Advanced Thermodynamics and Molecular Simulations
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Lecture - 27
Lattice Model of Liquid Solutions II

Hello, all of you, so in the last lecture we started discussing the lattice model of solutions. We have discussed the assumptions in the model. So, I will continue from the point where I left and discuss how can we derive the expression for the Helmholtz free energy density using the lattice model and then using the ideas that we have discussed earlier we will find out the expressions for the binodal, spinodal and critical point for the case of the lattice model.

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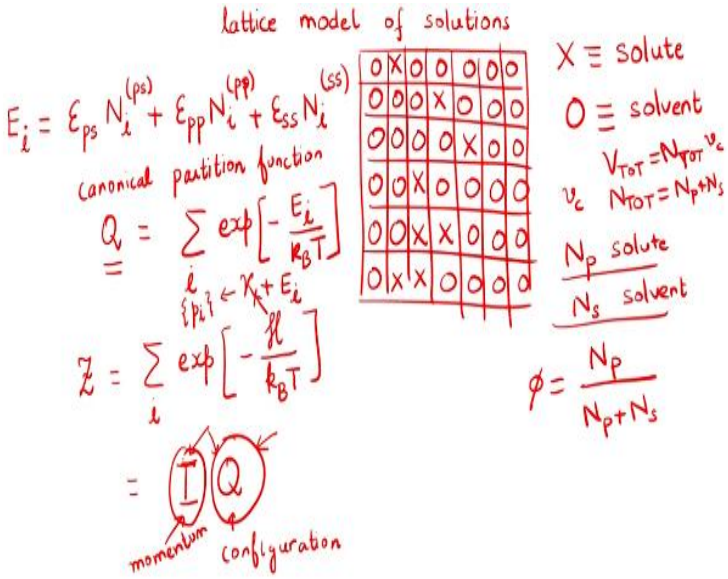
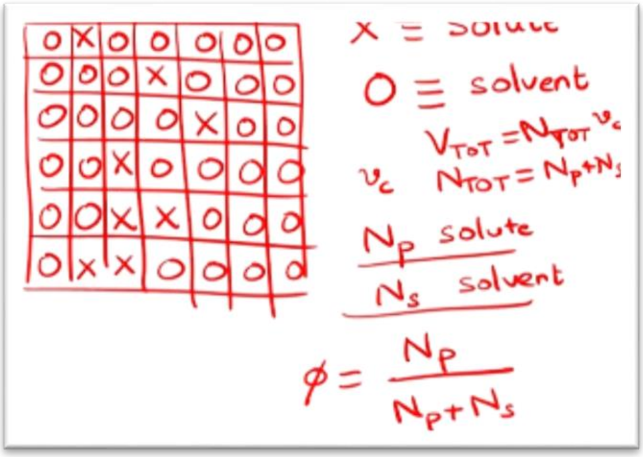


So, where we have been so far is we assumed that we are having a lattice and the solute and solvent molecules cannot just be anywhere they need to occupy positions on the lattice which pretty much reduces the dimensionality of the problem as we have discussed last time. So, we can have solvent molecules depending on the number of solvents, they will occupy so many sites or cells in the lattice and the remaining positions will be occupied by the solute molecules. So, X here is my solute and O here is the solvent.



So, clearly both of them are assumed to occupy the same volume that is equal to the lattice volume, that is v_c we have N_p solute and N_s solvent molecules and therefore I can define the volume fraction as-

$$\phi = \frac{N_p}{N_p + N_s}$$

because the volume occupied by both are assumed to be the same.

And then where we have been so far is we define the expression of energy for a configuration i as the energy of polymer solvent contacts multiplied with number of such contacts and the energy of polymer contacts multiplied with the number of such contacts and the energy of solvent-solvent contacts multiplied with the number of such contacts.

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

Clearly we can have many configurations which refer here to the different positions of the solute and solvent molecules. The total number of molecules are fixed you can say N_{TOT} is $N_p + N_s$ and since the volumes are the same, the total volume is simply N_{TOT} multiplied by v_c.

So, now if I have to define; the partition functions for this ensemble. We can assume that the volume is constant which indeed the case here, so we are working with the canonical partition function which is given as-

$$Q = \sum_i \exp\left[-\frac{E_i}{k_B T}\right]$$

Now the key point here is we are not looking at the momenta of the molecules and therefore we are only looking at the configurational part of the system and that will basically contain only the information regarding the positions, not the momentum. Nonetheless we can define the partition function for this system as Q here, but then if I also had to include the momentum contribution to that, if you think about it. I can write that as something like-

$$Z = \sum_{i} \exp\left[-\frac{H}{k_B T}\right]$$

And $H = K_i + E_i$

Now that kinetic energy part if you think about it that is going to be a function of momentums only. So, therefore what this amounts to is saying that we have a configurational part that we are discussing here and there is some other part. Let me give it the name I, which refers to the momentum part of that.

$$Z = Q.I$$

The reason why I can factorize this partition function into these two contributions is because the kinetic part does not depend on the position. So, we are only dealing with this part of the thing and it turns out that the first part can be analytically evaluated, under certain assumption I will not get into that. But for this particular lattice model that is inconsequential because the positions are fixed as we had discussed earlier. So, nonetheless now assuming that we are still working with the configurational partition function and everything else that we have derived is still holds true we may have some correction because of momenta but not within the context of the lattice model.

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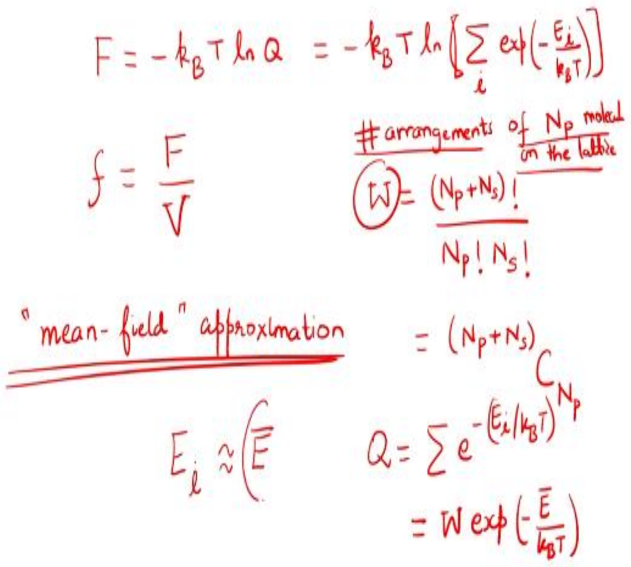

$$F = -k_B T \ln Q = -k_B T \ln\left[\sum_i \exp\left(-\frac{E_i}{k_B T}\right)\right]$$

$$f = \frac{F}{V}$$

arrangements of N_p molecul on the lattice

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

"mean-field" approximation

$$E_i \approx \bar{E}$$

$$Q = \sum e^{-(E_i/k_B T)} = W \exp\left(-\frac{\bar{E}}{k_B T}\right)$$

We can define the Helmholtz free energy as-

$$F = -k_B T \ln Q = -k_B T \ln\left[\sum_i \exp\left(-\frac{E_i}{k_B T}\right)\right]$$

We can evaluate that by enumerating over all the possible configurations and once we have that we can find the Helmholtz free energy density as the ratio of Helmholtz free energy with the volume or Helmholtz free energy per unit quality.

$$f = \frac{F}{V}$$

So, this is where we are after but it turns out that even that is of course simpler than doing it for a continuous system but even then the possibilities are not very small we have to think of all the possible arrangements of the molecules and if you think about it the number of arrangements here can be thought of the number of ways in which I can arrange N_p molecules or particles on the lattice because once I have chosen the position of the solute molecules then the positions of the solvent molecules are automatically fixed that is true when we assume that each site is occupied by either a solute or solvent molecules we do not have any empty sites there that again comes down to the idea of incompressibility, we are assuming both to have the same volume and the overall density of the system is constant and therefore there are no empty sites present on the lattice.

So, within that particular assumption the number of ways in which I can arrange Np molecules is given as something like-

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

So, W we can evaluate but for each of these W confirmations, the E_i are going to be different they will depend on the values of the number of contacts in that configuration and of course the ε value we have assumed to be constant. So, the number of contents contacts however us going to vary. So, we will make use of what is known as a mean field approximation to further simplify the problem and the assumption says that I will assume that all these energies in different configuration can be approximated by it is average value and since then I can find the average value I can basically simplify my partition function, so my Q would then be-

$$E_i \approx \bar{E}$$

$$Q = \sum_i e^{-\frac{E_i}{k_B T}} = W \exp\left(-\frac{\bar{E}}{k_B T}\right)$$

and how do we evaluate this E bar is the following.

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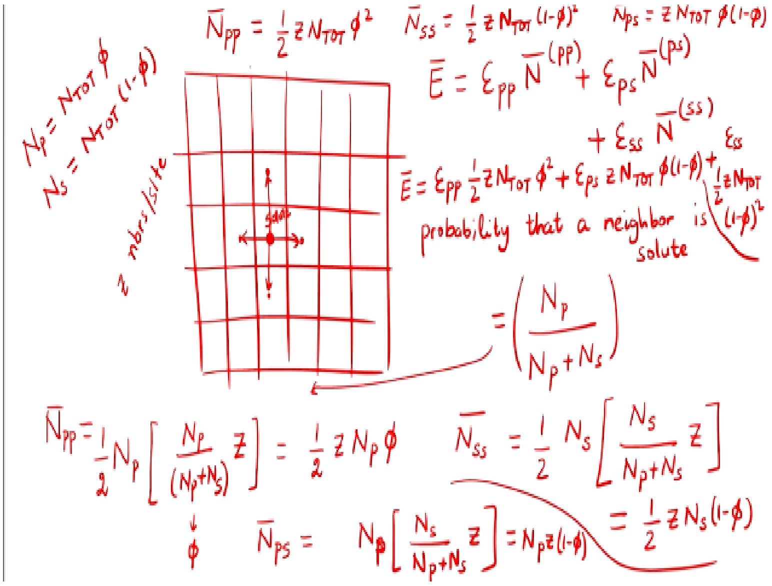
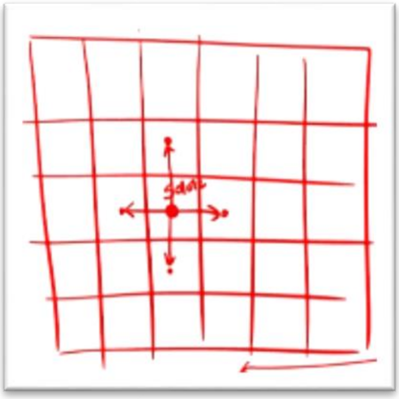


So, basically, the question that I am trying to ask, let us say if I look at any particular site on the lattice, and let us say if it is occupied by the solute molecules.



Then, what is on an evidence the number of solute-solute contacts around it, what is on an evidence the number of solute solvent contacts around it and what is on an average solvent, solvent contacts but for solute molecules that is not counted of course for a solvent molecule we can count those contacts as well. Essentially we are interested in E bar as-

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

So, for a solute contact you can see that there are in total Z neighbors, where Z is the coordination number. So, in total we have Z neighbors per side and what is the probability that this any of these neighbors is occupied by a solute molecule. So, probability, that a neighbor is solute that is not very difficult to evaluate, that probability is essentially equal to the probability of any site being occupied by the solute molecules and that is given by the number of solute divided by the total number of molecules in the system.

$$probability\ of\ any\ site\ occupied\ by\ solute = \left(\frac{N_p}{N_p + N_s}\right)$$

So, as Np increases we of course have higher probability that a site is occupied by the solute molecules and when Np is equal to the N_{ToT} that is there is no solvent molecules clearly the probability goes to 1 because all the sites are occupied by the solute molecules. So, now if I multiply this probability with the probability of having a solute in the first place we get the probability of the solute-solute contact happening there, what we can also do is we can look at each of the solute molecules in total there are Np of them and find the number of contacts as Np multiplied with the probability that we had there multiplied with Z. So, Z are the total number of neighbors every solute molecules have and each of them can be a solute with a probability of Np by Np plus Ns. So, the total number of the solute-solute contacts can be estimated to be this. Now when we are doing that we are going over every solute molecules and multiplying with the probability that the neighbors is a solute. So, clearly we will double count the contacts in this way because every contact will have two solute molecules. Since I am counting over all the solute molecules, we will basically be counting every contact twice. So, therefore, we will divide this quantity by 2. So, what we essentially have is half Z Np and this quantity is Φ as we had discussed half Z Np Φ.

$$\overline{N}^{pp} = \frac{1}{2} N_p \left[\frac{N_p}{N_p + N_s} \, Z \right] = \frac{1}{2} Z N_p \phi$$

Similarly, we can go ahead and find the number of solvent segment contacts. So, in total we have Ns solvent molecules probability that a neighbors is-

$$\overline{N}_{ss} = \frac{1}{2} N_s \left[\frac{N_s}{N_p + N_s} \, Z \right] = \frac{1}{2} Z N_s (1 - \phi)$$

Finally, I can go ahead and find the number of solute solvent contacts that is again, first I locate how many solute molecules that we have that is Np. The probability that the neighbors is solvent is Ns by Np plus Ns multiplied with Z. And now I am looping over all the solute molecules but I am counting the solute solvent contacts, so in this case we will not be having the double counting problem. So, this will appear simply like-

$$\overline{N}_{ps} = N_p \left[\frac{N_s}{N_p + N_s} . Z \right] = N_p Z (1 - \phi)$$

So, now since-

$$N_p = N_{TOT} \phi$$

$$N_s = N_{TOT} (1 - \phi)$$

If I put that thing in here what we find is the evidence number of the solute-solute contact is equal to-

$$\overline{N}_{pp} = \frac{1}{2} Z N_{TOT} \phi^2$$

$$\overline{N}_{ss} = \frac{1}{2} Z N_{TOT} (1 - \phi^2)$$

$$\overline{N}_{ps} = Z N_{TOT} \phi (1 - \phi)$$

So, using this we can then find the expression of the average energy as-

$$\bar{E} = \epsilon_{pp} \frac{1}{2} Z N_{TOT} \phi^2 + \varepsilon_{ps} Z N_{TOT} \phi (1 - \phi) + \varepsilon_{ss} \frac{1}{2} Z N_{TOT} (1 - \phi)^2$$

So, with this now I can take the Z N_{ToT} by two common from there and I can estimate my average energy as-

$$\bar{E} = \frac{ZN_{TOT}}{2}\left[\varepsilon_{pp}\phi^2 + \epsilon_{ss}(1-\phi)^2 + 2\varepsilon_{ps}\phi(1-\phi)\right]$$
$$= \left(\varepsilon_{pp} + \varepsilon_{ss} - 2\varepsilon_{ps}\right)\phi^2 - 2\varepsilon_{ss}\phi + \varepsilon_{ss} + 2\varepsilon_{ps}\phi$$

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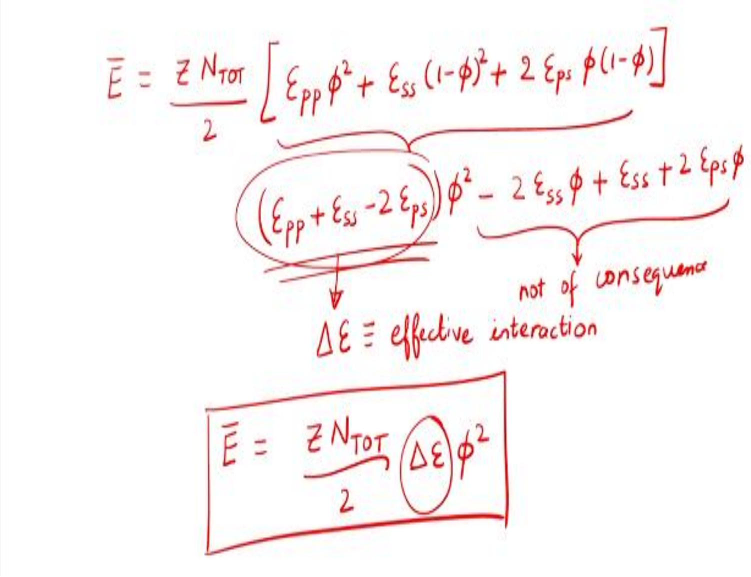

For what we will discuss it turns out that these linear terms are of no consequence in discussing the mixing and phase separation behavior. I will not derive it but you can do the derivation keeping the linear terms and you will figure out that these terms are not of consequence for what we are discussing. So, we only look at the quadratic term right here and this particular quantity is what I referred as something like-

$$\left(\varepsilon_{pp} + \varepsilon_{ss} - 2\varepsilon_{ps}\right)\phi^2 = \Delta\varepsilon$$

that is in some sense characterizes the effective interaction. So, therefore have E bar is equal to-

$$\bar{E} = \frac{ZN_{TOT}}{2}\Delta\varepsilon\,\phi^2$$

So, before we proceed let us say I want to focus on this effective interaction part and try to argue why we need to have this kind of a term representing the effective interaction here. So, the idea goes like this.

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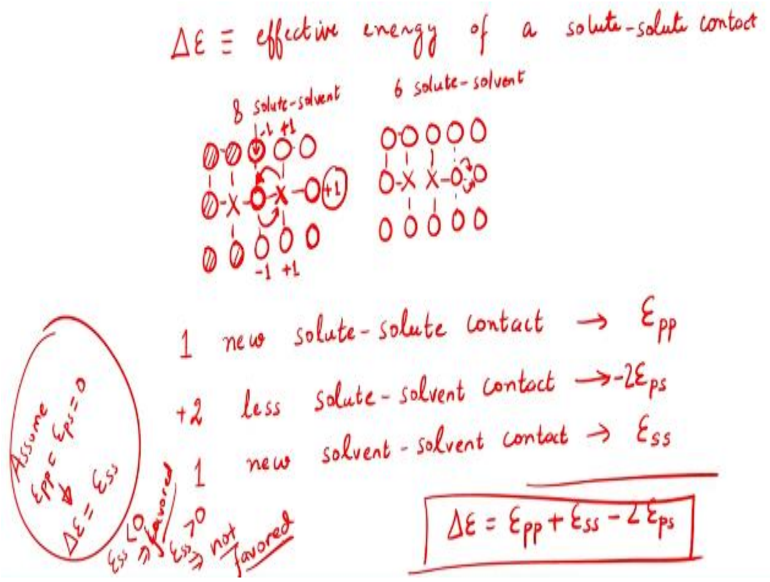
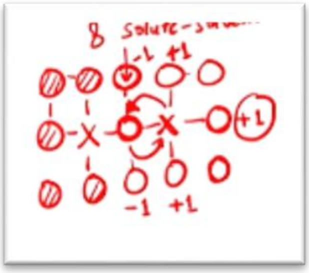
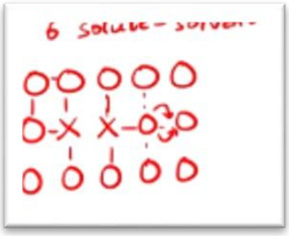


So, the Δ ε essentially characterizes the effective energy of a solute-solute contact and the reason why it is true, is let us say for example I am looking at a small part of the lattice, were we have some solvent molecules and two solute molecules and in this particular configuration there is no solute-solute contact.



Old arrangement of molecules

Now, let us say if I want to find the energy change when this solute swaps it's position with the adjacent solvent molecules so, that the two solute molecules come together, so the new configuration then would be, so we have formed a new solute-solute contact, but while doing that something else also happened. The number of the solute solvent contacts and the number of solvent-solvent contacts also changed while doing that. So, we clearly formed one new solute-solute contact and since that has energy of ε_{pp}, so we get that energy there. Now let us look at, what is the change in the number of solute solvent contacts?



New arrangement of molecules

So, in this case this guy was earlier forming four contacts with the solvent molecules and this guy two was forming four contacts with the solvent molecules, so in total we had eight solute-solvent contacts. In the new configuration this guy is forming three contacts with solvent molecules and this guy is also forming three contacts, so in total now we have only six solute solvent contacts. So, therefore, we have two less solute solvent contacts and that will result in an energy change of - 2 ε_{ps}.

Now, let us look at the solvent contacts. So, for many of the solvent molecules there is pretty much no change only for some there is a change, let us say if I start with this guy right here, so it was having two contacts earlier still it is forming to contact the new configuration there is no change for this guy as well but, if I look at this guy earlier it was forming a contacts with a solvent molecule, but now it is forming a contact with a solute molecule. So, in this case there is a change by, so this guy underwent a change of - 1 that is the decrease in the number of the solvent-solvent contacts. This guy was earlier having a contact with a solute molecule and now it is not having it so this guy will be basically be forming a new solvent-solvent contact earlier it was not present it was forming contact with the solute molecule all the other contacts remain as it is, so both of these basically cancel. The same is true for these two guys this guy have found a new solvent from a contact, so there is a plus one here as a solvent molecule has moved in and this guy is not affected. If I look at this particular guy in there, so earlier it was forming two contacts but now it is forming three contacts there but this contact we have already counted. So, we have actually one extra solvent- solvent contact that has been formed.

Similarly, I can go over others basically there is no effective change in this guy, this guy, this guy and so on. So, we have one new solvent-solvent contact or pair, only one new pair has formed and that will give me an energy of ε_{ss}.

So, in total when the two solute molecules came together the energy change is-

$$\Delta E = \epsilon_{pp} + \epsilon_{ss} - 2\varepsilon_{ps}$$

So, it is not only the solute-solute interaction that determines whether the solutes will come together, but it is also the solute solvent and solvent-solvent interaction that dictates this particular process. Let us take an example, let us imagine that my ε_{pp} and ε_{ps} is equal to zero. Now in this particular case what are we going to have in this case Δ ε is simply ε_{ss}. So, even though; there is no energy change because of the solute itself because solute the energy interaction energy of solute with solvent or other solute is zero. But since the solvent, solvent contacts are changing there is an energy change when two solutes come together and when this energy change is negative then we can say that the solute-solute contact is favored. On the other hand if this energy change is positive, then it is clearly not favored and this pretty much is responsible for in the case of liquid water the hydrophilic and hydrophobic behavior.

So, basically it does not really matter or it is not only important that we look at the solute-solute interactions alone even if the solute and solute interactions are favored. What is also important and actually what is more important is what is the solvent-solvent interaction and what is the solute-solvent interactions and it is that dictates the solubility of the solute in any particular media. So, let us say for example if two solute molecules want to come together that coming together will be dictated by in which solvent I am doing the experiment on and the role of solvent actually happens to be much more important in any cases particularly when we are working in the dilute concentrations, because we simply have more solvent-solvent interactions present in the system as opposed to solute-solute interactions.

So, that is the thing that we have to keep in mind, but let us get back to our partition function and see how far we have gotten so far.

So, that is the thing that we have to keep in mind, but let us get back to our partition function and see how far we have gotten so far. So, I have said that my Q is in mean field approximation as-

$$Q = W \exp\left(-\frac{\bar{E}}{k_B T}\right)$$

$$F = -k_B T \ln Q = -k_B T \ln W + \bar{E}$$

Now if I compare this with the expression of the Helmholtz free energy F is equal to U - T S. So, U here is the same as the E bar. So, essentially this quantity has to be T S and therefore S= k_B ln W which is of course true as we have discussed earlier in this course.

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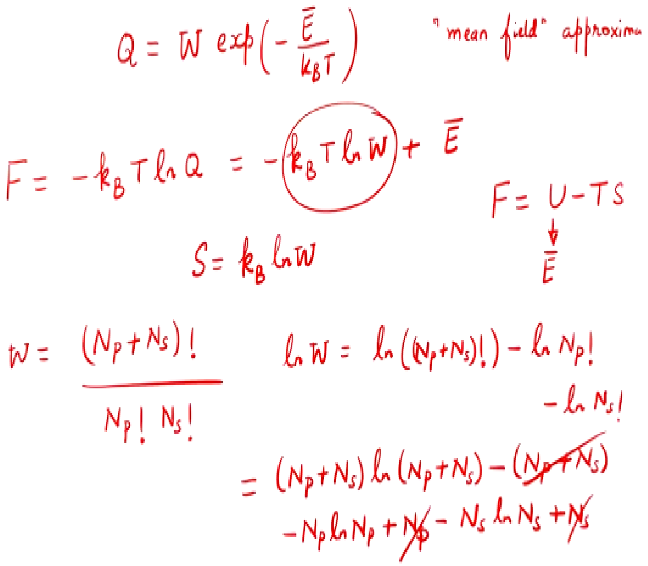

So now,

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

$$\ln W = \ln((N_p + N_s)!) - \ln N_p! - \ln N_s!$$

$$= (N_p + N_s)\ln(N_p + N_s) - (N_p + N_s) - N_p \ln N_p - N_s \ln N_s + N_s$$

$$S = k_B[(N_p + N_s)\ln(N_p + N_s) - N_p \ln N_p - N_s \ln N_s]\, N_p \ln(N_p + N_s) + N_s \ln(N_p + N_s)$$

$$S = k_B\left[-N_p \ln\frac{N_p}{N_p + N_s} - N_s \ln\frac{N_s}{N_p + N_s}\right]$$

So now,

$$-N_p = N_{TOT}\phi;\ \frac{N_p}{N_p + N_s} = \phi;\ N_s = N_{TOT}(1 - \phi);\ \frac{N_s}{N_p + N_s} = (1 - \phi)$$

So therefore I can write-

$$S = k_B N_{TOT}[-\phi \ln \phi - (1 - \phi)\ln(1 - \phi)$$

So, if I put this expression of S back in the expression of F that we had there what we will have is-

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$$F = \bar{E} - TS$$

$$= \frac{1}{2} z N_{TOT} \Delta\varepsilon \, \phi^2 + k_B T \overset{N_{TOT}}{\wedge} \left[\phi \ln \phi + (1-\phi) \ln (1-\phi) \right]$$

$$= N_{TOT} k_B T \left[\phi \ln \phi + (1-\phi) \ln(1-\phi) + \underbrace{\left(\frac{1}{2} \frac{z \Delta\varepsilon}{k_B T} \right)}_{\hookrightarrow -\chi} \phi^2 \right]$$

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

$$\chi = \text{solvent quality} = -\frac{1}{2} \frac{z \Delta\varepsilon}{k_B T}$$

$$F = \bar{E} - TS$$

$$= \frac{1}{2} Z \, N_{TOT} \, \Delta\epsilon \, \phi^2 + k_B T \, N_{TOT} [\phi \ln \phi + (1-\phi) \ln(1-\phi)]$$

$$= N_{TOT} k_B T [\phi \ln \phi + (1-\phi) \ln(1-\phi) + \left(\frac{1}{2} \cdot \frac{Z \, \Delta\epsilon}{k_B T} \right) \phi^2$$

And this if I divide by the volume gives me the Helmholtz free energy density, so this is-

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

So,

$$\chi = solvent \; quality = -\frac{1}{2} \cdot \frac{Z \Delta\epsilon}{k_B T}$$

So, basically, we have been able to evaluate the expression of F for the lattice model. Now, once we have that now we can go ahead and find the phase behavior by basically using the apparatus that we have discussed earlier we can find the second derivative and determine whether we have a tendency of mixing or for phase separation and then we can also find the expression of binodal, spinodal and critical point and that we will take it in the next lecture.

So, with that I want to conclude here, thank you.