Advanced Thermodynamics and Molecular Simulations
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Lecture -28
Lattice Model of Liquid Solutions III

Hello all of you, so in the last couple of lectures we have been discussing the lattice model of solutions and we have been able to obtain the form of the Helmholtz free energy density for the lattice model of solution. So, today I will use that function ‘f’ to find the mixing and phase behaviour and more importantly the expression for the binodal, spinodal and critical point. We already have obtained the expressions but we will do it for this particular model.

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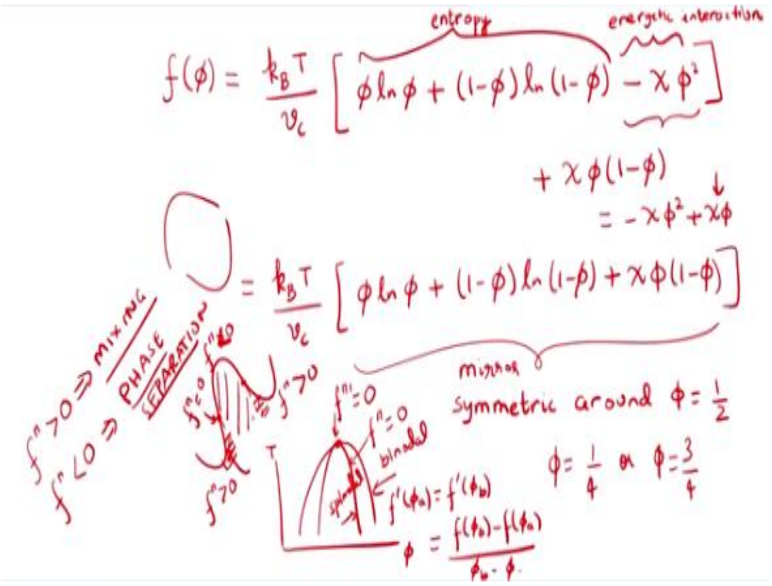

So, where we have been so far is the Helmholtz free energy density of the lattice model of solution is given by-

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

So, the first two terms are basically coming from the entropy and the last term is coming from the energetic interactions. Now what I will do here is I am going to replace this quantity with $\chi \Phi$ multiplied with $1 - \Phi$ with a plus sign that will essentially mean $\chi \Phi^2 + \chi \Phi$ that means I am going to add an extra linear term in this expression. The reason why we do that is first of all the linear terms does not matter we already have discussed this in the context of computing the effective interactions. So we ignored all the terms with powers of Φ less than 2. So, first of all this will have no consequence in terms of the final results but what it does is that it makes this function ‘f’ look nicer and the reason why it happens is because in this new expression, if I replace Φ with 1 - Φ, we essentially get the same expression. So, we can try if I replace Φ with 1 - Φ, we get pretty much the same expression what this essentially translates to is that this function then become symmetric around phi equal to 1 by 2.

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

So, let us say for example, if I look at either side of Φ equal to 1 by 2 let us say if I compare Φ equal to 1 by 4 or Φ equal to 3 by 4 that means, if I go 1 by 4 to the left of 1 by 2 and 1 by 4 to the right of 1 by 2 we will have the same expression so we have a mirror symmetry so as to speak around Φ equal to 1 by 2 and later on we will see that this also give rise to a common tangent of slope ‘0’ that makes the expression simpler to look.

So, with this particular idea let us now first see when do we have the mixing and phase separation behaviour in this particular system. So, for that the first thing I told you is that if f double prime is greater than 0 then we have mixing and if f double prime is less than zero then we have phase separation and that was discussed in the context of block graphs which were like having a single maxima or minima, for the case when you have multiple of them in that case we have discussed the idea of spinodal that was the point where f double prime is equal to 0 between the spinodal we have a regime that is unstable in which f double prime is less than 0 in this regime f double prime is higher than 0 on this side and this side and between these 2 points we have some sort of a meta stable regime then we already have discussed this.

So, ultimately if I want to establish these things basically ultimately we have to find the derivatives of ‘f’ right and later on we have also discussed that if I look in for example, in terms of the temperature volume fraction phase diagram I can define binodal curve, spinodal curve and they will merge at the critical point and the critical point is given as f triple prime is equal to 0 and of course a spinodal is given as f double prime equal to 0 and binodal is given as-

$$f'(\phi_a) = f'(\phi_b)$$

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

So, the advantage of using a mirror symmetric expression is that this quantity becomes equal to 0 because the common tangent that we will draw and we will see in the more details is going to be along the horizontal line and therefore the slope is going to be 0 and that will make the expression simpler.

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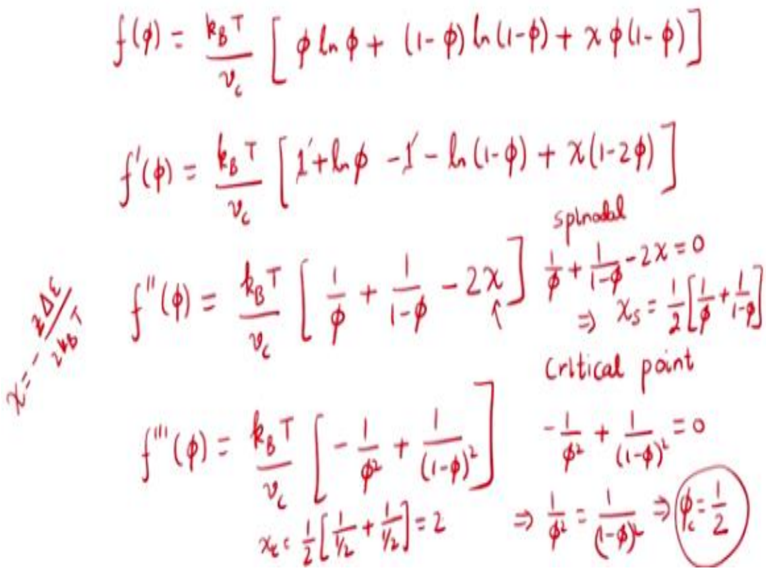

So, let us go ahead and first try to find the derivatives of f of Φ. So, we are starting with f of Φ is equal to-

$$f(\phi) = \frac{k_BT}{v_c}[\phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)]$$

$$f'(\phi) = \frac{k_BT}{v_c}[1 + \ln(\phi) - 1 - \ln(1-\phi) + \chi(1-2\phi)]$$

$$f''(\phi) = \frac{k_BT}{v_c}[\frac{1}{\phi} + \frac{1}{1-\phi} - 2\chi$$

$$f'''(\phi) = \frac{k_BT}{v_c}[-\frac{1}{\phi^2} + \frac{1}{(1-\phi)^2}$$

For critical point –

$$-\frac{1}{\phi^2} + \frac{1}{(1-\phi)^2} = 0$$

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

That is true when $\phi_c = \frac{1}{2}$

Now we of course also need to find the χ value so keep in mind here that χ is inversely proportional to the temperature so the effect of the temperature is contained in the variable chi right. Just like we had for temperature higher than critical point we said that we will be in a single phase regime the similar thing can also be applied for the χ variable because χ is a function of temperature. So, we have to find the χ value for the critical point and this we can find by first finding the spinodal expression. From spinodal what we find is that-

$$spinodal = \frac{1}{\phi} + \frac{1}{1-\phi} - 2\chi = 0$$

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

Now since the binodal curve also passes through the critical point if I find the value of spinodal at Φ equal to 1 by 2 that is the critical point value we should find the χ value at the critical point. That is χc is equal to-

$$\chi_c = \frac{1}{2}\left[\frac{1}{\frac{1}{2}} + \frac{1}{\frac{1}{2}}\right] = 2$$

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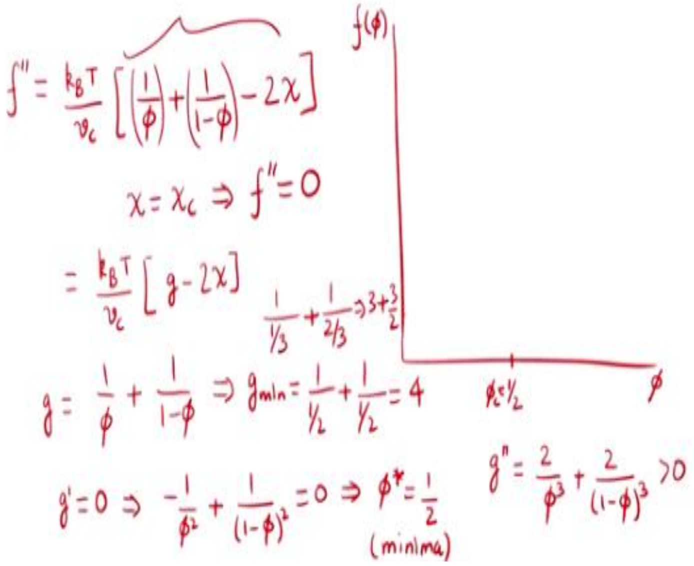

$$f'' = \frac{k_B T}{v_c}\left[\overbrace{\left(\frac{1}{\phi}\right)+\left(\frac{1}{1-\phi}\right)}-2\chi\right]$$

$$\chi = \chi_c \Rightarrow f'' = 0$$

$$= \frac{k_B T}{v_c}\left[g - 2\chi\right]$$

$$\frac{1}{1/3} + \frac{1}{2/3} \Rightarrow 3 + \frac{3}{2}$$

$$g = \frac{1}{\phi} + \frac{1}{1-\phi} \Rightarrow g_{min} = \frac{1}{1/2} + \frac{1}{1/2} = 4$$

$$g' = 0 \Rightarrow -\frac{1}{\phi^2} + \frac{1}{(1-\phi)^2} = 0 \Rightarrow \underset{(minima)}{\phi^* = \frac{1}{2}}$$

$$g'' = \frac{2}{\phi^3} + \frac{2}{(1-\phi)^3} > 0$$

So, if I now want to plot what my f of Φ, look like as a function of the Φ variable although we do not know the form yet, the few things we know there is a critical point around Φ equal to 1 by 2 and for χ_c value of 2. So, let us first look at what is the behaviour we expect for χ higher than the χ_c value and χ less than the χc value. So, we have already found the-

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

And for χ equal to χc we know that the f double prime is equal to 0. So, I can basically write this expression as something like-

$$f'' = \frac{k_B T}{v_c}[g - 2\chi]$$

Where

$$g = \frac{1}{\phi} + \frac{1}{1-\phi}$$

And,

$$g' = -\frac{1}{\phi^2} + \frac{1}{(1-\phi)^2} = 0$$

and this happens for Φ value is equal to 1 by 2.

Now we can go ahead and find the second derivative to see whether it is going to be a maxima or a minima and what we find is it is equal to-

$$g'' = \frac{2}{\phi^3} + \frac{2}{(1-\phi)^3}$$

So, clearly, this is higher than 0 because Φ is between 0 to 1. So, this is a point of minima, so the minimum value of the function g is-

$$g_{minima} = \frac{1}{\frac{1}{2}} + \frac{1}{\frac{1}{2}} = 4$$

For any other value of Φ this quantity is going to be more than 4 we can try plugging in a value let us say for example, we are doing it for Φ equal to 1 by 3 so we have 1 by 1 by 3 + 1 by 2 by 3 and that gives me 3 + 3 by 2 that is clearly more than 4

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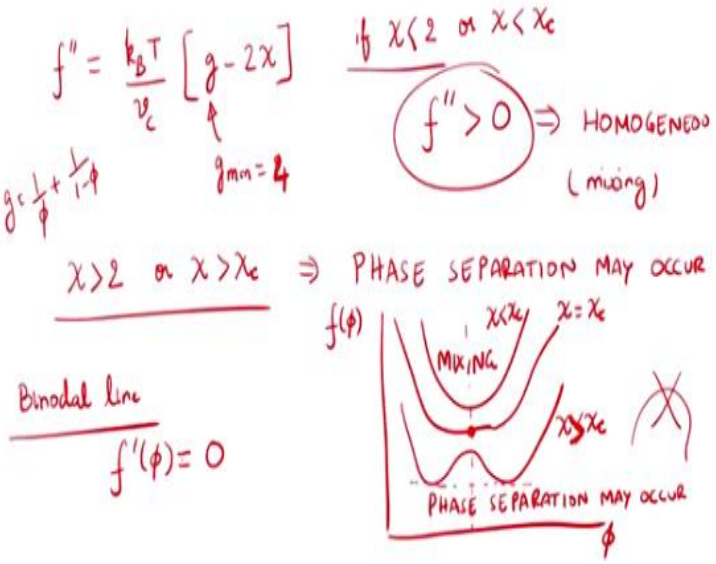


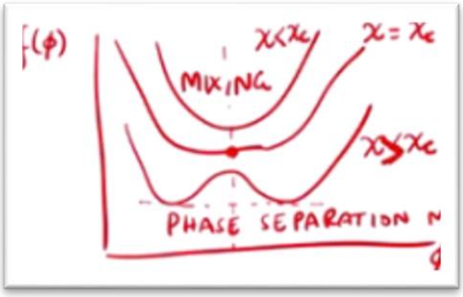
So, what this means then is my-

$$f'' = \frac{k_B T}{v_c}[g - 2\chi]$$

so the minimum value is equal to 4. So, if χ happens to be less than 2 we can be certain that f double prime is always higher than higher than 0 and when that happens we can be certain that the system will form a homogeneous solution or mixing will happen. So, in other words since χ_c is equal to say, is equal to 2 we can say, if χ is less than χ_c then we always have the mixing behaviour. On the other hand, when χ is higher than 2 or when χ is higher than χ_c. Clearly, we can have situations where f double prime happens to be negative but that will not happen for all the values of Φ because for very small value of Φ the quantity g that is 1 by Φ + 1 by 1 – Φ has very high value. Let us say if I plug in Φ equal to 0, there we are going to have g equal to infinity.

So, we will not have a situation where f double prime will be less than 0 for all values of Φ. So, we can never have a situation of complete de mixing so as to speak or complete phase separation but phase separation may occur for certain value of Φ.

So, what this translates to is the following so in my f Φ versus Φ curve we know that this situation happens for χ higher than χc and for that situation as we had discussed the curve should look something like that because only then we have mixing for all values of Φ then as I start increasing the value of χ we are going to a regime where we can have phase separation. And I give you this discussion where when we have this kind of functional form then we can have phase separation. We will never have a situation where it is fully convex because completely mixing is not possible in this situation so for χ less than χ_c this can be the behaviour so therefore what we can say is that, for χ is equal to χ_c that is the spinodal point this f double prime becomes equal to 0 so that is where we can say we have an onset of the phase separation behaviour.



So, what we have been trying to establish is the different phase regimes for this particular problem and we found that there is a variable χ_c that dictates that phase separation behaviour for χ value less than χ_c we have always mixing, for χ value higher than χ_c we can have a situation of phase separation.

Now the advantage of the mirror symmetry around Φ equal to 1 by 2 is first of all I have drawn the curves all which were mirror symmetric already but the advantage comes in when I try to draw a common tangent in the case of χ higher than χ_c and that common tangent will then have a slope of 0. So, the binodal line is therefore given as $f'(\Phi) = 0$ and the expression of that we had already evaluated earlier. So, this is the expression of the binodal line. This is the expression of the spinodal and here is the value of critical point.

So, in this particular discussion what I wanted to establish is that within certain assumptions we can make twine models which qualitatively describe the phase behaviour of solutions and the particular example that we were focusing on was on looking at the mixing and phase separation behaviour so we have been able to both derive the function f and to so its usefulness in characterizing the mixing and separation behaviour and it turns out and we have discussed in detail that if I know ‘f’ I can pretty much get the entire phase behaviour this is one way of doing it for the lattice model of course, when we are coming to the molecular simulation part we will be doing the same exercise more rigorously for a more elaborate phase space.

So, before I conclude here, let me tell you that this lattice model of solutions even when it is quite simplistic finds its use in many applications than we can imagine. So, I have taken an example of a liquid solution where solute and the solvent molecules were of the same volume but it also finds use in the study of polymers where polymers are clearly much larger than the solvent molecules.

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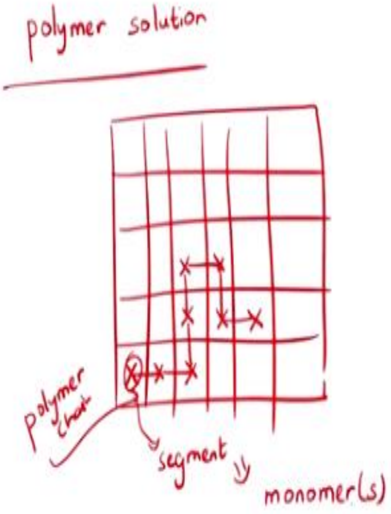
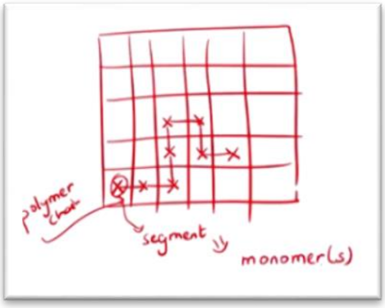


So, in that case what we assume for a polymer solution and I will not really completely derive the expressions for this particular case. So what I assume there is that the individual units of polymer which may be consisting of one monomeric unit or few monomeric unit they occupy the same volume as a solvent molecule. So, in every cell I will not place the entire polymer chain instead I will place them in multiple cells connected together so this entire thing that I am drawing right here represents a polymer chain and one of these is a segment of the polymer chain that may be a monomer or a set of monomers.



Again this is a toy model but it happens to have too much applicability in polymer physics and the reason, being that you may imagine that the simulation of polymeric systems is even more complicated than the simulation of simple simpler systems where the solute and solvent molecules are of the same size because, the polymer chain itself can take many possible configuration. So, until so far, when we are doing the liquid solution, we did not worry about the configurations of the molecules themselves we worried about the configuration of all the molecules together so their relative positions with respect to each other.

But in the polymer case the configuration of the polymer chain itself or the structure of the polymer chain itself adds a huge burden to the few to the phase space and therefore it is even more complicated to simulate and therefore in the polymer solution literature it is very common to use lattice models both theoretically and in simulations to simulate that.

More importantly this idea of lattice simulation has also picked pace in the study of biological systems. For example, phenomena such as self-replication can be described within a lattice model kind of a framework if we think about it, we are looking at a biological problem that is, in some sense even more complicated and the twine model that we are building is therefore even more simpler but nonetheless those kind of lattice models happens to have great utility in extracting the physical behaviour the qualitative behaviour regarding those systems.

So, with that I wanted to conclude the discussion today, thank you.