Introduction to Polymer Physics
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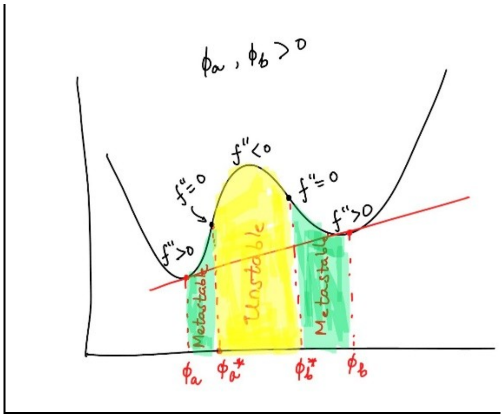
Lecture-31
Phase Separation Regime,
Introduction to Lattice Model of Solutions

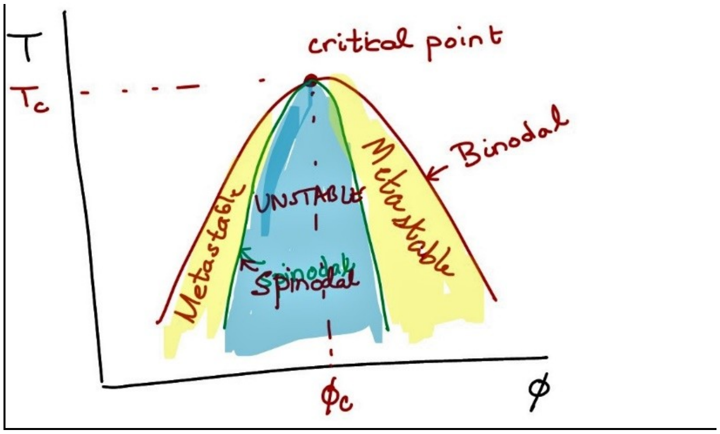
Welcome in the last class we have been discussing about the mixing and phase separation behavior of solutions that we can get using the Helmholtz free energy density and we have talked about various regions of phase separation- the Metastable and unstable regions and so on.

So, basically just to recall what we have said so far is if we want the system to phase separate it must have the Helmholtz free energy function must have regions where f'' is less than 0 that is a requirement for phase separation and of course I have already said that there is a possibility that the system is completely convex but in that case we will have a complete phase separation no coexistence so, the solute will face separate totally in one phase and solution phase will contain only the solvent.

If I want to have some sort of a coexistence of solute in the two phases the free energy curve should look something like this and in that curve I noted that there are two inflection points and if I want to know the phase coexistence I should draw a common tangent that will tell me these points will correspond to the concentrations at equilibrium when the two phases coexist and then we can separate the regions on the curve and between the points and I said that this particular reason that is in between these two points are known as the unstable region and if I look at the other two reasons, that is right here and right here then these two regions are referred as the metastable region and the difference here is the following that if we are in the unstable region any small difference will lead to phase separation but if we are in a metastable region we are in some sort of a local minimum small disturbances will not lead to a phase separation it can remain there for very long time only a large disturbance can take it to a phase separated state.



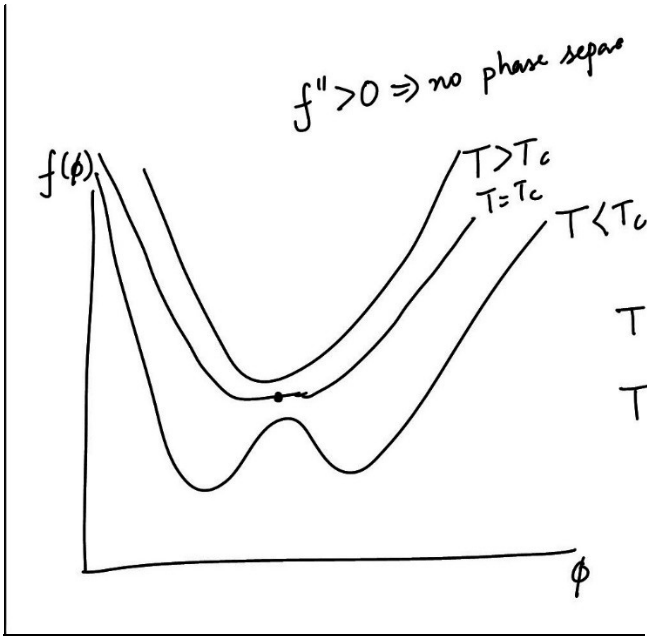
So, now we can also talk about something referred as a critical point and the idea is something like this since the function f is also a function of temperature and in so forth we have not really discussed the role of temperature. But temperature plays a very important role if I look at the temperature versus composition phase diagram the graph looks something like this.



So, the graph will change as the temperature changes as I am looking now at the role of temperature versus ϕ. So, this corresponds to these red dots here and then we can say that my unstable region is here on the plot, below the spinodal and the metastable region are between the spinodal line and the binodal line, so this is unstable and this is metastable and this again is metastable.

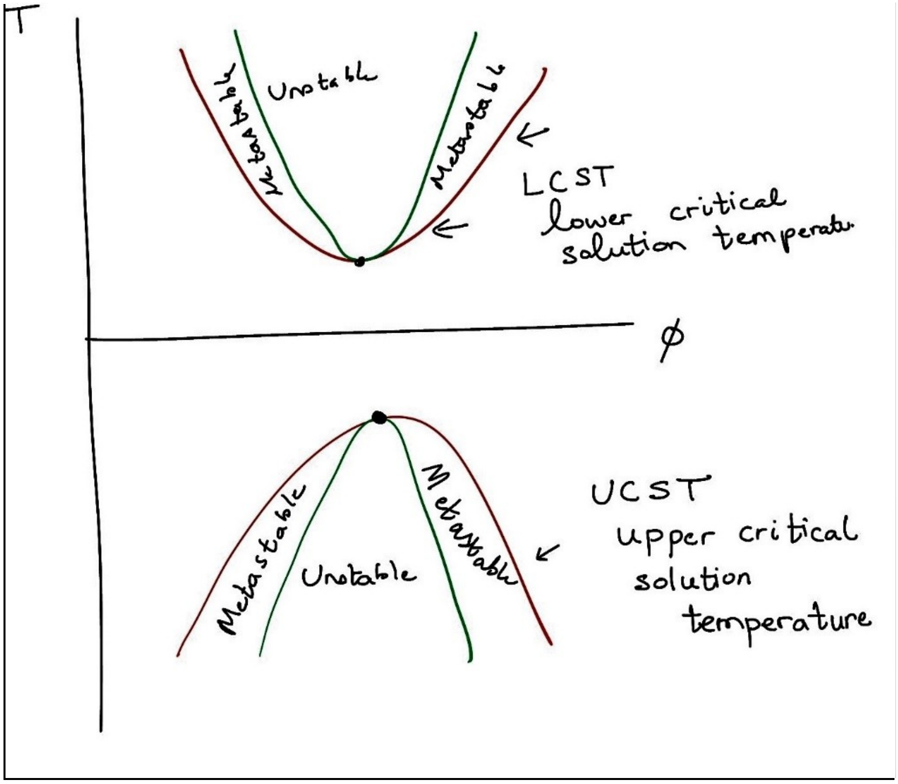
So, earlier what we have shown here the temperature was assumed to be constant and now I am telling you that what happens when temperature is changed and this point where the binodal and spinodal meets is referred as the critical point and referred as TC. I can also define a critical composition ϕ_c and the idea here is that if T is higher than TC then there will be no phase separation as you can see in the plot so when T is higher than TC we are above the envelope of phase separation, so there is no phase separation taking place. If T is less than TC then phase separation can occur and the phase separation can be unstable or metastable depending on what concentration we are lying in.

So, if I now look at that particular function f of ϕ as a function of temperature. This graph should also change to reflect the fact that there is no phase separation for T higher than TC and we know the behavior when there is no phase separation.



When there is no phase separation when my graphs would look like that because that corresponds to f double prime higher than 0 that is no phase separation. This would happen for T higher than TC. As soon as the T becomes smaller than TC we should start to have a phase separation characterized by the shape of graph like this that we have already used earlier. So, just at the brink of the critical point you can imagine that there is one point where inflection has begun to start just higher than the critical point we do not have any phase separation and below the critical point we start to have a phase separation. So, we will use this idea over and over in the polymer solution theory.

We will use something known as solvent quality that depends on temperature in place of temperature but let us come back to that later. What happens especially in the case of polymer solutions is sometimes the system shows slightly opposite behavior than what we have seen here.



So, now in the case that we have discussed earlier that was this particular that case that was right here in this case what we saw was the T higher than TC there is no phase separation but if I look at this particular graph then for T less than TC there is no phase separation. So, solutions with so this particular behavior are known as UCST or upper critical solution temperature and things with show this behavior are known as LCST or lower critical solution temperature.

So, there are two kinds of behavior that we can have in temperature versus composition space you can either have a UCST behavior or a LCST behavior, accordingly the metastable and unstable regions will also change. So, in this case we have the metastable and an unstable region as well.

So, now everything said and done we still do not know what the function f of ϕ is if we know its particular say I can talk about the mixing and phase separation behavior. But we have so far not discussed how we get that particular function f of (ɸ, T) that is the Helmholtz free energy density.

So, now I will try to discuss how can we get that particular function again we will derive it for a liquid solution that is continuing a binary system of a solute in a solvent and then we will extend the idea to a polymer solution and then once we have done that then we can talk about the mixing and phase behavior of polymer solutions okay. So, obviously there are two ways to get f of (ɸ, T) one way is by theory as with everything else either we can do some kind of a theory or some kind of an experiment. If you think of doing an experiment one possibility is for example I measure the osmotic pressure versus the volume fraction favorable to measure the osmotic pressure I do not know how we will do that but let us say we have some mechanism to measure the osmotic pressure as a function of composition we know osmotic pressure depends on the function f so we can get f from there.

If on the other hand if I am looking at a theory where should we start? So I will start with some basic ideas of classical I would say classical mechanics and then see like how exactly we go about getting the energy functions that we need. If you have done thermodynamics you must know that F of (ɸ, T) is related to the equation of states that we derive. Again we typically do not derive it, it is typically either experimentally obtained or there is some correlation that people hypothesize or things of that sort. But if we have to start from theory let us say for ideal gases, we know that we can use kinetic theory and obtain relation for PV = NRT.

So, let us go back there let us try to see how can we build a theory to determine the function f of (ɸ, T) so in classical mechanics ultimately everything comes down to something known as a classical Hamiltonian. In fact the same idea also apply in quantum mechanics except that the Hamiltonian there is an operator as opposed to a function expression here. So, the Hamiltonian is defined in terms of the positions of the constituent particles and their momentum. So, for any system that contains some collection of atoms if I want to find the energy of the system as I should start with the classical Hamiltonian that will depend of course on the position of particles and momentum of particles.

$$H\left(\{\vec{r}_i\},\{\vec{p}_i\}\right)$$

$$Here\,\vec{r}_i=\vec{r}_1,\vec{r}_2,\vec{r}_3\ldots\ldots\ldots\ldots\ldots\vec{r}_n\,refers\,¿\,position\,of\,particles$$

$$\vec{p}_i=\vec{p}_1,\vec{p}_2,\vec{p}_3\ldots\ldots\ldots\ldots\vec{p}_n\,refers\,¿\,momentum\,of\,particles$$

Now as we know from classical mechanics this would be composed of two terms- a kinetic energy term and a potential energy term. So, kinetic energy term I can write as

$$K.E=\sum_i \frac{\vec{p}_i^{\,2}}{2m_i}$$

And then you will have a potential energy which in this case will be dependent on the positions of particles because ultimately where this energy the energy comes from the energy comes from the interaction between particles and we have discussed earlier that the interactions eventually depend on the positions of particles and the distances between them. So, there is no velocity component that comes typically in the potential energy, potential energy typically I would say always for all the cases we will do will only be a function of the positions of particles because ultimately the positions can change with time this will give rise to different interaction energy between the particles in the system and eventually the total energy of the entire system.

$$P.E=U\left(\{\vec{r}_i\}\right)$$

$$H\left(\{\vec{r}_i\},\{\vec{p}_i\}\right)=\sum_i \frac{\vec{p}_i^{\,2}}{2m_i}+U\left(\{\vec{r}_i\}\right)$$

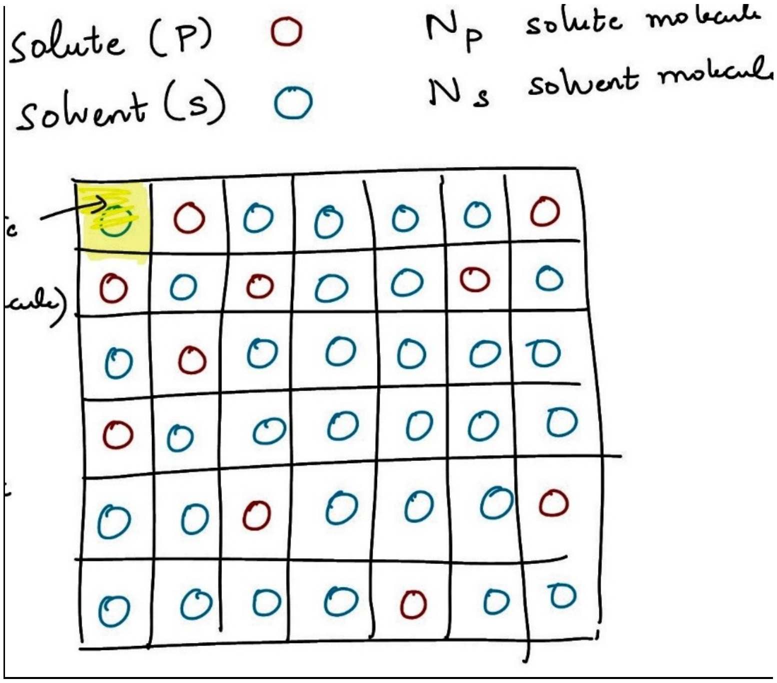
So, now we have a way to find the classical Hamiltonian of the system, the only difficulty here is if I look at the phase space of a large system that is thermodynamic in nature. Let us say if we look at a liquid solution and we talk in terms of the energy of that system. We are talking about a collection of like moles of the molecules that are present of solute and solvent if I think of say moles of solute and solvent we have moles multiplied by 3 coordinates moles multiplied by 3 momenta that is 10 to the power 23 to the power 10 to the power 24 both of them and of course the keeping track of all those positions and momenta is simply impossible even if we managed to do it for a large system of course we can do it for a smaller system that is the basis of what we discussed as the molecular dynamics but for large systems it does not really make sense of talking about the positions and momentum of particles because even if we are able to compute that by some means it is very difficult to make sense of those positions and momentum and try to relate the energies to those quantities.

So, what typically people do in most of classical mechanics or classical physics is we make some sort of toy models and what the toy models do is they decrease the phase space of the system that is to say that in reality the system will be having I would say a hundred thousand different coordinates one hundred thousand different momenta if I make at toy model I will decrease by an order of say thousand or ten thousand. So, that I will work with say ten positions and ten momenta things of that sort something that is more tractable and something that allows us to make some sort of a theory based on that.

So, the basic scheme is something like this so how do we get f of (ϕ, T) we have to get from the positions and momentums because of course if I get the Hamiltonian I know everything else but this is impossible to track. So, what we do is we make a toy model and we get a Hamiltonian for the toy model and using that we can get f of (ϕ, T). Let us call it some $\tilde{f}$ because in any case it depends on the model of course the models model dependent and we hope that this $\tilde{f}$ is approximately equal to the actual f of (ϕ, T).

So, this is the typical scheme that is being followed if you think of like toy models how do they work we have already demonstrated the whole idea of random walks thinking of polymer chains as walk of a drunkard left and right was a toy model and it was able to give us scaling laws. So, in a similar vein we will discuss the toy models that give us f of (ϕ, T) and we hope that they capture the thermodynamic behavior of polymer solutions but we start with liquid solutions and see how we go.

So, one of the toy models will discuss is known as the Lattice model of solutions and the basic scheme here is the following so instead of assuming that the solute and solvent particles let us again the solute particle is represented by P and solvent by S, so of course in a real system the solute and solvent particles can move anywhere and they will have very large numbers of positions and Momentum's or the phase space to reduce the phase space what we assume is these molecules move on a lattice that is to say that they cannot really move in a continuous space they are moving in some sort of a grid and let me represent the solute molecules by a red color and solvent molecules by a blue color. So, you can have these cells of the lattice occupied by the solvent molecules and of course the remaining slides are occupied by the solvent molecules.



So, again we can talk in terms of say some N_p solute molecules and N_s solvent molecules and what we also assume is the volume of each of the molecule is same as the cell volume that is to say the volume of each of the molecules is same as the volume of the cell, let us call this VC so

VC = solute volume = solvent volume

So, of course this is clearly not true for the actual system because solute and solvent can differ in size. But let us see like at least at a qualitative level whether this model is able to provide some understanding or not of course we can make more generalities such as we can make the cell size is different and things of that sort but that would anyway kill the simplicity of the model and any hope to go towards a very large free space is I think futile because the number of molecules are anyway large. So, given its weaknesses, given the simplicity that is of course telling us that it is this cannot be true. We will see how this model is still very successful in giving the phase behavior that of the in giving the function f of (ϕ, T) and the phase behavior since we have already discussed that if we have the function f we can predict the phase behavior.

So, now in this particular model I can define the volume fraction in this case anyway thus the volumes of solute and solvents are the same so I can define the solute volume fraction as solute volume by total volume which is simply by-

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

$$\text{¿}\frac{N_p}{N_p+N_s}$$

$$\text{¿}\frac{N_p}{N_{tot}}$$

So, in the next class using this particular description we will go on to find out the expression for the Helmholtz free energy density of the polymer solutions and then we will extend the idea to a polymer solution in other polymeric systems.

With that I conclude, thank you.