Introduction to Polymer Physics
Dr. Amit Kumar
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture – 05
Thermodynamics of Polymer Solutions

So hello, in the previous lecture we started a discussion on Thermodynamics of Polymer Solutions. So, we discuss the case of an ideal solution and introduced the concept of lattice approach to calculating entropy change of mixing and Gibbs energy change of mixing. And then we started discussing the thermodynamic behavior of polymer solutions. So, in particular we introduced the Flory Huggins theory as the as the main theory that we will be discussing in this course for the describing the thermodynamic behavior of polymer solutions.

So, we in the previous lecture we covered the portion the combinatorial entropy portion of this Flory Huggins theory. So, in today's lecture we will continue that discussion and we will complete the development of this Flory Huggins theory and the Flory Huggins equation for describing a polymer solution thermodynamics.

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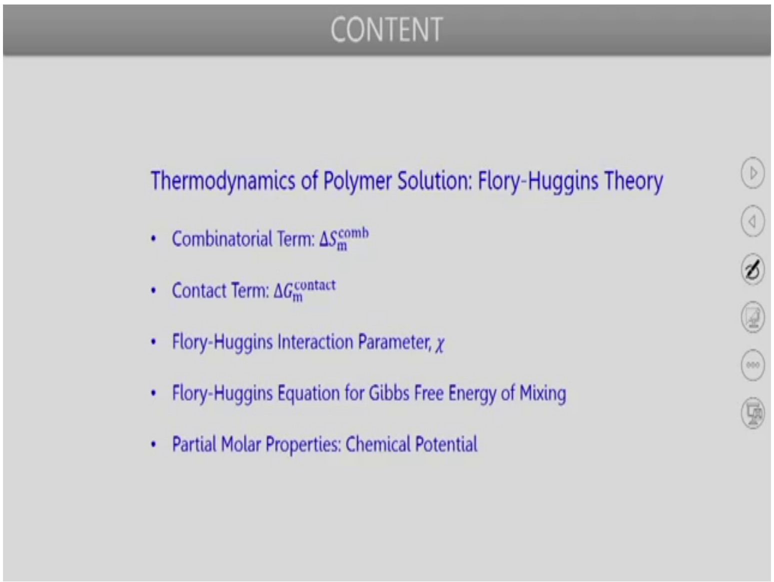

CONTENT

Thermodynamics of Polymer Solution: Flory-Huggins Theory

- Combinatorial Term: ΔS_m^{comb}
- Contact Term: $\Delta G_m^{contact}$
- Flory-Huggins Interaction Parameter, χ
- Flory-Huggins Equation for Gibbs Free Energy of Mixing
- Partial Molar Properties: Chemical Potential

Regards the content of this lecture we will briefly summarize the discussion from the previous lecture on the combinatorial term. And then we will develop another term which is referred to as a contact term and then this term basically accounts for the intermolecular interactions. So, if you remember in the previous lecture we when we discussed the combinatorial entropy term there the interaction was assumed to be absent. So, initially the change in entropy purely due to the different confirmations that a polymer or polymer chains can adapt that was considered and neglecting the effect of interactions.

So, that led to the combinatorial entropy term which will have a contribution towards the Gibbs energy of mixing. Today we will discuss another term which will account for the presence of intermolecular interactions between polymer chains and the solvent molecules. That will refer to as a contact term and the, and while discussing this contact term we will also introduce parameter which is called the Flory Huggins interaction parameter.

So, this parameter is an important measure of the solvent polymer interactions. So, we will introduce this and then we will completely complete the development of the Flory Huggins equation to calculate the Gibbs energy change of mixing, for a polymer solution. And after that we will briefly introduce the concept of partial molar properties specially focusing on chemical potential because it is an important property which is related to other exponentially measurable quantities as well. So, we will discuss that and we will see how the application of Flory Huggins theory leads to certain expressions for the chemical potential as well as quantities like activity.

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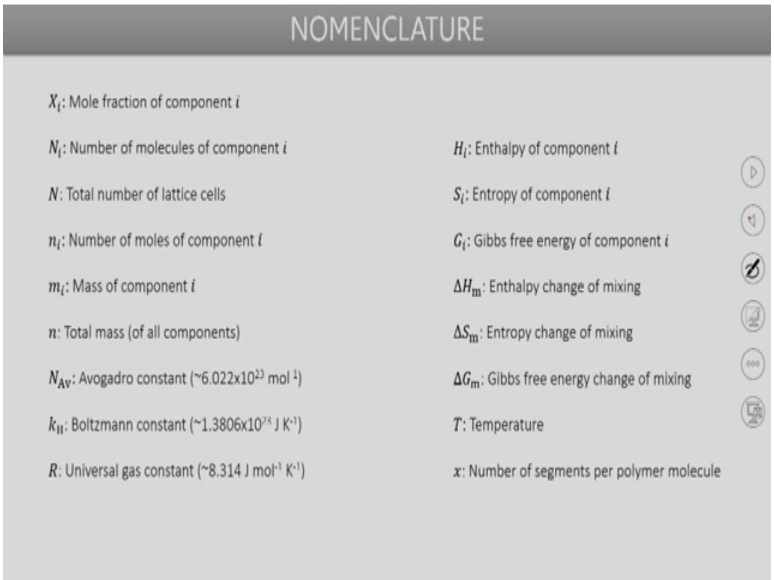

NOMENCLATURE

X_i: Mole fraction of component i

N_i: Number of molecules of component i

N: Total number of lattice cells

n_i: Number of moles of component i

m_i: Mass of component i

n: Total mass (of all components)

N_{Av}: Avogadro constant (~$6.022\text{x}10^{23}$ mol^{-1})

k_B: Boltzmann constant (~$1.3806\text{x}10^{23}$ J K^{-1})

R: Universal gas constant (~8.314 J mol^{-1} K^{-1})

H_i: Enthalpy of component i

S_i: Entropy of component i

G_i: Gibbs free energy of component i

ΔH_{m}: Enthalpy change of mixing

ΔS_{m}: Entropy change of mixing

ΔG_{m}: Gibbs free energy change of mixing

T: Temperature

x: Number of segments per polymer molecule

So, the nomenclature that we introduced in the previous lecture the same nomenclature will follow today as well as and when some new term is introduced the corresponding definition of that term will be provided whenever we encounter it. So, apart from all the apart from all the terms that are listed here we may come across some other terms as well during our discussion today. So, as and when such terms appear or such quantities appear we will introduce them.

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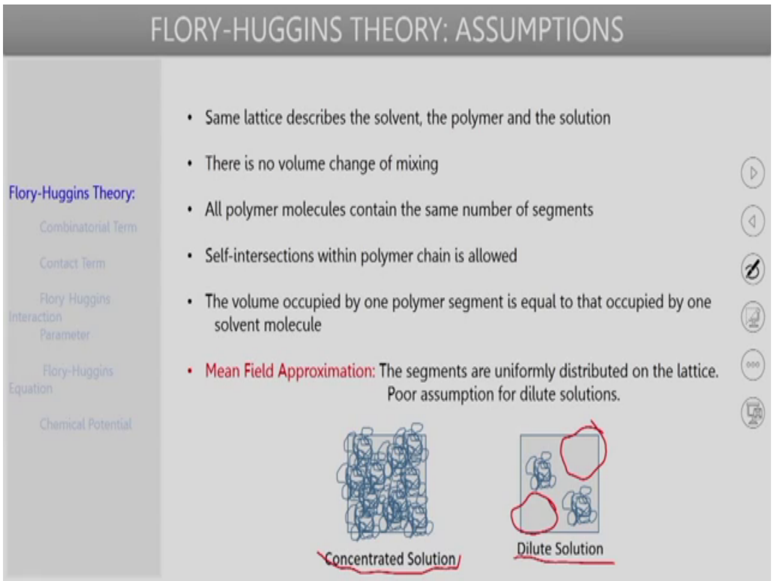

FLORY-HUGGINS THEORY: ASSUMPTIONS

Flory-Huggins Theory:
Combinatorial Term
Contact Term
Flory Huggins Interaction Parameter
Flory-Huggins Equation
Chemical Potential

- Same lattice describes the solvent, the polymer and the solution
- There is no volume change of mixing
- All polymer molecules contain the same number of segments
- Self-intersections within polymer chain is allowed
- The volume occupied by one polymer segment is equal to that occupied by one solvent molecule
- Mean Field Approximation: The segments are uniformly distributed on the lattice. Poor assumption for dilute solutions.

So,; before moving on with the discussion on Flory Huggins theory and development of Flory Huggins equation, let us just briefly summarize what we discussed about the Flory Huggins theory in the previous lecture. So, some of the key assumptions involved in Flory Huggins development of the Flory Huggins theory are the first one is that it is a lattice based model.

So, the model itself is a lattice based model where the solvent molecules the polymer as well as the polymer solution that forms all these three cases are considered to be on a lattice. And, the as a key assumption here is that for describing the arrangement of solvent molecules pure solvent molecules as well as pure polymer molecules and the polymer solution for all these three cases the same kind of lattice is used in Flory Huggins theory. Apart from that we considered no volume change of mixing.

So, the fact that the same identical lattice is considered for the 2 components as well as for the solution, that itself leads to the fact that there is no volume change of mixing associated. So, volume change of mixing is assumed to be 0 in Flory Huggins theory another at least during the derivation the assumption is that all polymer molecules that are being considered have the same number of segments. So, all polymer molecules have the same size and they are mono disperse. Towards the end of today's lecture we will see that even for poly disperse samples the equations can be applied with only very slight modification; but the derivation that we will carry out that is initially only for mono dispersed sample polymers with identical number of segments. The other assumption is that within a polymer chain the self intersections are allowed.

So, if you have a different polymer chains then their segments need not intersect, but for given polymer chains intersection between different segments of that same polymer chain that is self intersections that are allowed. And, this is basically the way in which the different configurations or confirmations of the system are counted for calculating entropy change the, combinatorial entropy change. During that the way in so, in the last lecture we discussed that one by one the polymer molecules I introduced in a in the lattice. Until all the polymer molecules occupy and positions on the lattice and then the solvent molecules are filled in. And this is the approach is to calculate the different number of distinguishable arrangements possible which can be used to calculate the entropy and entropy change.

So, during that process of introducing the polymer molecules one by one and there and for each polymer molecule introducing the segment one by one on the lattice. There the self intersections between segments of the same polymer chain are neglected that is so that is one of the one more assumption of this theory. And one of the other assumptions is that the polymers segment and the solvent molecule have the same size. So, a given polymer segment essentially is defined based on the fact that it should have the same size the same volume as the as a solvent molecule.

So, after that finally, one of the key assumptions and limitations of this theory is the mean field approximation which we also discussed in the previous lecture. Where when you when the polymer chains are being introduced onto the lattice. It is assumed that when a new segment or new polymer chain is being added to the lattice. The already added polymer segments are uniformly distributed across the entire lattice.

So, that is what is called the mean field approximation. And if we let us say have a concentrated polymer solution then this assumption is not that bad it is ok, but if we have a dilute solution in that case, the this assumption is quite limiting because, it is a very poor assumption for high dilute solution. So, through these couple of cartoons just see why this mean field approximation is not a good assumption for dilute solutions. So, so for this concentrated solution that we have drawn here this rough carton. The one can see the polymer chains are packed quite closely to each other and they are entangled with each other as well.

So, here one can safely say that the segments that polymer segment distribution across the entire volume of the solution that is shown that is relatively uniform. So, the making a mean field approximation here we will not actually lead to; significant error whereas, if we look at the dilute solution case here what we have is polymer chains which are isolated and well separated from each other.

So, in the solution we have polymer chains occupying certain volumes, but much of the volume of the solution is occupied by solvent molecules. So, in this case assuming that the polymer segments are uniformly distributed throughout that is a poor assumption because, if we consider let us say these regions of volume here. So, in these regions actually there are no polymer molecules present so no polymer segments are present as well. So, assuming that the polymer molecules are uniformly present that is a mean field approximation is not a very good assumption for dilute solution case.

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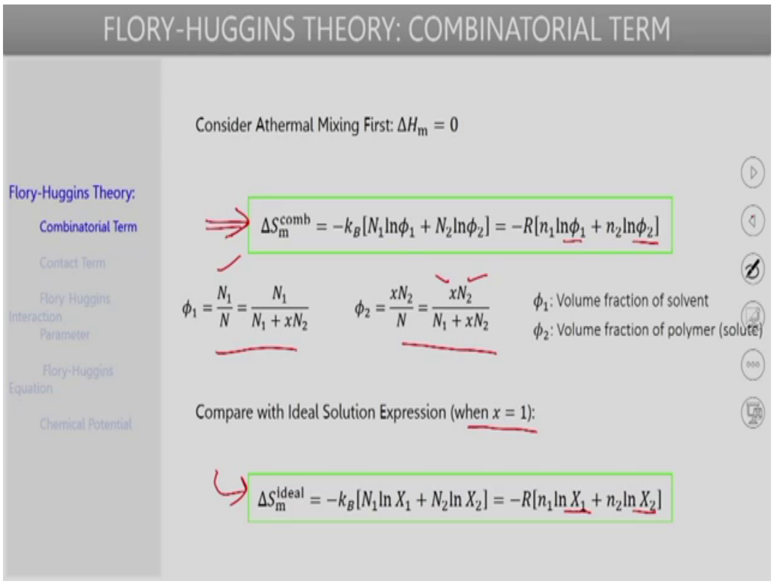

FLORY-HUGGINS THEORY: COMBINATORIAL TERM

Consider Athermal Mixing First: $\Delta H_m = 0$

$$\boxed{\Delta S_m^{comb} = -k_B[N_1 \ln\phi_1 + N_2 \ln\phi_2] = -R[n_1 \ln\phi_1 + n_2 \ln\phi_2]}$$

$$\phi_1 = \frac{N_1}{N} = \frac{N_1}{N_1 + xN_2} \qquad \phi_2 = \frac{xN_2}{N} = \frac{xN_2}{N_1 + xN_2}$$

ϕ_1: Volume fraction of solvent

ϕ_2: Volume fraction of polymer (solute)

Compare with Ideal Solution Expression (when $x = 1$):

$$\boxed{\Delta S_m^{ideal} = -k_B[N_1 \ln X_1 + N_2 \ln X_2] = -R[n_1 \ln X_1 + n_2 \ln X_2]}$$

Next let us just briefly summarize the combinatorial term the combinatorial entropy term that we discussed in the previous lecture and after we summarize. And that then we will move on to the contact term and further on. So, in the previous lecture if you the first as a first step we assume that the mixing is athermal, which means that there is no enthalpy change of associated with the mixing of a polymer and the solvent. And this athermal mixing is an initial assumption we will see that when we discuss the contact term.

There this, the athermal mixing that part that assumption will be relaxed, but for calculating the combinatorial entropy which is purely based on the different number of confirmations that the polymer chains can adopt. So, for calculating that term this assumption of no enthalpy changes of mixing essentially, no interactions that is made. So, with athermal mixing assumption initially; we developed the combinatorial entropy term to be what shown here. So, we saw that although the steps involved a; large number of mathematical manipulations but finally, the expression that we get is quite simple. So, the entropy change a combinatorial entropy change of mixing is just minus R n 1 l n phi 1 plus n 2 l n phi 2 where phi 2 and phi 2 the respective volume fractions of the solvent and the polymer in the solution.

So, in terms of the number of molecules of the solvent present which is N 1 and the number of molecules of the polymer present which is N 2. And also the number of segments per polymer chain which is this x. So, in terms of these one can define these volume fractions and this volume fractions basically are what appear in the combinatorial entropy term. If we contrast this with the expression for ideal solution which we also developed initially in the previous lecture; we see that thus do the 2 equations have very similar in form the only difference is that in the ideal solution case the mole fractions appear here and here. Where is whereas, for the polymer solution case in the case of a thermal mixing the volume fractions appear in these 2 places.

So, that is a only difference, but as we will see this the difference itself actually you can lead to large difference in the value of the entropy chain that is calculated using these 2 equations. So, one additional point here is that the expression that we will have here this will reduce to the ideal solution expression which is here. In the limit when this X equal to 1 which is quite obvious. So, when X is equal to 1 which means the number of segments in the polymer chain is 1.

It means that the solute which the solute actually is now a simple molecule which has the same identical size as a solvent. So, in that case of course, we will we should be able to get back the ideal solution expression from the polymer expression that we have developed here. And if you if you substitute X equal to 1 in the in these equations here, you will see that the ideal solution expression for delta S is obtained.

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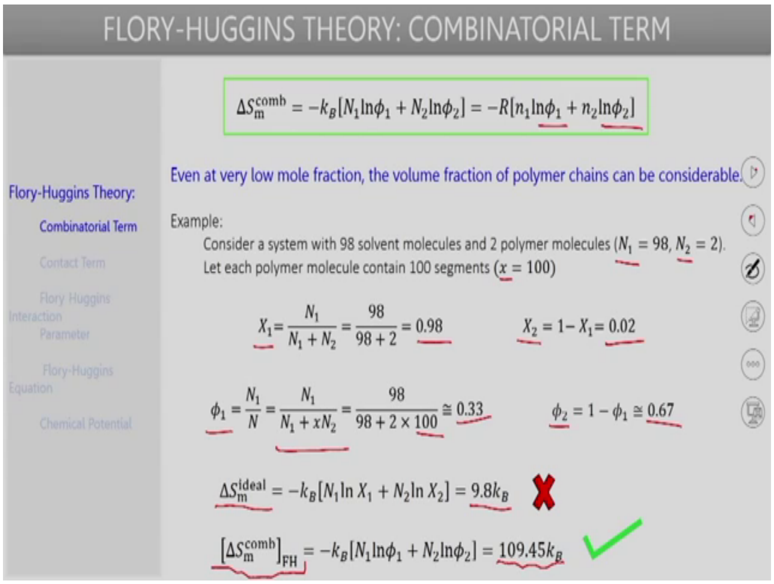

FLORY-HUGGINS THEORY: COMBINATORIAL TERM

$$\boxed{\Delta S_m^{comb} = -k_B[N_1 \ln\phi_1 + N_2 \ln\phi_2] = -R[n_1 \ln\underline{\phi_1} + n_2 \ln\underline{\phi_2}]}$$

Even at very low mole fraction, the volume fraction of polymer chains can be considerable.

Example:

Consider a system with 98 solvent molecules and 2 polymer molecules ($\underline{N_1} = 98$, $\underline{N_2} = 2$).

Let each polymer molecule contain 100 segments ($\underline{x} = 100$)

$$\underline{X_1} = \frac{N_1}{N_1 + N_2} = \frac{98}{98+2} = \underline{0.98} \qquad \underline{X_2} = 1 - X_1 = \underline{0.02}$$

$$\underline{\phi_1} = \frac{N_1}{N} = \underline{\frac{N_1}{N_1 + xN_2}} = \frac{98}{98 + 2 \times \underline{100}} \cong \underline{0.33} \qquad \underline{\phi_2} = 1 - \phi_1 \cong \underline{0.67}$$

$$\underline{\Delta S_m^{ideal}} = -k_B[N_1 \ln X_1 + N_2 \ln X_2] = \underline{9.8k_B}$$ ✗

$$\underline{[\Delta S_m^{comb}]_{FH}} = -k_B[N_1 \ln\phi_1 + N_2 \ln\phi_2] = \underline{109.45k_B}$$ ✓

So, let us just quickly have a look at this combinatorial entropy term a bit more; in terms of some numbers and examples. Just to get a feel of how the presence of these volume fractions instead of mole fractions how that leads to a much different value of the entropy change that will be there. So, one thing about the polymer chains or polymer molecules as solute is that even if they are present in very low mole fraction. So, even if the number of polymer molecules is small compared to the number of solvent molecules; even then because of because the size of a poly molecule is very large compared to a solvent molecule.

The volume fractions of the poly molecule molecules or the polymer in the solution will be significant or even though its mole fraction is small. So, let us consider an example here so, let us say we have a system which contains 98 solvent molecules and 2 polymer molecules just to make it a round number of 100. So, we have this system and let us say that each polymer molecule which is a chain like molecule contains 100 connected segments. So, in this case the N 1 is 98 N 2 is 2 and X which is the number of segments where polymer molecule let us 100.

Now let us see let us first calculate the mole fractions. So, the mole fraction X 1 which is just N 1 by N 1 plus N 2, that comes out to be 0.98 for the solvent. And X 2 which is the mole fraction for the polymer that of course, will be 1 minus X 1 which is 0.02. So, we have binary mixture here so, X 1 plus X 2 the sum of mole fractions will be 1. So, X 2 will be 1 minus X 1 which is point 0 2. Next let us calculate the volume fractions so; the volume fraction phi 1 is given by N 1 divided by N 1 plus x N 2. So, we see that because the value of x is 100, because of that the volume fraction of solvent is now 0.33. Through although the mole fraction is 0.98, the volume fraction we see is actually 0.33 only. And so the volume fraction of the polymer which is phi 2 will be 1 minus phi 1which is 0.67.

So, again volume fraction also the sum of volume fractions will be 1. So, phi 2 will be 1 minus phi 1 for this binary mixture. And finally, let us do the calculations for ideal entropy and then the combinatorial entropy that we get from Flory Huggins theory. So, for the ideal entropy case if we do a calculation based on the equation for ideal entropy change or entropy change for ideal solution. Then we get this number 9.8 K B for this particular case where K B is the Boltzmann constant.

And, if we use this calculation for a polymer solution it will be an incorrect calculation it will give an incorrect result as well. So, this for a polymer solution this is not the correct result. For a polymer solution because the polymer chains are long and connected to each other the correct expression to is the combinatorial entropy term derived for the Flory Huggins theory. And if we do the calculation using that equation the Flory Huggins combinatorial entropy term, it comes out to be 109.45 K B, which is the correct which will be the correct value for polymer solutions.

So, we see that the presence of volume fractions in this Flory Huggins expression for combinatorial entropy. That actually leads to in this particular case an order of magnitude increase in the actual entropy the change that is happening compared to what we will get if we had an ideal solution; so, with that summary of what we covered in the last class an example to illustrate the points.

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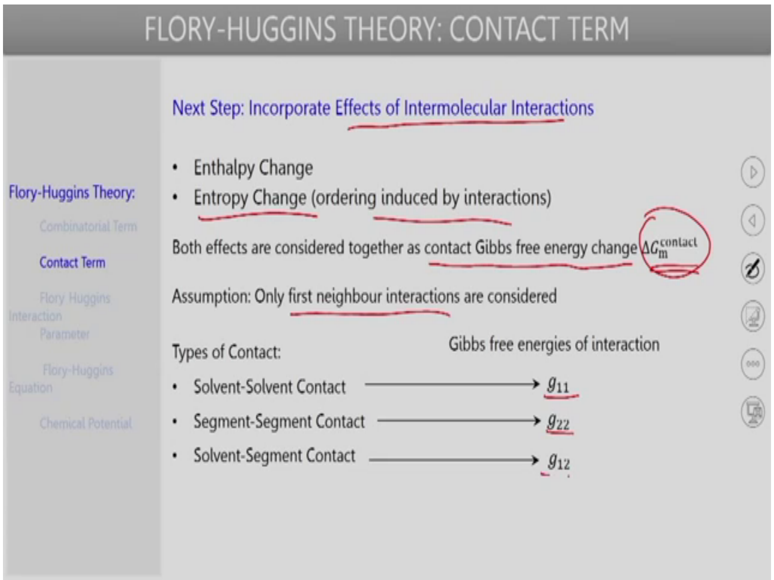

FLORY-HUGGINS THEORY: CONTACT TERM

Next Step: Incorporate Effects of Intermolecular Interactions

- Enthalpy Change
- Entropy Change (ordering induced by interactions)

Both effects are considered together as contact Gibbs free energy change $\Delta G_m^{contact}$

Assumption: Only first neighbour interactions are considered

Types of Contact: Gibbs free energies of interaction

- Solvent-Solvent Contact $\longrightarrow g_{11}$
- Segment-Segment Contact $\longrightarrow g_{22}$
- Solvent-Segment Contact $\longrightarrow g_{12}$

Let us move on to the other contribution to this Flory in this Flory Huggins theory and that is due to the intermolecular interactions. So, in the first part we calculate the entropy change, which was purely combinatorial in the sense that the no effect of any interactions was considered. And only because the polymer chains are long and connected and can adopt multiple confirmations only due to this reason many different distrigutual arrangements were possible. And due to that an entropy change or mixing was there, which was the combinatorial term that we discussed previously.

Next now if we now so, that was a athermal mixing, now if we consider the effect of intermolecular interactions as well. So, polymer solvent molecules they will of course have intermolecular interactions and the interaction between the two need not be of the same type. So, if we consider intermolecular interactions then in Flory Huggins theory the incorporation of this effect of intermolecular interaction that will of course, be through an enthalpy change of mixing. So, if you have intermolecular interactions present upon mixing one would expect enthalpy to change.

So, we will have a nonzero enthalpy change of mixing, but apart from that that will not be the only effect of these intermolecular interactions. Apart from in non zero enthalpy change of mixing; entropy change of mixing will also be affected by the presence of intermolecular interactions. The reason for this is if we have intermolecular interactions present that these interactions actually might lead to some kind of ordering or some kind of reduction in the randomness of the arrangement of molecules.

So, the presence of interactions can result in some kind of ordering and that intern can lead to an additional entropy change apart from the combinatorial entropy chain that we already discussed previously. So, this ordering induced by interactions that is the other effect. Now in this Flory Huggins theory we will consider both these effects together through a single term, which is the Gibbs energy change of mixing through contact interactions.

So, so we will consider this contact Gibbs free energy change of mixing delta G m contact and in this term both the effects the enthalpy change of mixing as well as the entropy change due to some kind of ordering in the presence of interactions both these effects will be captured in this delta G m contact term. So, the one assumption that we are making here is that the interaction the inter molecule interaction that we are considering, they are limited only up to the distance of first neighbors of the molecules. So, long range interactions we are neglecting.

So, in any case in the absence of any charged, charges in the system the interactions that are present to be of the Van der Waals kind of non bonding interactions. They are typically short range so; this is a reasonable assumption for such systems. If you have long range interactions present then of course, this assumption is not a very good one, but from our case we will consider only first neighbor interactions which is good enough assumption for short range interactions.

So, let us talk about that different types of contacts that might be present when we form this polymer solution which contains solvent molecules as well as polymer molecules which in turn are composed of polymer segments. So, we can have solvent-solvent contact, where two solvent molecules are close to each other and they are interacting with each other. We can have segment-segment contact where two different polymer segments are close to each other and they are interacting with each other through non model interactions.

So, here we are not considering two segments which are let us say directly bonded to each other along given polymer chain. We are considering segments which are essentially not directly bonded to each other and interacting through non bonded interactions. So, we can have the segment-segment contact interactions apart from that we can also have a solvent segment interaction. So, a given polymer segment might be surrounded by solvent molecules. So, those interactions those contacts will lead to some kind of interaction which will call the solvent segment interaction.

So, the Gibbs free energy associated with these three types of interactions let us represent them by small g 1 1 small g 2 2 for the solvent-solvent and segment-segment contact interactions. And for the solvent segment interaction let us say the corresponding Gibbs free energy of this contact is g 1 2 and these all these quantities are for single contacts. So, for a single solvent-solvent contact the corresponding Gibbs energy let us say g 11 for a single solvent segment contact let us say g 1 2 and so on.

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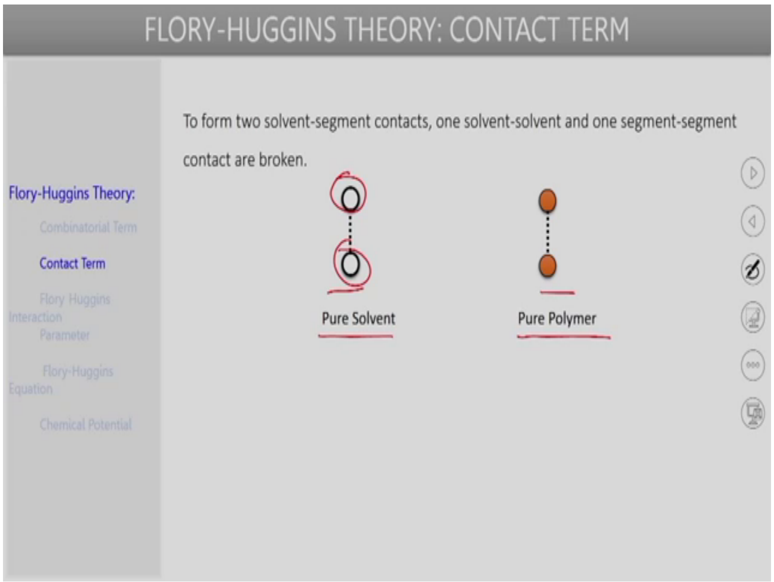

FLORY-HUGGINS THEORY: CONTACT TERM

Flory-Huggins Theory:
Combinatorial Term
Contact Term
Flory Huggins Interaction Parameter
Flory-Huggins Equation
Chemical Potential

To form two solvent-segment contacts, one solvent-solvent and one segment-segment contact are broken.

Now, let us look at this the contacts in a bit more detail and what happens when this pure solvent. And the pure polymer is mixed together what happens to the contacts how new contacts form an old contacts are disrupted. So, for the formation of two segments solvent contacts so, two contacts points between solvent molecules and segment polymer segment for a formation of two such contacts one solvent-solvent contact on an average will break and one segment-segment contact will break.

So, if we consider let us say a pure solvent and focus on two solvent molecules these 2. And if we consider again a pure polymer here and consider the contact interaction between 2 polymer segments represented by these orange circles here. So, initially in the pure species will have the in the solvent we will have solvent-solvent interactions only in the pure polymer will have only segment-segment interactions. Now, let us say and we are focusing on one solvent-solvent interaction here and one polymer segment-segment interaction here.

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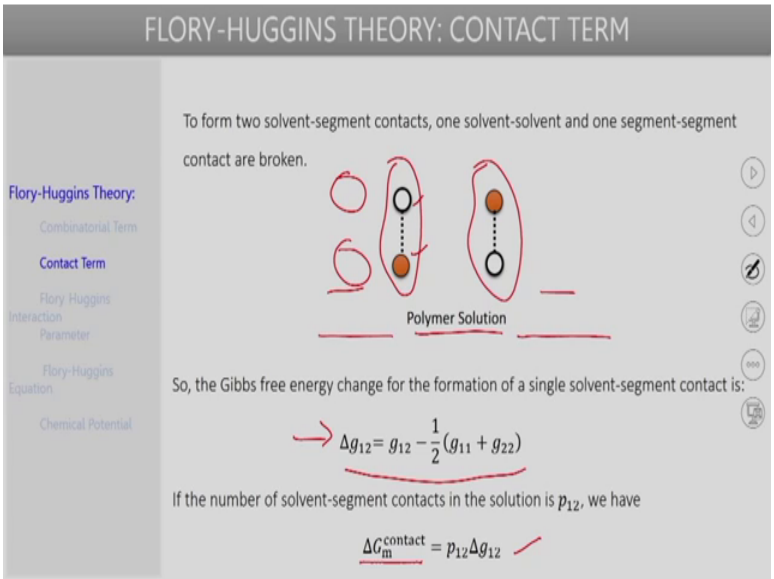

FLORY-HUGGINS THEORY: CONTACT TERM

To form two solvent-segment contacts, one solvent-solvent and one segment-segment contact are broken.

So, the Gibbs free energy change for the formation of a single solvent-segment contact is:

$$\longrightarrow \underbrace{\Delta g_{12} = g_{12} - \frac{1}{2}(g_{11} + g_{22})}$$

If the number of solvent-segment contacts in the solution is p_{12}, we have

$$\underline{\Delta G_m^{\text{contact}}} = p_{12}\Delta g_{12}$$

Now, let us say when we mix the two and atom positions gets rearranged and we get a situation like this. So, here now if we see in this polymer solution that has now formed, we have a form two contacts and both of these are segment solvent contact. So, one solvent-solvent contact got broken one segment-segment contact got broken and two new solvent segment contacts got formed. So, that is based on this observation one can basically define the Gibbs free energy change for the formation of a single solvent segment contact. So, that can be defined through the equation that is written here.

So, this delta g 1 2 that is equal to g 1 2 minus half of g 1 1 plus g 2 2 and this factor half comes because two solvent segment contacts form when one solvent-solvent and one segment-segment contacts get broken. So, the corresponding Gibbs energy change will be given by the expression here. Now let us say that the number of such solvent segment contacts is p 1 2 in the entire solution that has formed. So, the total Gibbs energy change the total contact Gibbs energy change of mixing will simply be given by the product of this p 1 2 times this delta of this small g 1 2.

So, this p 1 2 is a total number of solvent segment contacts present in the entire solution. And the delta g 1 2 is the Gibbs energy change associated with the formation of a single solvent segment contact. So, their product will actually give the entire Gibbs energy change a contact term for the Gibbs energy change of mixing. So, we have this expression here, now let us see if we can come up with an expression for this quantity p 1 2 which is a total number of segment solvent contacts in our polymer solution. So, to for that let us start by considering a single polymer or focusing on a given polymer chain in our lattice.

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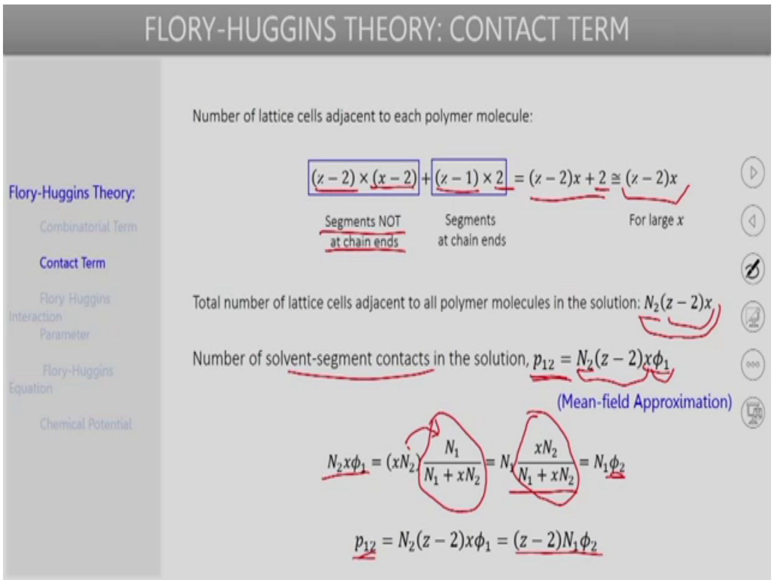

FLORY-HUGGINS THEORY: CONTACT TERM

Flory-Huggins Theory:

- Combinatorial Term
- Contact Term
- Flory Huggins Interaction Parameter
- Flory-Huggins Equation
- Chemical Potential

Number of lattice cells adjacent to each polymer molecule:

$$\boxed{(z-2)\times(x-2)}+\boxed{(z-1)\times 2}=(z-2)x+2\cong(z-2)x$$

Segments NOT at chain ends

Segments at chain ends

For large x

Total number of lattice cells adjacent to all polymer molecules in the solution: $N_2(z-2)x$

Number of solvent-segment contacts in the solution, $p_{12}=N_2(z-2)x\phi_1$

(Mean-field Approximation)

$$N_2x\phi_1=(xN_2)\frac{N_1}{N_1+xN_2}=N_1\frac{xN_2}{N_1+xN_2}=N_1\phi_2$$

$$p_{12}=N_2(z-2)x\phi_1=(z-2)N_1\phi_2$$

So, for a given polymer chain, if we count the number of lattice cells that are adjacent or neighboring to this polymer chain. Then that counting can be done in the following manner. So, we will have two terms, the first term here the term here this basically this product corresponds to segments of polymer chain that are not at the chain ends.

So, all the polymer segments which are not chain ends so, if we have total x segments in a given polymer molecule. Then in that case the number of segments which are not chain ends will be x minus 2 because we are considering only linear polymers which will have two chain ends. So, if we remove those two chain ends do not consider that for this term. Then we will have x minus 2 segments and each of these x minus 2 segments will have z minus 2 adjacent lattice cells to them.

Now, this z minus 2 comes because of the fact that for a given polymer segment which is not a chain in it will be connected to two other polymer segments. So, if we have this one polymer segment it will be connected in to next volume segment here and a previous polymer segment. So, if the overall coordination of the lattice is z which means the total number of nearest neighbors is z for a given polymer segment. Then two of those positions are already occupied by the two segments that are bonded to to the segment that we are considering.

So, if we subtract that 2 then z minus 2 number of cells lattice cells around this segment are other adjacent cells. Which are available for occupation by solvent molecules as well as segments from other polymer chains or distance more distance polymer segments in the same chain as well. So, so this z minus 2 is because of that and x 2 is because we have x minus 2 such segments plus we have another term accounting for the contribution from the chain ends. So, we have two chain ends because we are considering linear polymers.

So, for each chain end, each chain end actually is connected only to one more segment the previous segment along the chain ok. So, if we have this as the chain end this will be connected to one segment here, but on the other side there would not be any connection. So, if the overall coordination of the lattice is z, then z minus 1 adjacent sites will be again available for occupation by other solving molecules or other segments.

And only this one segment which is to which this chain end is connected that cell is not available. So, for chain ends the two chain ends will have for each of them will have z minus 1 at adjacent lattice cells available. Now if we simplify this expression what we get is this z minus 2 times x plus 2. Now if the x is the large so, for a for long polymer chains typically the value of x will be quite large. So, for large x this 2 this plus 2 here that can be neglected we can just say that the total number of lattice cells adjacent to a given polymer molecule is just z minus 2 times x ok.

So, now proceeding from here now, if we know that if the total number of polymer molecules in the solution is N 2 so, if for a given polymer molecule we have z minus 2 times x number of adjacent lattice cells. Then for all the N 2 polymer molecules together, the number of adjacent lattice cells that we can get is just N 2 multiplied by z minus 2 times x ok. So, now this gives a total number of adjacent cell for all polymer molecules, our aim is to come up with the number for the contact interactions. And now how many contact contacts are there solvent segment contacts are there. So, the if this is the.

Student: Ok.

Total number of adjacent cells for polymer molecules, then we need to next find out how many of these cells are actually occupied by solvent molecules. And that number will give us a total number of segments solvent contact present in the solution. So, to do that again the mean field approximation is invoked in this Flory Huggins theory. So, mean field approximation what here what its implying is that the overall volume fraction the solvent in the entire solution, that same volume fraction can be used to calculate the number of cells adjacent to given polymer molecules which will be occupied by the solvents.

So, if you have a bunch of polymer molecules and we have identified the neighboring cells or adjacent cells. Then some of them will be occupied by solvent molecules some others can be occupied by other polymer segments as well. So, using mean field approximation what we say is that out of these adjacent cells the phi 1 fraction of these adjacent cells will be occupied by solvent molecules only. So, that leads to an expression for this quantity p 1 2 and if we then just try to simplify this expression further.

So, we have this N 2 times x times phi 1 these three terms appearing in the expression for p 1 2. So, phi 1 we can write in this manner and then we can take this the N 1 out and the x N 2 we can take here. So, just rearranging we get this expression and this quantity this ratio is nothing, but phi 2. So, essentially N 2 times x times phi 1 and that can be simplified to N 1 times phi 2. So, now, again based on this simplification the expression for p 1 2 becomes z minus 2 N 1 times phi 2.

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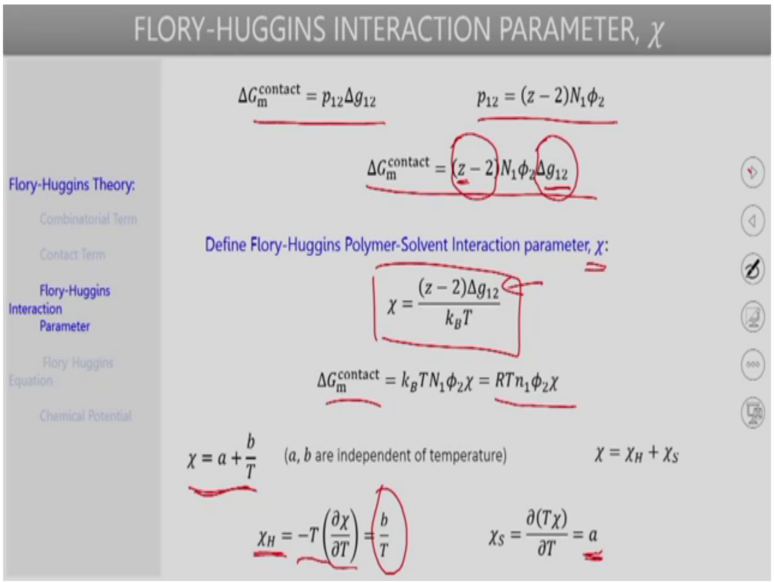

FLORY-HUGGINS INTERACTION PARAMETER, χ

Flory-Huggins Theory:

- Combinatorial Term
- Contact Term
- Flory-Huggins Interaction Parameter
- Flory Huggins Equation
- Chemical Potential

$$\Delta G_m^{contact} = p_{12}\Delta g_{12} \qquad p_{12} = (z-2)N_1\phi_2$$

$$\Delta G_m^{contact} = (z-2)N_1\phi_2\Delta g_{12}$$

Define Flory-Huggins Polymer-Solvent Interaction parameter, χ:

$$\boxed{\chi = \frac{(z-2)\Delta g_{12}}{k_B T}}$$

$$\Delta G_m^{contact} = k_B T N_1 \phi_2 \chi = RTn_1\phi_2\chi$$

$$\chi = a + \frac{b}{T} \quad (a, b \text{ are independent of temperature}) \qquad \chi = \chi_H + \chi_S$$

$$\chi_H = -T\left(\frac{\partial\chi}{\partial T}\right) = \frac{b}{T} \qquad \chi_S = \frac{\partial(T\chi)}{\partial T} = a$$

So, once we have an expression for p 1 2 we can plug that back into the expression for the contact Gibson energy change of mixing. So, the contact Gibson energy change of mixing it is given by this expression p 1 2 by this. So, combining these two, the expression for the contact Gibson energy change of mixing is z minus 2 N 1 phi 2 times this delta g 1 2 term. So, what in this theory what is done next is the details of the lattice which are contained here so, this z is a lattice coordination numbers that contains details are the lattice that is being used.

So, that term as well as this delta g 1 2, which is the Gibbs energy change associated with the formation of polymer solvent segment contact. So, these terms are basically combined into a single parameter and that parameter is called the chi parameter or the Flory Huggins polymer solvent interaction parameter. So, this parameter is defined in this manner. So, z minus 2 times delta g 1 2 just divided by K B T. So, we see that both the details of the lattice contained in the coordination number z, as well as the delta g 1 2 term.

Both of these terms are subsumed or combined to in this Flory Huggins interaction parameter term which is also called the chi parameter. And this chi parameter basically is a measure of the polymer solvent interactions. So, next now if once we have this chi parameter defined if we substitute this in the expression for the contact Gibbs free energy of mixing. Then we will get an expression like this so, delta G m contact is just R T times n 1 phi 2 chi. So, let us just look at this chi parameter in little bit more detail here. So, this chi parameter can in general be expressed as in the form of a plus b by T, where a and b are independent of temperature. So, we see that this chi parameter is a temperature dependent dimensionless quantity. And the temperature dependence normally can be expressed as a plus b by T.

The chi parameter if we see here it contains this delta g 1 2 term so in inside it the chi parameter contains both an entropic contribution as well as an enthalpy contribution because, the Gibbs free energy of course, will contain both these terms. So, one can also think of chi parameter as consisting of an entropic contribution chi H plus an entropic contribution chi S. And it can be shown based on the discussion that we have been having it can be shown that this chi H the enthalpy contribution. That is given by minus T times this partial derivative del chi del T. And when applied to this formula that leads to just b by T so the enthalpy term is the one which is temperature dependent and that can be shown to be equivalent to b by T.

Similarly, the entropic term that will be given by the partial derivative of T times chi with respect to temperature and that will simply be the parameter a from this expression. So, we see that this the entropic term is actually does not come out to be a temperature dependent term. It is a enthalpic term that is temperature dependent. Now, that we have defined the Flory Huggins interaction parameter and use that to come up with an expression for the contact Gibbs energy change of mixing. And the fact that we have already developed an expression for the combinatorial entropy change of mixing. Now, we can combine both these terms to get in the overall that overall Gibbs free energy change of mixing associated with the formation of polymer solutions.

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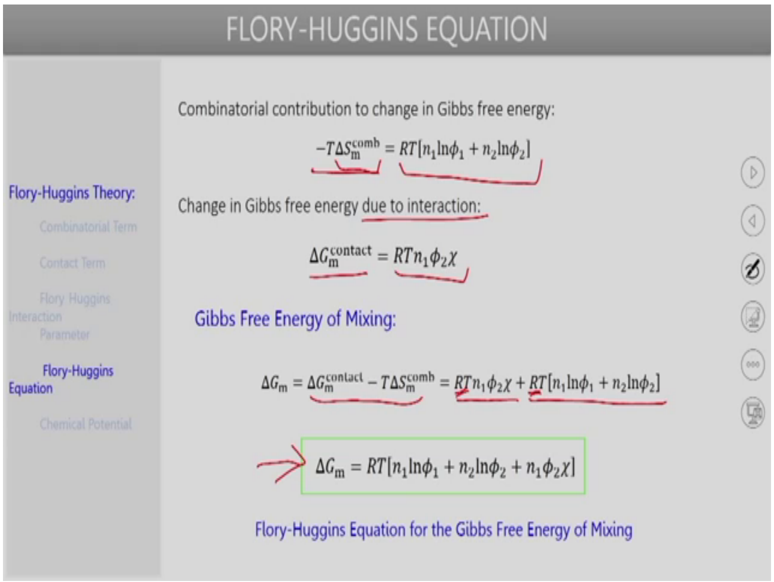

FLORY-HUGGINS EQUATION

Flory-Huggins Theory:

- Combinatorial Term
- Contact Term
- Flory Huggins Interaction Parameter
- **Flory-Huggins Equation**
- Chemical Potential

Combinatorial contribution to change in Gibbs free energy:

$$-T\Delta S_{\mathrm{m}}^{\mathrm{comb}} = RT[n_1 \ln\phi_1 + n_2 \ln\phi_2]$$

Change in Gibbs free energy due to interaction:

$$\Delta G_{\mathrm{m}}^{\mathrm{contact}} = RT n_1 \phi_2 \chi$$

Gibbs Free Energy of Mixing:

$$\Delta G_{\mathrm{m}} = \Delta G_{\mathrm{m}}^{\mathrm{contact}} - T\Delta S_{\mathrm{m}}^{\mathrm{comb}} = RT n_1 \phi_2 \chi + RT[n_1 \ln\phi_1 + n_2 \ln\phi_2]$$

$$\rightarrow \boxed{\Delta G_{\mathrm{m}} = RT[n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1 \phi_2 \chi]}$$

Flory-Huggins Equation for the Gibbs Free Energy of Mixing

So, the combinatorial contribution to the Gibbs free energy change that will just be minus T times the entropy change of the other combinatorial entropy change. So, that if we substitute the expression for the combinatorial entropy change that we had developed earlier. That if this expression out to be R T times n 1 l n phi 1 plus n 2 l n phi 2. Similarly the other contribution due to the interaction or intermolecular interactions that is this contact Gibbs energy change of mixing and that we just saw is R T n 1 phi 2 chi.

So, we combine these two to get the Gibbs energy change of mixing for polymer solution and that expression by combining these two terms we can get this expression here. So, R T you will see R T is common to both these so we can take this R T term outside. And the final expression for the Flory Huggins equation for Gibbs energy change of mixing that is given by R T n 1 l n phi 1 plus n 2 l n phi 2 plus n 1 phi 2 chi.

So, this is the expression the key expression for the Flory Huggins theory and that is that gives the Gibbs free energy change of mixing. And this Gibbs free energy change of mixing is a very important quantity for describing the phase behavior of solutions. Because starting from here many other quantities can be calculated which are related to phase behavior polymer solutions. So, let us now that we have develop the complete Flory Huggins equation let us just briefly discuss some of the features some of this equation as well as some of it is limitations.

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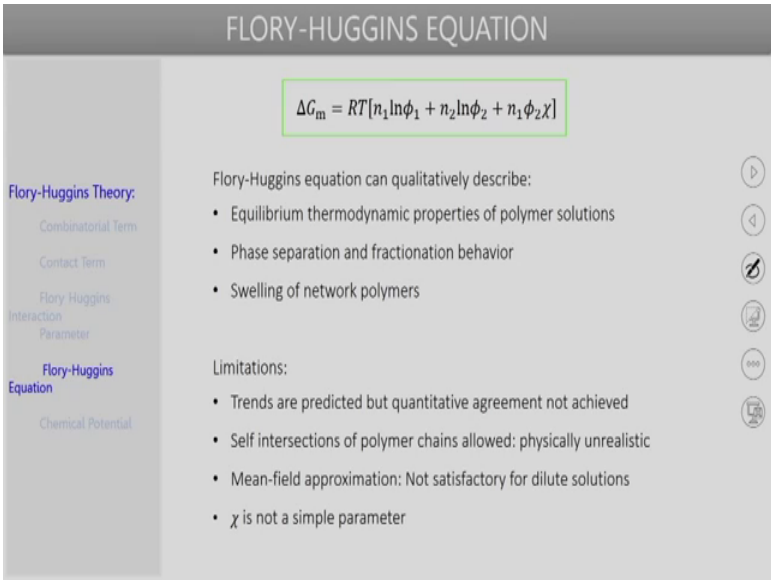

FLORY-HUGGINS EQUATION

Flory-Huggins Theory:

Combinatorial Term

Contact Term

Flory Huggins Interaction Parameter

Flory-Huggins Equation

Chemical Potential

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

Flory-Huggins equation can qualitatively describe:

- Equilibrium thermodynamic properties of polymer solutions
- Phase separation and fractionation behavior
- Swelling of network polymers

Limitations:

- Trends are predicted but quantitative agreement not achieved
- Self intersections of polymer chains allowed: physically unrealistic
- Mean-field approximation: Not satisfactory for dilute solutions
- χ is not a simple parameter

So,; Flory Huggins theory the good thing about it is that its relatively simple theory and simple expression that we get here, but can still qualitatively describe a lot of different kinds of behavior. So, the equilibrium thermodynamic properties of polymer solutions the qualitative trends it can predict well.

Similarly, the phase separation behavior so if we have a polymer solution where the interactions are not good and phase separation occurs. So, that phase separation behavior which again is connected to fractionation as well. So, these kind of behaviors are also qualitatively well described by Flory Huggins theory. And swelling of network polymers that solves something Flory Huggins theory describes well and there are other applications as well, but these are the important ones.

Next let us talk about some of the limitations of Flory Huggins theory. So, it is a simple theory and so of course, there will be some limitations. So, one thing one of this limitation is that it predicts the qualitative trends well for a lot of different cases, but it does not give good quantitative agreement will experimental data in general while calculating the combinatorial entropy term in this theory. The self intersection of polymer segments is actually allowed which is not a realistic assumption.

As we have discussed many times already the mean field approximation is the probably the more important weaknesses of this theory. And it is a more apparent for the case of dilute polymer solutions where the assumption of uniform presence of polymer segments is actually not valid much. So, it is not satisfactory for dilute solutions. The chi parameter that we have, that we have defined it is not the very simple parameter it is depends on Gibbs free energy change of contact formations and contains entropic as well as enthalpy contributions. So, it is not a simple parameter and in some cases it is actually also shown to be dependent on the polymer volume fractional concentration.

So, so that is another limitation apart from this the fact that the same lattice is being used for the solvent the polymer as well as the solution that is formed. So, that itself is a kind of a limiting assumption. So, and it is something that need not be true for many cases. So, these are some of the limitations of Flory Huggins theory, but that does not mean that this theory is not very useful.

In fact, the point of time when this theory basically was develop this was a landmark development in the field of polymer solution thermodynamics. And even now the theory actually gives a very good qualitative description of various strengths related to the behavior of polymer solutions. So, it is relatively simple, but quite good theory. And even the most sophisticated theories that have been developed later on, many of them actually used Flory Huggins theory as a starting point and then further refine it to get better predictions and agreement with the data.

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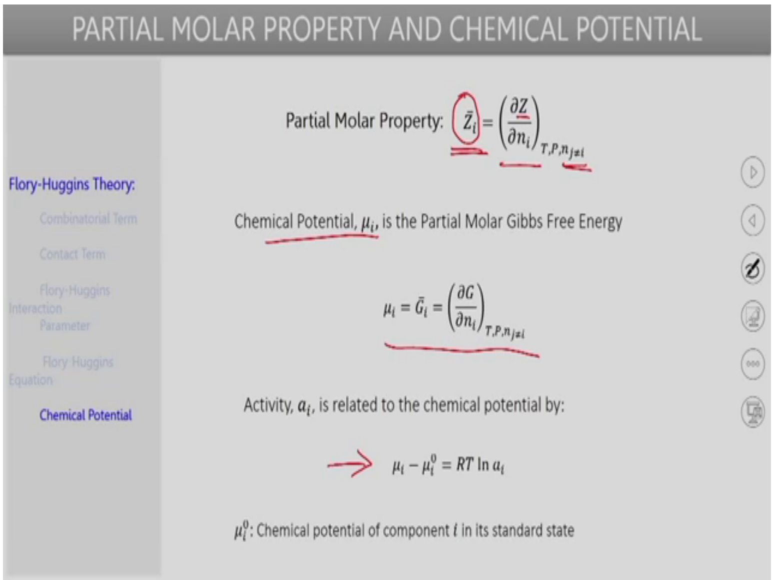

PARTIAL MOLAR PROPERTY AND CHEMICAL POTENTIAL

Flory-Huggins Theory:

- Combinatorial Term
- Contact Term
- Flory-Huggins Interaction Parameter
- Flory Huggins Equation
- Chemical Potential

Partial Molar Property: $\bar{Z}_i = \left(\frac{\partial Z}{\partial n_i}\right)_{T,P,n_{j\neq i}}$

Chemical Potential, μ_i, is the Partial Molar Gibbs Free Energy

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Activity, a_i, is related to the chemical potential by:

$$\mu_i - \mu_i^0 = RT\ln a_i$$

μ_i^0: Chemical potential of component i in its standard state

So, now that we have develop the Flory Huggins equation and talked about the Flory Huggins equation and the theory in some detail. Let us see how we can extract some useful thermodynamic quantities from the equations that we have developed till now. So, before we move on let me introduce this concept of partial molar properties. So, those of you who have take courses in chemical thermodynamics you will be well familiar with the this term. So, partial molar property of a given component in a solution is basically measure of a how much a given property will change or a given solution property will change when a very small amount of a certain component is added to that solution.

So, let us say if we are talking about any property represented by Z ok. So, this Z that we have here it can be the Gibbs energy the enthalpy the volume any thermodynamic property of interest. So, the corresponding partial molar property is given by Z i bar that is a representation. And it is defined as the partial derivative of Z with respect to n i which is the number of moles of this component i. Keeping the temperature pressure and the number of moles of all other components in the system constant. So, it basically as I just mentioned is a measure of how much a certain property changes when we add this very small amount of a certain component to the solution or mixture.

So, the partial molar property that is of most interest towards is what is called the chemical potential, which we will represent by mu i. And this chemical potential is nothing, but the partial molar Gibbs free energy. So, the change in Gibbs free energy as of a given solution associated with the addition of a very small amount of certain component. That change basically is what this is partial what this chemical potential of that component signifies. So, since it is a partial molar Gibbs energy mathematically one can define it like this. And from here another important expression that is of interest to us is basically the relation between this chemical potential and activity of a solution or activity of a given component in a solution. So, this activity is related to chemical potential through the expression here which states that mu i minus mu i naught is equal to R T l n a i.

Here mu i is of course, the chemical potential of component i in the solution, a i is the activity of component i in the solution, mu i naught is the chemical potential of component i in its standard state. So, in general the standard state will be if we have a liquid, then the standard state can be the particular component in it is pure state at the same conditions as the solution is that. So, mu i naught is the standard state chemical potential of component i. Now this mu i minus mu naught which is equal to R T l n a i.

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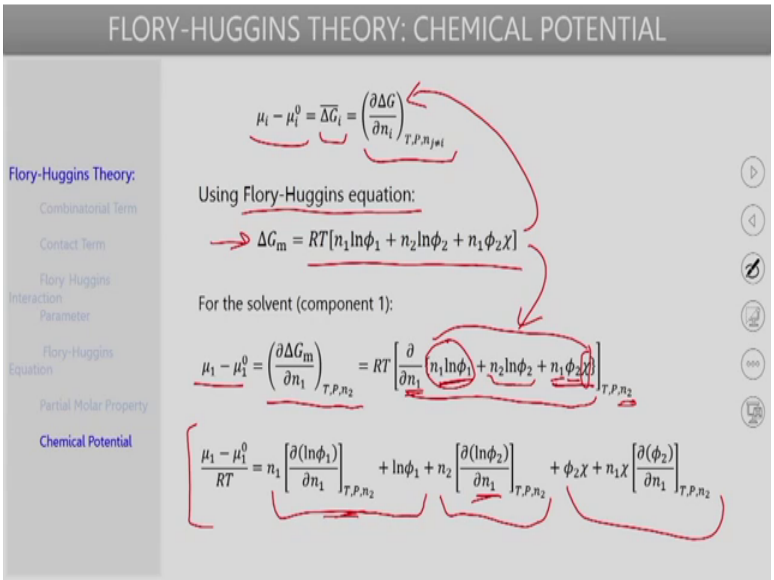

FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

$$\mu_i - \mu_i^0 = \overline{\Delta G_i} = \left(\frac{\partial \Delta G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Using Flory-Huggins equation:

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

For the solvent (component 1):

$$\mu_1 - \mu_1^0 = \left(\frac{\partial \Delta G_m}{\partial n_1}\right)_{T,P,n_2} = RT\left[\frac{\partial}{\partial n_1}\{n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1\phi_2\chi\}\right]_{T,P,n_2}$$

$$\frac{\mu_1 - \mu_1^0}{RT} = n_1\left[\frac{\partial(\ln\phi_1)}{\partial n_1}\right]_{T,P,n_2} + \ln\phi_1 + n_2\left[\frac{\partial(\ln\phi_2)}{\partial n_1}\right]_{T,P,n_2} + \phi_2\chi + n_1\chi\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}$$

This is actually also a partial molar property and it is a partial molar property of the Gibbs energy change of mixing. So, this mu i minus mu i naught can be shown to be the partial molar Gibbs energy change of mixing. And again mathematically we can define it like this. Now if we use the Flory Huggins equation that we have developed for the Gibbs energy change of mixing for a polymer solution.

So, the equations that you have discussed till now for the partial molar property the chemical potential the activity. Those equations are general thermodynamic equations valid for any kind of solution. Now if you consider the specific case of a polymer solution, then the Gibbs energy change of mixing we can described by the Flory Huggins equation here. So, if we substitute this expression here then we can come up with an equation for the chemical potential of any component i.

So, let us focus on the solvent phase so for the polymer solution that we have we have a binary mixture of a polymer and a solvent. So, let us first consider the solvent phase which is component 1 so for that this mu i minus mu mu i naught if we can say i equal to 1 for the solvent. Then we get mu 1 minus mu 1 naught equal to this partial molar Gibbs free energy of mixing. And we can substitute the Flory Huggins equation here and then carry out the differentiation to obtain an expression.

So, in the next couple of slides just walk through this derivation step by step. So, so next the mu i mu 1 minus mu 1 naught by R T this quantity here that basically if we split or expand this partial derivative into multiple terms. Then if we are taking first the partial derivative this term n 1 l n phi 1 with respect to del del n 1. Then using product rule we will get these two terms. So, the partial derivative of this term actually leads to these two terms here. Then the partial derivative of the this second term here, if we take the partial derivative with respect to n 1. Then we will get only this one term, the reason for this is in taking this partial derivative the n 2 is considered to be maintained constant.

So, while taking the derivative and 2 can be taken outside and only this l n phi 2 the derivative l n phi 2 with respect to n 1 has to be taken. And in the third again we have n1 and phi 2 both of which will contribute to the partial derivative with respect to n 1. So, again using product rule chi we are assuming to be this Flory Huggins interaction parameter chi will assumed to be independent of n 1. So, in that case by product rule again we will get these two terms as a result of differentiation of this third term here. Now, in the next slide again look at all the terms that we have in more detail.

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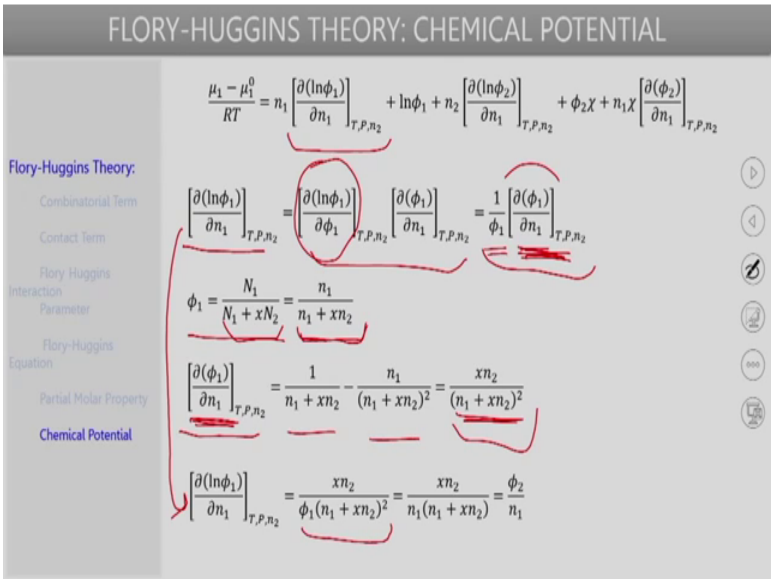

FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

Flory-Huggins Theory:
- Combinatorial Term
- Contact Term
- Flory Huggins Interaction Parameter
- Flory-Huggins Equation
- Partial Molar Property
- Chemical Potential

$$\frac{\mu_1 - \mu_1^0}{RT} = n_1 \underbrace{\left[\frac{\partial(\ln\phi_1)}{\partial n_1}\right]_{T,P,n_2}} + \ln\phi_1 + n_2\left[\frac{\partial(\ln\phi_2)}{\partial n_1}\right]_{T,P,n_2} + \phi_2\chi + n_1\chi\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}$$

$$\left[\frac{\partial(\ln\phi_1)}{\partial n_1}\right]_{T,P,n_2} = \left[\frac{\partial(\ln\phi_1)}{\partial \phi_1}\right]_{T,P,n_2}\left[\frac{\partial(\phi_1)}{\partial n_1}\right]_{T,P,n_2} = \frac{1}{\phi_1}\left[\frac{\partial(\phi_1)}{\partial n_1}\right]_{T,P,n_2}$$

$$\phi_1 = \frac{N_1}{N_1 + xN_2} = \frac{n_1}{n_1 + xn_2}$$

$$\left[\frac{\partial(\phi_1)}{\partial n_1}\right]_{T,P,n_2} = \frac{1}{n_1 + xn_2} - \frac{n_1}{(n_1 + xn_2)^2} = \frac{xn_2}{(n_1 + xn_2)^2}$$

$$\left[\frac{\partial(\ln\phi_1)}{\partial n_1}\right]_{T,P,n_2} = \frac{xn_2}{\phi_1(n_1 + xn_2)^2} = \frac{xn_2}{n_1(n_1 + xn_2)} = \frac{\phi_2}{n_1}$$

So, this is the expression that we got by expanding and take applying product rule and taking the partial derivative with respect to n 1 for the different terms in the Flory Huggins equation. Next let us consider some of the derivatives that is still here part by part or one by one. So, let us consider this term first so this term del l n phi 1 by del n 1 again that we can write in this form del n phi by del phi 1 multiplied by del phi 1 by l n n 1.

So, this derivative is nothing, but 1 by phi 1 that is the standard derivative formula for when you are taking log the derivative of a log of something. And this second term will remain here. Now, again let us look the second term this one in more detail. For that lets to evaluate this term here, we first need to know how phi one are the volume fraction of a solvent depends on n 1. So, phi 1 is defined as capital N 1 by capital N 1 plus x times capital N 2 that is a volume fraction of the solvent.

And in terms of the number of moles we can just write phi 1 in this form. And that can be done by just converting the number of molecules here to number of moles by applying the Avogadro constant as the factor. And that Avogadro constant will cancel in both the numerator and the denominator and you will just get this expression for phi 1.

So, now that we have this expression for phi 1, we can differentiate that with respect to n 1. And this derivative upon differentiation will lead to two terms and these two terms actually can be combined into the single term here. So, we have this single term and we see that this single term that we have can be further simplified. But before doing that lets go back to the this term so this is a term that we actually need. So, this term is just 1 over phi 1 multiplied by this derivative here.

So, that derivative is shown here which is this term so if you multiply this by 1 over phi 1. Then we will get this equation which will give the partial derivative of l n phi 1 with respect to n 1. So, now, we know that phi 1, phi 1 itself is defined as n 1 by n 1 plus x n 2. If we substitute that here then upon simplification we just end up with this ratio phi 2 by n 1 that is that is a partial derivative of l n phi 1 with respect to n 1. So, we see that after mathematical manipulations and simplification we get a quite simple expression for this partial derivative ok.

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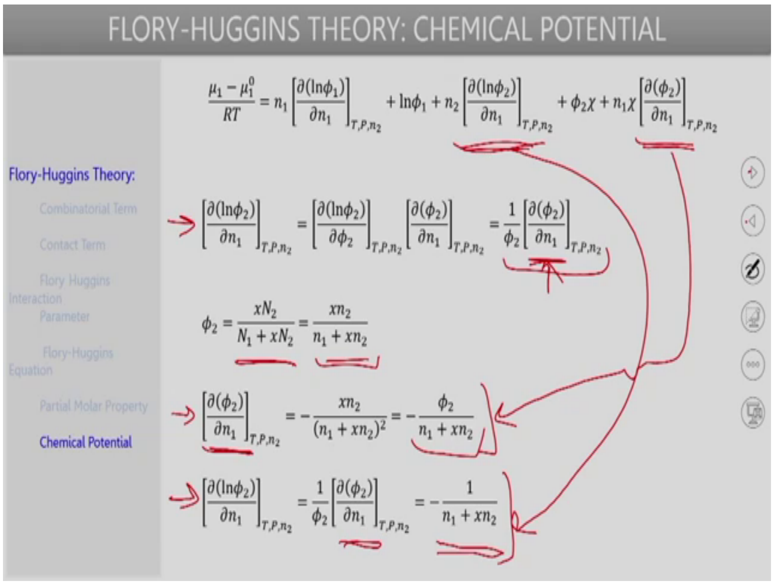

FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

$$\frac{\mu_1-\mu_1^0}{RT}=n_1\left[\frac{\partial(\ln\phi_1)}{\partial n_1}\right]_{T,P,n_2}+\ln\phi_1+n_2\left[\frac{\partial(\ln\phi_2)}{\partial n_1}\right]_{T,P,n_2}+\phi_2\chi+n_1\chi\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}$$

$$\left[\frac{\partial(\ln\phi_2)}{\partial n_1}\right]_{T,P,n_2}=\left[\frac{\partial(\ln\phi_2)}{\partial \phi_2}\right]_{T,P,n_2}\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}=\frac{1}{\phi_2}\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}$$

$$\phi_2=\frac{xN_2}{N_1+xN_2}=\frac{xn_2}{n_1+xn_2}$$

$$\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}=-\frac{xn_2}{(n_1+xn_2)^2}=-\frac{\phi_2}{n_1+xn_2}$$

$$\left[\frac{\partial(\ln\phi_2)}{\partial n_1}\right]_{T,P,n_2}=\frac{1}{\phi_2}\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}=-\frac{1}{n_1+xn_2}$$

So, now let us consider the second term the second partial derivative which is del l n phi 2 by del n 1. So, for this again the similar approach as the what we did for the del l n phi 1 del n 1 term in the previous slide the same approach can be used. And finally, the partial derivative can be expressed as 1 over phi 2 del of phi 2 del n 1. So, next to evaluate this partial derivative let us see how phi 2 depends on n 1. So, that again based on a definition of phi 2 in terms of number of molecules the same can be converted to the to number of moles and the expression that we get is this here.

So, now that we have this expression for phi 2 we will try to differentiate that with respect to n1. And the partial derivative that we get here upon simplification is just phi 2 over minus of phi 2 over n 1 plus x n 2. Now, if this partial derivative expression is substituted here then we will get an expression for this partial derivative as well. So, substituting that so, we get 1 over phi 2 this partial derivative which is here so, upon simplification the expression that we get is minus of 1 over n 1 plus x n 2.

And that is the expression for partial derivative of a natural log of phi 2 with respect to n 1. So, we will see that we have both these derivatives partial derivative that we have these two terms for both of them we have define or come up with simplified expressions. So, for this partial derivative we have this expression here and this partial derivative we have this expression here.

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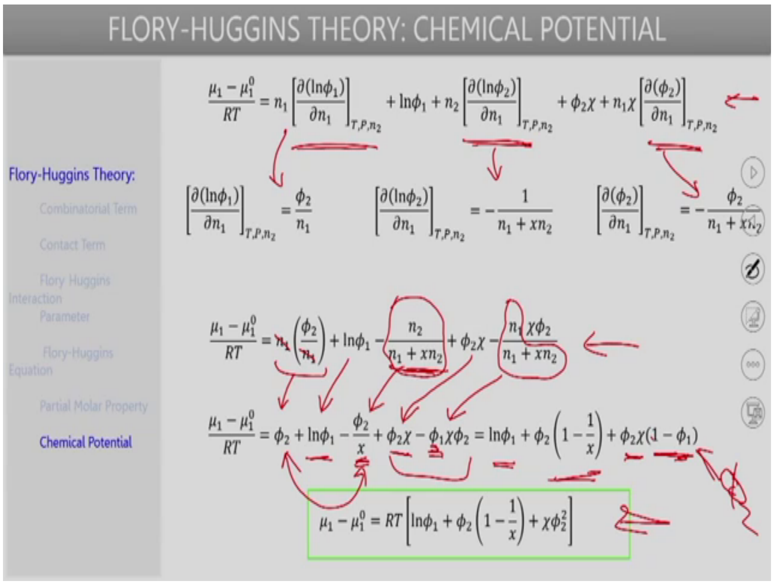

FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

Flory-Huggins Theory:

Combinatorial Term

Contact Term

Flory Huggins Interaction Parameter

Flory-Huggins Equation

Partial Molar Property

Chemical Potential

$$\frac{\mu_1-\mu_1^0}{RT}=n_1\left[\frac{\partial(\ln\phi_1)}{\partial n_1}\right]_{T,P,n_2}+\ln\phi_1+n_2\left[\frac{\partial(\ln\phi_2)}{\partial n_1}\right]_{T,P,n_2}+\phi_2\chi+n_1\chi\left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}$$

$$\left[\frac{\partial(\ln\phi_1)}{\partial n_1}\right]_{T,P,n_2}=\frac{\phi_2}{n_1} \qquad \left[\frac{\partial(\ln\phi_2)}{\partial n_1}\right]_{T,P,n_2}=-\frac{1}{n_1+xn_2} \qquad \left[\frac{\partial(\phi_2)}{\partial n_1}\right]_{T,P,n_2}=-\frac{\phi_2}{n_1+xn_2}$$

$$\frac{\mu_1-\mu_1^0}{RT}=\cancel{n_1}\left(\frac{\phi_2}{\cancel{n_1}}\right)+\ln\phi_1-\frac{n_2}{n_1+xn_2}+\phi_2\chi-\frac{n_1\chi\phi_2}{n_1+xn_2}$$

$$\frac{\mu_1-\mu_1^0}{RT}=\phi_2+\ln\phi_1-\frac{\phi_2}{x}+\phi_2\chi-\phi_1\chi\phi_2=\ln\phi_1+\phi_2\left(1-\frac{1}{x}\right)+\phi_2\chi(1-\phi_1)$$

$$\boxed{\mu_1-\mu_1^0=RT\left[\ln\phi_1+\phi_2\left(1-\frac{1}{x}\right)+\chi\phi_2^2\right]}$$

So, next if we consider again the complete expression we have three partial derivative terms in this expression this as well as this one. And we have already come up with the expression simplified expression for all of these and the corresponding simplified expression for this one is here for this term here this expression and for the last partial derivative we have this expression here. So, if you substitute all of these in the original equation, this equation if you substitute all these three terms; we get this equation here and again we will have we will need to simplify a bit.

So, from this equation which is obtained by substitution if we simplify so let us go again term by term. So, this term of course, becomes just phi 2 because n 1 n 1 these will cancel, l n phi 1 let us leave it as it is this term here. This actually this term becomes phi 2 by x, because if you look at this term here this is n 2 by n 1 plus x n 2 and we know that phi 2 is x times n 2 by n 1 plus x n 2. So, this term can simply be represented as phi 2 by x 4th term again we will we are leaving as it is. And this last term here this ratio in this term, this n 1 by n 1 plus x n 2 we know that this ratio is just a definition of phi 1. So, last term becomes phi 1 times chi parameter times phi 2.

So, in the next step we can combine these two terms because phi 2 is common. So, these 2 by combining become phi it becomes phi 2 1 minus 1 by x 1 here. This l n phi 1 is the l n phi 1 that we have here and the last term again from these two terms this phi 2 chi can be taken common outside. So, we get 1 minus phi 1 this one here. Now this 1 minus phi

1 it is a binary mixture, so, 1 minus phi 1 will be simply be phi 2. So, the final expression where this 1 minus phi 1 this is nothing but phi 2 so, based on that the final expression that we get for mu 1 minus mu 1 naught is R T l n phi 1 plus phi 2 times 1 minus 1 by x plus chi times phi 2 square.

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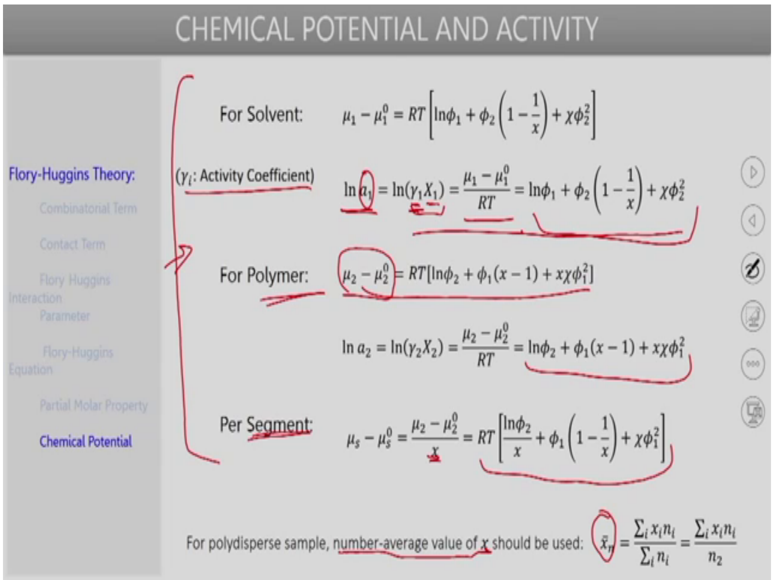

CHEMICAL POTENTIAL AND ACTIVITY

Flory-Huggins Theory:

Combinatorial Term

Contact Term

Flory Huggins Interaction Parameter

Flory-Huggins Equation

Partial Molar Property

Chemical Potential

For Solvent: $\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$

(γ_i: Activity Coefficient) $\ln a_1 = \ln(\gamma_1 X_1) = \frac{\mu_1 - \mu_1^0}{RT} = \ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2$

For Polymer: $\mu_2 - \mu_2^0 = RT[\ln\phi_2 + \phi_1(x-1) + x\chi\phi_1^2]$

$\ln a_2 = \ln(\gamma_2 X_2) = \frac{\mu_2 - \mu_2^0}{RT} = \ln\phi_2 + \phi_1(x-1) + x\chi\phi_1^2$

Per Segment: $\mu_s - \mu_s^0 = \frac{\mu_2 - \mu_2^0}{x} = RT\left[\frac{\ln\phi_2}{x} + \phi_1\left(1 - \frac{1}{x}\right) + \chi\phi_1^2\right]$

For polydisperse sample, number-average value of x should be used: $\bar{x}_n = \frac{\sum_i x_i n_i}{\sum_i n_i} = \frac{\sum_i x_i n_i}{n_2}$

So, for that is the expression that we have developed for the solvent using Flory Huggins against theory or Flory Huggins equation. And we know that this chemical potential difference is related to the activity. So, this l n a1 we know is just given by mu1 minus mu1 naught by R T; so, the l n of the activity of solvent that will be given by this expression her.

Now the activity of any component a1 can also be represented as product of it is mole fraction X1 and what is called the activity coefficient gamma 1. So, this gamma i these are referred to activity coefficient and these are basically quantities which connect the activity to the mole fraction. So, any activity a i is simply gamma i times x i. So, we see that both the activity as well as activity coefficients can be obtained from this whole expression here for the solvent. Similarly we can do a similar kind of a derivation for the polymer as well which we have not shown but doing that similar kind of derivation following similar steps one can get for the polymer this expression.

And again the activity and activity coefficient can be obtained from the chemical potential difference and that comes out to be what shown here. And if one wishes to just consider the chemical potential or chemical potential on per segment basis. So, this is for entire polymer molecules if you are considering let us say chemical potential per segment, then we can just consider this and divide that by the number of segments x per molecule.

So, that will give us an expression like this, on a per segment basis. So, one last point to discuss here before concluding is that all the expressions that we have here it is fine, if you have a mono dispersed polymer sample. So, if we have polymers where all the chains of the same length have the same number of segments for that all these expressions are fine, but usually we will have poly dispersed samples. So, for poly dispersed samples there is not much modification that needs to be done in these equations. The only thing is that the number of segments x poly disperse samples where the chain lengths multiple different chain lengths of polymers are present. So, for such samples the number average value of this number of segments x has to be taken ok.

So, this number average x let us represent that by x n bar that is simply defined as sigma x i n i by sigma n i where i cycles or i is the index which runs through over all the different sizes of polymer chains that are present in a poly dispersed sample ok. So, so if that is the case then sigma n i in the denominator that we have here that sigma n i is nothing, but just n 2. So, the summation of all the polymers numbers of polymer chains of different means that some all done here we do not have number of polymer chains here we have the number of moles.

But, all the number of moles, that summation will simply be equal to the total number of moles of the polymer present in the solution ok. So, we see that for a poly disperse sample wherever the number of segment x appears in any equation. Whereas the definition of volume fraction or the Flory Huggins equation for Gibbs energy change of mixing or for chemical potential or activity everywhere if we replace this x by it is number average value. Then we can apply the same equations for a poly dispersed samples as well whether polymer chain lengths can be different.

So, we will conclude today’s lecture here. So, what we have discussed in the last couple of lectures basically is a description of polymer solutions using a lattice based theory and the theory is referred to as a Flory Huggins theory. So, using that we developed expressions for combinatorial entropy change of mixing as well as the Gibbs energy change of mixing, because of the presence of interactions, we combined these two to get the overall Flory Huggins equations.

In that Flory Huggins equation we have applied to calculate the chemical potential and activity of a solvent and polymer in the solution. So, in the next lecture we will continue our discussion of thermodynamics of polymer solutions. We will look at the phase behavior of polymer solutions as well as the solubility of polymers in different solvents. So, what kind of parameters can be defined to quantify or determine how soluble a given polymer is in a certain solvent?

So, these kind of discussions we will carry forward in the next lecture.