Polymer Physics

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Lecture - 04
Thermodynamics of Polymer Solutions

So, in the last couple of lectures we have been discussing the conformation of isolated polymer chains primarily, we have looked at the different models for ideal polymer chains describing the conformation end to end distance and other dimensional properties of a such chains. We also, towards the end of the previous lecture briefly discussed the behavior of real polymer chains in solutions.

So, in today's lecture we will be carrying forward our discussion of polymer solutions further and today we will specifically focus on the study of Thermodynamics of Polymer Solutions. So, studying the thermodynamic behavior of polymer solutions is important, because it can help in the prediction of phase behavior of polymer solutions. A polymer solutions are widely encountered in many applications and it is a, the prediction of phase behavior is important in many applications as well.

Further, knowledge of thermodynamics of polymer solution can actually help in a establishing or determining whether given polymer is soluble in a given solvent or to what degree are given polymer dissolves in a solvent. Apart from that miscibility in polymer blends is also something where the studying the thermodynamics of polymer solutions in blends is important. So, let us look at the content of today's lecture what we will be going through in the present lecture.

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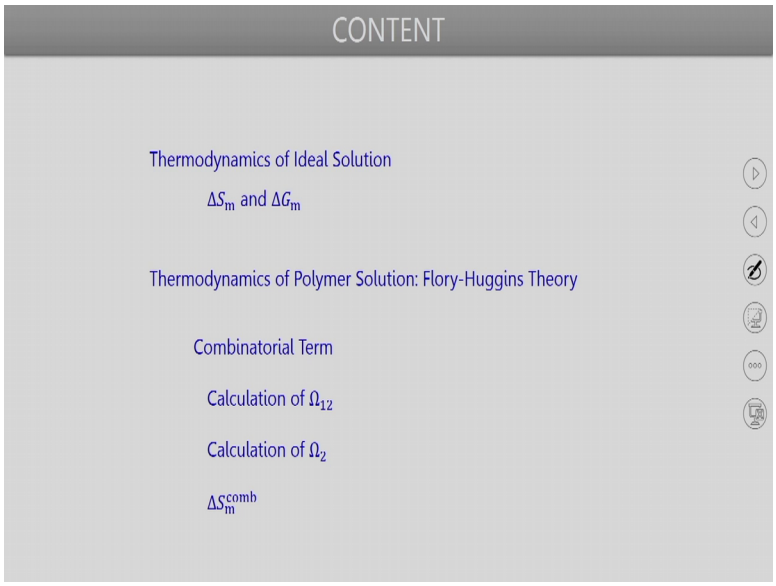

So, we will actually begin by a discussion of thermodynamics of ideal solutions. So, before we move on to studying the thermodynamic behavior of real solutions and theory describing that, we will first start off by talking about the thermodynamics of ideal solutions. And specifically we will look at the how the expressions for entropy change of mixing or Gibbs energy change of mixing can be obtained. Then we will move on to the study of thermodynamics of polymer solutions and there we will focus on a particular theory which came about in the early 1940s.

But, it is the beauty of this theory is that it is a relatively simple theory, but it is still able to capture many of the qualitative features the displayed by polymer solutions. So, we will for study this theory which is known as Flory Huggins theory. So, we will study the thermodynamic behavior of polymer solutions within the framework of this Flory Huggins theory.

And in this lecture we will only partly be covering this theory and in the next lecture we will we will complete the discussion on this theory. So, in today's lecture we will specifically focus on using the Flory Huggins theory to determine what is called a combinatorial term and calculation of certain quantities, as well as calculation of a particular component of the entropy change of mixing. So, we have a few symbols here which might not be very clear right now, but by the time this lectures I hope that all the symbols and the meanings will be clear.

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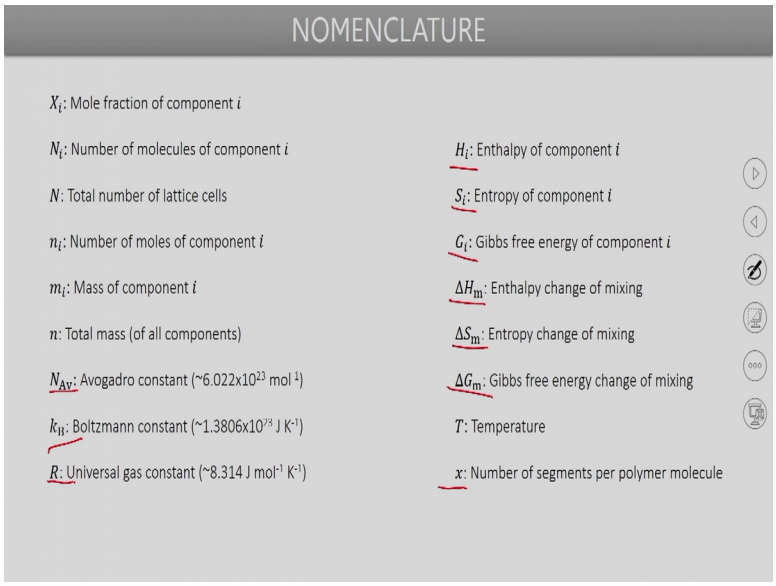

So, before we move on let us just briefly look at the nomenclature that is relevant for today's lecture. So many of these symbols we have already discussed in the very first lecture on in introduction to polymers, there is some new symbols specifically symbols related to a thermodynamic quantities. So, symbol for enthalpy the standard symbol is h; so H i will represent of a particular component i; similarly, S i for entropy of i, G i for the Gibbs free energy of component i in any mixture.

Further we are talking polymer solutions which are actually mixtures. So, we will be focusing on quantities like enthalpy change of mixing which will be represented by delta H m delta S m will represent the entropy change of mixing. And delta G m will represent the Gibbs energy free energy change of mixing. T of course, will stand for temperature. This symbol x will be using this symbol to denote the number of segments in a given polymer chain or polymer molecule.

So, again when we discuss the Flory Huggins theory the what is meant by a segment of a polymer molecule that will become clear. Apart from that the Avogadro constant Boltzmann constant, Universal gas constant these are the standard constant that we will come across during our discussion today.

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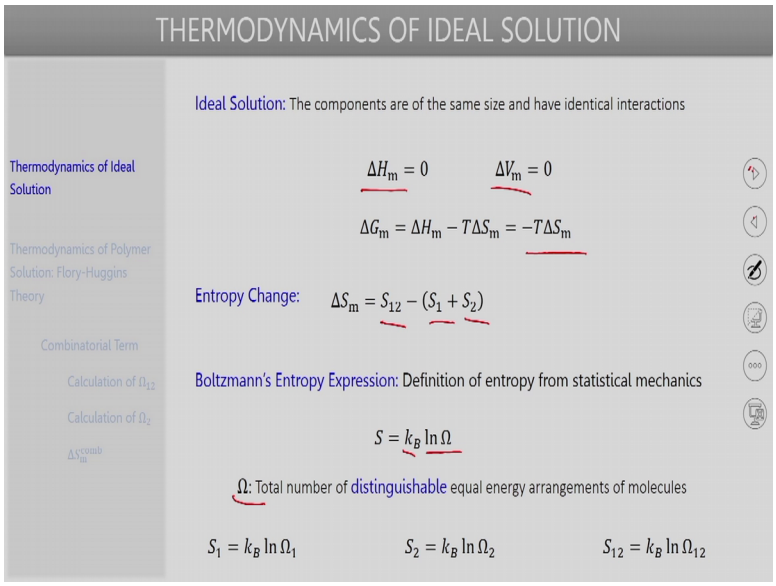

So, let us begin. Before moving on to studying the behavior of polymer solutions let us begin by the simplest case which is that of an ideal solution. So, let us see how one can basically derive the basic equations for change in entropy and Gibbs free energy change of mixing for ideal solutions. So an ideal solution; and the definition of ideal solution can be a solution where the components being mixed are or of the same size; pretty much the same size and the interactions are also almost identical.

So, what we mean by identical interactions is that the interaction. Let us consider for example, a binary solution or a binary mixture where we have two components. Let us say the component 1 is the solvent component, two is the solute and then we mix the two to form the solution. Then in an ideal solution the interaction between molecules of type one will be similar to the interactions between molecules of type b or type 2. And the cross interactions between molecule of type 1 and molecule of type 2 that also will be similar to the like interactions between 1 1 or 2 2 molecules. So, all the interactions will have similar strength. So, an ideal solution basically again is where the interactions are similar and sizes are also similar.

So, from thermodynamic point of view: an ideal solution is defined by a solution whose formation actually does not lead to a change in change in enthalpy and a change in volume as well. So, both the enthalpy change of mixing and the volume change of mixing denoted by delta V m here. So, both of these quantities are actually 0 for an ideal

solution. So, since the sizes are identical when the components are mixed then sizes being identical and the there being no difference in interactions, their volume also does not change. And since the interactions are similar the enthalpy also does not change upon mixing.

So, the definition of Gibbs energy change of mixing is just delta H of mixing minus T times delta S of mixing that is the standard definition an of any Gibbs energy change or Gibbs free energy change. So, for ideal solution since the since the enthalpy change of mixing is 0. The Gibbs energy change can simply be expressed in terms of the entropy change of mixing multiplied by minus T. So now, this Gibbs free energy change of mixing is an important quantity and the thermodynamics of ideal solution as well as polymer solution in both the cases what we will try to do is come up with an expression for this Gibbs free energy change of mixing. Because, once we have an expression for this many other quantities like the chemical potential or the activity coefficients such quantities can be determined starting from here. So, it is an important quantity and our aim here is to establish relations for the Gibbs free energy change of mixing.

So, since for an ideal solution Gibbs free energy change of mixing is directly related to the entropy change of mixing. Here what we will do is first try to establish an expression for the entropy change of mixing. So, entropy change of mixing is basically defined as the change in entropy due to the formation of the mixture. So, for an ideal solution although the enthalpy change of mixing volume change of mixing are 0 the entropy change of mixing as we will see is not actually 0.

So, entropy change of mixing is defined as the difference between the entropy of the mixture that is formed and the respective entropies of the pure species 1 and 2 which we are mixed to form the solution. So, before we go ahead what the for today's discussion what we need is a what is called a statistical mechanical definition of entropy. So, this definition of entropy is provided by Boltzmann and that is why this expression in the formula for entropy is refer to as the Boltzmann entropy formula.

So, a what this expression states is that the entropy of a collection of molecules is basically Boltzmann constant multiplied by the natural log of a quantity omega. And this omega is nothing but the different number of distinguishable equal energy states or equal energy arrangements that are possible for this given collection of molecules. So, if we

have a set of molecules or collection of molecules the number of different ways in which we can arrange these molecules, with each arrangement being distinguishable from the other, but having the same energy; so now the number of such different states or arrangements that is referred to as this quantity omega.

So this, with this Boltzmann entropy expression now what we will do is write down this the entropy of the individual components 1 and 2 as well as the entropy of the mixture in terms of this Boltzmann entropy formula. So, the S 1 will be just k B times l n omega 1, S 2 will be k B times l n omega 2, and S 12 will be k B times l n omega 12. Where, the omegas are again the respective distinguishable arrangements that are possible in the different cases that we have here, for the pure components and the mixture.

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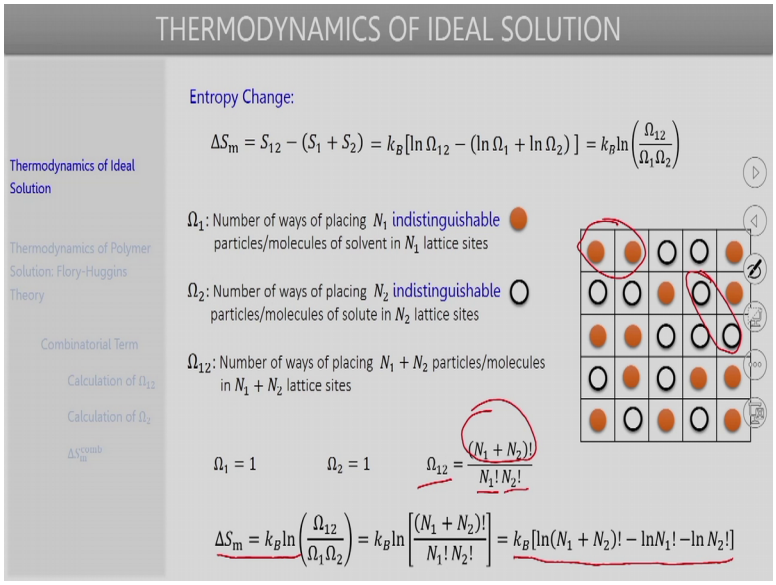

So, again the formula for entropy changes S 12 minus S 1 plus S 2. So, if we substitute the expressions for an these entropy is using the Boltzmann formula, then we get the following expression which again can be simplified to get an expression like this: k B multiplied by natural log of the ratio of omega 12 by omega 1 multiplied by omega 2. So, with this expression in place now all we need to do is come up with expressions for these three quantities: omega 1 omega 2 and omega 12. So, if we have expression for these three quantities those can be substituted here and one can get a expression for the entropy change of mixing for ideal solution.

So, to do that let us first consider a model for this ideal solution behavior that we are discussing. So, the model that we will be using for further derivation basically is what is called a Lattice model. And here what is assumed is that for a whether its pure component or a mixture all the molecules basically occupy distinct sites on a on a lattice. So, for such a kind of a model omega 1 basically will be the number of different ways in which N 1 indistinguishable particles from molecules of the solvent can be placed on N 1 lattice sites or lattice cells. Similarly omega 2 will be the number of ways in which the N 2 indistinguishable molecules of the solute can be placed on the N 2 different lattice sites.

So, in the our discussion we will represent the solvent molecules by this solid or in circle and the solute molecules by this empty black circle. And we say indistinguishable in both the cases that is the word which has been highlighted here and. So, we say that both in both the cases and molecules are indistinguishable, because the molecules in both the cases correspond to those of pure components. So, for pure components all the different molecules will pretty much be indistinguishable from each other.

So, in both these cases the N 1 molecules in the first case of the solvent and the N 2 molecules in the second case for the solute they are indistinguishable. Now if we mix a N 1 molecules of the solvent N 2 molecules of the solute then will form a mixture containing N 1 plus N 2 molecules. And the lattice model that we are employing or will be employing basically requires that this N 1 plus N 2 molecules of the mixture of the solution; I will placed on N 1 plus N 2 lattice cells or lattice sites.

So, representation of a typical lattice of the mixture or solution that is formed, that is shown here. So, here we see that the molecules of the solvent that is solid or in circles and the molecules are solute are kind of randomly distributed over the different lattice cells. And for simplicity we are showing a two dimensional lattice in reality of course as lattice will be three dimensional. So, here we are showing as square lattice the actual lattice can be cubic in three dimensions or it can have any other shape as well.

So now, that we have defined our lattice in this way, the two things that we can directly notice is that the omega 1 and omega 2 will be one each. The reason for that is that omega 1 omega 2 correspond to the number of distinguishable arrangements of the pure solvent molecules and the pure solute molecules, but all the pure solvent molecules are

identical similarly all this a pure solute molecules are also identical. So, if we want to place N 1 identical solvent molecules on N 1 cells of any kind of lattice then there is only one way to do it. If we try to let say swap two different molecules here, then we will not end up with an arrangement that is distinguishable from the previous one.

So, essentially there is only one way to place a N 1 identical molecules of solvent on N 1 cells of a lattice. Similarly for solute also you have N 2 identical molecules or solute so on a lattice containing N 2 cells there is only one way in which they can be placed. So, again the number of arrangement is one and. So, omega 1 and omega 2 are both unity.

But for the case of mixture: the case of mixture actually the situation is different, because now the all the particles are not actually identical; in the solution of the mixture that here we have both solvent molecules, and the solute molecules present as shown in the representative lattice here. And the there are actually because there are two different types of molecules now there are many possible ways of arranging these molecules on this lattice cells. So, the omega 12 in this case is actually not 1, but it is given by this kind of an expression.

So, omega 12 for this case is given by N 1 plus N 2 factorial divided by N 1 factorial times N 2 factorial. So, the numerator here in this expression, the numerator here N 1 plus N 2 factorial basically provides a different number of ways in which one can place N 1 plus N 2 of these molecules on N 1 pus N 2 number of cells in our lattice.

But if we if we consider only the numerator we are actually over counting the number of distinguishable arrangements, because even for a mixture of or a binary mixture placed on the lattice here there are many arrangements. Out of the N 1 plus N 2 factorial arrangements that we have counted there many arrangements which will actually be duplications or in other sense which will be indistinguishable from each other.

So, this the denominator contains N 1 factorial and N 2 factorial these two terms; these two terms basically take care of the fact that when if we consider just N 1 plus N 2 factorial arrangements we are over counting and we are actually counting many arrangements which are actually identical. So, that scaled by these two quantities and we get the overall number of arrangements in the case of mixture.

So, to further illustrate this point let us consider again the lattice that shown here. And here, let us say if we swap any two molecules of the same type. So, let us say we swaped two molecules of the solvent these two. So, after swapping we see that the arrangement of the overall lattice remains unchanged. So, because we have N 1 identical molecules of the solvent on the lattice these N 1 factorial terms come into play here, because these N 1 solvent molecules their internal swapping and rearrangement basically will not lead to any change in the overall arrangements

So this, the N 1 plus N 2 factorial this term has to be divided by N 1 factorial. Similarly if we consider any two solute molecules and let us say we swap them, so in this case we have swap these two molecules. And again we see that swapping any two randomly chosen solute molecules also does not create any new arrangement. So, to account for such identical again cases of resulting from the swapping of different solute molecules this N 2 factorial term also has to be considered here.

So, overall the omega 12 term is represented by a ratio of N 1 plus N 2 factorial and N 1 factorial times N 2 factorial. So, if we now substitute all the expressions for omega 1 to omega 1 and omega 2 in the expression for entropy change of mixing then we end up with in this expression here. So, we see that the expression that we have obtained here contains factorials of different terms.

So, next what we will see is that in the case of N 1 plus N 2 factorial or N 1 factorial n to factorial these terms there is an approximation that can be made provided the numbers N 1 and N 2 are quite large. So, this approximation is referred to a Stirling approximation, its valid for cases where N is large. So, what it states is that the natural log of N factorial is approximately equal to N times ln N minus N provided N is large.

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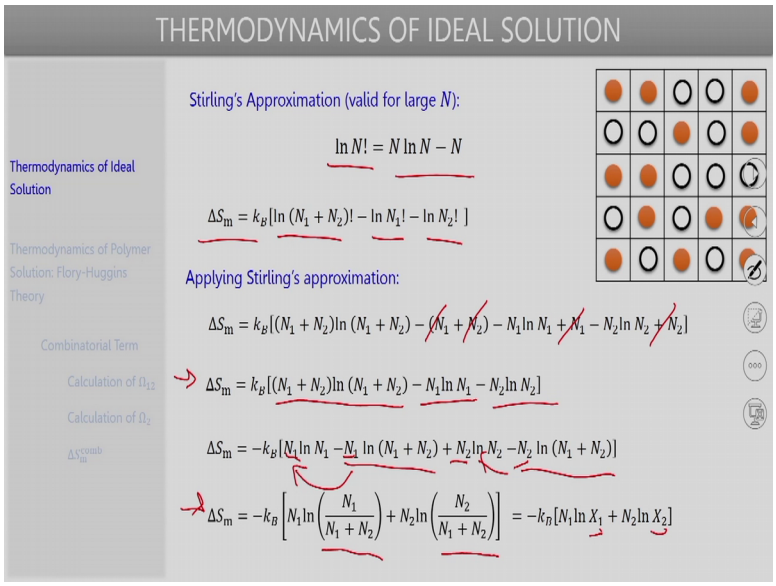

So, in a typical scenario for a given solution when we are mixing two substances; the number of molecules usually will be very large. So, N 1 N 2 are large quantities so typically the Stirling's approximation will be valid. So now, let us apply the stirlings approximation to the entropy change of mixing that we have derived just now. So, we can apply Stirling's approximation to all these terms.

So, we have three terms containing natural log of factorials. And in all these terms the quantities N 1 N 2 and N 1 plus N 2 are quite large, so a sterling approximation can be applied to all of them, and if we do that then the expression for the entropy change of mixing gets simplified like this. And now here we see that this minus N 1 term will cancel this plus N 1 here, this plus N 2 will cancel the this minus N 2 again will cancel this plus N 2 here. So, canceling these terms and again simplifying and rearranging. In the next step we can say that the entropy change of mixing can be represented by this equation here.

Now, this term here again we can split into two terms say its N 1 plus N 2 multiplied by ln N 1 plus N 2. So, we can write it as N 1 ln N 1 plus N 2 plus N 2 ln N 1 plus N 2. And we can split this into two terms and then combine respective terms with the these two terms. So, splitting in splitting can be done in this fashion. So, we have one term here and term here, and this term will be combined with this and similarly this term we can combine with this, because in both these cases N 1 is common here in both these terms N

2 is common. So, we combine and finally end up with this kind of an expression for the entropy change of mixing. So, we see that inside the log we get these ratio N 1 by N 1 plus N 2 and N 2 by N 1 plus N 2. And as we know these ratios basically are nothing but the respective mole fractions.

So, these ratios can be expressed as the respective mole fraction fractions X 1 and X 2. And the expression for entropy change of mixing as you see has simplified to negative a Boltzmann constant multiplied by N 1 ln X 1 plus N 2 ln X 2.

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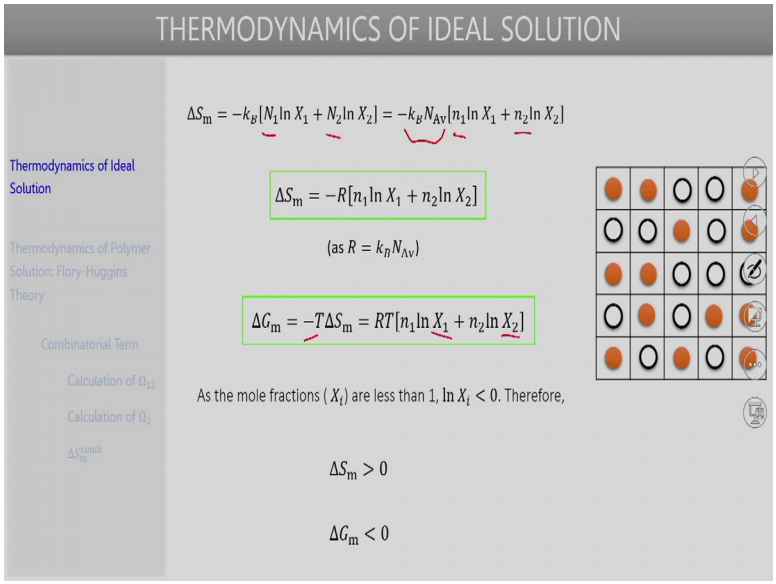

And, now if we want to change from the number of molecules N 1 and N 2 to the number of moles small n 1 and small n 2. Then the factor of Avogadro number will appear. So, the number of molecules N 1 will just be equal to the Avogadro number multiplied by number of moles N 1 small n 1. Similarly the number of molecules capital N 2 will be equal to Avogadro number times number of moles small n 2. So,. So,.

So, now, the these two constants Boltzmann constant Avogadro constant they can be combined together and their product is nothing but the universal gas constant. So finally, upon simplification and combining constants the expression for the entropy change of mixing that we get is that delta S of mixing is equal to minus R number of moles n 1 times ln X 1 plus number of moles of solute n 2 times ln X 2.

So, this is the entropy change of mixing for an ideal solution and if we just multiply this entropy change of mixing by minus T we will get the Gibbs energy change of mixing the expression for that which is nothing but RT and whenever the next one plus n 2 and X 2. So, this is a standard thermodynamic result which one can obtain from classical thermodynamics as well, but here what we have used is to use the statistical definition of entropy, and the concept of a lattice model to perform this derivation because the same will be used in the case of polymer solution as well.

So, we see that this mole fractions X 1 and X 2 will of course, be less than 1. So, since these are less than one their natural logs ln of X 1 ln X 2 both will be negative or less than 0. So, what that implies is that the, entropy change of mixing will always be positive for ideal solutions and the Gibbs energy change of mixing will always be negative for ideal solutions. So, with that introduction to ideal solution thermodynamics of ideal solution behavior let us now move on to the case of polymer solutions and see how the scenario is different there.

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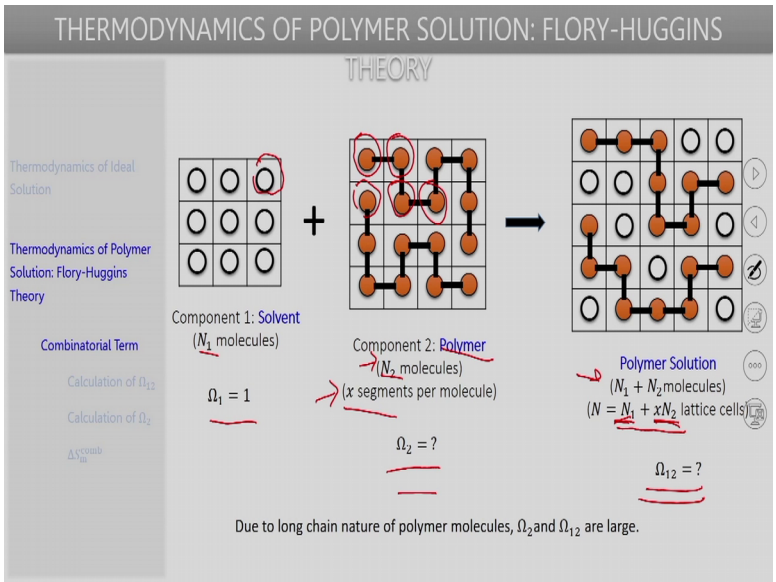

So, let us consider the thermodynamics of polymer solutions. So, in this case let us say that we have again; as we did for the case of ideal solutions we will adopt what is called a lattice model, because the theory that we will be discussing one for polymer solution which is the Flory Huggins theory that is based on the lattice model of this polymer solution.

So, here let us first consider component 1 which is a solvent and let us say we have N 1 molecules of this pure solvent, and that occupies a certain lattice. So, each molecule of the solvent occupy individual cells in the 2D square lattice; that we have shown here, but as mentioned in the actual case the will have a 3D lattice. And here we have shown a square lattice where was 3D version will be a cubic lattice, but Flory Huggins theory is actually not just limited to consideration of; not just limited to cubic lattice other kinds of lattice geometries also are fine.

So, let us say that component solvent molecules N 1 molecules occupy N 1 lattice cells. And next let us say that we add polymer molecules to this solvent to form our solution. So, for the polymer molecules; the polymer molecules here are represented by these orange circles connected through these black bars. Individual units of the polymer molecules are connected to each other through the bonds. So, the component two which is the solute in our case is the polymer and that also is represented on a lattice in this Flory Huggins against theory.

So, as a representation here we have shown only two polymer molecules, but let us say for the general case for the development of this theory we have a total of N 2 number of polymer molecules. So, one polymer molecules here is basically one chain of polymer, so N 2 polymer molecules means N 2 chains of polymer. And another detail is that, for each polymer molecule or for each polymer chain we have x segments. So, the orange circles that we have here these basically are referred to as segments in Flory Huggins theory.

So, for in this representative example we have a two polymer chains each having eight segments, but for the general case for the development of the theory we will consider N 2 polymer molecules and with each polymer molecule having x number of segments. So, if we combine the polymer with the solvent the what the theory assumes is that the solution that forms is also, can also be described on a lattice. And the nature of the type of the lattice for the solvent molecules and the pure polymer molecules as well as a polymer solution, the type of lattice is identical or the same for all the three cases.

So, that is one of the assumptions of this Flory Huggins theory, which need not be very realistic, because strictly speaking the molecular arrangement in polymer pure polymer or impure solvent need not follow a similar kind of lattice structure. So, in any case that

is one of the assumptions. And so mixing the polymer N 2 molecules of polymers and N 1 molecules of the solvent gives us our polymer solution having N 1 plus N 2 molecules. So, in the case of solvent we have N 1 molecules occupying N 1 lattice cells. In the case of polymer we have N 2 molecules occupying x times N 2 lattice cells, because each molecule basically contains x segments. In the case of a polymer each segment occupies one lattice cell. So, we have x times N 2 cells which are being occupied by x times N 2 polymer segments.

So, another assumption this Flory Huggins theory is that the volume of a given polymer segment and the volume of a solvent molecule they are identical. So, volume of polymer segment and a volume of a solvent molecules shown here these are assumed to be same in this Flory Huggins theory. So, when we combine them the polymer solution that forms it can will contain N 1 molecules of solvent N 2 molecules of the polymer. But since, each polymer molecule occupies x times or x number of cells because it has x number of segments, so a total number of lattice cells in the polymer solution that sum. So, the total number of lattice cells that will be occupied is N 1 plus x N 2; where N 1 lattices are occupied by the solvent molecules and x times N 2 lattice cells are occupied by the different polymer segments that we have.

So, with this kind of description will now proceed to find out how the thermodynamic properties or property changes can be obtained for such cases. So,. So, if we again go back to the quantities omega 1 omega 2 and omega 12. So, if we look at these quantities omega 12 as well. So, omega 1 is pure solvent where we have N 1 molecules placed on N 1 cells of a lattice. So, since all the molecules are identical there is only one way or one arrangement here, so omega 1 again is 1.

But in the case of polymer molecules, although all the polymer molecules again in this theory are also assume to be identical of the same length, but the but their connectivity actually leads to a situation where omega 2 actually is not unit its, it has will we have will have a value much higher than 1. So, all the polymer molecules are identical since the segments are connected in a given polymer chain that actually leads to the a possibility of multiple distinguishable arrangements, and omega 2 as we will see will be much larger than 1.

Similarly when we have polymer solution of course omega 12 will be much larger than 1. But, here again I mean apart from the fact that we have two different types of molecules again the polymer chains are also this being connected internally, they can adopt different confirmations and that will further add to the different number of distinguishable arrangements. So, both omega 2 and omega 12 need to be calculated and that is the essence of this Flory Huggins theory how the approach used to calculate these two quantities and from there of course the entropy change of mixing can be calculated.

So, as we discussed the long chain nature of polymer molecule as well as the fact that the segments are connected to each other that leads to multiple different conformational possibilities for the polymers. And hence the omega 2 and omega 12 are large.

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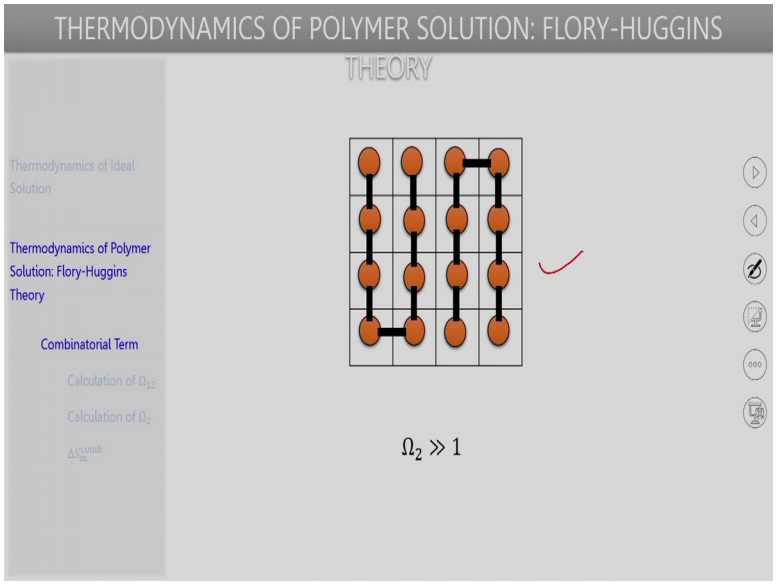

So, again let us just consider a illustrative example for the same thing. So, let us focus just at the pure polymer case, the lattice containing pure polymer molecules. So, in this representative case this, what is shown here is one possible confirmation that the two polymer molecules can have. Similarly the two polymer molecules can also adopt different conformation that is shown here or the conformation adopted can change to something like this.

So, these are three just three sample or representative sample confirmations of the polymer that is shown there are many other confirmations that are possible. And, due to the fact that multiple confirmations can be adopted by the polymer chains the number of

distinguishable arrangements of these chains on the lattice is also quite large. So, also that is why omega 2 will be much larger than 1. And similarly for the polymer solution also similar case is there. So, omega 12 also will be much larger than 1.

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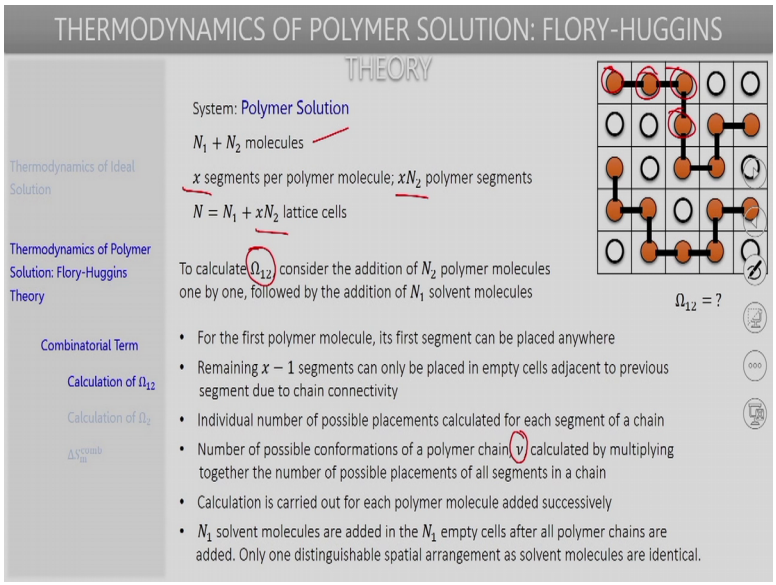

So before we go ahead, in today's lecture we will focus on only a one part of the Flory Huggins theory and that part deals with the case where we are considering the mixing of the solvent with the polymer as a thermal mixing. So, a thermal mixing is a mixing where the enthalpy change of mixing is 0. So, what we are assuming is that in a thermal mixing the interactions again are similar to each other or the interactions the difference in interactions between polymer-solvent and polymer-polymer or solvent-solvent; these different interactions are not that important and ultimately the enthalpy of mixing is 0.

So, this is something that not, that is not very realistic, but to develop this theory as a starting point we will consider the case of a thermal mixing of our polymer solution, where the enthalpy changes even the complexity due to the interactions is not accounted for. But, what we will do is in the next lecture we will incorporate some other terms which account for the interaction present and take into the consideration the fact that enthalpy change of mixing actually is not 0.

So, in today's discussion all that we are doing is trying to come up with an expression for the entropy change of mixing from what is called a purely combinatorial perspective, we are not taking into consideration any difference in interactions. So, so the discussion

today is limited to the case of our assumption of a thermal mixing where the delta g of mixing is 0 in the next lecture we will relax our assumption and add extra terms to develop the complete theory.

So, let us look at the polymer solution as our system which again is a model where all the solvent molecules and polymer molecules are placed on a lattice. So, in this system we have as we discussed we have N 1 plus N 2 molecules, we have. For each polymer molecule x segments are there, so a total of x times N 2 polymer segments are there. So, these are the individual polymer segments and the total of x times N 2 polymer segments are there. Total number of lattice cells is N 1 plus x N 2. So, N 1 is number of molecules of solvent and x times N 2 is a number of molecules of polymers segment, and one cell is occupied either by a solvent molecule or by a polymer segment.

Now, our aim is to calculate an expression or develop an expression for omega 12. So, here will what we will do is to develop an expression; we will consider that the lattices initially empty and it is filled by first adding the polymer molecules to the lattice one by one, and then at the end adding all the solvent molecules to the remaining empty sites. So, as we are adding the polymer molecules one by one will also try to come up with an expression for the different possible arrangements that the polymer molecules can adopt and using that will try to come up with an expression for omega 12. So, in for this step by the addition of polymer molecules, let us say instead initially we consider lattice to be completely empty and we are trying to add the first polymer molecule to this lattice. So, again for each polymer molecule that that is being added the addition will be done segment by segment.

So, the first segment of the first polymer molecule when we try to add that the entire lattice is empty in the entire lattice is available for adding this first segment of first polymer molecule. So, if we have a N 1 plus x N 2 times a number of lattice cells available, so those many possible possibilities are there for placing the first segment of the first polymer molecule. Now the second next segment of this first polymer molecule that cannot be arbitrarily placed anywhere, because it has to be connected to the first segment that was placed on the lattice. So, due to the connectivity of polymer chain we see that already this some restriction.

So, the next segment can only be placed in one of the adjacent or neighboring cells of the first segment that has been placed. So, the after placing the first segment of this first polymer molecule the remaining x minus 1 segment, so to relax segments are there. So, the remaining x minus 1 segments, they can only be placed in empty cells which are adjacent to the previously added segments; because they have to be connected to the previously added segment, so for the chain connectivity to be there.

Next, for each segment of the chain the individual number of possible arrangements that are there that is counted or calculated. So, the individual number of possible placements for each segment is calculated. And for a polymer chain the number of possible confirmations that that can be there for a given polymer chain that will represented by represent by this symbol nu in our discussion and that is calculated was simply by multiplying together all the different possible placements of all the segments that we have considered for that chain.

So, just a continuous multiplication of the different possible placements or all this chain segments of a given chain, when they are multiplied together that will give us the number of possible confirmations that a given chain will adopt. And as the polymer molecules are added successively the different number of possible confirmations each polymer molecule that is being added; the how many confirmations it can adopt that is calculated.

And finally, when all the polymer molecules have been added and that the different possible arrangements are there they have been calculated the remaining empty cells will be N 1, and the remaining N 1 solvent molecules will be added to those N 1 cells. So, again the solvent molecules are indistinguishable. So, there is only one way to add the N 1 solvent molecules to the remaining empty N 1 cells of the lattice, so only one distinguishable. So, a spatial arrangement for this solvent molecule addition will be there, because all the solvent molecules are identical.

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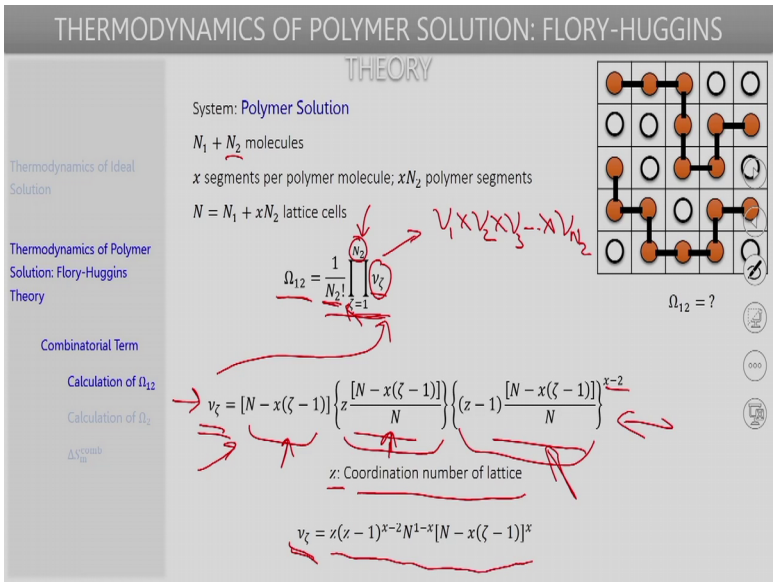

Next, let us try to calculate this quantity omega 12, that is our aim here; to calculate omega 12 as well as omega 2 and then to calculate the entropy change of mixing. So, this omega 12 based on our previous discussion if since we have a total of N 2 number of polymer chains, the omega 12 actually can be simply written in this form 1 by N 2 factorial. And this symbol here, this symbol here basically is the symbol for a continuous product. So, just like capital sigma is a symbol for summation this capital pi is symbols for continuous product, so what this means is that we are multiplying nu 1 with nu 2 with nu 3 and so on with nu N 2.

So, all these nu's which basically correspond to the different number of confirmations of the individual polymer chains. All these nu's are multiplied together in this term here and then it is divided by N 2 factorial, because at the end all the N 2 polymer molecules in themselves are identical. So, we are not considering the polymer molecules to have different length or in a different chemical identity all the polymer molecules have the same number of segments and they are identical. So, to account for the over counting due to the fact that polymer molecules themselves are identical this factor N 2 is used in a denominator here.

Next, let us focus on this quantity nu. So, in this expression, in this continuous product here that we have here this zeta here; this zeta that basically is a kind of an index for this product. So, zeta basically runs to all the different polymer chains that we have in our

system. So, zeta equal to 1 corresponds to the first polymer chain that is added zeta equal to 2 corresponds to a second polymer chain that we are adding to the lattice and so on all the way up to N 2, because we have N 2 number of polymer chains. So, this will run up to N 2. Now the expression for nu zeta that is important, because once we have that expression that week that we can back substitute here and then try to simplify and come up in the expression for omega.

So, for expression for zeta or nu zeta; basically a different number of confirmations possible for the chain number zeta that is being added to our lattice. So, that is given by the expression that we have shown here, we here at this quantity z is called the coordination number of the lattice. So, whatever lattice we are considering we are showing us planar square lattice, but it is irrespective of the type of lattice the only detail of the lattice that is important that comes into the theory at least at this point is a coordination number of the lattice. So, even if there we have some other lattice the if we know the coordination number of the lattice then we can just introduce that quantity as z in these expressions. And we will see that later on the in the expression for the entropy change of mixing this coordination number does not feature at all. So, in the final expression becomes independent of the type of lattice being considered.

So here, actually we have three terms and each term has some physical meaning. So, the first term basically corresponds to the number of ways in which the first segment that you are adding of this chain number zeta, that the number of in ways in which the first segment can be placed in the lattice; that is this term. This second term is corresponds to the number of ways in which; the second segment can be placed of this chain number zeta in the lattice. And this actually is a product of actually x minus 2 terms you see this power raised to the power x minus 2. So, they are x minus 2 terms here and these correspond to the remaining addition of the remaining x minus 2 segments of the chain number zeta.

So, we will not go into the detail of the these terms. The one thing to point out here is that in the derivation of this expression here an assumption is made in the Flory Huggins theory is called the mean field assumption. So, what that assumption states is that: when a given segment is added in a lattice then it is assumed that the previously added segments are homogeneous geneously distributed throughout their lattice. So, if a given in the polymer segment is being added though all the other segments that have already

been added to the lattice, they are assumed to be uniformly distributed across a lattice. That is the mean field a assumption or mean field approximation of Flory Huggins theory. So, using mean field approximation, actually this the second term in this third term can be written.

So, this mean field approximation which says that the segment distribution or polymer segments distribution is uniform throughout the polymer solution or the lattice that kind of a approximation is for a concentration in a concentrated solution that is a reasonable approximation, because you will have polymer, chains, and segments distributed almost throughout the solution. But for a dilute solution that approximation is severely limiting as we will notice or note later on. So, this nu zeta the number of confirmation of this zeta is chain that the expression that we have here this expression can be simplified and the final expression that we obtain is shown here.

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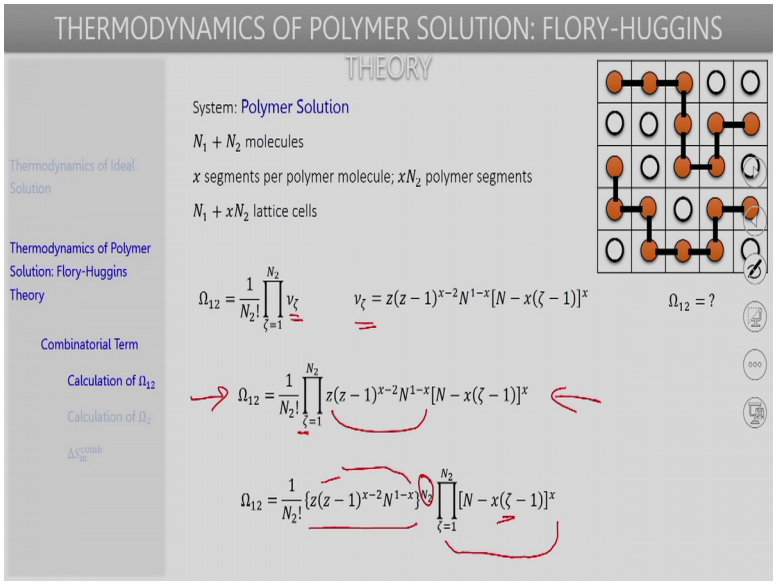

Next if we substitute the expression for nu zeta from the previous slide here. So, in the nu zeta that we had from the previous slide is a simplified version. We substitute that in the expression for omega 12 the resulting expression that we get is shown here. So, these expressions might seem a bit long, but we will see that later on after appropriate mathematical manipulations all the final expression that we will get will be relatively simple. Mathematically, it will be as simple as the expression that we get forgot was an ideal solution although the form will be slightly different.

So, now again from this expression here the these terms can be taken out, because these terms do not depend on the zeta over which the product is being taken. So, these terms can be taken outside and if we take their terms outside power of N 2 comes over all these terms, because this is a these terms are actually getting multiplied N 2 times if we expand this product. So, when we take them out this term will get raised to the power N 2 here. And this will remain inside the product, because we have a zeta containing term here.

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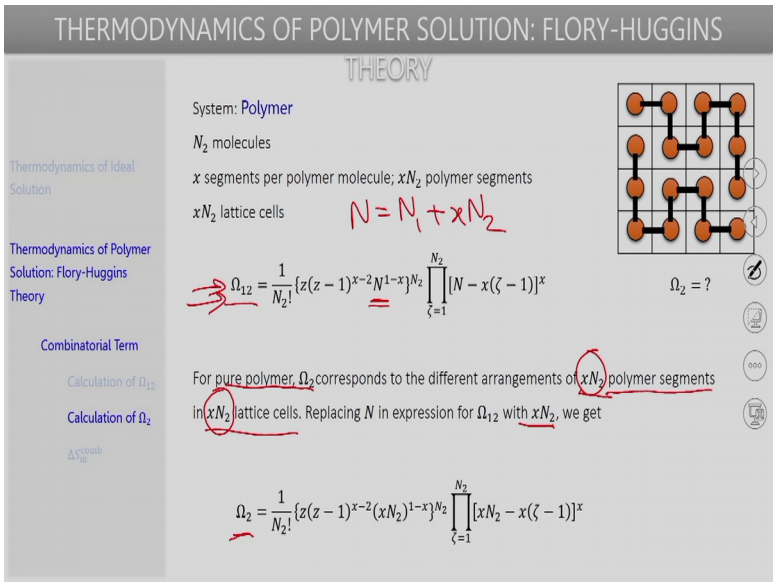

So, in any case said this is the expression that we get. And again now if we consider the case of pure polymer, so apart from omega 12 the whose expression we have obtained the expression for omega 2 that is the number of possible arrangements for the pure polymer chains on the lattice that is also something that we need to calculate, because that is its not trivial to find that out.

So but, since we have already obtained an expression for omega 12 get an expression for omega 2 which is that for a pure polymer that becomes simple, because the similar kind of a similar kind of a approach can be adopted as was done for this polymer solution case where the polymer molecules are being added one by one. And just once the polymer molecules are being added successively the different arrangements possible can be counted.

So, similar approach can be used the only difference here is that; now the total x N 2 polymer segments that we have they are getting added to only x N 2 lattice cells for the

case of pure polymer. In the case of polymer solution this x N 2 polymer segments will being added to N 1 plus x N 2 lattice cells, whereas now for pure polymer they are getting added to this x N 2 lattice cells. So, in the x this expression here just replacing this term N where this N is nothing but N 1 plus x N 2. So, if we replace this N by x N 2 then we can just obtain the an expression for omega 2. So, the expression for omega 2 that applies for a pure for the pure polymer is this.

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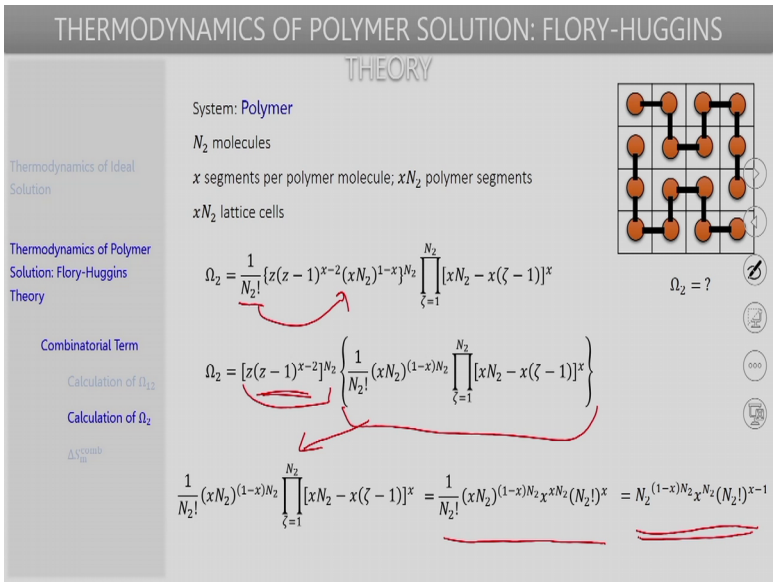

And, again in this expression we can make certain simplifications. So, if we start from that expression and we rearrange the terms a bit. So, we take these terms outside take this N 2 in here and this term this terms we have taken outside. So, we the bracketed term that we have created just by rearranging the some of the other terms. So, the bracketed term basically can be further simplified. So, the bracketed term is again shown here or written here. So, it can be simplified to this form ok. And again this is just simple mathematical manipulations over you can just work through it and verify that for this simplification will lead to this expression.

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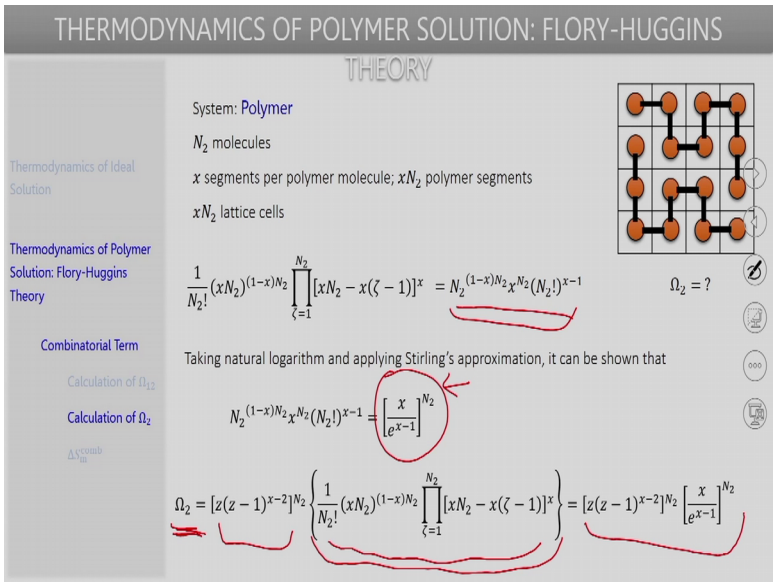

And the expression that we have obtained there, that expression which is shown here; that expression can again be further simplified if we take natural log apply sterlings approximation and do some many mathematical manipulations. So, it can be shown that this term here is equal to this quantity x by e to the power x minus 1 to the power whole to the power N 2.

So, now that we have simplified this term the omega 2 which was a product of this term as well as this bracketed term. So, this bracketed term we have simplified in this form. So finally, the expression for omega 2 becomes what is shown here. So, we get a relatively simple simpler expression now.

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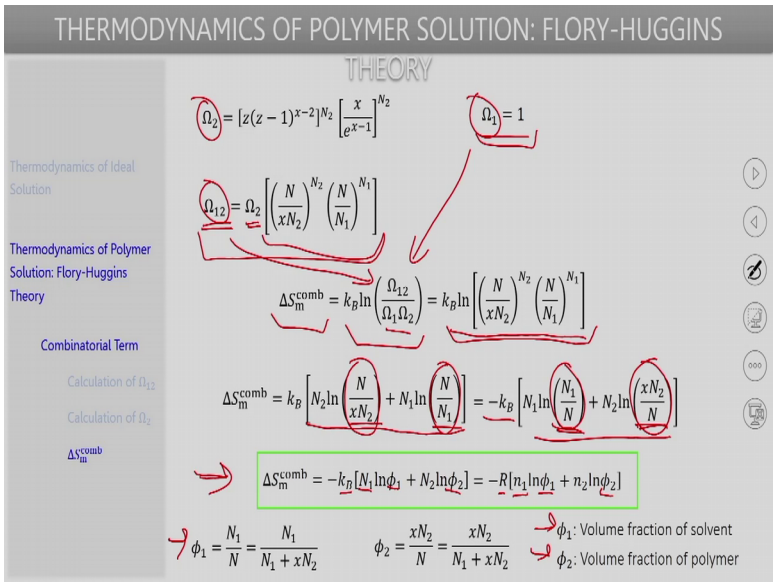

So, for omega 2 as we discussed we get simplified expression like this. Omega 12 we are we are not going to the detail mathematical manipulations here, but for omega 12 it can be shown again using some mathematical manipulations and application of again Stirling's approximation and so on. It can be shown that omega 12 is basically given by as can be given as a product of omega 2 and this bracketed quantity. Omega 1 which is the for the pure solvent that is that is again just one because for a pure solvent we have N 1 identical solvent molecules which have to be placed on N 1 lattice cells, so there is only one possible arrangement. So, omega 1 is just one.

So, now for the combinatorial entropy term; here the from the definition we have this delta S combinatorial S Boltzmann constant times natural log of this ratio and if, we substitute the expression for omega 12 as well as omega 2 n omega 1 from these expressions if you substitute all of these here. So, if you substitute all these three here then we end up with this equation for our combinatorial entropy change.

So,. So, if we again take the natural log then this is this expression that we have this can be further simplified as shown here. And again some just taking the reciprocal of these terms inside the natural log. So, we are inverting these terms. So, here you see it is N 1 by N and x N 2 by and instead of N by N 1 and N by x N 2. So, so if we invert these then basically a minus sign will come outside. So, the expression for delta S combinatorial can be written like this.

Now these two quantities, these this ratio as well as this ratio these ratios if we represent by phi 1 and phi 2 then the expression for combinatorial entropy change of mixing according to Flory Huggins theory will be given by this expression. And again if we wish to change from number of molecules to number of moles then the Boltzmann constant will change to the universal gas constant.

So, this is the expression for combinatorial entropy according to Flory Huggins theory. Here the phi 1 and phi 2 if you notice carefully the phi 1 and phi 2 which correspond to this ratio N 1 by N N x N 2 by N these two are basically the volume fraction of the solvent phi. So, phi 1 is the volume fraction of the solvent and phi 2 is the volume fraction of the polymer in the solution. So, phi 1 is defined as N 1 by N which is N 1 by N 1 plus x N 2 phi 2 is x N 2 by N. So, if we if you we recall the lattice model for our polymer solution there we have N 1 plus x N 2 total number of cells N 1 cells are occupied by solvent molecules.

So, the volume fraction of solvent in that kind of an arrangement will just be N 1 by N 1 plus x N 2. So, that is what this phi 1 is. Similarly for the polymer the polymer molecules actually occupy x times N 2 cells, because each we have N 2 polymer molecules and each polymer molecule occupies x number of cells because it contains x segments. So, there the volume fraction will simply be the number of cells occupied by total number of cells which is again x N 2 divided by N 1 plus x N 2. So, phi 1 and phi 2 as mentioned are the respective volume fraction of the solvent and the volume fraction of the solute or the polymer.

So, we will conclude or stop this lecture here, where we have developed an expression for the combinatorial entropy change of mixing which purely depends on the different ways in which the polymer chain can arrange itself for the different conformation the polymer chain can adopt leading to entropy change of mixing. Apart from this here in this discussion we have completely ignored any interactions or difference in interactions. We said that the for this part we are assuming a thermal mixing.

But, in the next lecture what we will do is extend this theory to incorporate the effect of different interaction between the polymer molecules and the solvent molecules. And after incorporation of that effect of interactions the final expression that will obtain for the

delta g or the Gibbs energy change of mixing that will be the that will give us the Flory Huggins equation for the Gibbs energy change of mixing.