Introduction to Polymer Physics
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Lecture-35
Lattice Models of Polymeric Systems

Welcome in the last lecture we have discussed the lattice model of solutions and then very briefly we discussed like how we can extend that to polymer solutions. So, we will take it further today and then talk about the phase behavior of polymer solution using the lattice model. So, what we are developing is the lattice model of polymer solutions. So, again as I have said we will use the analogy of a lattice just to simplify the analysis so again it is a toy model we are going to make similar approximations of mean field and all that in fact we will not completely derive the expression as they are in the books but they are very similar to what we have done for a liquid solution.

So, now one thing we noted in the last class was compared to the solution model where we assumed that solute and solvent are the same size we can no longer assume that instead what we assume is instead of individual polymer chains present in a lattice side we will have segments of polymer chains which are present and these have the same volume. So, segment volume is taken equal to solvent volume and that is equal to the v_c the cell volume that we have discussed earlier.

So, now within that model we can imagine that we have polymer chains and the segments are connected as we have done in the context of random walk on a lattice and the remaining positions are occupied by solvent molecules. So, now instead of N_p and N_s solute and solvent what we do have is we have N_p polymer chains of let us say some N segments each and we have N_s solvent molecules and then we said that if I compare the different terms in the expression we derived for liquid solutions what we can note here that the solute entropy and solvent entropy they are the same in the case of a liquid solution which will not be true in this case because the segments of a polymer chain are connected together so they will have substantially lower entropy then compared to the solute which was present in the liquid solution model.

So, using this idea the polymer entropic term will be divided by N that is the number of segments in a polymer chain solvent entropy term remains unchanged and the solute solvent interaction term also remains unchanged. So we can write equation as-

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

So, now one thing you can see is unlike the earlier case where I can replace ϕ by 1 - ϕ and we get the same expression and that is why we said we have a mirror symmetry around ϕ = ½ .This we cannot do here because if I replace ϕ by 1 – ϕ we will have like 1 - ϕ by N there so this is no longer symmetric as we had earlier, so no not symmetric now ϕ = ½ which also means that the common tangent is not horizontal okay and in that case we know how to find the coexistence line. So, coexistence line given by-

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

So, now let us go ahead and try to find the binodal, spinodal and critical point for this function graph but we already have noted that the function is no longer symmetric it can be anti-symmetric like this that means it will have a common tangent that is no longer horizontal alright. So

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

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

Using this expression of f' and using the expression for coexistence line or binodal we can get the binodal curve from here but let’s say we go ahead and try to find the spinodal and critical point. For spinodal we are interested in the second derivative it is-

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

So from here spinodal line we can write as-

$$\chi_s=\frac{1}{2}\left[\frac{1}{\phi N}+\frac{1}{1-\phi}\right]$$

Now for the critical point I should go to the third derivative. It is equal to-

$$f^{'''}=\frac{k_B T}{v_c}\left[\frac{-1}{\phi^2 N}+\frac{1}{(1-\phi)^2}\right]=0=\text{¿}\left(\frac{1-\phi}{\phi}\right)^2=N$$

$$\frac{1-\phi}{\phi}=\sqrt{N}$$

$$\phi_c=\frac{1}{1+\sqrt{N}}$$

This is our critical value. Let us see what happens when we use a minus value then we have-

$$\frac{1-\phi}{\phi}=-\sqrt{N}$$

$$so,\phi=\frac{1}{1-\sqrt{N}}<0\ for\ N\gg 1$$

In this case here we can pretty much forget about this solution and then if I want to find the critical solvent quality I can simply plug in the expression ϕ_c in the expression of the spinodal and what I do get is this-

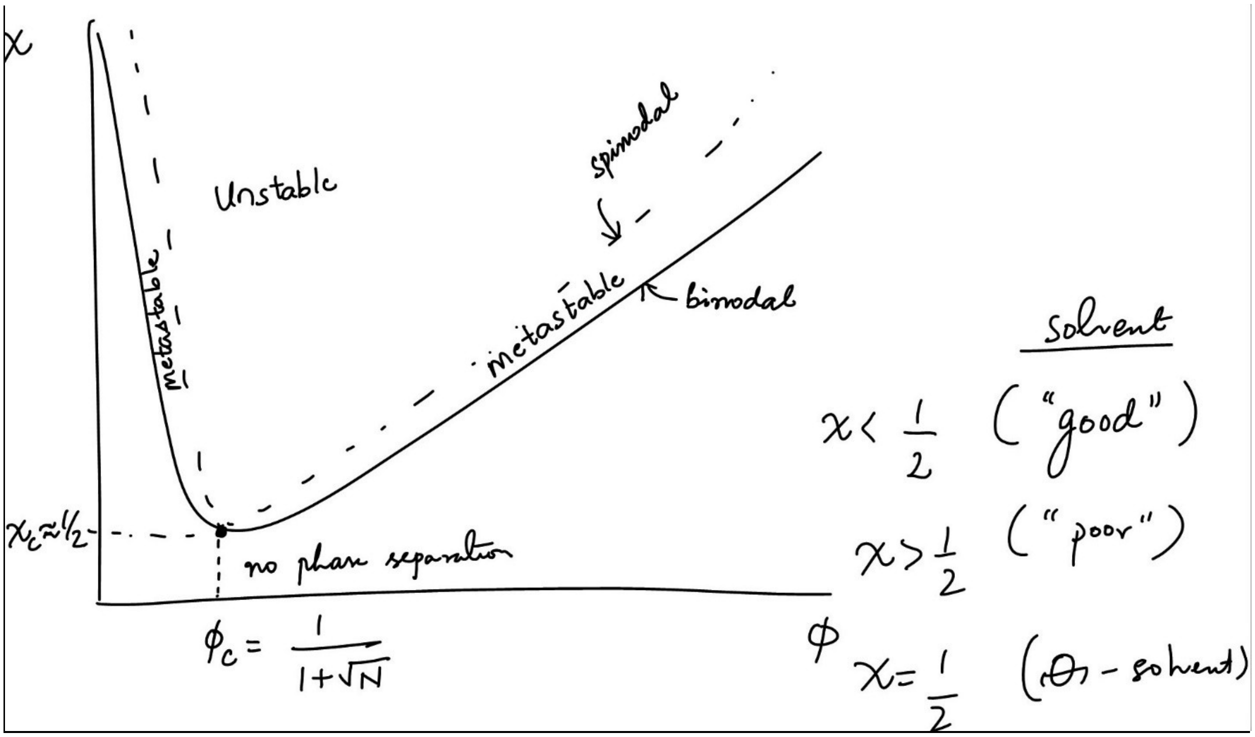
$$\chi_c=\chi_s(\phi_c)=\frac{1}{2}\left[\frac{1}{\phi_c N}+\frac{1}{1-\phi_c}\right]=\frac{1}{2}\left[\frac{1}{N(1+\sqrt{N})}+\frac{1+\sqrt{N}}{\sqrt{N}}\right]$$

So the χ_c will then be something like this if you look at these terms then for large value of N what you can see that the first term is anyway much smaller compared to the second term so, we can drop the first term in the second term we have like 1 by root N + 1, 1 by root N is anyway small because N is very high. So, what do we get is-

$$\chi_c \approx \frac{1}{2}$$

If I now look at the phase diagram for a polymer solution there is two things to note here and the critical volume fraction which was ½ for the case of a liquid solution is now something like 1 by 1 + $\sqrt{N}$ that is very small compared to 1 for N larger than 1 actually it becomes 0 in the limit and it is infinite and the critical solvent quality which was to 2 earlier is now ½ for large value of N actually it approaches there for I would say even substantially smaller values like 300 or 200 then also you will get a value very close to ½ .

So, with these two things if I look at the phase behavior the first thing to notice is it is going to be highly un symmetric then the critical volume fraction is like 1 by 1 + $\sqrt{N}$ and χ_c is approximately equal to ½ and again we can have a spinodal so here is my binodal that I have to get my solution of the coexistence curve equation with the only detail here that the common tangent is not horizontal then this is my spinodal that we have derived and this is of course my critical point. There is also metastable region and unstable region and below this value we have no phase separation.



In fact then this value of ½ has a very important meaning in the polymer language because if χ is less than ½ I call my solvent to be good. If χ is much higher than or higher than ½ I call my solvent to be poor or bad and if Chi = ½ then this represents what is known as a θ solvent that is in between the good and poor limits just like what we showed for a single chain we can now think at a thermo dynamic behavior level that the good solvent will have no phase separation bad solvent or a poor solvent is when we will have a phase separation and a θ is just the brink of these those two extremes.

So, it turns out that if I now want to look at different kinds of polymer system of course we can go through the full derivation but just looking at the expression we began with give us good clues to derive expression for different polymer systems even different from polymer solutions.

So, let us say for instance I am interested in the behavior of a polymer melt. So, polymer melt contains only two species you have polymer A of volume fraction ϕ polymer B of volume fraction $1 - \phi$ and we have no solvent. Let us say the polymer A has N_A segments per chain polymer B has N_B segments per chain. We can build the expression of f by simply writing the entropy and interaction terms just like we did for a polymer solution.

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

Since we do not have any solvent in the system we do not have to worry about the solvent entropy and then of course we have a χ this is no longer the solvent quality. It is between A and B, so I can call it χ_{AB} that represents the energetic interaction between polymer A and polymer B.

And then I can go ahead and try to do the calculation of binodals spinodal and critical point for the polymer melt as well. So, the by this way the very simple idea of a lattice model can be extended for different kinds of polymer systems and although we have limited ourselves so only two components we can think of three component as well. So, now you will have three entropy terms and you may have various combinations of the energetic interaction terms.

So, let us say if we have A, B and C now we can write like I like-

$$f=\frac{k_B T}{v_c}\left[\frac{\phi_A}{N_A}\ln\phi_A+\frac{\phi_B}{N_B}\ln\phi_B+\frac{\phi_c}{N_c}\ln\phi_c+\chi_{AB}\phi_A\phi_B+\chi_{BC}\phi_B\phi_C+\chi_{CA}\phi_C\phi_A\right]$$

This is the benefit of the toy model that it allows us it provides us an easy way to construct the Helmholtz free energy density of my polymer systems and using that by the math that we have done we can go ahead and try to find the binodals spinodal and critical point and we can actually draw a phase diagram of the sort that we have we have discussed here.

So, I will provide some examples in the course that you can work through and try to apply the same concepts that we have just used here for somewhat different types of polymer systems.

So, with that I conclude, thank you.