Introduction to Polymer Physics
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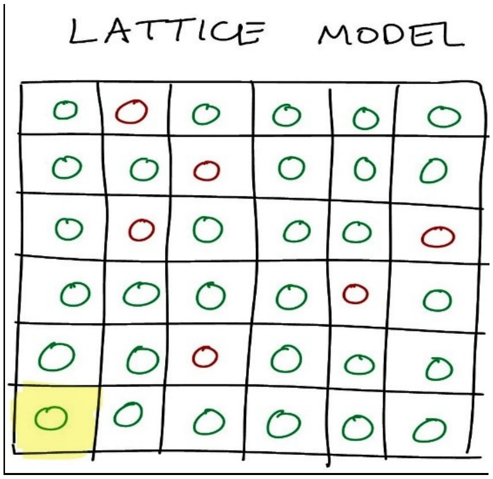
Lecture-32
Lattice Model of Solutions - I

Welcome in the last class we have been discussing the toy model that we can use to find the Helmholtz free energy density f of (ϕ, T) and the particular toy model we have been working on is the lattice model of solutions. We will take it further and discuss how we can derive the expression for F the Helmholtz free energy density for this model of solutions and then using that we can analyze the behavior of polymer solutions again using a lattice model that is basically an extension of what we are doing right now.

So, just to recap the basic assumption that we have made so far is instead of being anywhere in the 3 dimensional space the solute and solvent molecules of my model can only occupy positions on a lattice which can be a lattice in 2 dimensions three dimensions and we are assuming that there are only 2 components solute refer as P and I will use the red color for the solute and a solvent which I refer as S and I am using a green color for the solvent and these positions on the lattice are either occupied by a solvent or a solute and of course as we will discuss there can be many, many possible confirmations or configurations representing the position of the solute and solvent molecules on the lattice and this is one particular configuration that I have just drawn.



We have N_p solute molecules in red color and N_s solvent molecules in green color and both of them for sake of simplicity are assumed to occupy the same volume that is the volume of solute is equal to volume of solvent is equal to the cell volume of my lattice that is the volume of any particular cell that of course same for all those cells and let us say this quantity is equal to some V_c. Of course we can generalize to different volume of solvent and solute but that would take away the simplicity of the model has in any case the model is at best qualitative because we have already restricted the motion of molecules to be on a lattice instead of being on a 3 dimensional space.

So, given this particular approximation I can define the volume fraction of solute as-

$$Volume\,fraction\,of\,solute = \phi = \frac{N_p}{N_p + N_s} \vee \frac{N_p}{N_{tot}}$$

Similarly for the solvent this has to be (1 – ϕ) because the positions are either occupied by a solute or a solvent this has to be-

$$Volume\,fraction\,of\,solvent = \left(1 - \phi\right) = \frac{N_s}{N_p + N_s} \vee \frac{N_s}{N_{tot}}$$

Here, $N_{tot} = N_p + N_s$.

What we also assume in this model is a solute or a solvent molecule in the system only interact with its closest neighbors that is we ignore all the interactions with neighbors which are farther off than the closest neighbor of course that will only work for very short range kind of interactions, the kind of things that we have assumed in the excluded volume theory that we have discussed earlier and between the neighbors they interact by so we can say interaction energy between neighbors is ϵ_{pp} ϵ_{ps} or ϵ_{ss} depending on what combination it is. So, for example ϵ_{pp} is for solute- solute ϵ_{ps} for solute-solvent and ϵ_{ss} for solvent- solvent.

So, if we assume these values of interaction energy between closest neighbors we can talk about the total energy of the lattice in a particular configuration that is for a particular arrangement of solute and solvent molecules the lattice and this I can write as the following energy of or total energy of configuration i is given as-

$$\text{Total Energy of Configuration } i = E_i = \epsilon_{pp} N_i^{pp} + \epsilon_{ps} N_i^{ps} + \epsilon_{ss} N_i^{ss}$$

Here

$$N_i^{pp} = \text{number of solute} - \text{solute pairs}; N_i^{ps} = \text{number of solute} - \text{solvent pairs} \wedge N_i^{ss} = \text{number of solvent} - \text{solvent}$$

So, this is however the total energy of a given configuration and of course there can be many possible confirmation that we can find by the convenient tricks how many confirmations we do have in the system. So, before we go further I will define a quantity that is known as the partition function using which I can discuss the free energy of the system. So, I will take a small detour and define what is known as the partition function often represented as Z and Z by definition is-

$$Z = \sum_i \exp\left(\frac{-E_i}{k_B T}\right) = \sum_i \exp(-\beta E_i)$$

Here i= all configurations, $\exp\left(\frac{-E_i}{k_B T}\right)$ = Boltzmann Factor and $\beta = \frac{1}{k_B T}$

So, essentially what Z is the sum over the Boltzmann factors of all possible confirmations or configurations or what is also known in statistical mechanics as microstates. If you have had a course on static mechanics you must have known this as the sum over all microstates. But essentially it is all possible confirmations or configurations which are present in the system. We simply compute the Boltzmann factor and sum them up and that is what we get is known as the partition function.

So, there are two major roles of this Z in the context we are discussing and that will suffice for the discussion that we will do in polymer physics course in general. So, the significance or the role of Z are essentially two-

1. We already have said that probability of occurrence of any particular configuration, so probability of configuration i to occur let us call this some p_i it should be proportional to the corresponding Boltzmann factor this we had discussed earlier i.e.

$$p_i \propto \exp\left(\frac{-E_i}{k_{BT}}\right)$$

so Z in some sense work as a normalization factor and why is that because if I simply sum over all the configurations the Boltzmann factors basically we get a net sum that represents the total probability of all possible confirmations and so if I divide the quantity we have-

$$p_i = \frac{\exp\left(\frac{-E_i}{k_{BT}}\right)}{Z}$$

I should get the absolute probability for that configuration to occur because we are simply dividing the probability of that particular configuration divided by the sum of all configurations and because sum of all probabilities must =1. Therefore,

$$\sum p_i = 1$$

2. Partition function is as generating function for other energy functions. For instance all that means is like if I know Z, I can get to know all the other energy functions that I need in thermodynamics. So, for example if I do something like that-

$$\frac{E_i \exp(-\beta E_i)}{Z}$$
$$¿$$
$$\frac{-\partial lnZ}{\partial \beta} = \frac{-1}{Z}\frac{\partial Z}{\partial \beta} = \frac{-1}{z}\sum_i -E_i \exp(-\beta E_i) = \sum_i ¿$$

This expression by definition is the probability for the configuration i, as we have derived earlier and therefore this is sum over i E_i p_i so if I multiply the energy value for the configuration with the probability of occurrence and I sum them up what I know, what I get is what is known as mathematical expectation or the average value, so this gives me essentially the expected expectation or mean value of the energy. So,

$$\sum_i E_i p_i = \acute{E}$$

So, we can see from here that if I want to know the mean energy of the system we can do some manipulation with Z and we can we can get that. I will not go through all the possible other variables but the basic ideas applied. If I know the Z, I can find other thermodynamic functions with much ease that is the only thing I need to know.

It turns out that the Helmholtz free energy is-

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

And Helmholtz free energy density is-

$$f=\frac{F}{V}=\frac{-k_B T}{V}\ln Z$$

If I want to find the Helmholtz free energy density which was the objective that we started with all I need to know is my Z because if I know the Z and if I know the volume, volume of course we know from the lattice model itself the number of cells multiplied by the volume gives me the volume of the lattice and so knowing the Z we can get the function f.

So, now the question is like how we find the Z so to get Z there are of course couple of approaches either we can do a simulation look at all the possible configurations the system has or the most probable configuration confirmations get the energies and using that try to compute the partition function. It turns out that we do not directly get the partition function but something of that sort, I am not getting into that. What I will discuss is what is known as the mean field theory that really simplifies our task and give us a good analytical expression for the for the Z partition function Z.

So, the mean field theory and of course just like the name says is the mean field it is actually an approximation than being exact and the approximation is that what we assume is instead of the different confirmations having different energies we assume that all the confirmations have a mean energy $\acute{E}$. So, the assumption is like all configurations have mean energy $\acute{E}$ because if I do that then Z which was summed over all the Boltzmann factors-

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

Now if all the E_i is approximated to be equal to $\acute{E}$ then this is simply exponential of - beta $\acute{E}$ which then would be something like-

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

Where W is number of possible configurations, and we know that N_p is solute molecules N_s is Solvent molecules. The number of ways to arrange them on the lattice is given by simple common tricks and it is equal to the number of possible confirmations. The W is-

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

Although we have taken example of solute and solvent you can have apples and oranges the number of ways to arrange the say 5 apples and 10 oranges on 15 sites is given by like 15 factorial divided by 5 factorial multiplied by 10 factorial this is a standard formula.

So, we know what W is, the only challenge is how to get $\acute{E}$. So, we have already said that my E_i is-

$$E_i = \epsilon_{pp} N_i^{pp} + \epsilon_{ps} N_i^{ps} + \epsilon_{ss} N_i^{ss}$$

Here, N_i^{PP} is the number of solute- solute pairs and ϵ_{pp} is the interaction energy between the molecules in that pair, the same thing for solute solvent pairs and same thing for solvent- solvent pairs. So, $\acute{E}$ has to be average of that where $\acute{N}$ is now the average number of pairs-

$$\acute{E} = \epsilon_{pp} \acute{N}^{pp} + \epsilon_{ps} \acute{N}^{ps} + \epsilon_{ss} \acute{N}^{ss}$$

Here, $\acute{N}^{PP}$ is average number of solute- solute pairs $\acute{N}^{PS}$ is the average number of solute solvent pairs and $\acute{N}^{SS}$ is the average number of solvent- solvent pairs and this quantities we can get by simple probability rules. So, we know that each of the sides can be occupied by the solute with the probability ϕ and then let us say that particular site is occupied by the probability ϕ then it has z neighbors small z neighbors we have z is the coordination number and they can be a solute also with a probability ϕ because ϕ is the fraction of the solute molecules in the system.

So, if I think of any position on the lattice it may contain a solute molecule with a probability of ϕ and this will then have z neighbors which is = 4, 4for square lattice and each of them can also be a solute with probability ϕ each. So, if I multiply ϕ with zϕ, I get the total number of the total probability of having a pair of solute and solute in a given side and this if we multiply with the total number of sides I should get the total number of such solute- solute pairs in the system. The only thing is that if I am doing this way I always do a double count because when I come and look at the neighbors of this one side then we will again find that this also has 4 neighbors, one of them that is already counted and so we always have a double counting of the pair's if we proceed in the way I have suggested. So, we have to divide this by 2 we had 2 accounts for the double counting and this is then-

$$\acute{N}^{pp}=\frac{N_{tot}\phi\cdot z\phi}{2}=\frac{1}{2}N_{tot}z\phi^{2}$$

The same thing applies for a solvent- solvent pair except that now the probability to find a solvent on a given side is 1 – ϕ, again we have z neighbors and they can also be a solvent with a probability of 1 – ϕ again we have double counting and now what we get is this,

$$\acute{N}^{ss}=\frac{N_{tot}(1-\phi)\cdot z(1-\phi)}{2}=\frac{1}{2}N_{tot}z(1-\phi)^{2}$$

The same idea can be applied for solute- solvent pair. So, now every site can be a solute with a probability of ϕ and then it can again have z neighbors which can be solvent with a probability of 1 – ϕ this time we do not have to divide by 2 because we are looking at pairs of different species. So, I am looking at the solvent neighbors of every side. So, if I go to the next side again I will look at solvent neighbors assuming that the site is occupied by the solute. So, in this case we do not have any double counting in the picture.

$$\acute{N}^{ps}=N_{tot}\phi\cdot z(1-\phi)$$

So, using these 3 formulas I can plug that in the equation for $\acute{E}$ and what I will get is the following is this,-

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

¿ $$\frac{N_{tot}z}{2}\left[\phi^{2}\epsilon_{pp}+(1-\phi)^{2}\epsilon_{ss}+2\phi(1-\phi)\epsilon_{ss}\right]$$

So with this I stop here in the next lecture we will take it further and go on to find the expression for the Helmholtz free energy density for the lattice model and using that we can then extend and talk about the mixing and phase behavior that we have discussed earlier, now given the functional form of the Helmholtz free energy density.

So, with that I stopp here, thank you.