Introduction to Polymer Physics

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Lecture – 07

Phase Behaviour of Polymer Solutions and Blends

So, hello everyone, we have been discussing the thermodynamics of polymer solutions in the last few lectures. So, we have discussed the Flory Huggins theory and used it to derive an expression for the Gibbs free energy change of mixing for a polymer solution. We also discussed the Flory Huggins interaction parameter what is its significance how it depends on temperature.

We have discussed the solubility parameter approach, which can be used to get a feel of the solubility of a polymer in a given solvent. So, although it might not provide very accurate results it might be limited to only polymers and solvents which are nonpolar, but still it is a useful method through which one can determine or get an idea of whether a certain polymer is soluble in a given solvent.

So, we will continue our discussion of this topic of thermodynamics of polymer solutions. And in today's lecture we will focus on the phase behavior and specially the phase separation of a polymer solution. So, we will look at the phase diagrams the concept of critical temperatures in this phase diagrams in the present lecture. We will also start our discussion on the thermodynamics of polymer blends towards the end of this lecture.

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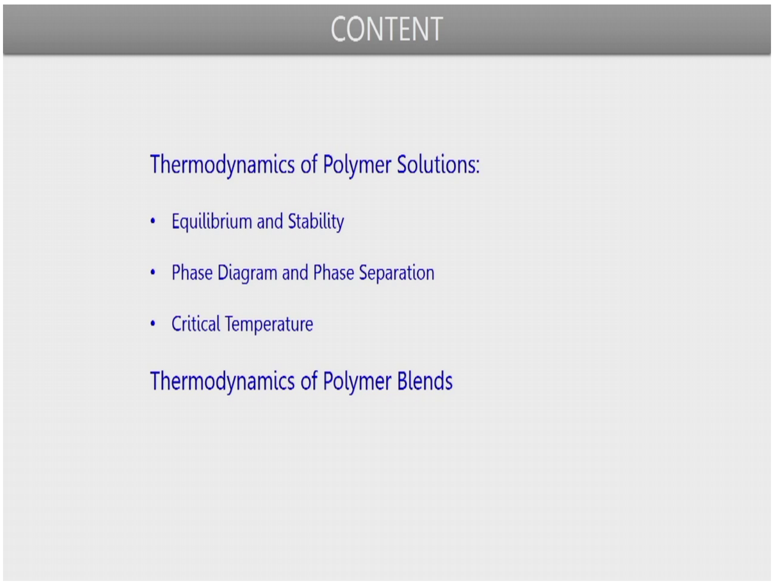

CONTENT

Thermodynamics of Polymer Solutions:

- Equilibrium and Stability
- Phase Diagram and Phase Separation
- Critical Temperature

Thermodynamics of Polymer Blends

So, specifically in the present lecture we will first talk about the condition of the equilibrium and that of stability of a polymer solution that is formed by mixing and polymer in a solvent. So, what is the condition for the solution to actually form and when even if it can form, whether that solution will remain stable or whether it will tend to separate into different phases. So, the conditions for these we will look into these topics through graphical as well as mathematical approach.

We will discuss the phase behavior of this polymer solutions using Flory Huggins theory, and we will also talk about the phase separation behavior. We will also discuss what is called the critical temperature associated with the phase behavior of polymer solution. So, specifically we will talk about 2 types of critical temperature, the lower critical solution temperature and the upper critical solution temperature. And as I mentioned we will also briefly start our discussion of the thermodynamics of polymer blends towards the end of this lecture.

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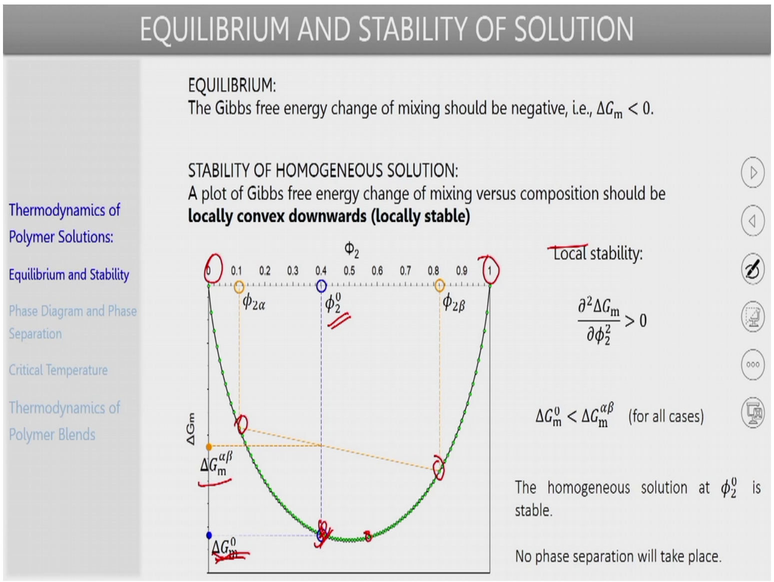

EQUILIBRIUM AND STABILITY OF SOLUTION

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

Phase Diagram and Phase Separation

Critical Temperature

Thermodynamics of Polymer Blends

EQUILIBRIUM:
The Gibbs free energy change of mixing should be negative, i.e., $\Delta G_m < 0$.

STABILITY OF HOMOGENEOUS SOLUTION:
A plot of Gibbs free energy change of mixing versus composition should be **locally convex downwards (locally stable)**

~~Local~~ stability:

$$\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} > 0$$

$\Delta G_m^0 < \Delta G_m^{\alpha\beta}$ (for all cases)

The homogeneous solution at ϕ_2^0 is stable.

No phase separation will take place.

So, when we talk about equilibrium when we if we mix a polymer in a solvent to form a polymer solution. So, the equilibrium condition for equilibrium is that the Gibbs energy change of mixing must be negative. So, the solution will form only when the Gibbs energy of the system actually goes down or decreases.

So, which implies that the delta G of mixing must be negative now that is fine if we mix a polymer solvent and if the Gibbs free energy of the mixture is lower than the sum of the Gibbs free energies of the individual components, then that will give a negative delta G of mixing and that will satisfy the equilibrium condition that delta G should be less than 0.

However, even if that condition is satisfied there is no guarantee that the solution that has formed upon mixing of the 2 components, that solution will remain stable. So, if the we mix 2 tuned components solvent and the polymer and a we form a solution. Then if the solution that is formed can separate into 2 different phases and that separation if that separation can actually lead to further reduction of the Gibbs free energy of the system. Then that phase separation actually will take place and ultimately we will end up with a system having 2 distinct phases one which will be rich in the polymer and the other which will be rich in the solvent.

So, the delta G being less than 0 that is of course, required for the solution to form, but even if that condition is satisfied there is no guarantee that homogeneous solution that is formed it will remain stable it. So, some other conditions need to be looked upon which will help us determine whether the solution I that is found will remain stable or whether it will it is unstable and it will phase separate into different phases. So, the condition for stability of a homogeneous solution is that, if we construct a plot of the delta G of mixing against composition.

So, for our case we will consider the volume fraction of the polymer in the solution as the measure of composition so, that we have been representing as phi 2. So, phi 2 will be the measure of our composition. So, if we plot delta G of mixing against phi 2. So, if that plot is a convex downwards throughout, then we can say that throughout the composition range the solution homogeneous solution that has formed is stable.

However, if that is not the case, then there will be regions in which the stability condition will be violated and the solution homo homogenous solution will actually separate into different phases. So, as to further reduces give it is Gibbs free energy. As we just discuss the stability condition is that the delta G of mixing curve should be locally convex downwards. So, if we look at a typical delta G of mixing curve of this type plotted with respect to phi 2, then the locally convex downwards which implies local stability is will look something like this.

So, here we see that throughout the composition means that is from phi 2 equal to 0 to phi 2 equal to 1, throughout this range the plot is actually convex downwards. So, what this means is that throughout this composition range, the solution that has formed will be stable. So now, that is a graphical condition for stability, equivalently we can also state the conditions for stability in mathematical form that condition of local stability is that the second derivative of the delta G of mixing with respect to phi 2 that should be greater than 0.

So, this is a necessary condition for stability if; this condition is satisfied only then stability can be expected. And if this condition is violated if delta G the secondary of delta G of mixing is less than 0, then the solution that is formed will be actually unstable. So, we will discuss these things in more detail further on this lecture. So, let us consider a solution that is formed at this composition phi 2 naught. This is approximately 0.4 so, the solution contains around 0.4 volume fraction of polymer and remaining will be solvent.

So, corresponding to this composition if we form a solution the delta G of mixing is given by the delta G m naught here, and let us for the sake of argument, let us see what happens if this solution homogeneous solution that has formed at this condition if that separates into 2 different phases. So, whether that separation into 2 different phases whether that will lead to a further reduction of delta G of mixing or not let us find out.

So, let us say that this at the, this composition the solution that has formed that phase separates into 2 phases one having compression corresponding to that point, and the other having composition corresponding to this point. And let us say the corresponding compositions are phi 2 alpha and phi 2 beta and the 2 phases that are formed are the alpha phase and the beta phase.

So now, the if we consider these 2 phases of phases then the delta G of mixing with respect again to the pure component of components. That is a pure solvent in pure polymer the delta G of mixing for this system, which consists of 2 phases will be given by the delta G m alpha beta that shown here. And we see that this delta G m alpha beta is clearly higher than the delta Gm naught which we got if the solution remained homogenous and did not phase separate. So, since this delta Gm naught is less than the delta Gm alpha beta, and that will be true for any point on the curve that we have here.

So, whether we choose this point in this point here or whether we choose this point or any other point, that point will always have given lower gives delta G of mixing compared to a phase separated system containing 2 distinct phases. So, for all cases what this implies is that the homogenous solution will be stable and it will not phase separate into 2 distinct phases. So, no phase separation will take place.

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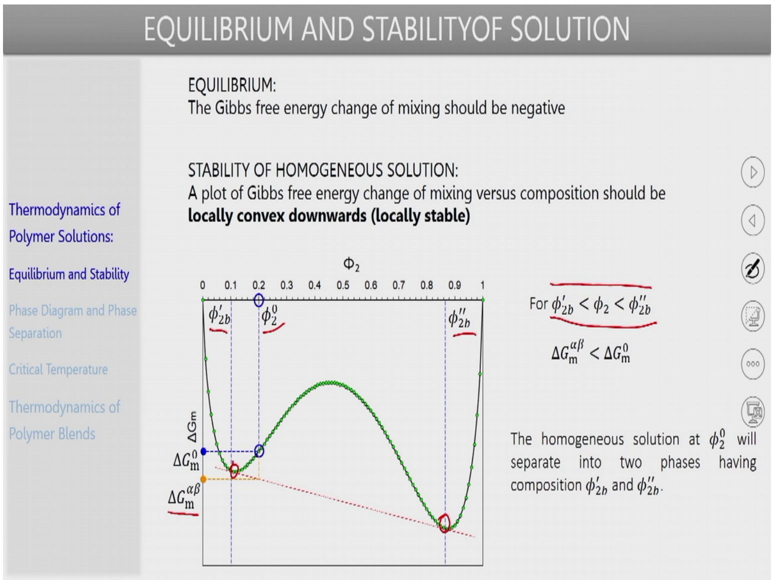

EQUILIBRIUM AND STABILITYOF SOLUTION

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

Phase Diagram and Phase Separation

Critical Temperature

Thermodynamics of Polymer Blends

EQUILIBRIUM:
The Gibbs free energy change of mixing should be negative

STABILITY OF HOMOGENEOUS SOLUTION:
A plot of Gibbs free energy change of mixing versus composition should be **locally convex downwards (locally stable)**

For $\phi'_{2b} < \phi_2 < \phi''_{2b}$

$\Delta G_m^{\alpha\beta} < \Delta G_m^0$

The homogeneous solution at ϕ_2^0 will separate into two phases having composition ϕ'_{2b} and ϕ''_{2b}.

So, if we now consider a curve of delta Gm which actually is not convex downwards throughout, but actually shows a concave region in the middle part, then things become a bit more interesting. By drawing what is called a common tangent to the this curve where which shows 2 min minima, we can identify a 2 points which let us call as phi 2 b prime and phi 2 b double prime, these 2 points are what is called the binodal points. And these 2 points de market regions of stability for a system of this that shows this kind of a behavior.

So, if we have a solution that forms at that composition it will be stable. And similarly any solution that forms above phi 2 b double prime, above that composition that will also be stable. And this method by which we have identified the 2 points phi 2 b prime and phi 2 b double prime, that method is called the common tangent rule. So, basically what we have done is drawn a common tangent to the 2 regions of the curve that shown minima. And this common tangent construction gives us the binodal points.

So, we see that in this particular case the curve is asymmetric, and the 2 minima basically have different depths. So, as before cases with a curve this delta Gm plot or curve is asymmetric. For such cases the binodal points will not actually entirely coincide with the points of the minimum in those regions. So, the phi 2 b prime here it will not coincide with the minimum here. Similarly, the phi 2 b double prime that will also need not coincide with the minimum here. If we consider the region between phi 2 b prime and phi 2 b double prime.

So, that region is demarcated by this range. And that region is the region in which phase separation will take place. So, this region between where the composition is greater than phi 2 b prime and less than phi 2 b double prime. That is a region between the binodal points, that part is referred to as a miscibility gap, because that is a region where the polymer solution will not be remain homogeneous and it will not be miscible and it will have a tendency to separate into 2 different phases.

Now let us again look at a homogeneous solution having a certain composition in the region of miscibility gap. And let us see what happens in this case. So, let us say this phi 2 naught is that composition that we have again identified. But we see that this composition lies in a region where the solution need not be stable. So, it lies in the miscibility gap. So, core corresponding to this composition phi 2 naught the delta G m naught can be obtained like this. And if in instead of having this homogenous solution here, if we if the solution separates into 2 phases corresponding to compare.

The 2 binodal compositions, then the Gibbs free energy change of mixing delta G m alpha beta. So, again let us call that 2 phases that have formed as alpha and beta phase. So, the Gibbs free energy change of mixing will be given by this point here. So, we clearly see in this case that the Gibbs free energy change of mixing actually has reduced when phase separation takes place. What we can infer from here is that, if we have a try to form a homogeneous solution having a composition phi 2 naught in this case, then that homogeneous solution will tend to separate into 2 different phases.

So, as to further minimize it is Gibbs free energy. And that composition of the 2 phases will correspond to that 2 binodal points that we have identified using the common tangent rule. And it is important to note that separation in 2 phases having the binodal composition that will give a give the minimum possible Gibbs free energy and that is why that separation is thermodynamically favored and it happens.

We can also consider any other point in this miscibility gap region some at let us say some other phi 2 naught, and for this case also we can identify that delta G m naught if solution where homogenous and if instead if it phase separates into 2 phases having the binodal compositions.

So, if it again phase separates into solution having these 2 compositions. Then the corresponding delta G m alpha beta again can be identified like this. And we see that again the delta G m alpha beta is less than the delta G m corresponding to the pure homogeneous solution. So, again the phase separation will be favored because it reduces the Gibbs free energy change of mixing. So, for it what one can see is that for any composition in the miscibility gap region which is in this range.

So, for any phi lying in this range between the binodal points, it will always so happen that the phase separation will be thermodynamically favored because there are corresponding delta G of mixing will get reduced upon separation in 2 phases corresponding to the binodal compositions, phi 2 b prime and phi 2 b double prime. So, in the miscibility gap the phase separation will always be favored a thermodynamically.

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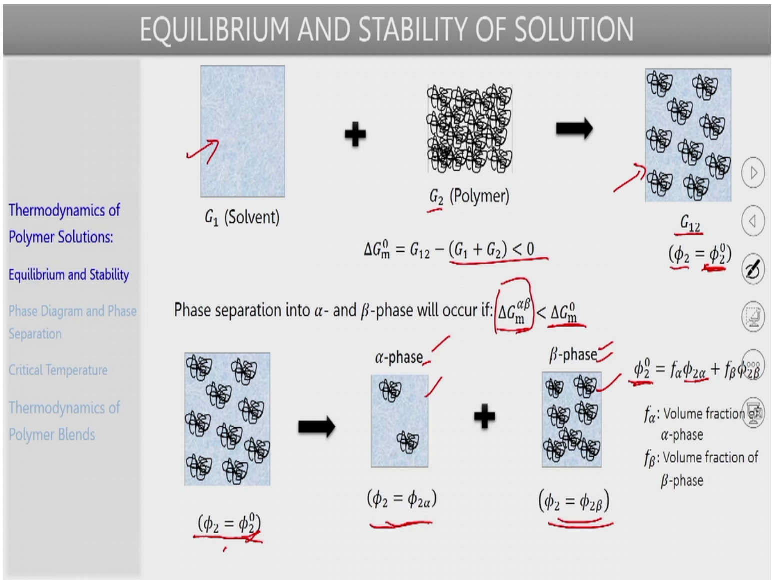

EQUILIBRIUM AND STABILITY OF SOLUTION

Thermodynamics of Polymer Solutions:

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Critical Temperature

Thermodynamics of Polymer Blends

G_1 (Solvent) + G_2 (Polymer) → G_{12} $(\phi_2 = \phi_2^0)$

$\Delta G_m^0 = G_{12} - (G_1 + G_2) < 0$

Phase separation into α- and β-phase will occur if: $\Delta G_m^{\alpha\beta} < \Delta G_m^0$

$(\phi_2 = \phi_2^0)$ → α-phase $(\phi_2 = \phi_{2\alpha})$ + β-phase $(\phi_2 = \phi_{2\beta})$

$\phi_2^0 = f_\alpha \phi_{2\alpha} + f_\beta \phi_{2\beta}$

f_α: Volume fraction of α-phase

f_β: Volume fraction of β-phase

Next let us just schematically try to represent what we have been discussing thus far. So, let us say that this box here this contains the pure solvent. And it is Gibbs free energy let us say is G 1 and if we add a polymer to this solvent having Gibbs free energy G 2.

Then we will end up with a solution where the polymer will be dissolved in the solvent, and let us say the Gibbs free energy of this system is G 1 2 and the volume fraction of polymer let us say is phi 2 naught for this case. So, this case represents a homogeneous solution that has formed. So now, again depending on what this composition is whether this lies in the miscibility gap or whether it lies in the stable region that will decide whether this homogeneous solution is stable or whether it will prefer to separate into 2 different phases.

So, the delta G of mixing of course, is given by G 1 2 minus G 1 plus G 2. And that should be less than 0 for the solution to form at all. Now if this phase separation in of this homogenous solution at this composition that phase separation takes place into an alpha phase and a beta phase having compositions phi 2 and phi 2 beta respectively. So, that phase separation will occur if the delta G of mixing corresponding to the formation of these 2 phases is lower than the delta G of mixing corresponding to the homogenous solution that we have.

Ultimately the whether the solution that has formed is stable or not, that will always be dictated by whether the solution formed can further reduced Gibbs free energy of mixing by separating into 2 different phases. And we notice at this phase separation that takes place here the alpha phase and the beta phase. So, one phase will be rich in the solvent the other phase will be rich in the polymer.

And the overall volume fraction phi 2 naught in the homogenous solution that can be that will be equal to the volume fraction of an alpha phase that has formed multiplied by the volume fraction of polymer in that alpha phase, plus the volume fraction of the beta phase that has formed, which has f beta times the volume fraction of polygons in that bet beta phase.

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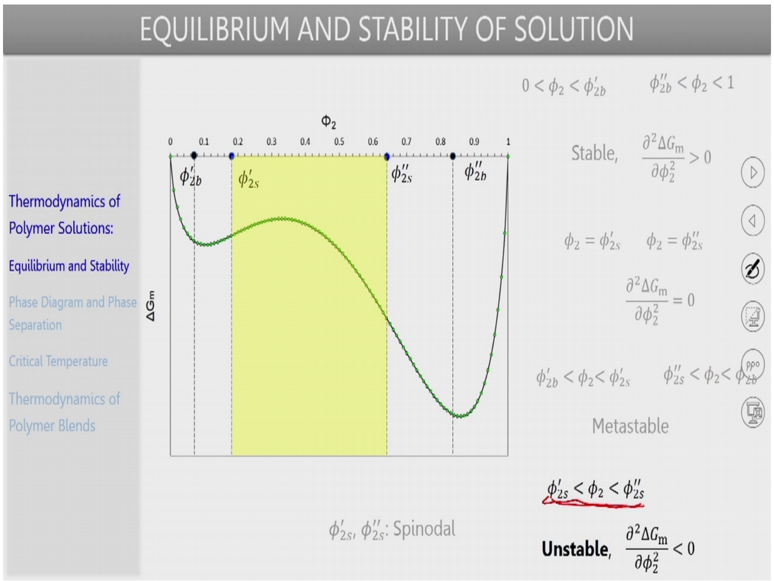

EQUILIBRIUM AND STABILITY OF SOLUTION

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$0 < \phi_2 < \phi'_{2b}$ $\phi''_{2b} < \phi_2 < 1$

Stable, $\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} > 0$

$\phi_2 = \phi'_{2s}$ $\phi_2 = \phi''_{2s}$

$\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} = 0$

$\phi'_{2b} < \phi_2 < \phi'_{2s}$ $\phi''_{2s} < \phi_2 < \phi''_{2b}$

Metastable

$\phi'_{2s} < \phi_2 < \phi''_{2s}$

Unstable, $\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} < 0$

ϕ'_{2s}, ϕ''_{2s}: Spinodal

So, if we look at again a delta G of mixing versus phi 2 curve which shows a tool in the convex regions along with a concave kind of region in the middle, then using as just discussing the common tangent rule we can construct this dashed red line as a common tangent to the 2 regions.

And that common tangent can be used to identify the binodal compositions phi 2 b prime and phi 2 b double prime. So now, in the 2 regions denoted by volume fraction below phi 2 b prime or volume fraction above phi 2 b double prime. So, in these 2 regions which are shown as shaded in green here the solution will be stable and this second derivative of Gibbs free energy will be greater than 0 which is the necessary condition. So, it has to be satisfied.

So, the solution will be stable because if a solution forms in these composition ranges then no kind of phase separation will further reduce it is Gibbs free energy if we consider now a couple of other points on this graph. So, let us consider 2 points phi 2 prime s and phi 2 prime double s which has shown here. So, these 2 points have been identified as the points at which the second reality of the delta G of mixing is 0 ok. So, the 2 points in this curve where this del square delta Gm del phi 2 square is 0, those 2 points are called the spinodal points, and they are represented as phi 2 prime s and phi 2 phi 2 s double prime.

So, these spinodal points basically demarcate the region where the second derivative is positive and where the second derivative is negative so, if we now consider the range shown here also shown as a shaded region in the graph, as well as the range here which again is shown as a shaded region. So, these 2 compositions correspond to those between the binodal composition the spinodal compositions.

So, if we consider these ranges, the solution if it is forms if the, we have a certain solution that forms with a composition lying in these ranges and the solution is set to be metastable ok. So, this spinodal points basically demarcate the regions up to which the solution will be metastable. And if we go to compositionally in that lies between the 2 spinodal points.

So, if the composition is between phi 2 s prime and phi 2 s double prime, then in that case the solution if the solution forms having a composition in this range, then the solution will be unstable and of course the second derivative of Gibbs free energy is less than 0.

So, it will necessarily be unstable. So now, let us just briefly discuss what is the difference between the metastable region and the unstable region. So, in the metastable region as well as the unstable region thermodynamically the favorable state will be the phase separated state where the solution separates into 2 phases having the 2 binodal compositions so that it can further reduce it is Gibbs free energy; however, in the metastable region for this phase separation to occur which is thermodynamically favorable for this phase separation to occur a certain kind of barrier needs to be crossed.

So, in the metastable region the phase separation will typically take place through a mechanism called nucleation and growth. For the new for the nuclei of a critical size to form which can further grow and finally, lead to phase separation, certain kind of activation barrier will need to be crossed. So, a metastable region solution actually in the metastable region although thermodynamically speaking it should always phase separate it can stay in that region, provided that the activation barrier for this formation of a nuclear of critical size is not overcome.

So, that is a metastable region. Now in the unstable region which lies between the 2 spinodal points, in that region the space separation will actually be completely spontaneous. So, even the tiniest fluctuation in let us say composition will induce phase separation. So, any solution that forms in the unstable region will spontaneously phase separate into 2 different phases corresponding to the binodal compositions and reduce it is Gibbs free energy. This kind of a phase separation which takes place in the unstable region that is region lying between the 2 spinodal compositions.

This type of phase separation is referred to as spinodal decomposition. So, again to distinguish between the 2 spinodal decomposition takes place in the unstable region. And it is induced by the tiniest of fluctuations in the system. Whereas, the nucleation and growth mechanism first phase separation that takes place in the metastable region, and for the nucleation to start and progress a certain barrier needs to be crossed for a nuclei of a critical size to form, which can then grow and lead to phase separation.

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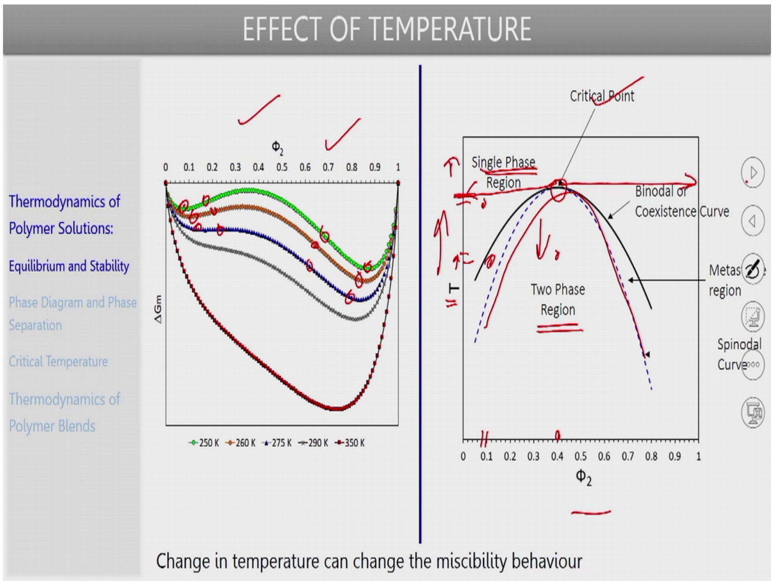

EFFECT OF TEMPERATURE

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

Phase Diagram and Phase Separation

Critical Temperature

Thermodynamics of Polymer Blends

Change in temperature can change the miscibility behaviour

Next now look at the effect of temperature on the miscibility or behavior of polymer solution. So, here what we have done is a shown a plot of delta G of mixing versus phi 2 at several different temperatures. So, we see that for this particular case as the temperature is being increased from 250 Kelvin onwards, we see that the delta G of mixing graph progressively becomes more and more negative.

So, what that suggests is that the miscibility of the polymer in the solvent is increasing and if we go to high enough temperatures, which is 350 k in this case then the miscibility gap basically completely disappears and we have a solution which will be completely homogeneous throughout the composition range.

So, if we look at the lowest temperature in this graph (Refer Time: 25:33) that the one at 250 Kelvin. So, we see that let us say the binodal compositions are somewhere here, if we go up in temperature to 260 Kelvin the binodal compositions are shifting a bit. And further at higher compositions or higher temperatures the binodal composition will further shift.

So, what we see is that as a temperature is being raised where in this case the miscibility gap actually keeps decreasing at, and at high end enough temperature, the system becomes miscible over the entire composition range. In this particular case increasing temperatures are actually increasing miscibility. So, change in temperature are always leads to change in miscibility behavior, but it need not be that increasing temperature always increases.

Miscibility there can be cases where increasing temperature can decrease miscibility, but for the particular example that we are considering here. It is clear that as a temperature is being increased the composition over which the solution will be stable that composition range keeps on increasing.

So now from the Gibbs energy versus phi 2 curve drawn at different temperatures we can actually use information from this curve to construct what is called a phase diagram of temperature versus volume fraction. So, this T versus phi 2 phase diagram, this we can construct if we have the Gibbs free energy change of mixing curves as a function of phi 2 at different temperatures. To construct a curve on the right hand side this curve if you want to construct this what we need to do is identify first all the binodal points on the Gibbs free energy curve.

So, if we let us have the binodal points here and here at a certain temperature, then at that particular temperature on the right hand side curve. We can mark 2 points corresponding to the binodal compositions phi 2 b prime and phi 2 b double prime. Similarly, at a higher temperature the binodal points will shift. So, let us say the binodal points are here now. So, again at that higher temperature, we can again mark the 2 binodal points.

So, in this way if we keep going up in temperature and identifying the binodal points from the Gibbs free energy curve and plotting that those points on this T versus phi 2 curve, then we will get this the solid black curve that shown on the right hand side. And that curve basically is referred to the binodal curve.

So, if we look at this T versus phi 2 curve on the phase diagram on the right hand side in more detail, we can identify 2 region regions in this phase diagram. The region lying inside this binodal curve so, the binodal curve we just discussed is constructed by identifying the binodal points from that delta G versus phi 2 plot and this is shown as the solid black line here.

So, binodal curve basically demarcates the single phase region and the 2 phase region. So, if we have we added temperatures in composition which lie outside the binodal curve so, it if we are at this point, then if the mixing takes place at that place at that composition and at that temperature. So, this temperature let us say an some composition here.

If mixing is taking place at that kind of a condition, then a single homogenous phase will form and it will be stable; however, in the 2 phase region that we have here again if we try to form a mixture at this curve point let us say which corresponds to some volume fraction let us say around 0.4 and some temperature here.

So, in this at this point if the mixture or solution is formed it will the prefer to phase separate into 2 phases. And so, this region under the binodal curve is referred to as that 2 phase region, because the solutions formed at these conditions at this temperature in composition under the binodal curve region, they will tend to phase separate into 2 phases. So, the black line as I just mentioned is a binodal curve it is also referred to as a coexistence curve in on this phase T versus phi 2 phase diagram.

Now, if you look at this one more curve on this diagram, which is shown as the dashed blue line, that curve is a referred to as the spinodal curve. And to construct this curve again the, this delta G m versus phi 2 that plot can be used.

And again at different temperatures the spinodal points where the second derivative becomes 0, those points can be identified and, and at different temperatures those spinodal compositions can be plotted. And if you plot this mineral compositions as a function of temperature, then we will get the spinodal curve which is shown as the dashed blue line here.

So, the region between the binodal and the spinodal curve that is the metastable region that we previously discussed. So, so, if we have solution that forms at a certain composition that corresponds to this point. So, at a certain temperature and a certain composition, which corresponds to this point if we form a solution that solution actually really metastable.

Thermodynamically it will prefer to phase separate because that will reduce it Gibbs free energy it is Gibbs free energy. But for phase separation to occur a certain barrier for nucleation has to be crossed. So, if enough energy for crossing that barrier is not present the phase separation might not spontaneously take this.

So, that is a metastable region. And the region under the spinodal curve so, if we have this spinodal here, that this region under the spinodal curve that region de denotes the unstable region; where if we form a solution in with composition temperature in that region then it will always spontaneously phase separate by spinodal decomposition into 2 different phases. And finally, the maximum so, the curve that we have drawn here it basically shows a maximum.

So, the maximum point of both the binodal and the spinodal curve actually coincide, and that point where both the binodal and spinodal curves show a maximum that point is referred to as a critical point. So, again I would like to emphasize that this kind of a phase diagram T versus phi 2 phase diagram, this kind of diagram is will be seen if the miscibility is actually increasing with increasing temperature. So, we see that as we go up in temperature the miscibility is increasing and above this critical point if they are above this critical temperature, then for the entire composition range above this temperature all always a single phase will form.

So, if we cross this critical temperature, then the system will become completely miscible over the entire composition range. So, miscibility is increasing with temperature above the critical temperature the system becomes completely miscible for all values of phi 2. So, that is valid only if miscibility is increasing with temperature; there are cases where miscibility actually can decrease with temperature as well. So, in that case the T versus phi 2 diagram actually will look inverted.

So, we will discuss those the phase diagrams in a bit more detail after some time in this lecture. So now, we have talked about the graphical or we have discussed the phase separation behavior from a graphical perspective or graphical approach. Next let us try to explore the same concepts mathematically.

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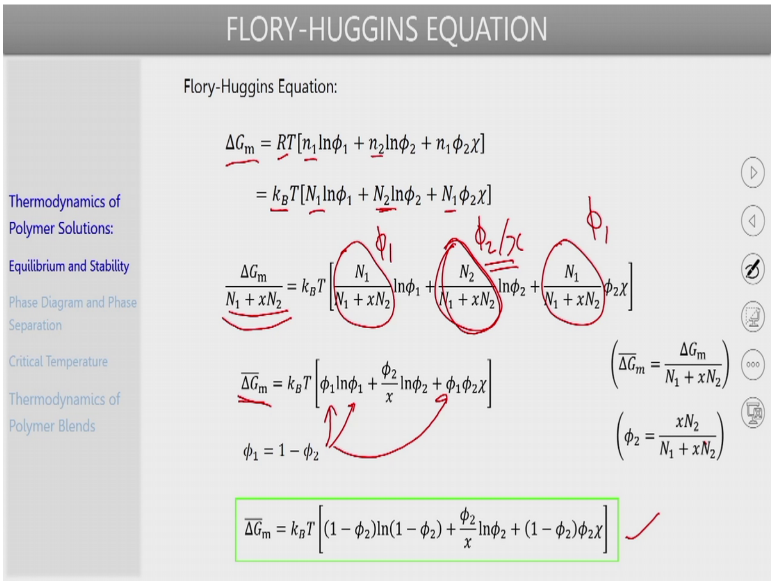

FLORY-HUGGINS EQUATION

Flory-Huggins Equation:

$$\Delta G_m = RT[n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1\phi_2\chi]$$

$$= k_B T[N_1 \ln\phi_1 + N_2 \ln\phi_2 + N_1\phi_2\chi]$$

$$\frac{\Delta G_m}{N_1 + xN_2} = k_B T\left[\overset{\phi_1}{\frac{N_1}{N_1 + xN_2}} \ln\phi_1 + \overset{\phi_2/x}{\frac{N_2}{N_1 + xN_2}} \ln\phi_2 + \overset{\phi_1}{\frac{N_1}{N_1 + xN_2}} \phi_2\chi\right]$$

$$\left(\overline{\Delta G}_m = \frac{\Delta G_m}{N_1 + xN_2}\right)$$

$$\left(\phi_2 = \frac{xN_2}{N_1 + xN_2}\right)$$

$$\overline{\Delta G}_m = k_B T\left[\phi_1 \ln\phi_1 + \frac{\phi_2}{x} \ln\phi_2 + \phi_1\phi_2\chi\right]$$

$$\phi_1 = 1 - \phi_2$$

$$\boxed{\overline{\Delta G}_m = k_B T\left[(1 - \phi_2)\ln(1 - \phi_2) + \frac{\phi_2}{x} \ln\phi_2 + (1 - \phi_2)\phi_2\chi\right]}$$

So, for a polymer solution we have derived the expression for delta the Gibbs free energy, energy change of mixing using the Flory Huggins theory.

So, the Flory corresponding Flory Huggins equation relates the delta G of mixing with the volume fractions of the polymer and the solvent, and it contains a parameter called the chi parameter. We can also write this delta G m in terms of the number of molecules capital N 1 capital N 2 instead of the number of moles small n 1 and small n 2.

So, both are equivalent only difference is that instead of universal gas constant we now will have Boltzmann constant here. So now, using this Flory Huggins equation we will like to mathematically explore the stability condition that we have discussed previously.

To do that let us try to first recast this Flory Huggins equations so, that the delta Gm is expressed only as a function of phi 2. Because we see that the stability condition stay is related to the second derivative of delta Gm with respect to phi 2. So, let us try to reformulate this equation. So, that delta Gm is expressed only as a function of phi 2 and we eliminate other quantities like phi 1 N 1 and N 2. So, to do that let us divide both sides by the total number of sites so, N 1 plus x N 2.

So, if you recall the development of the Flory Huggins equation. So, there that the Flory Huggins theories way is a lattice based theory. So, we assume the polymer and the solvent to be in the solution to be present on a lattice. And the total number of lattice sites or cells is equal to N 1 plus x N 2; where N 1 is a number of solvent molecules N 2 is a number of polymer molecules. And x is a number of segments in a single polymer molecule or a single polymer chain.

So, if we divide this delta Gm by the number of lattice cells, that will allow us to express the delta Gm in terms of phi 2 only. So, on the right hand side we get this term. And if you call this term this ratio is nothing but the definition of phi 1, the volume fraction of the solvent. Similarly, this term that we get this actually can be related to phi 2 the volume fraction of the solute or the polymer. And again this is this is also phi 1; this one was also phi 1. This again if you recall this will come out to be phi 2 by x.

So, if we make these replacements, then the expression that we get is kb T times phi 1 ln phi N plus phi 2 by x l N phi 2 plus phi 1 phi 2 a chi. And the delta Gm bar that we have shown here, that is just the delta Gm divided by N 1 plus x N 2. So, that is the basically the Gibbs energy change of mixing per unit lattice site. Phi 2 if is again defined as x N 2 by N 1 plus x N 2. So, that is why this ratio we could write as phi 2 by x. So, finally, this phi 1 and phi 2 their sum is 1 because we have binary solution of polymer and solvent.

So, phi 1 plus phi 2 will always be one. So, phi even we can write as 1 minus phi 2 if we substitute those this in these 2 places as well as here, then we get the expression for delta Gm bar. So, delta Gm expressed on per unit lattice cell basis as shown here. So now, we see that the delta Gm bar that we have it is expressed only as a function of phi 2.

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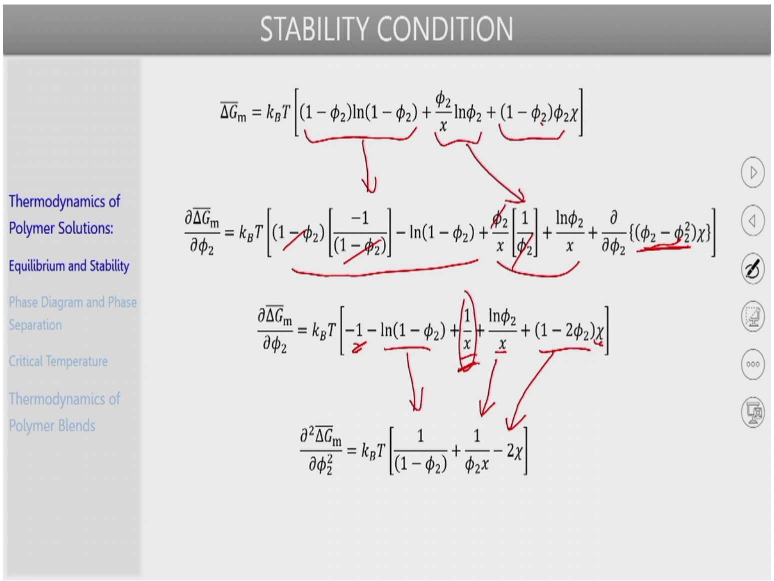

STABILITY CONDITION

Thermodynamics of Polymer Solutions:

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$$\overline{\Delta G}_m = k_BT\left[(1-\phi_2)\ln(1-\phi_2) + \frac{\phi_2}{x}\ln\phi_2 + (1-\phi_2)\phi_2\chi\right]$$

$$\frac{\partial\overline{\Delta G}_m}{\partial\phi_2} = k_BT\left[(1-\cancel{\phi_2})\left[\frac{-1}{(1-\cancel{\phi_2})}\right] - \ln(1-\phi_2) + \frac{\phi_2}{x}\left[\frac{1}{\cancel{\phi_2}}\right] + \frac{\ln\phi_2}{x} + \frac{\partial}{\partial\phi_2}\{(\phi_2-\phi_2^2)\chi\}\right]$$

$$\frac{\partial\overline{\Delta G}_m}{\partial\phi_2} = k_BT\left[-1 - \ln(1-\phi_2) + \frac{1}{x} + \frac{\ln\phi_2}{x} + (1-2\phi_2)\chi\right]$$

$$\frac{\partial^2\overline{\Delta G}_m}{\partial\phi_2^2} = k_BT\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} - 2\chi\right]$$

So, starting from this expression of delta Gm bar, now let us start differentiating this with respect to phi 2. So, we know that the stability conditions are defined based on the second derivative of the delta Gm with respect to phi 2. So, will successive successively differentiate the expression that we have obtained for delta Gm.

We will differentiate it 2 times and the expression that we get for the second derivative, then we will relate it to 0 and c whatever the conditions that that we come up with. The first derivative if we see here if we are differentiating this with respect to phi 2 we can differentiate this using the product rule.

Similarly, this also can be differentiated using the product rule. And here this is we can re express this simply as phi 2 minus phi 2 square. So, that is what we have done here. And these 2 terms come from the differentiation of this term; these 2 come if we differentiate this. So, upon further simplification we see that this of course, this can these 2 will cancel similarly the phi 2 will cancel this phi 2 here. So, upon further simplification, you will get a minus 1 here and then this term 1 by x here l n phi 2 by x. And the derivative of phi 2 minus phi 2 square, that will come out to be 1 minus 2 phi 2 and chi will remain.

So, in this discussion what we are assuming is that the Flory Huggins parameter is independent of composition. So, we have discussed earlier that the flow against the parameter is a function of temperature ah; however, we have till now neglected the dependence of Flory Huggins parameter on composition.

So, here also in the current discussion also we will assume that chi is independent of phi 2; however, it must be noted that there are systems and cases in which this chi parameter can actually be a function of the volume fraction of the other composition of the polymer. So, but such systems we are neglecting in the current discussion. So, next if we again differentiate this one more time to get the second derivative which we want.

So, the derivative of this term will be 0, 1 by x is also a constant with respect to phi 2. So, differentiating this will also result in a 0 term. So, from this we will get this term and differentiation of this will get this term. And finally, differentiating this will just result in a minus 2 times chi.

So, this is the expression for the second derivative of delta Gm that we have obtained. And based on the stability criteria that we have discussed earlier, what we can say is that, if this value is less than 0, then the solution that has formed is definitely unstable. And it will spontaneously phase separate into 2 distinct phases corresponding to the binodal compositions.

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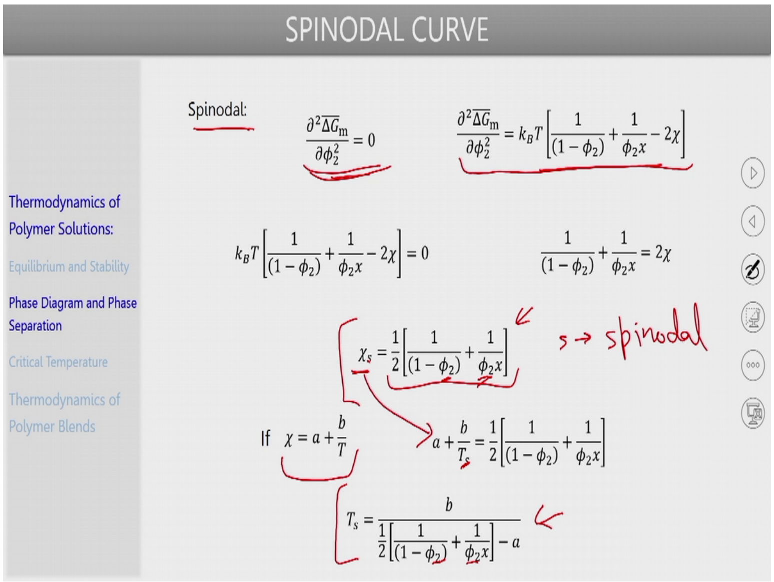

SPINODAL CURVE

Thermodynamics of Polymer Solutions:

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Spinodal:

$$\frac{\partial^2 \overline{\Delta G}_m}{\partial \phi_2^2} = 0 \qquad \frac{\partial^2 \overline{\Delta G}_m}{\partial \phi_2^2} = k_B T \left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} - 2\chi\right]$$

$$k_B T \left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} - 2\chi\right] = 0 \qquad \frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} = 2\chi$$

$$\chi_s = \frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right]$$

$s \to$ spinodal

$$\text{If } \chi = a + \frac{b}{T} \qquad a + \frac{b}{T_s} = \frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right]$$

$$T_s = \frac{b}{\frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right] - a}$$

Now let us consider the case or the point where the second derivative is actually 0.

So, this condition defines the spinodal points as we have discussed earlier. So, if we said the second derivative of Gibbs free energy to 0 and we already have derived the expression for the second derivative Gibbs energy to be this. Then if we set this expression to as 0 then just rearranging the terms we get that 1 over 1 minus phi 2 plus 1 over phi 2 x that will be equal to 2 times chi. And finally, the chi s where the subscript s s denotes spinodal.

So, the subscript s here denotes the spinodal point. So, the chi or the Flory Huggins parameter of corresponding to the spinodal condition in the spinodal point is expressed in terms of the volume fraction of the polymer and the number of segments using this expression here. So, the applying the spinodal condition basically leads us through this expression and finally, if we assume chi to be a function of T of this form.

So, if we say that chi is a plus b by T, which we have discussed earlier also and it is commonly assumed temperature dependence of the Flory Huggins interaction parameter.

So, if we assume that and then here instead of chi s we can substitute substitute that by a plus b by T s; where this subscript s again represents the temperature corresponding to the spinodal point. So, if we do that and if we again finally, rearrange the terms what we get is the an expression for the spinodal temperature, or the temperature at spinodal point. Essentially this expression that we have or the previous expression this for T s and chi s, these 2 represent what is called the spinodal curve.

So, if we consider different values of phi 2 in these expressions that will give us different values of chi s or T s. So, using this equation, one can actually plot chi s versus phi 2. So, as kind of a spinodal plot of Flory Huggins parameter as a function of phi 2 similarly using this equation here one can construct the spinodal curve which corresponds to the temperature versus phi 2 plot for the spinodal points.

So, using Flory Huggins theory these are the 2 equations for the spinodal curve that we obtain, one for the Flory Huggins parameter and the other equivalently for the temperature.

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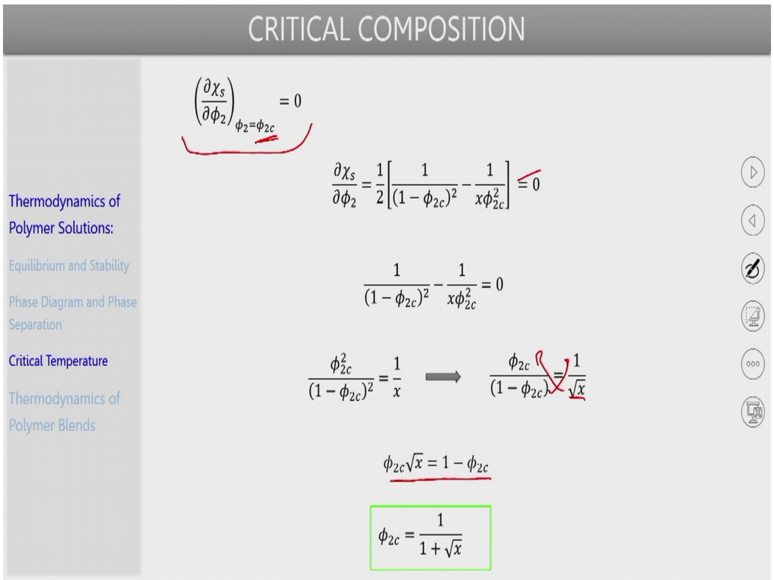

CRITICAL COMPOSITION

Thermodynamics of Polymer Solutions:

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Thermodynamics of Polymer Blends

$$\underbrace{\left(\frac{\partial \chi_s}{\partial \phi_2}\right)_{\phi_2=\phi_{2c}}}= 0$$

$$\frac{\partial \chi_s}{\partial \phi_2} = \frac{1}{2}\left[\frac{1}{(1-\phi_{2c})^2} - \frac{1}{x\phi_{2c}^2}\right] = 0$$

$$\frac{1}{(1-\phi_{2c})^2} - \frac{1}{x\phi_{2c}^2} = 0$$

$$\frac{\phi_{2c}^2}{(1-\phi_{2c})^2} = \frac{1}{x} \Longrightarrow \frac{\phi_{2c}}{(1-\phi_{2c})} = \frac{1}{\sqrt{x}}$$

$$\underline{\phi_{2c}\sqrt{x} = 1 - \phi_{2c}}$$

$$\boxed{\phi_{2c} = \frac{1}{1+\sqrt{x}}}$$

Now if we if we remember that the maximum of the spinodal curve coincides with the maximum of the binodal curve and that corresponds to the critical point. The critical point basically can be mathematically identified by this condition; where if we plot chi s versus phi 2 then that will show a extreme a maximum or a minimum.

So, essentially the derivative of chi s with respect to phi 2 will be 0 at that critical point. And let us say the composition and the critical point be represented by phi 2 c. So, applying this condition for the critical point, what we get is first using the expression that we had derived for chi s in the just previously. We can differentiate that once with respect to phi 2 to get this expression. And we can we will set that equal to 0 to get the critical point.

Again we further simplify the expression and rearrange the terms, and upon rearrangement what we get finally, is that this ratio phi 2 c by 1 minus phi 2 c that is comes out to equal to 1 over square root of x.

And from this expression again by rearranging we can obtain an expression for phi 2 c in terms of x. We can take the square root of x up here and we can take this up here. So, we will get this expression and finally, the expression for phi 2 c will be 1 over 1 plus square root of x. So, that is the composition corresponding to the critical point that we obtain by setting the derivative of chi s with respect to phi 2 as 0.

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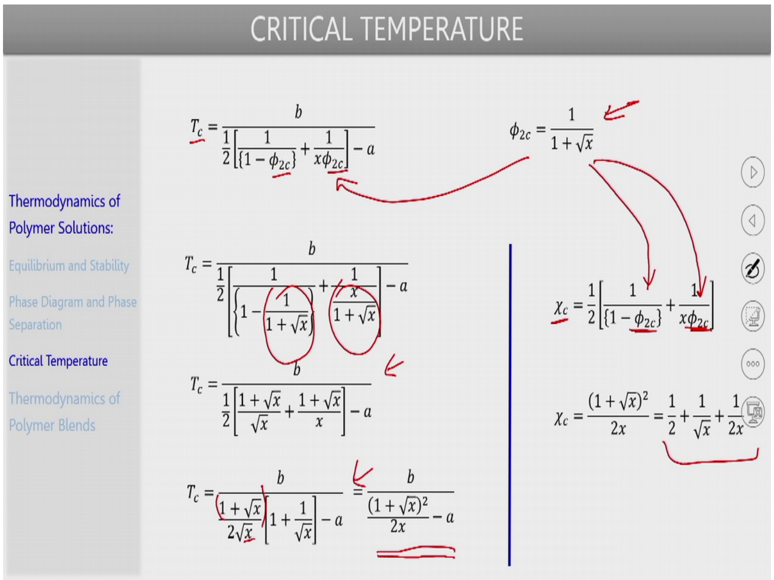

CRITICAL TEMPERATURE

Thermodynamics of Polymer Solutions:

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Thermodynamics of Polymer Blends

$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1}{\{1-\phi_{2c}\}} + \frac{1}{x\phi_{2c}}\right] - a}$$

$$\phi_{2c} = \frac{1}{1+\sqrt{x}}$$

$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1}{\left\{1-\frac{1}{1+\sqrt{x}}\right\}} + \frac{\frac{1}{x}}{\frac{1}{1+\sqrt{x}}}\right] - a}$$

$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1+\sqrt{x}}{\sqrt{x}} + \frac{1+\sqrt{x}}{x}\right] - a}$$

$$T_c = \frac{b}{\frac{1+\sqrt{x}}{2\sqrt{x}}\left[1+\frac{1}{\sqrt{x}}\right] - a} = \frac{b}{\frac{(1+\sqrt{x})^2}{2x} - a}$$

$$\chi_c = \frac{1}{2}\left[\frac{1}{\{1-\phi_{2c}\}} + \frac{1}{x\phi_{2c}}\right]$$

$$\chi_c = \frac{(1+\sqrt{x})^2}{2x} = \underbrace{\frac{1}{2} + \frac{1}{\sqrt{x}} + \frac{1}{2x}}$$

Equivalently for T c the critical temperature, critical temperature again corresponds to the temperature which will be observed at the critical compositions.

So, in the expression for the spinodal temperature that we have derived previously if we substitute the critical composition in place of the compositions, and the critical composition expression we have already derived to be this if we substitute. These expressions here, then we will get an expression for the critical temperature. So, substituting phi 2 c here as well as here and then further simplifying, we can simplify the terms and we will get an expression of this kind. And then taking out this term as this n 1 plus square root of x as common we will get this expression.

And again simplifying that further the final expression that we obtain is this so, T c is equal to b over 1 plus square root of x squared divided by 2 x minus a. So, a and b again as the parameters which relate the Flory Huggins interaction parameter to temperature. Similarly, the critical Flory Huggins parameter, critical for Flory Huggins interaction parameter again that we can find by substituting the expression for phi 2 c in these 2 places.

So, the critical Flory Huggins interaction parameter chi c we can obtain by substituting this expression in these 2 places. And upon substitution and simplification what we get finally, is that chi c is equal to half plus 1 over square root of x plus 1 over 2 x. So, what that this shows is that, as the time as the number of segments of the polymer chain becomes become longer, the value of this critical Flory Huggins interaction parameter will approach 0.5.

And in the limit when x is infinity it will become 0.5, but for any real system x will be large number in 100s or thousands, but it will not be infinity. So, typically chi c will be found to be in the range of 0.5 to 0.7.

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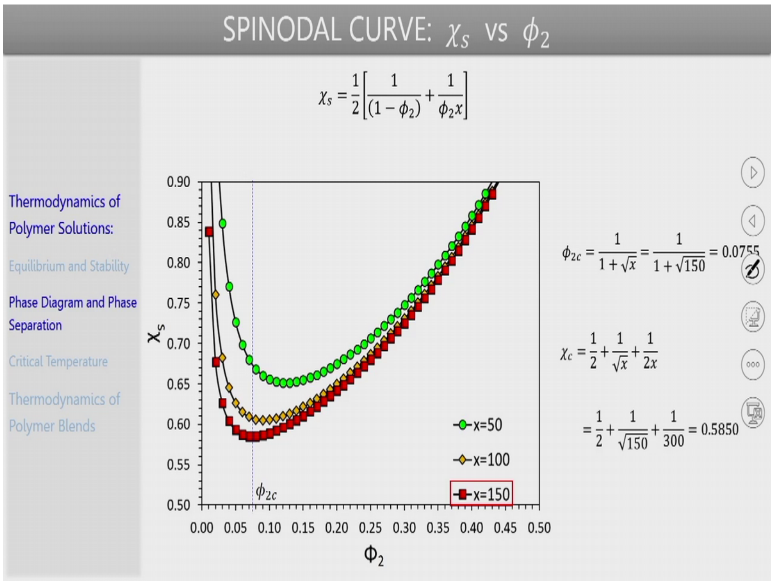

SPINODAL CURVE: χ_s vs ϕ_2

$$\chi_s = \frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right]$$

Thermodynamics of Polymer Solutions:

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$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{150}} = 0.0755$$

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{x}} + \frac{1}{2x}$$

$$= \frac{1}{2} + \frac{1}{\sqrt{150}} + \frac{1}{300} = 0.5850$$

So, if we now let us say use the expression that we have derived for considering the spinodal conditions. So, the Flory Huggins interaction parameter corresponding to the spindle condition if we use that equation of chi s versus phi 2 and if we plot this so, on the x axis if we plot phi 2 and on the y axis if we plot chi s which is found using the this equation here, then depending on the value of x was the number of polymer segments that we have we observe a shift downwards and towards the left as the number of segments is being increased from 50 to 150.

So, if we consider the case of this 50 segments, then the critical composition mathematically we can calculate using the expression we have derived. And that comes out to be a point around 0.1239. And if we mark that on the graph and if you also calculate the critical Flory Huggins interaction parameter chi c using again the expression, that we have derived that comes out to be around 0.6514.

So, will we see that it lies between 0.5 and 0.7 and we can mark it here so, this the critical points that do we calculate that corresponds to minimum on this curve. And that is what the mathematical condition was which was used to derive these expressions. Similarly, if we increase the value of x and do repeat the calculations this is at phi 2 c actually goes down and the chi c also goes down.

So, the curve has shifted to downwards and towards the left and at even higher values of x which in which means longer polymer chains, then also phi 2 c further reduces and similarly chi c also reduces further. So, what we observe here is that as the polymer chain length is being increased, the critical composition progressively decreases and also the value of the critical Flory Huggins interaction parameter that also decreases.

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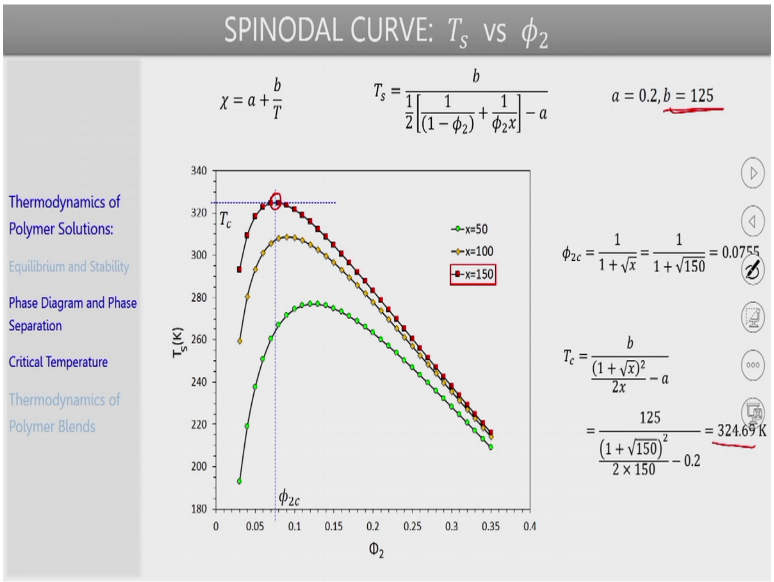

SPINODAL CURVE: T_s vs ϕ_2

$$\chi = a + \frac{b}{T} \qquad T_s = \frac{b}{\frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right] - a} \qquad a = 0.2, b = 125$$

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$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{150}} = 0.0755$$

$$T_c = \frac{b}{\frac{(1+\sqrt{x})^2}{2x} - a} = \frac{125}{\frac{(1+\sqrt{150})^2}{2 \times 150} - 0.2} = 324.69\ \text{K}$$

Next we can also construct spinodal curves of temperature versus phi 2 instead of chi versus phi 2.

So, for that we will use the temp temperature the expression for temperature, that we have derived corresponding to the spinodal condition. And again here at different values of phi 2 we can calculate the value of T s and plot that to obtain the curves. And again if we change the value of x we will get different curves. So, here we have shown 3 curves again at the same 3 values of x that we used previously at x equal to 50, 100 and 150. And for this specific case we have used a equal to point to be equal to 0.5 just as an example. So, b v c is positive in this case.

So far these values the curves that we obtain are shown here in in this plot. And we see that as we go from smaller to longer polymer chains that is as we increased x from 50 to 150, the curves actually shift up and towards the left. So, again if we perform calculations for the x equal to 50, if we find out phi 2 c that will come out to be the same as what we did for the case of chi s versus phi 2. So, we get 0.1239 as a (Refer Time: 51:54) composition same as before and if we find out T c that comes out to be 276.9 Kelvin.

So, that corresponds to them again the maximum point here which is the critical point. So, that is the T c. Similarly, if we increase x to 100 then phi 2 c decreases as previously whereas, T c increases in this case to 308.64 and that corresponds to the critical point on this curve. And finally, for the longest polymer chains having x equal to 150. Phi 2 c will further decrease and T c will increase to 320 almost 325 Kelvin in this case. And that these 2 points will correspond to the maximum here which is the critical point for this curve.

So, the kind of behavior that, we see here is it is a specific to the parameter b that we have chosen here ok.

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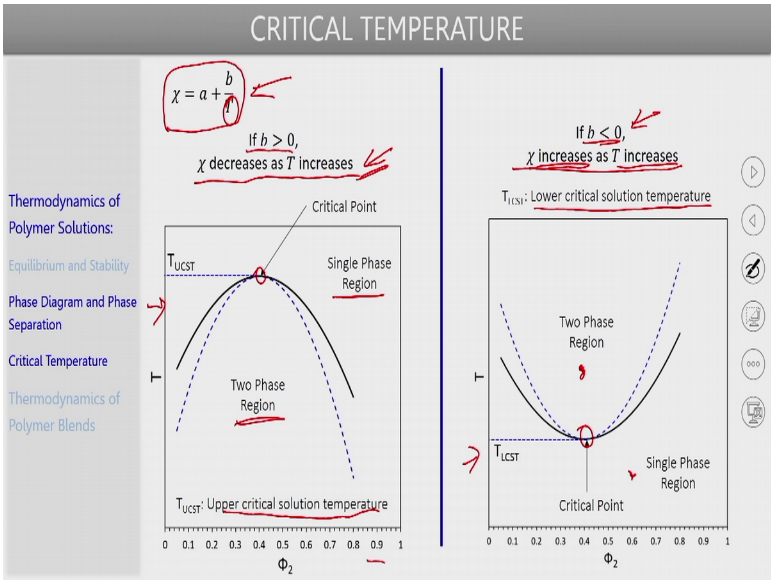

CRITICAL TEMPERATURE

Thermodynamics of Polymer Solutions:

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Critical Temperature

Thermodynamics of Polymer Blends

$\chi = a + \frac{b}{T}$

If $b > 0$, χ decreases as T increases

T_{UCST}: Upper critical solution temperature

If $b < 0$, χ increases as T increases

T_{LCST}: Lower critical solution temperature

Let us consider that critical temperature in a bit more detail. So, we have assumed chi to depend on temperature using this kind of an expression. Now if b is greater than 0, this we have discussed briefly in previous lecture as well, but now we will discuss these conditions in a bit more detail. So, if b is greater than 0 b what we can say is that chi is chi will decrease as temperature increases. So, if b is positive if T is T is increasing this second term will actually decrease and chi will also decrease.

So, for such a case if we draw the phase diagram it will look something like what is shown here and it will show a maximum. So, again the solid black line shows the binodal and the dashed black line shows a spinodal compositions.

Or the binodal and spinodal curves and the binodal marks the separation between the single phase region and the 2 phase region. So, single phase region is region outside the binodal 2 phase is inside the binodal. And we see that the top point we have said that as a critical the maximum. Other temperature corresponding to that the top point is referred to as UCST or the upper critical solution temperature ok.

So, this is a temperature such that above this temperature the solution will the single phase solution will be stable throughout the composition range. Next if we consider a different case where b actually is decreasing with or b is less than 0. So, in this case if b is less than 0 if we again assume this functionality then chi will increase as pressure increases.

So, if so, what we know is that a decrease in chi actually favors mixing and then increasing chi works against miscibility. So, if chi if temperature is increasing and if that is leading to increase in chi, then what that implies is that in increase in temperature actually in this case lowest miscibility. That is in contrast to this case.

So, in the case on the left side since chi is decreasing with temperature increase. So, miscibility is actually increasing as temperature increases and at high enough temperature the system becomes miscible over the entire composition range. But now let us get back to this condition. So, here temperature increase leads to chi increase.

So, that leads to decrease in miscibility. So, the a typical temperature versus phi 2 phase diagram for this case will show a minimum. And again the solid curve is the binodal the dashed curve is the spinodal curve and the 2 phase region is the region above the binodal single phase region is a region below the binodal in this case.

So, if we are in a region then if the solution forms in this region it will spontaneously phase separate into 2 different phases. And if we are in the single phase region then the solution that forms will be stable and remain homogeneous and single phase. So now, in this case again the critical point can be identified as the point corresponding to the minimum of both the binodal and spinodal curves and the temperature corresponding to this critical point that is referred to as a lower critical solution temperature.

So, this temperature basically represents the temperature at above which immiscibility or phase separation can be seen. So, below this lower critical solution temperature no image no phase separation will occur and the single phase will remain stable throughout the composition range.

But if we go above this lower critical solution temperature, then depending on the composition that we are at phase separation can occur. So, these are 2 representative cases one in which miscibility actually increases with increasing temperature the other in which miscibility decreases with increase in temperature there can also be cases where this b actually changes sign with temperatures.

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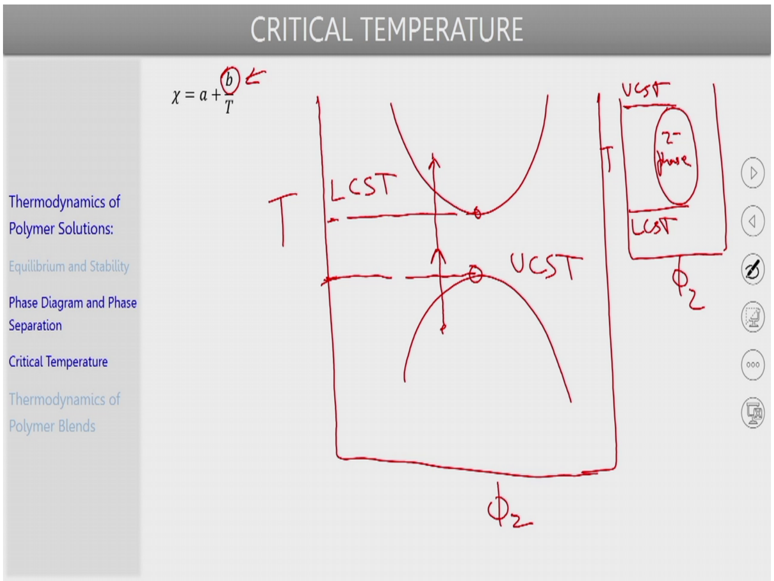

CRITICAL TEMPERATURE

$\chi = a + \frac{b}{T}$

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

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Thermodynamics of Polymer Blends

So, instead of b being (Refer Time: 57:22) in greater than 0 throughout or less than 0 throughout if b, changes sign with temperature. Then that kind of behavior that kind of change in sign will can reflect in the phase diagram as well. So, apart from the simple phase diagrams that we have discussed in the previous slide, some other kind of phase diagrams can also be seen in polymer solutions where the term actually shows both LCST. So, this is the LCST here because it corresponds to the minimum of the binodal. And the same solution at a different temperature it can show a UCST as well.

So, this more complex kind of phase behavior can be observed for cases where the parameter b actually changes sign with change in temperature. So, we can have a case shown here where as temperature is increased initially the miscibility is increasing so that from let us say a 2 phase mixture as temperature increase will become a single phase and miscibility will increase but as temperature is further increased the. So, system can again become immiscible and separated in 2 phases.

So, such kind of more complex phase diagrams of course, are also seen for different polymer systems. So, in this particular case the LCST is lying above the UCST one can also have a case. So, there is some few systems which show a phase behavior which is kind of a closed loop ok. So, here the UCST is a lying above the LCST, and this region is the 2 phase region inside this closed loop.

So, all sorts of different phase behaviors are possible. And we have tried to discuss some of the typical phase behavior and phase separation behavior observed in polymer solutions in our discussion today. Now that discussion basically completes how our study of the thermodynamics of polymer solutions and it is phase behavior phase separation behavior critical temperatures. So, all those things we have tried to discuss graphically as well as mathematically.

Next we will just briefly introduce the concept of thermodynamics of polymer blends in this lecture and we will carry forward that discussion in the next lecture as well.

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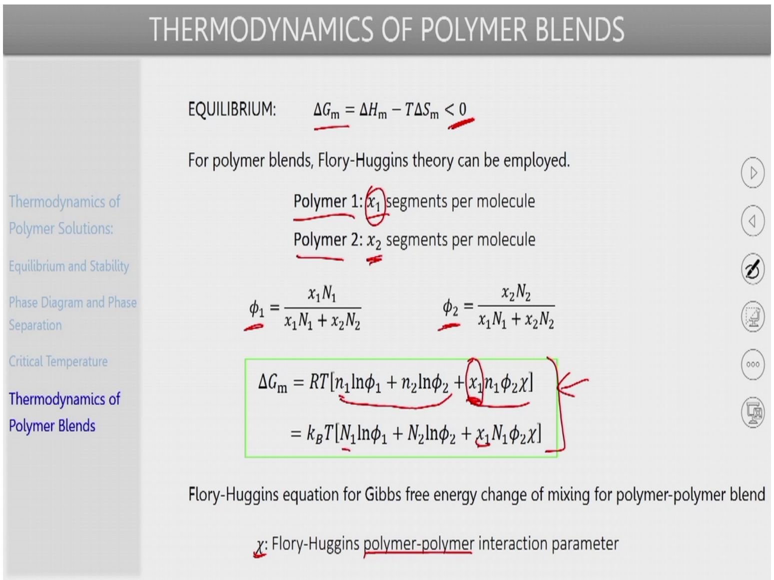

THERMODYNAMICS OF POLYMER BLENDS

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

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Critical Temperature

Thermodynamics of Polymer Blends

EQUILIBRIUM: $\Delta G_m = \Delta H_m - T\Delta S_m < 0$

For polymer blends, Flory-Huggins theory can be employed.

Polymer 1: x_1 segments per molecule

Polymer 2: x_2 segments per molecule

$$\phi_1 = \frac{x_1N_1}{x_1N_1 + x_2N_2} \qquad \phi_2 = \frac{x_2N_2}{x_1N_1 + x_2N_2}$$

$$\boxed{\begin{aligned}\Delta G_m &= RT[n_1\ln\phi_1 + n_2\ln\phi_2 + x_1n_1\phi_2\chi] \\ &= k_BT[N_1\ln\phi_1 + N_2\ln\phi_2 + x_1N_1\phi_2\chi]\end{aligned}}$$

Flory-Huggins equation for Gibbs free energy change of mixing for polymer-polymer blend

χ: Flory-Huggins polymer-polymer interaction parameter

Polymer blends represents a uniform mixtures of 2 different polymers. So, a polymer solution is where you have a polymer being dissolved in a solvent whereas, in a polymer blend both components are polymers. So, you have 2 different polymers that are mixed together. And depending on their mutual interactions they can either be immiscible.

So, where they do not do not mix, they can be partially miscible or they can be in some cases perfectly miscible as well. So, we have seen that the polymer solution thermodynamics can be described using the Flory Huggins theory. So, slight modification of Flory Huggins theory actually can be used or the slight modification of Flory Huggins equation for polymer solution can be used for polymer blends.

So, the same similar Flory Huggins theory applies to polymer blends as well. And the equation that we get that will also be similar to the Flory Huggins equation. The only difference now is that since both the components are polymers polymer 1 and 2. So, we need to define x 1 as I and x 2 as the 2 quantities x 1 being the number of segments per molecule of polymer 1 and x 2 being the number of segments of molecules for polymer 2.

So, now based on this definition the definition of the volume fractions phi 1 and phi 2 that also will change a bit, phi 1 can be represented as x 1 n 1 by x 1 plus x 2 n 2. And phi 2 will be x 2 n 2 by x 1 n 1 plus x 2 n 2. So, the definitions are similar to a polymer solution only difference is that this x 1 appears now. Because the first component is not a solvent it is also a polymer and it also contains multiple segments.

So, based on these considerations the Flory Huggins equation for the delta G of mixing for a polymer blend actually comes out to be what shown here any one of these 2 equations, both are equivalent one is in terms of number of moles the other in terms of number of molecules. So, the if you note look carefully at this equation. The only difference is that. So, the first 2 terms are identical the entropy terms are identical the interaction term the contact term actually is slightly different because of the presence of this extra x 1.

So, the number of polymers segments of polymer one that appears in the contact term here. So, that is the only difference if we compare this to the Flory Huggins equation for a polymer solution ok. So, of course, the equilibrium conditions where thermodynamically will always be that delta G of mixing that should be less than 0.

So, that will be true for any system it a little bit true for the mixing of a polymer blend as well. So, the equation that we have shown here that is the called the Flory Huggins equation for the Gibbs free energy change of mixing of polymer-polymer blend. It is very similar to the equation for a polymer solution only this extra x 1 term appears.

And the chi now, the chi that appears here that is called the Flory Huggins polymer -polymer interaction parameter. So, for a polymer solution if you recall the chi was the Flory Huggins polymer solvent interaction parameter. For polymer blends it is the polymer -polymer interaction parameter.

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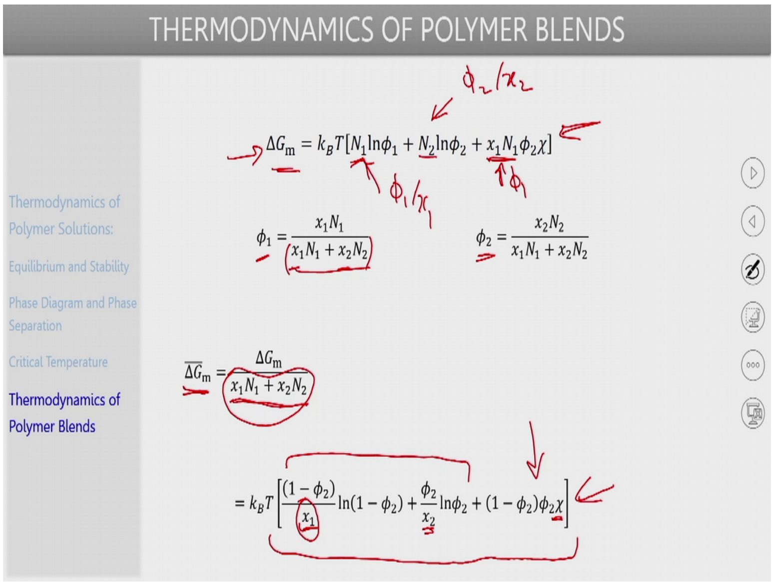

THERMODYNAMICS OF POLYMER BLENDS

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

Phase Diagram and Phase Separation

Critical Temperature

Thermodynamics of Polymer Blends

ϕ_2/x_2

$$\Delta G_m = k_B T[N_1 \ln\phi_1 + N_2 \ln\phi_2 + x_1 N_1 \phi_2 \chi]$$

ϕ_1/x_1

ϕ_1

$$\phi_1 = \frac{x_1 N_1}{x_1 N_1 + x_2 N_2} \qquad \phi_2 = \frac{x_2 N_2}{x_1 N_1 + x_2 N_2}$$

$$\overline{\Delta G_m} = \frac{\Delta G_m}{x_1 N_1 + x_2 N_2}$$

$$= k_B T\left[\frac{(1-\phi_2)}{x_1}\ln(1-\phi_2) + \frac{\phi_2}{x_2}\ln\phi_2 + (1-\phi_2)\phi_2\chi\right]$$

And so, now that we have an expression for delta G m and phi 1 and phi 2 as well for a polymer blend. If we again divide this delta Gm by the number of lattice cells so now since we have a polymer blend.

The we have n 1 molecules of polymer one n 2 molecules of polymer 2, each molecule of polymer one contains x 1 segments each molecule of polymer 2 contains x 2 segments the total number of cells is x 1 n 1 plus x 2 n 2. So, if we divide this delta Gm by x 1 n 1 plus x 2 n 2, then if we again concession here we are basically dividing all the terms on the right hand side by x 1 n 1 plus x 2 n 2.

So, this first term, upon division by this quantity, this first term will you will see will become phi 1 by x 1. This term will become phi 2 by x 2. This n 2 and at least this if we divide this x 1 n 1 by this quantity, then we will end up with just a phi one term here. And upon doing that the final expression that we get for delta G m again expressed on per unit lattice cell basis. So, the final expression that we have is again in terms of phi 2 only.

So, this is the expression, and if we compare it to the expression for polymer solution, then the only difference that one can see is that you get an x 1 term here as well ok. So, but that extracts one term actually has a significant impact on the phase behavior of polymer blends.

So, one thing that can be inferred is that now these 2 terms that 2 entropic terms they will be quite small because both are divided by x 1 and x 2 which are large numbers, typically on the order of 100's or 1000's. So, these 2 terms will be small. So, for polymer blends actually the contact or the interaction term involving the interaction parameter that becomes quite important in describing the phase behavior.

So, we will conclude today's lecture here. And where we have discussed in detail the phase separation behavior of polymer solutions, both graphically as well as mathematically we have used the Flory Huggins equation and derived the stability conditions, and derived equations for the spinodal curve and so on.

And towards the end we started our discussion of thermodynamics of polymer blends; where we saw that Gibbs free energy change of mixing that expression is very similar to that for a polymer solution except for the presence of one extra term ah; however, the Gibbs free energy change of mixing in a polymer blend, actually is influenced much more by the interaction of contact term because the entropy term in is quite small.

So, the phase behavior is much more strongly influenced by the contact term involving the interaction parameter. And we based on the expression of the Gibbs energy that we have derived for the polymer blend, what we will do in the next lecture is continue this discussion and try to derive the expressions for spinodal curve and try to draw some phase diagrams for polymer blends as we will to better illustrate and understand the phase behavior.

And after blends we will also briefly discussed the phase behavior of copolymers block copolymers especially. We will not go into too much detail because a bit of an advanced topic, but we will just briefly illustrate and outline the key features associated with phase behavior of block copolymers.

Thank you.