments at least may have the volume of an order of magnitude similar to a water molecule. We can always decompose a large polymer chain into smaller segments we can have say 1000 segments or 10000 segments. Each of those segments then have a volume similar to a solvent molecule so in that context instead of putting an entire polymer chain on a given cell I will now put a segment in a given cell and now we will perform a random walk on a lattice just like we have discussed in random walk models we have done earlier in the in the course.

So, the main idea is that once the segments are connected and they are moving on a lattice this happens with a much lower entropy then compared to the case where segments would not have been connected or rather speaking we can say that the solute where smaller in size or comparable to water molecules or solvent molecules. So, what it turns out then is if I want to go from this model a liquid solution model to a polymer solution model all I have to do is simply divide the first term by N because the polymer entropy is very reduced very less compared to the solvent entropy where N is the number of segments of polymer chain in fact we can pretty much also drop the first term because polymer entropy in any case will be very smaller compared to the entropy of solvent molecules.

So, you will take start from this point and then discuss the phase behavior in the case of a polymer solution, thank you.