# Introduction to Polymer Physics
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## Lecture-33
## Lattice Model of Solutions - II

Welcome in the last class we have been discussing the lattice model of solutions and we have already went half way through the derivation of the expression for the Helmholtz free energy density. So, I will quickly recap that derivation we have been doing and then we will take it further and complete the derivation that we have been working on. So, just to recap we are working on the lattice model of solutions where we assume that we have certain number of solute and solvent molecules in the system, which are constrained to move on a lattice instead of moving everywhere in 3d space and the and of course both solute and solvent are assumed to occupy the same volume that is equal to the lattice volume and it is equal to the cell volume in the lattice.

So, until so far what we have done is we have derived within what is known as the mean field approximation that assumes that all configurations have the same energy $E_i$ within that approximation I said that the partition function which generally is the sum over Boltzmann factors of all configurations i with all configurations with energy $E_i$-

$$Z=\sum_i \exp\left(-\beta E_i\right)$$

If I assume the $E_i$ approximately equal to the mean energy I can write this as-

$$Z=W\exp\left(-\beta E_i\right)$$

Here $W=\frac{\left(N_p+N_s\right)!}{N_p!\,N_s!}$ and also we derived the expression for $\acute{E}$ as-

$$\acute{E}=\frac{1}{2}N_{tot}\,z\left[\epsilon_{pp}\phi^2+\epsilon_{ss}\left(1-\phi\right)^2+2\epsilon_{ps}\phi\left(1-\phi\right)\right]$$

So, if you look at this particular term and keeping in mind where ultimately I am interested in the free energy i.e.-

$$F = -k_B T \ln Z$$

And actually divided by volume of that quantity F by V and in that quantity I only care about the quadratic terms in ϕ and the reason is because ultimately the behavior of mixing and phase separation is dictated by the second derivatives. So, since we, only care of $f''$ for mixing or phase separation. We can drop all the linear terms, that are terms containing either ϕ or a constant that we can drop because any way we are interested in second derivatives okay and if that is somewhat confusing to you, you can try doing a separate derivation starting from the terms we have ignored and in the end you will see that those terms are really having no significance in the larger scheme of things because ultimately we are going for the second derivatives of the function f that I will derive.

So I will collect the terms that contains second power of ϕ that is $\epsilon_{pp}\phi^2$ here. So, this term will retain so let me write on top what will retain. In the second term there is $\epsilon_{ss}\phi^2$ and then we have two more terms which are of lower order they will be ignored and similarly in the last term we have 2 $\epsilon_{ps}\phi^2$ and we also have a 2 $\epsilon_{ps}\phi$ which is a linear term and we can ignore that. So, using this idea I can get the expression for $\acute{E}$. Now we are left with the terms

$$\epsilon_{pp}\phi^2 + \epsilon_{ss}\phi^2 - 2\epsilon_{ps}\phi^2$$

So, again if you have any confusion you can try retaining the linear terms and continue derivation and then see how does it affect the end results with regard to the mixing and phase separation behavior that we are going to discuss and what you will find out is that that dropping the linear term has no consequence in the final results that we are after.

So, what we get is $\acute{E}$ now is-

$$\acute{E}=\frac{1}{2}N_{tot}z\phi^2\left[\epsilon_{pp}+\epsilon_{ss}-2\epsilon_{ps}\right]$$

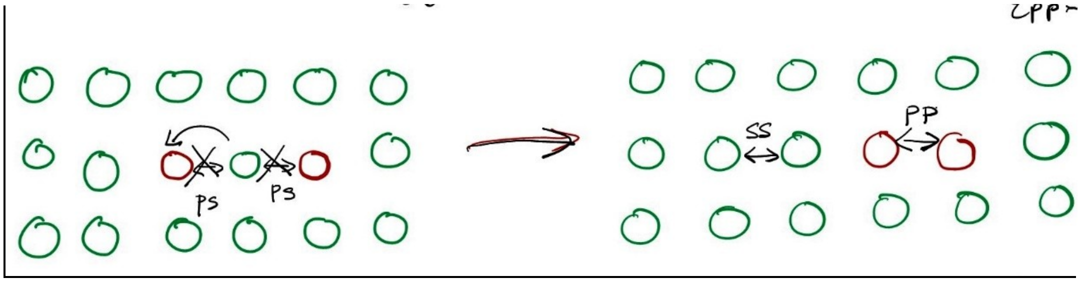
$$Now\,we\,can\,write\,\Delta\epsilon=\left[\epsilon_{pp}+\epsilon_{ss}-2\epsilon_{ps}\right]$$

$$Therefore,\acute{E}=\frac{1}{2}N_{tot}z\phi^2\Delta\epsilon$$

So, before we go further in derivation let's pause for a moment and try to see like what does this, $\Delta\epsilon$ signify. So, we are interested in the total energy of the system and that energy is composed of solute- solute interactions, solute solvent interactions and solvent- solvent interactions and so $\Delta\epsilon$ in some sort represents the effective interaction that is present in the system. Okay, and now of course this $\acute{E}$ does not contain the entropic contribution the entropy will come separately. This contains in some sort the energetic or enthalpic contributions but in any case if this $\acute{E}$ is highly positive that would mean that the system will not like to mix it will have a tendency to phase separate. On the other hand if $\acute{E}$ is very negative that would mean the system will have a tendency to mix. So, this $\Delta\epsilon$ in some sense characterizes the enthalpic part of energy.

So, let us see let us think that we had the cross section of the system that we started with which was all solvent molecules and in between we have a solute in the middle and we have we have a solvent in the middle and then we have two solutes which are right now separated they are not together and let us say we are thinking about a process where these two molecules will come together.

So, in that case the new arrangement the two solute molecules come together this will be the new arrangement. Now let us think of like what is the energy gain or loss that happened as a result of this particular process where the solute molecules which were a bit farther came together and formed a new pair.



So, now if we look at this particular arrangement what you will notice is going from left to right we formed one additional pair of solute and then since this guy moved here the solvent moved here it also formed a new solvent- solvent pairs between these two. You can see like all the other pairs between solute and solvent remained unaffected except the ones I am looking at. And then you can also see that there were two pairs between solute and solvent which had to be sacrificed as a result of this process because the solute molecules came together they formed one contact so, we gained energy by one contact off or one pair of solute- solute one pair of solvent- solvent minus two pairs of solute and solvent that we had to sacrifice. So, the energy change in this process is-

$$\Delta E=\left(\epsilon_{pp}+\epsilon_{ss}-2\epsilon_{ps}\right)=\Delta\epsilon<0$$

So, if $\Delta\epsilon$ is less than 0, I will tend to form more pairs of solute and solute which if you now think of more number of solute molecules if the system favors the formation of solute-solute pairs that means system has a tendency to phase separate. Okay. So, this essentially means a tendency to phase separate. Now what is interesting here is the following that the phase separation or the $\Delta\epsilon$ is not really dictated by the solute- solute interactions alone they are also dictated by the solvent-solvent interactions. So, what happens for instance if $\epsilon_{ss}$ is like very negative and let us say $\epsilon_{pp}$ is 0 $\epsilon_{ps}$ is also 0 or close to 0. So, although the solute does not interact with the solvent and there is no interaction between solutes even then we can have phase separation because the solvent like itself much larger.

This is an example we have been giving about the hydrogen bonding in water. If the interaction between water molecules are so large then any solute which does not offer an energetic contribution in terms of either a solute solvent interaction or a solute- solute interaction will has to have to phase separate that is of course that is a limiting case because most of them will have some favorable interaction let us say a hydrogen bond with water and so on.

So, the key lesson from here is when we talk about the interaction between solute molecules and this is not example of polymer right now this can be any solution. When we take the interaction between solute molecules we have to think in an effective way in a sense that how are the solvent- solvent interactions and solute solvent interactions also affected by the contact of solute species.

So, in the in the polymer physics language we define a quantity named $\chi$ that is called a solvent quality. Right now we are not doing a polymer solution but let us say at least define the quantity. The quantity is defined also for a binary solution so that we can use it more effectively and we discuss about polymer solutions. So, we will define a quantity called solvent quality $\chi$ that is defined as-

$$\chi = \frac{-z\Delta E}{2k_B T}$$

And I can plug that in here and that I will have-

$$\frac{\acute{E}}{k_B T} = -N_{tot}\chi\phi^2$$

As in any case we do not look at the interaction values by themselves we look at how they compare to $k_B$T that is a thermal energy only if the energy is very high compared to thermal energy it can have any effect on the system because otherwise the system is entropy dominated and favors mixing.

So, let us keep that aside for a moment and let us go back to the expression of Z that we started with. So, Z is now-

$$\left(-\beta \acute{E}\right) = ¿ \ln Z = ¿ \ln W - \beta \acute{E}$$

$$Z = W \exp ¿$$

The Helmholtz free energy is-

$$F = -k_B T \ln Z$$

$$¿ - k_B T \ln W + \acute{E} = E - T\left(k_B \ln W\right)$$

The $\left(k_B \ln W\right)$ is a definition of Entropy S as given by Boltzmann.

So, Boltzmann really had a very funny life he derived this particular expression and no one agreed to that this expression of entropy and while he was he was living. Only after he died people saw value to his work and this expression is engraved on his grave is $S = k_B \ln \Omega$, $\Omega = W$ which was one of his most important contributions to today's thermodynamics. So, we just multiply the Boltzmann constant, so of course he did not call it a Boltzmann constant. He called it a constant k by the logarithmic of the number of possible states the system can have we get an expression for the entropy of the system. This is the Boltzmann formula now it is known in the thermodynamics.

So, now you can see this expression we have is $\acute{E}$ r - TS you can compare to the standard thermodynamic expression F = U - TS and note very clearly that U is basically my $\acute{E}$ and TS appeared as it is that we had there, okay. So although when I first define this quantity I did not make any particular link to the expression right here but now you can see for yourself that this is what it is. The $\acute{E}$ is some sort of internal energy of the system only thing is that it is derived in a mean field sense in the theory that we have discussed where we assume that all the configurations are having the same energy $E_i$.

So, now we know what W is and we know what $\acute{E}$ is. So, let us first look at ln of W. As we know W is-

$$W=\frac{(N_p+N_s)!}{N_p!\,N_s!}$$

Therefore,

$$\ln W=\ln\left[(N_p+N_s)!\right]-\ln\left[N_p!\right]-\ln\left[N_s!\right]$$

We will make use of what is known as the Sterling formula we had already used it in the context of random walk. So, for large N the ln of the factorial can be approximated as N ln N - and there was one more term there that we are also ignoring that is anyway smaller term compared to this ok. So, using this formula what we have is

$$\text{¿}(N_p+N_s)\ln(N_p+N_s)-(N_p+N_s)-N_p\ln N_p+N_p-N_s\ln N_s+N_s$$

$$\text{¿}-N_p\ln\frac{N_p}{N_p+N_s}-N_s\ln\left(\frac{N_s}{N_p+N_s}\right)$$

And this by definition is ϕ and 1 – ϕ and so we get-

$$\ln W\cong-N_p\ln\phi-N_s\ln(1-\phi)$$

So, now you can note again that ultimately-

$$N_p=N_{tot}\phi\wedge N_s=N_{tot}(1-\phi)$$

Therefore,

$$\ln W\cong-N_{tot}\left[\phi\ln\phi+(1-\phi)\ln(1-\phi)\right]$$

Now I will go back here put the expression of ln W here so it is $\acute{E}$ - $k_B$T ln W and $\acute{E}$ we have already obtained right here - $N_{tot}$ χϕ square multiplied by $k_B$T. Now I will go back here put the expression of ln W here so it is-

$$F=\acute{E}-TS=\acute{E}-k_BT\ln W$$

$$\text{¿}k_BT\left[-N_{tot}\chi\phi^2+N_{tot}\phi\ln\phi+N_{tot}(1-\phi)\ln(1-\phi)\right]$$

¿ $N_{tot} k_B T\left[\phi \ln \phi + (1-\phi)\ln(1-\phi) - \chi \phi^2\right]$

So, now we have expression for F and I have to divide this by volume to get the Helmholtz density.

$$\frac{F}{V} = \frac{F}{N_{tot} v_c} = \frac{k_B T}{v_c}\left[\phi \ln \phi + (1-\phi)\ln(1-\phi) - \chi \phi^2\right]$$

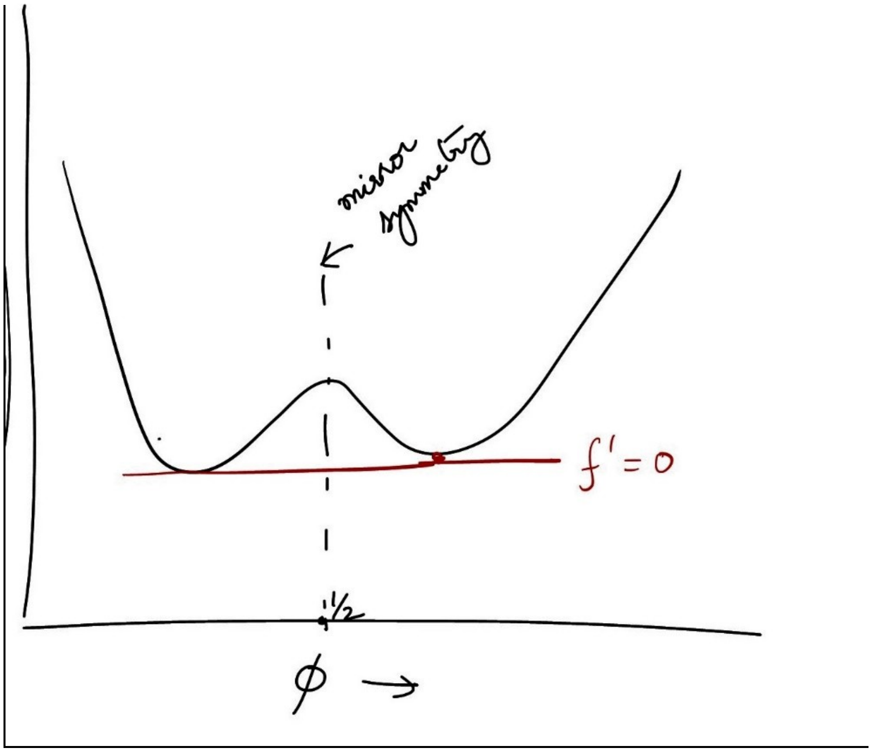
So, this is what we have got after we have dropped the linear terms in the energy expression and now I will play a small trick just for the expression to look slightly nicer. I will add some arbitrary linear term here we will see advantage of this in a moment. But basically we will add a term here which is a linear term which has no consequence in mixing behavior or phase separation behavior. The reason why we have added it the first reason is that now the expression looks somewhat symmetric. It looks like-

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

It is easier to remember but more importantly you can see $\phi$ there that if I switch $\phi$ by 1 – $\phi$, I do get the same result. So, we will have 1 - $\phi$ln of 1 - $\phi$+ $\phi$ln $\phi$+ $\chi$ multiply 1 – $\phi$ multiply $\phi$ that will be the same result that we have here.

So, if I look at the function plot that will have a symmetry around $\phi$= 1 by 2 so we have a mirror symmetry because if I simply replace $\phi$ by 1 – $\phi$ I get the same result. So, it must be symmetric with respect to $\phi$ = ½. So, the advantage is if I now draw a common tangent sorry for the poor drawing it will look straight. So, let me draw it again so it looks somewhat more symmetrical, so you can see if I draw a common tangent now that common tangent will be a horizontal line which corresponds to $f'$ = 0 and that simplifies our calculations. So, by adding a linear term we got this particular advantage in terms of our equation. So, now just to conclude we have been able to find this expression for the Helmholtz free energy-

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



This a function of ϕ and T and which is a symmetric expression and using that now I can go on and find the bimodal, spinodal and critical point and so on and again based on that theory we will go ahead and try to extend that to the polymer solutions.

With that I conclude here, thank you.