Polymer Chemistry

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Lecture - 25
Polymer Solutions

Welcome back to this course on polymer chemistry. Till now what we have been learning for last several lectures is how to synthesize different polymers, how to make different polymers, we have learnt different types of polymerization by which we can make polymers. And we now theoretically know that what once we do a polymer synthesis, what are the different types of molecular weight and what are the different types of molecular weight distribution we can get from our previous learning from last few lectures.

Now, what we are going to learn in next few lectures is that how to characterize. Once you made this polymer of course we want to know that what we have made both in chemical term; that means what is the constitution? What is the chemical constitution? What is the structure microstructure of the polymer, and also most important is what is the molecular weight of the polymers which we made, and what are the as you know that polymers seldom have unique; all the polymers chains have same molecular weight. So, there will be always a molecular distribution associated with when we make a polymer. So, for the polymers which we already synthesized how what is the molecular weight distribution? Now for that, what we will begin today is to understand polymers in solution.

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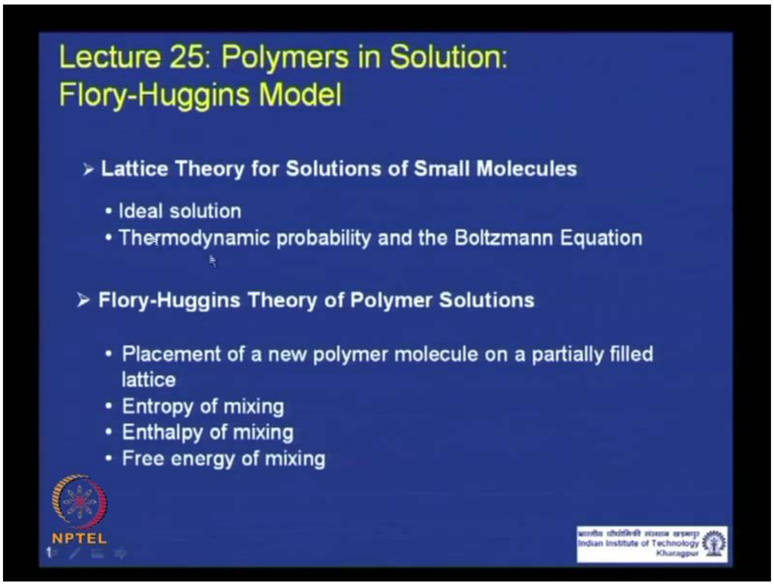

Lecture 25: Polymers in Solution: Flory-Huggins Model

- Lattice Theory for Solutions of Small Molecules
  - Ideal solution
  - Thermodynamic probability and the Boltzmann Equation
- Flory-Huggins Theory of Polymer Solutions
  - Placement of a new polymer molecule on a partially filled lattice
  - Entropy of mixing
  - Enthalpy of mixing
  - Free energy of mixing

And in today’s lecture, we are going to learn lattice theory of solutions for small molecules and then learn about ideal solutions, thermodynamic probability and distribution and the Boltzmann equation and then learn about polymer Huggins theory of polymer solutions; these are the sub topics which we will learn during this lecture.

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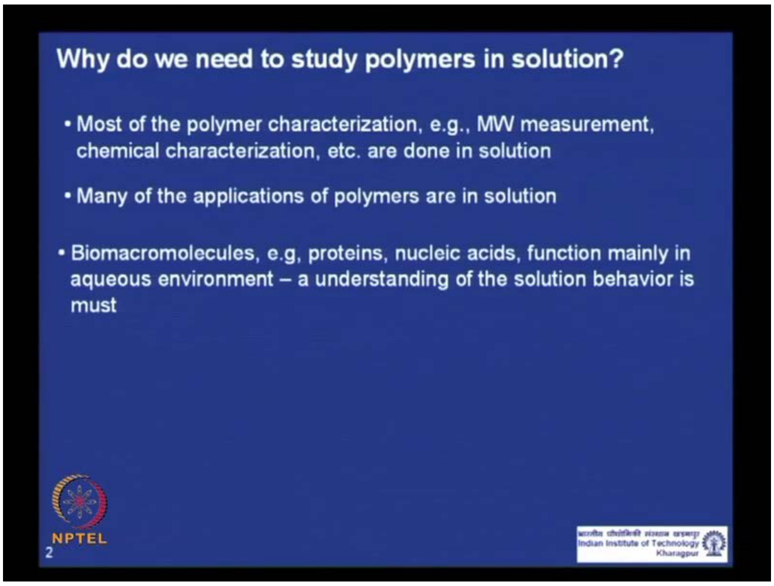

Why do we need to study polymers in solution?

- Most of the polymer characterization, e.g., MW measurement, chemical characterization, etc. are done in solution
- Many of the applications of polymers are in solution
- Biomacromolecules, e.g, proteins, nucleic acids, function mainly in aqueous environment – a understanding of the solution behavior is must

Now as I said that we are going to learn polymers in solutions or polymer solution. Now why do we need to study polymers in solution? As I was just mentioning that once we made this polymer, we must characterize both chemically and physically and one of the most important parameter is the molecular weight. Now as you will see in after few lectures that most of this polymer characterization techniques for example, molecular measurements, chemical characterization, etc are done in solution.

So unless we do not know how polymers behave in solution, we will not be able to understand how polymer characterization is done. Also many of the applications in beginning if you recall what I said that there are few applications or some applications where, though in not majority, a minor application of polymers where polymers are used in solution; for example, eye drop where the water solvable suppose active polymers are used, detergents and there are several applications where you will find that polymers are added in solution. So, polymers are used in the applications where the final form of the product is in solution form. So, we must know the behavior of the polymers in solutions to understand how we can utilize these synthesize polymers in those applications.

Also biomacromolecules for example, proteins, nucleic acids; though these polymers are not part of this course but as a comparison biomacromolecules they function mainly in aqueous environment and to understand the behavior of this biomacromolecules, one must understand the solution behavior of this molecules and the solution behavior of thermodynamics of polymer solutions is for a synthetic polymers are very similar to the treatment you will see for biomacromolecules. So, if you understand the thermodynamics of polymer solution for synthetic polymers, you will also be able to easily understand the behavior of macromolecules in solution biomacromolecules in solution.

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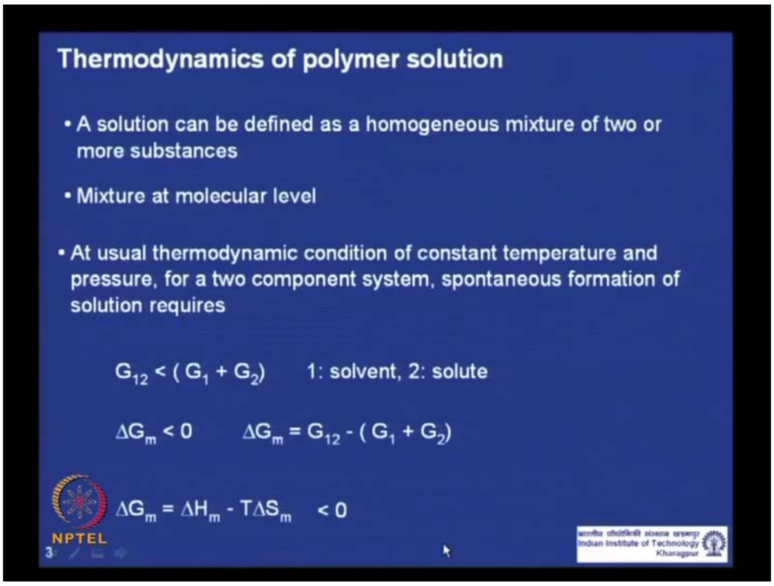

Thermodynamics of polymer solution

- A solution can be defined as a homogeneous mixture of two or more substances
- Mixture at molecular level
- At usual thermodynamic condition of constant temperature and pressure, for a two component system, spontaneous formation of solution requires

$G_{12} < (G_1 + G_2)$ 1: solvent, 2: solute

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

$\Delta G_m = \Delta H_m - T\Delta S_m \quad < 0$

So, let us start with thermodynamics of polymer solution and for a solution as we know that the solution can be defined as a homogeneous mixture of two or more substances; homogeneous means that the mixture is at molecular level. And of course we know that from our basic understanding of thermodynamics that usual thermodynamic condition of constant temperature and pressure, for a two component system, spontaneous formation of solution requires that the Gibbs free energy of the solution is lower than the sum of the Gibbs free energy of the solvent and the solute G 1 and G 2.

And in other words you can write that Gibbs free energy of mixing; Gibbs free energy which is given by the difference in the Gibbs free energy of the solution or the mixture and the sum of the individual Gibbs free energy of the solvent and solute should be negative too, so that the solution can form continuously. And we also know that the Gibbs free energy mixing can be expressed in terms of enthalpy of mixing and entropy of mixing. So, this should be lower than 0.

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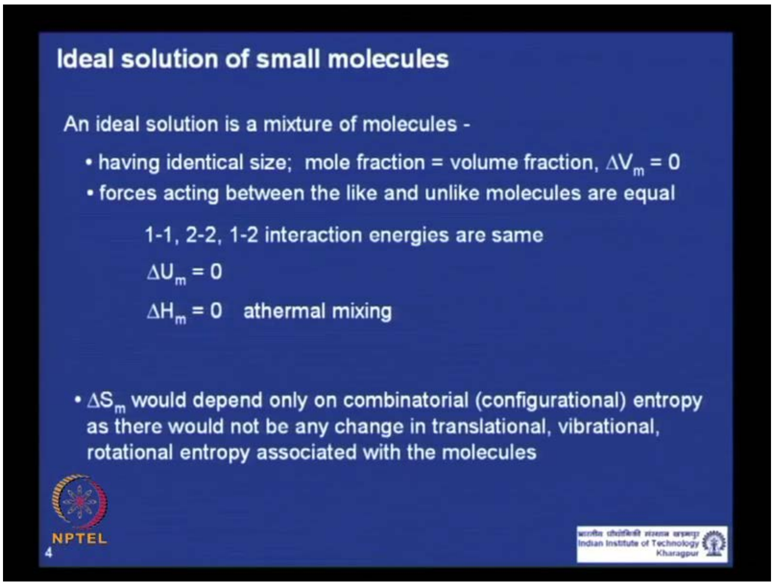

Ideal solution of small molecules

An ideal solution is a mixture of molecules -

- having identical size; mole fraction = volume fraction, $\Delta V_m = 0$
- forces acting between the like and unlike molecules are equal

1-1, 2-2, 1-2 interaction energies are same

$\Delta U_m = 0$

$\Delta H_m = 0$ athermal mixing

- ΔS_m would depend only on combinatorial (configurational) entropy as there would not be any change in translational, vibrational, rotational entropy associated with the molecules

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Now let us start with ideal solutions of small molecules. Now ideal solution is a mixture of molecules having identical size. We call a solution as ideal solution when the ingredients all the components solute and the solvent are having same size; the individual sizes, molecular sizes are same. And once the molecular size is same molar volume is same; the mole fraction would be equals to the volume fraction and the change in or volume of mixing would be 0. So, there will be no change in volume after mixing of the components. Now of course there is another condition that force acting between the like and the unlike molecules; similar and dissimilar molecules are equal or in other words if you have, say, 1 as your solvent and 2 as your solute, then interaction between 1-1 solute-solute solvent-solvent and 2-2 solute-solute is same as the interaction between the solute and solvent molecules which is 1-2 interaction.

So, if you replace one of the molecules, say, solute molecules or solvent molecules with another one, there should not be any change in the energy of the systems. So, energy of mixing should be 0 and as you have seen that volume of mixing is also 0. So, enthalpy of mixing should be 0. So, an ideal solution formation leads to a thermal mixing with no change in enthalpy of the system. Now if there is no change in the enthalpy of the system on mixing or when the solute and solvent mix and form a solution, the entropy of mixing delta S m would depend only on the combinatorial entropy.

The other entropies like transitional, vibrational, and rotational entropy are associated with molecules. They will not change at all because there is no change in thermal energy in the system delta H m is 0. So, those entropies will not change. So on mixing, the only change in the entropy would be the combinatorial entropy and what is the combinatorial entropy or configurational entropy is the number of ways you can arrange a different molecules. Number of distinguishable ways you can arrange different molecules; the more number of such numbers, then the entropy of mixing is higher. So, mixing becomes easier. Let us discuss little more in next page.

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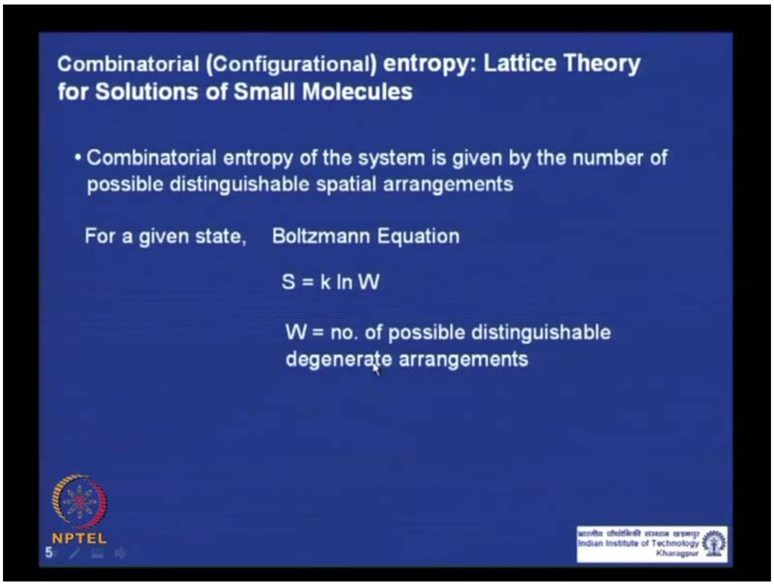

Combinatorial (Configurational) entropy: Lattice Theory for Solutions of Small Molecules

- Combinatorial entropy of the system is given by the number of possible distinguishable spatial arrangements

For a given state, Boltzmann Equation

$S = k \ln W$

W = no. of possible distinguishable degenerate arrangements

Combinatorial entropy of the system is given by the number of possible distinguishable spatial arrangements. So for a given state, we know from out statistical thermodynamics or statistical mechanics that Boltzmann equation gives the relation between the combinatorial entropy and W which is the number of possible distinguishable degenerate arrangement. W is the possible distinguish; all the arrangement you are doing by changing the position of the molecules has to be distinguished and they have to be of the same energy because in this case of ideal solution because interaction energies are same between like and unlike molecules So, once if you do interchange between solute and solvent molecules, they will produce degenerate arrangements.

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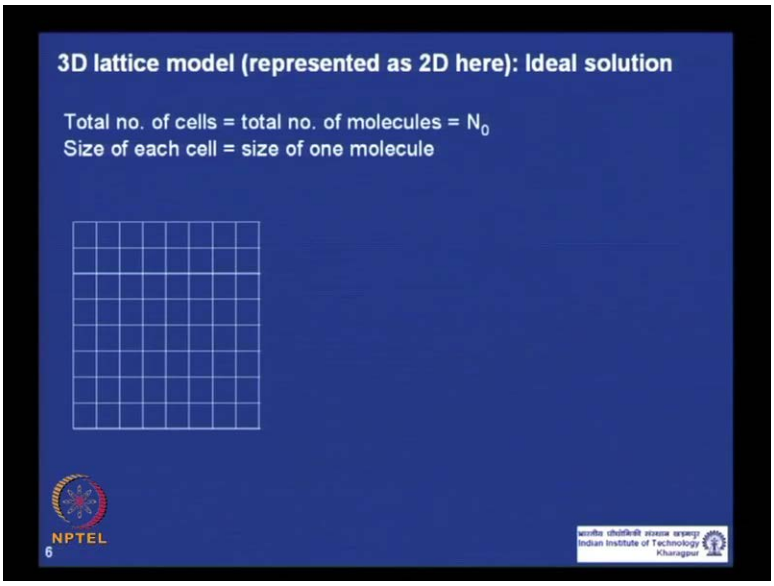

3D lattice model (represented as 2D here): Ideal solution

Total no. of cells = total no. of molecules = N_0
Size of each cell = size of one molecule

Now let us talk about how to calculate this combinatorial or configurational entropy and we are continuing our discussion with most simpler system of ideal solution.

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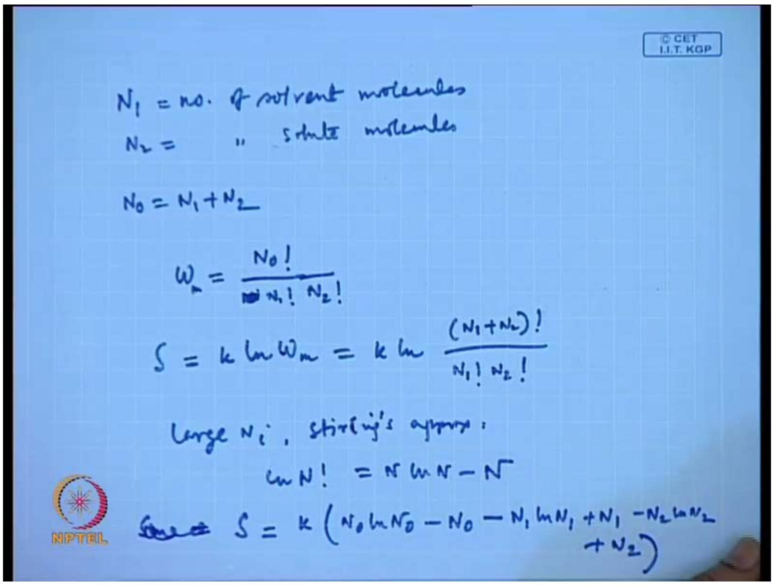

N_1 = no. of solvent molecules
N_2 = " solute molecules

$N_0 = N_1 + N_2$

$$W_m = \frac{N_0!}{N_1!\,N_2!}$$

$$S = k \ln W_m = k \ln \frac{(N_1+N_2)!}{N_1!\,N_2!}$$

Large N_i, Stirling's approx:

$$\ln N! = N \ln N - N$$

$$S = k\left(N_0 \ln N_0 - N_0 - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2\right)$$

And you have N 1 is the number of solvent molecule and N 2 is the number of solute molecules and N 0 is N 1 plus N 2 which is the total number of molecules. Now we have said or we have seen earlier that in case of ideal solution, the sizes of solute and the solvent molecules are similar. So, we can have a one 3D cell 3D lattice which have N 0 number of cells and the size of the cell of each cell is same as the size of the one molecule. Now in this slide it is shown as one of the 2D version of the 3D. You can imagine that it is it is a 3D lattice. So now, we have N 0 number of cells and N 0 number of molecules and each size of this cell is equal to the size of one molecule.

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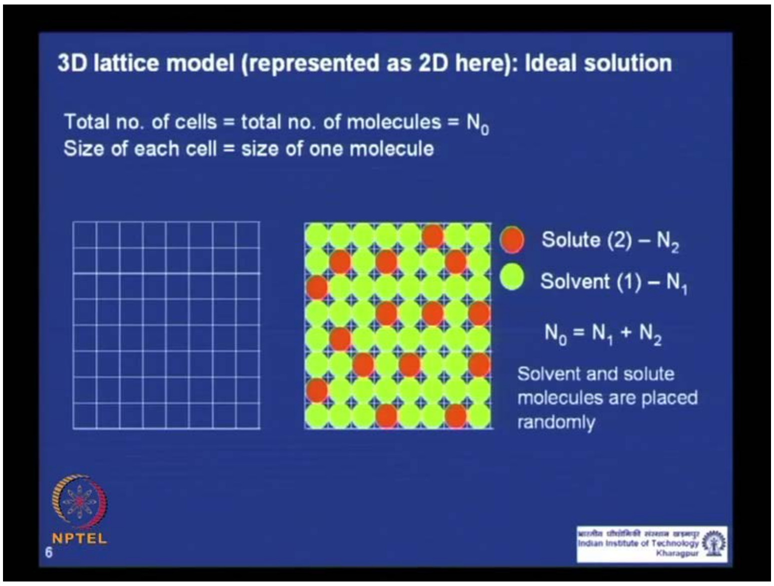

3D lattice model (represented as 2D here): Ideal solution

Total no. of cells = total no. of molecules = N_0
Size of each cell = size of one molecule

🔴 Solute (2) – N_2
🟢 Solvent (1) – N_1

$N_0 = N_1 + N_2$

Solvent and solute molecules are placed randomly

Now let us put or place the solute and solvent molecules; solute are and will be shown as number 2 in this course and it is typically shown as 2 and solvent will be represented as 1. So, N 2 number of solute molecules and N 1 number of solvent molecules which are shown in this colors and total N 1 and N 2 is the total number of molecules and they are placed randomly in this cell. So now, you have to calculate how many different ways you can arrange this molecules. Now total number molecule is N 0 which is N 1 plus N 2. So, total number of ways you can arrange these total molecules is factorial of N 0; this is the number of ways you can arrange all these molecules. Now, if you replace one solvent molecule with another or you can change the position of the solvent molecules with another solvent molecule, you can imagine that you are not creating another distinguishable arrangement.

If you replace this one with if you interchange this molecule with this molecule, you are getting the same arrangement. Basically there this two arrangement of replacing one solvent molecule or interchanging one solvent molecules with another or one solute molecule with another solute molecules will not give you any indistinguishable arrangement. So, these arrangements are overestimated. So, actual number of distinguishable arrangements would be; you divide by the N 1 factorial and N 2 factorial. So, quickly the combinatorial entropy will be given by Boltzmann equation. I will just do quickly N 1 factorial plus N 2 factorial divided by N 1 factorial and N 2 factorial. And you know for large N, large value of N i Stirling’s approximation gives you ln N factorial; this is from your previous mathematical knowledge. So, you can apply this and you can write S is equal to k N 0 ln N 0 minus N 0; this is N 0 factorial. So, you can just use this Stirling’s approximation and you get this expression.

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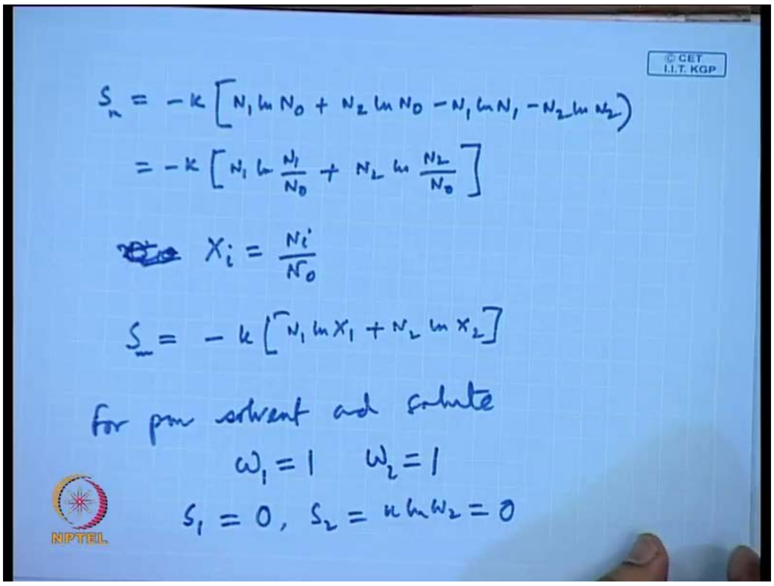

$$S_m = -k\left[N_1 \ln N_0 + N_2 \ln N_0 - N_1 \ln N_1 - N_2 \ln N_2\right)$$

$$= -k\left[N_1 \ln \frac{N_1}{N_0} + N_2 \ln \frac{N_2}{N_0}\right]$$

$$X_i = \frac{N_i}{N_0}$$

$$S_m = -k\left[N_1 \ln X_1 + N_2 \ln X_2\right]$$

for pure solvent and solute

$$\omega_1 = 1 \quad \omega_2 = 1$$

$$S_1 = 0, \; S_2 = k \ln \omega_2 = 0$$

Now I continue further simplification you will get. So, this k is Boltzmann constant that you known previously. Now mole fraction represented by X i or I can write capital X i mole fraction is N i by N 0. So, S could be given by k N 1 ln X 1 plus N 2 ln X 2. This is the S case for the mixture. So, I can write this is for the mixture S m. Now for pure solvent and solute, what will be the w? Number of ways you can arrange is 1 because no matter how many times you interchange the molecules you will always end up in same arrangement. So, this is the only one distinguishable way you can arrange a pure solvent or a pure solute. So, w 1 is 1 and w 2 for the solute is also 1. So, case one is 0 and S 2 is also k ln w 2 is 0. So, this is the combinatorial entropy for the mixture and this is entropy for the solvent and this is for the solute before mixture.

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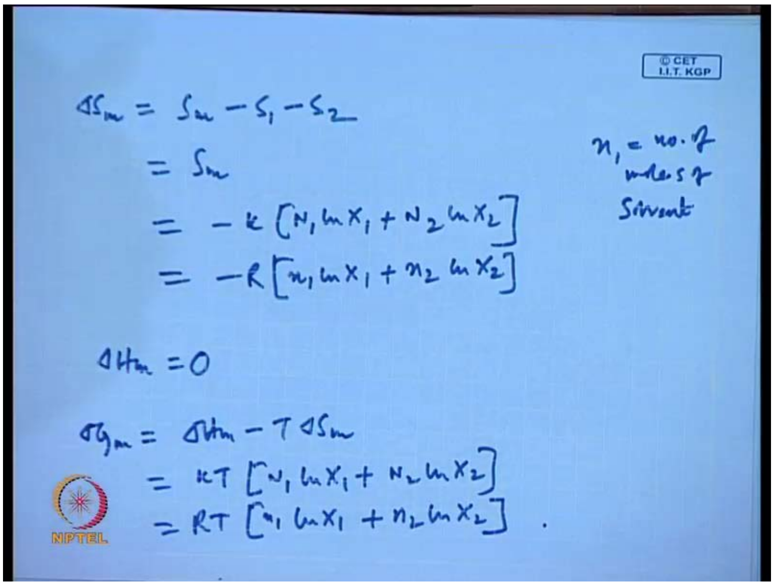

$$\Delta S_m = S_m - S_1 - S_2$$
$$= S_m$$
$$= -k\left[N_1 \ln X_1 + N_2 \ln X_2\right]$$
$$= -R\left[n_1 \ln X_1 + n_2 \ln X_2\right]$$

n_1 = no. of moles of solvent

$$\Delta H_m = 0$$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$
$$= kT\left[N_1 \ln X_1 + N_2 \ln X_2\right]$$
$$= RT\left[n_1 \ln X_1 + n_2 \ln X_2\right] .$$

So, what is the entropy of mixture mixing in this case is same; entropy of the mixture S 2 is given by S m and it is the same what we have seen earlier. You can multiply it both side by and convert it to; N 1 is the number of molecules solvent molecules and small n 1 lower case n is your number of moles solvent, number of moles of solvent. So, N 2 is the number of moles of the solute. Now what is del H m for the ideal solution is zero. So, del G m which is Gibbs free energy of mixture would be del H m minus T del S m; we get k T N 1 ln X 1 plus N 2 ln X 2 or R T N 1 ln X 1 plus N 2 ln X 2. So, this is your expression for Gibbs free energy of mixing Gibbs free energy. This is the mole fraction for solvent, this is for solute, this is number of moles for solvent, then this is number of moles for the solute.

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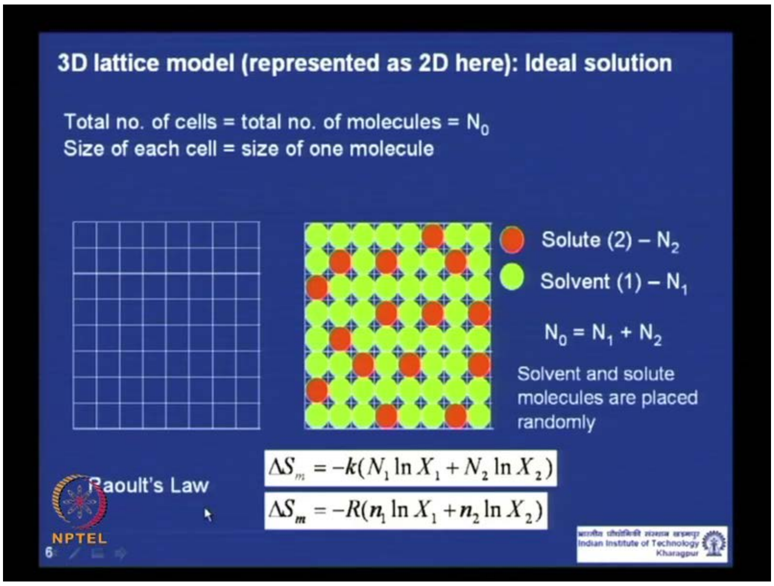

3D lattice model (represented as 2D here): Ideal solution

Total no. of cells = total no. of molecules = N_0
Size of each cell = size of one molecule

● Solute (2) – N_2
● Solvent (1) – N_1

$N_0 = N_1 + N_2$

Solvent and solute molecules are placed randomly

Raoult's Law

$$\Delta S_m = -k(N_1 \ln X_1 + N_2 \ln X_2)$$

$$\Delta S_m = -R(n_1 \ln X_1 + n_2 \ln X_2)$$

So, we can write for this ideal solution entropy of mixing is given by this expression and remember this is the same as we have seen from Raoult's law which keeps the expression of entropy of mixing for Gibbs free energy for the ideal solution.

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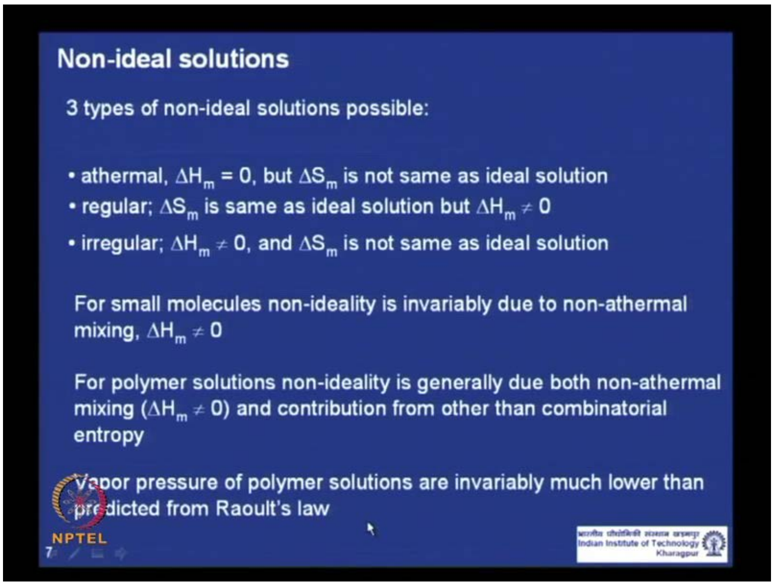

Non-ideal solutions

3 types of non-ideal solutions possible:

- athermal, $\Delta H_m = 0$, but ΔS_m is not same as ideal solution
- regular; ΔS_m is same as ideal solution but $\Delta H_m \neq 0$
- irregular; $\Delta H_m \neq 0$, and ΔS_m is not same as ideal solution

For small molecules non-ideality is invariably due to non-athermal mixing, $\Delta H_m \neq 0$

For polymer solutions non-ideality is generally due both non-athermal mixing ($\Delta H_m \neq 0$) and contribution from other than combinatorial entropy

Vapor pressure of polymer solutions are invariably much lower than predicted from Raoult's law

Now what about non-ideal solution? Now there could be three types of non-ideal solution; one is a thermal where del H m is 0, but del S m is not same as in case of what you have just seen for ideal solution. Second is regular solution; entropy of mixing is same as ideal solution but enthalpy of mixing is not 0. And third is irregular where enthalpy of mixing is not 0 and entropy of mixing also not same as the ideal solution. Now non-ideal solution of small molecules is invariably due to non-athermal mixing. As you know from your physical chemistry knowledge that any non-ideality which happens in case of solutions for small molecules are due to non-athermal mixing or delta H mixing is not equal to 0. For polymer molecules for polymer solutions this non-ideality is generally due to both. It is both for non-athermal mixing; del H mixing is not equals to 0 and also contribution from other than combinatorial entropy.

So in case of polymer solution, the non-ideal behavior of polymer solution or a polymer solution behave unlike a ideal solution of small molecule we juts discussed; because of both the reasons, in most cases, the enthalpy of mixing or enthalpy of solution for a polymer in a solvent is not equal to 0, delta h mixing is not equal to 0. And also for ideal solution, it is only the combinatorial entropy which contributes to the Gibbs free energy change for the mixing. In case of polymer solution, as we will see in a moment that, it is not only the combinatorial entropy; it is also the entropy change induced by the athermal process also contributes the Gibbs free energy of mixing. And in most cases vapor pressure of the polymer solutions are invariably much lower than what has been predicted from the Raoult’s law which is the law describing the ideal solution.

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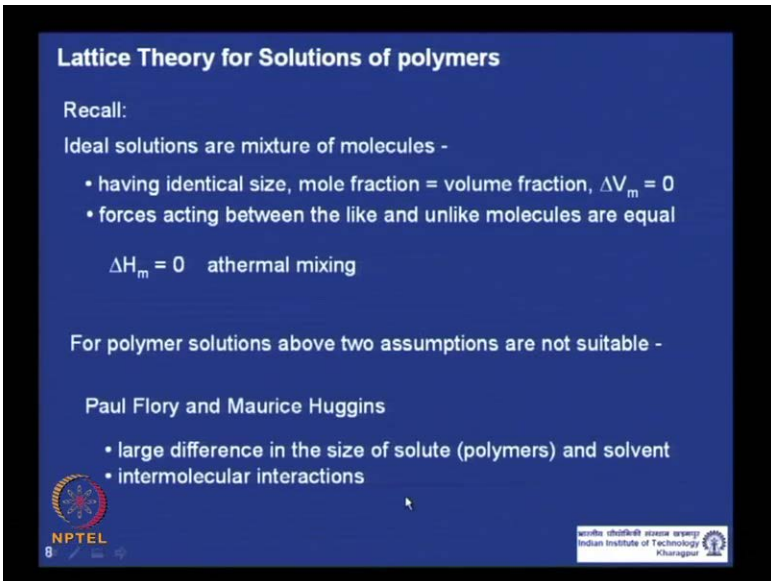

Lattice Theory for Solutions of polymers

Recall:

Ideal solutions are mixture of molecules -

- having identical size, mole fraction = volume fraction, $\Delta V_m = 0$
- forces acting between the like and unlike molecules are equal

$\Delta H_m = 0$ athermal mixing

For polymer solutions above two assumptions are not suitable -

Paul Flory and Maurice Huggins

- large difference in the size of solute (polymers) and solvent
- intermolecular interactions

So, how do get this combinatorial entropy or Gibbs free energy for mixing for the polymer solution? We have till now done the Gibbs free energy of mixing for solution ideal solution for small molecules. Now we will try to apply the same lattice theory to find out the Gibbs free energy of mixing for the polymer solvent mixture or a solution of a polymer in a solvent. Recall that in case of ideal solution, the molecules are having same size but in polymer obviously when you are dissolving a large polymer molecule in a solvent molecules, the size of polymer molecules are much higher than solvent molecules. So, this assumption which we made for ideal solution is not valid here; the sizes are solvent molecules and solute molecules. In this case, the polymer molecules is much higher is very different.

And in case in the ideal solution we had seen that del H mixing is 0 because of the force of like and unlike molecules are 1, 1 2, 2 is equals to 1, 2 and in most often interaction between polymer and a solvent molecule is not athermal. In most cases they are specific interaction between polymer and solvent molecule is different than the interaction between a solvent-solvent molecule or a polymer-polymer molecules. So, these are the two main difference of a polymer solution than an ideal solution of the small molecules. Now the two scientists Paul Flory and Maurice Huggins they proposed the theory which we will know in a minute which took consideration of the large difference in the size for the solute and this is polymers and the solvent and existence of the intermolecular interactions. So, now what we will do is we will explain or we will try to learn how the Paul Flory, Huggins theory was established using that same lattice theory which we just learnt for small molecules.

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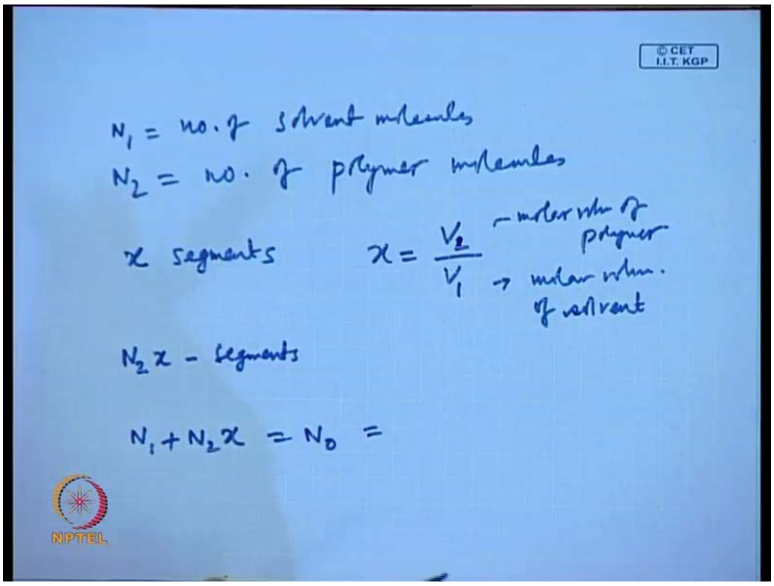

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N_1 = no. of solvent molecules

N_2 = no. of polymer molecules

x segments $\quad x = \frac{V_2}{V_1}$ – molar vol. of polymer; V_1 → molar vol. of solvent

$N_2 x$ – segments

$N_1 + N_2 x = N_0 =$

Again we will have the same 3D lattice in this case as well but here the difference is that N 1 is again the number of solvent molecules and N 2 is number of polymer molecules. Obviously, the sizes of the polymer molecules and the solvent molecules are different. So what we are doing, we breaking or dividing the polymer molecule in to x segments; dividing a single polymer molecule in to x segments where the size of the each segment is same as the size of a solvent molecule. So, x is v 2b y v 1 where v 2 is the molar volume of polymer and v 1 is the molar volume of solvent.

So, what we are doing? We are breaking polymer or dividing a single polymer chain in to x segments where the size of each segment is same as the solvent molecules. So, each polymer molecule has x segments. So, N 2 number of polymer molecules has N 2 into x segments. So, these are the total number of polymer segments in the solution or in the mixture. So, we require N 1 plus N 2 x which is N 0; this is the number of lattice we require where each size of each lattice is either same as the size of solvent molecules or same as the size for a segment of a polymer.

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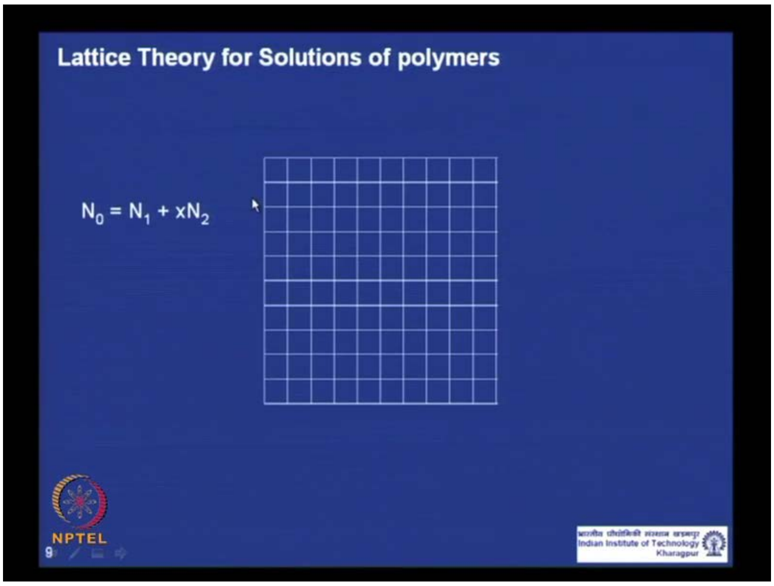

Lattice Theory for Solutions of polymers

$N_0 = N_1 + xN_2$

So, in general we have N 0 number of cells where N 1 is the number of solvent molecules and each size of the each cell is same as the size of the solvent molecules and x is number of segment of a single polymer chain and size of the segment is same as the size of the cell. So, we have N 0 number of cells; N 0 is given by N 1 plus x N 2.

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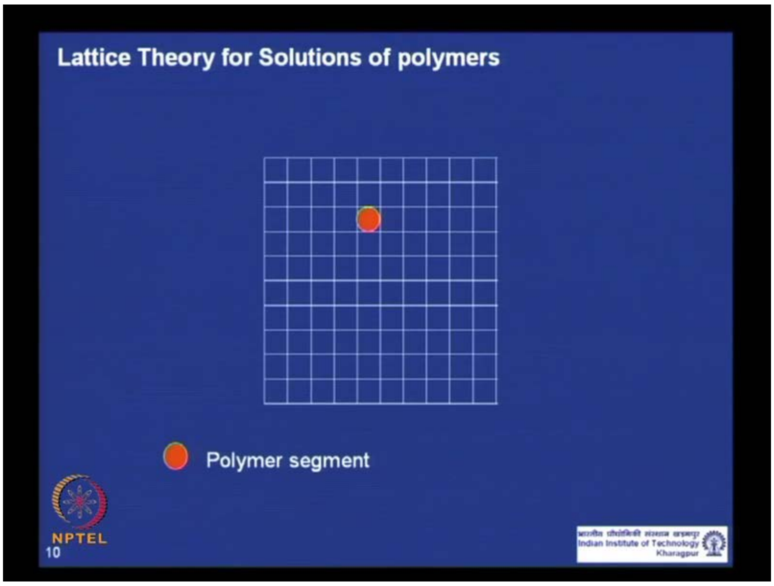

Lattice Theory for Solutions of polymers

● Polymer segment

What we are going to do is find out first how many different ways we can arrange the polymer segments. We are going to add the polymers in those in this 3D lattice, one after one; we are going to add the polymer chains in this lattice one after one, one segment after one segment and once we added all the polymer chains then we will add the solvent molecules. This is the approach what we are taking; we will add the polymers one by one and for single polymers we will add each segment one after one. Now how are we going to add this polymer segments.

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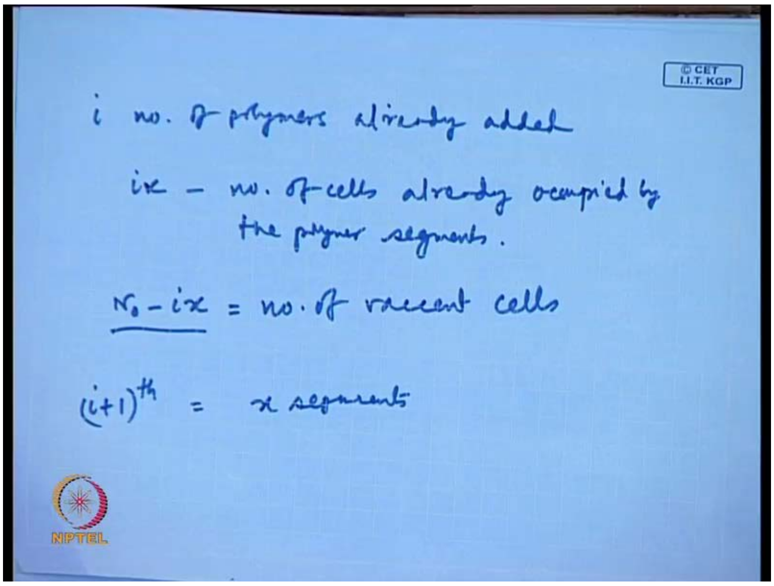

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i no. of polymers already added

ix – no. of cells already occupied by the polymer segments.

$\underline{N_0 - ix}$ = no. of vacant cells

$(i+1)^{th}$ = x segments

See since we have already i; i is the number of polymers already added. So, we have already added in this 3D lattice which are we are not showing; those i number of polymer molecules are not shown here to make this picture clear. So, you have to understand that there are already i number of polymers present which means i into x number of cells are already occupied. Each polymer has x number of segment if we had i number of polymers which is already added. So, i minus x cells are already occupied. So, how many number; this is number of cells already occupied by the polymer segments. So, N 0 minus i x is the number of vacant cell where in the next one, i plus 1 polymer chain we can place. This is the number of cells which are vacant, because N 0 was total number of cells and i x is the total number of cells that are already occupied.

So, N 0 minus i x is the number of vacant cells. So, this is the number of cells where we can place the next polymer molecule which is i plus 1th, i plus first. Now i plus this polymer chain has how many segments? Again x segments; this i plus 1, i plus first chain has x segments. So, the first segment of this polymers; let me write this. This is the number of vacant cells available for this i plus first polymer chains to get in. Now the first segment; now as I said earlier that I am showing this all are vacant, but these are all vacant i x number of cells are already blocked, already occupied. So, N 0 minus x i is the number of cells which are available.

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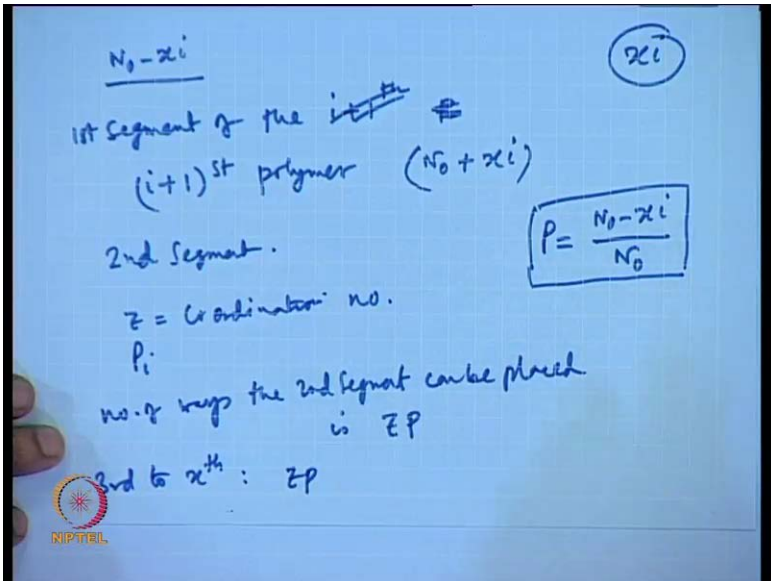

$N_0 - xi$

$\boxed{xi}$

1st segment of the ~~i^{th}~~

$(i+1)^{st}$ polymer $(N_0 + xi)$

$$\boxed{P = \frac{N_0 - xi}{N_0}}$$

2nd segment.

z = coordination no.

P_i

no. of ways the 2nd segment can be placed is zP

3rd to x^{th} : zP

So, how many different ways you can place the first segment of polymer? There are N 0 minus x i number of vacant cell. So, the first segment of i plus first polymer can we added how many different ways? Of course, it can be added any of these vacant cells. So, it can be added in this many ways. So, this is the number of vacant cells available for the segments to go in. So you can arrange, you can place or you can locate the first segment in any of these vacant cells. So, this is the number of ways you can add the first segment. What about the second segment? If I want to add another molecule, another segment, not molecule; if I want to add another segment where it has to stay of course unlike the small molecules where the molecules are apart from each other.

For polymers the segment has to be tied up because there the segments are joined to each other. So, they can be placed in any of this first level. So, if z is the coordination number which is the number of cells present in the first level, you can add in any of these cells. So, I can add, say, I can add here. So, second segment can be placed in any of this z cells. Now what is the chance that all the z cells are vacant; Remember the lattice already has x i number of block cell. So, it is not that all the z number of cells will be free for the second segment to go in; there is a probability. So if I write the probability as p I, then the number of ways the second segment can be placed is z p; p is the probability that the cell is vacant. Now what is that probability? Total number of empty cells is N 0 minus x i divided by total number of cells.

So, this is the probability; chances of that one of the cells if you choose and pick any of the cell from this lattice, this is the probability that it will be vacant because this is the number of cells which are vacant and this is the total number of cells present in the lattice. So, this is the probability and this is the second segment; number wise if second segment can be placed is z p. From third to the last which is x z how many different way you can add? You can add basically the same way; it is basically the same way you have added the second one, you have to add third, fourth, fifth, sixth, etc, the same way you have to arrange. So, each third segment can be placed again by z p way; four segments can be placed in z multiplied by p s and so on. So, total number of way is then.

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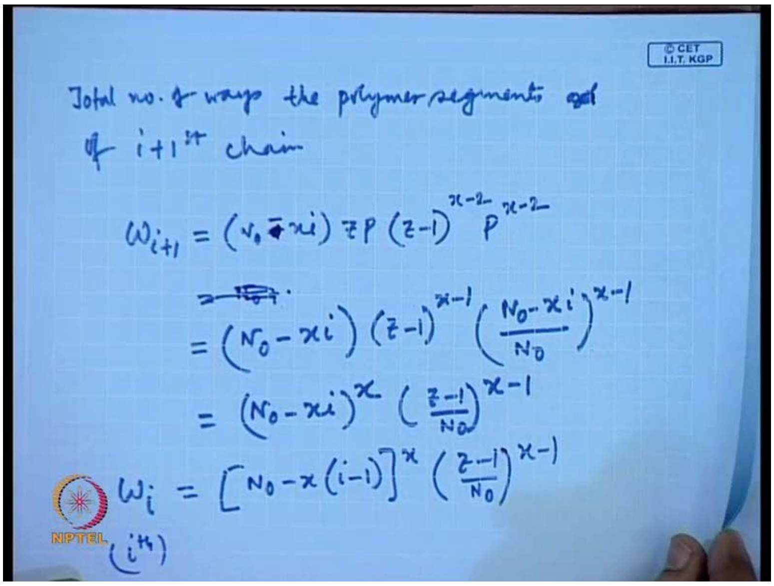

Total no. of ways the polymer segments of $i+1^{st}$ chain

$$\omega_{i+1} = (N_0 - xi)\, zp\, (z-1)^{x-2}\, p^{x-2}$$

$$= (N_0 - xi)\, (z-1)^{x-1} \left(\frac{N_0 - xi}{N_0}\right)^{x-1}$$

$$= (N_0 - xi)^{x} \left(\frac{z-1}{N_0}\right)^{x-1}$$

$$\omega_i = \left[N_0 - x(i-1)\right]^{x} \left(\frac{z-1}{N_0}\right)^{x-1}$$

(i^{th})

So, the total number of ways the polymer segments of i plus first chain can be placed and will be given by the multiplication of all this segments; first segment N 0 plus x i second segment z p. What I just missed here is that when you have one sample, second sample can be placed any of this z coordination number but for the third one, one is already blocked; one of the z is blocked. So, from third to last will be z minus 1 because one is already blocked; one of the neighbors is already blocked. So if I place third here, I can place third here; I can place here, I can place here, I can place here. One of this is already blocked; I cannot place here. So, it has to be z minus 1. Fourth one again z minus 1; so that is you have to remember, so z minus 1 p. So, this is for the second segment, this is for the second segment, and this is for the third to the last segment.

Now, what I will do? I will quickly go through the mathematical part, not plus this is minus. Now z, because z is quite high so I can again put z equals to minus z minus 1. So, I can make z minus 1; z z minus x minus 2 so that is x minus 1 and p x minus 1 and we know p is N 0 minus x i by N 0 that is x minus 1. So, I can rearrange it; x i bring that here, x and z minus 1 N 0 x minus 1. So, this gives the number of possible ways this i plus first chain gets introduced in the lattice when the lattice is already has i number of polymer chains present. So for simplicity what will be the i th chains, number of ways i th chains can be placed; N 0 x i would be i plus 1 is i. So, i would be i minus 1. So, this is the number of ways this i th chain i th polymer chain can be placed in the 3D lattice. So, now if you want to calculate the number of ways all this chain can be placed; we have to multiply by the possibilities of each individual chain.

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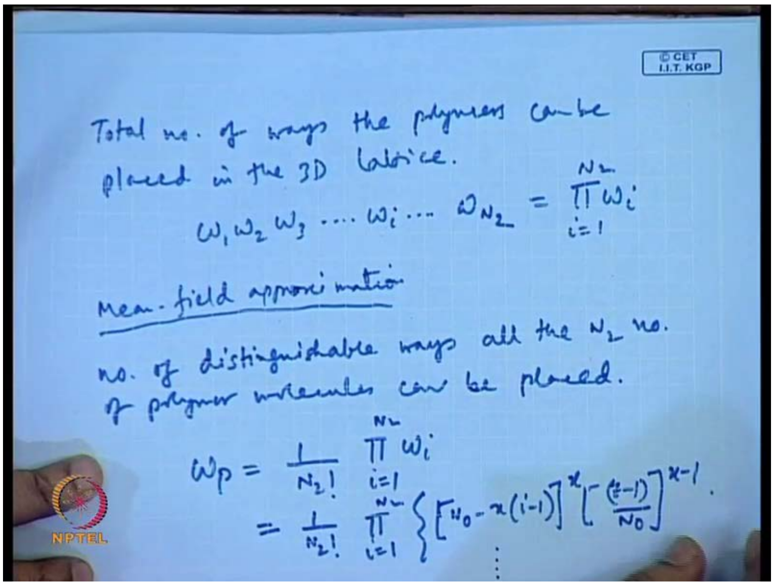

Total no. of ways the polymers can be placed in the 3D lattice.

$$\omega_1 \omega_2 \omega_3 \cdots \omega_i \cdots \omega_{N_2} = \prod_{i=1}^{N_2} \omega_i$$

Mean-field approximation

no. of distinguishable ways all the N_2 no. of polymer molecules can be placed.

$$W_p = \frac{1}{N_2!} \prod_{i=1}^{N_2} \omega_i$$

$$= \frac{1}{N_2!} \prod_{i=1}^{N_2} \Big\{ \left[N_0 - x(i-1)\right]^x \left[\frac{(z-1)}{N_0}\right]^{x-1} .$$

$\vdots$

So, the total number of ways the polymers can be placed in the 3D lattice will be given by w 1 w 2 w 3 w i N 2. By now one thing you must have noticed that what we are considering here that when you are finding the probability p, we are just taking that the chance or the probability of one cell being vacant is the number of vacant cell divided by the total number of cells.

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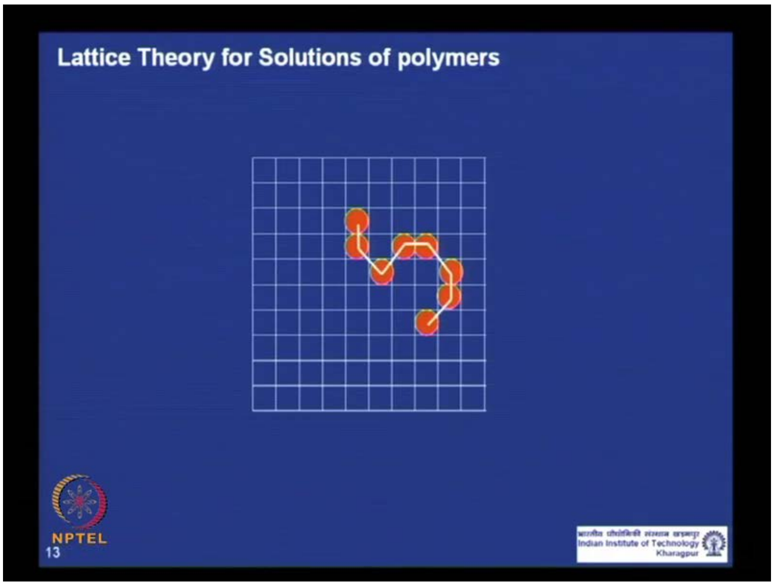

Lattice Theory for Solutions of polymers

Now, polymer chains in actual sense are these all segments are attached; for a single polymer chain all the segments are attached. So in true sense, the chances of finding a vacant cell near by a polymer chain would be lower than from a distance from a chain. What I am trying to explain is that the chances of finding one vacant cell near the polymer chain would be lower than if you go little distance from a polymer chain because of segments are attached. But we are not considering that; we are considering that whatever polymer segments are already present, they are distributed randomly. So, that is the assumption we are making and we are telling that is mean-field approximation where we are considering that all the segments which are already present in the 3D lattice are distributed randomly; they are not joined, they are distributed randomly.

So, we have found the number of distinguishable ways; all the N 2 number of polymer molecules can be placed, w p would be because each. Again like the ideal solution, the arrangements between a single polymer chains are identical. So, you have to divide by N 2 factorial by the total number of arrangements; these are the total number of distinguishable arrangements. Now I am not going to go in detail about the steps; this mathematical steps you can get or you can refer any of the standard text books, you will find out that different steps in between.

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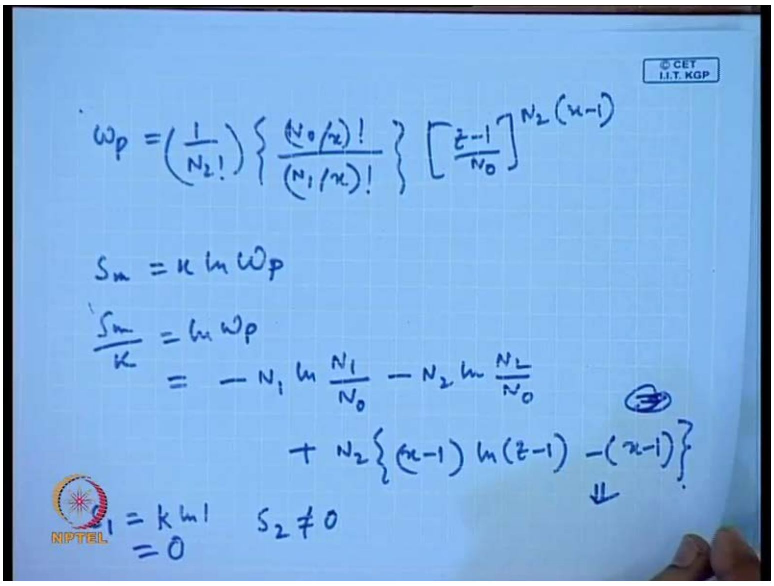

$$\omega_p = \left(\frac{1}{N_2!}\right)\left\{\frac{(N_0/x)!}{(N_1/x)!}\right\}\left[\frac{z-1}{N_0}\right]^{N_2(x-1)}$$

$$S_m = k \ln \omega_p$$

$$\frac{S_m}{k} = \ln \omega_p$$

$$= -N_1 \ln \frac{N_1}{N_0} - N_2 \ln \frac{N_2}{N_0}$$

$$+ N_2\{(x-1)\ln(z-1) - (x-1)\}$$

$$\Downarrow$$

$${}_1 = k \ln 1 \qquad S_2 \neq 0$$

$$= 0$$

I am going directly to the final expression of this number of ways this total number of N 2 chains can be placed in this three lattice which is number of distinguishable ways you can place the N 2 number of molecules in this sheet; it is given by the expression we just mentioned here. Now we just drop the steps and write the final step. So, this is the number way and all the polymers can be placed. Now once we had placed all the polymer molecules, now we can place the solvent molecules in the vacant cells. Now how many different ways the solvent molecules can be placed in the vacant cells? All the solvent molecules are identical. So, there is only one way you can place all the solvent molecules; if you change the places between the solvent molecules themselves, it does not given any indistinguishable arrangement.

So, this is the only one way you can place the solvent molecules. So, the total number of ways you can place both the polymers and the solvent molecules and complete or fill the three lattice will be given by this multiplied by one which will be this. So, w which is the total number of ways the entire 3D lattice containing N 1 solvent molecules and N 2 polymer molecules can be filled by this way. So, what will be the combinatorial entropy for this mixture? It is k ln w p or S m by k ln w p will be given by minus N 1 ln. So, this is what we get. This S m is the combinatorial entropy for the mixture of N 1 solvent molecules and N 2 polymer molecules.

Now what will be the S accommodated interval for the solvent. Again the number of ways you can arrange different solvent molecules is one. So it will be k ln 1, again 0; number of different ways you can add in this solvent molecules, but unlike the ideal solution case S 2 is not equals to 0 here because the amorphous polymer chain has different confirmations and so you can actually arrange the polymer chain in different ways; not only one way like small molecules. So, S 2 which is the combinatorial entropy for the polymer molecule is one is not equals to 0; it has significant value. So, what I will do; I will continue I will just take this, do one more step mathematical step for simplification.

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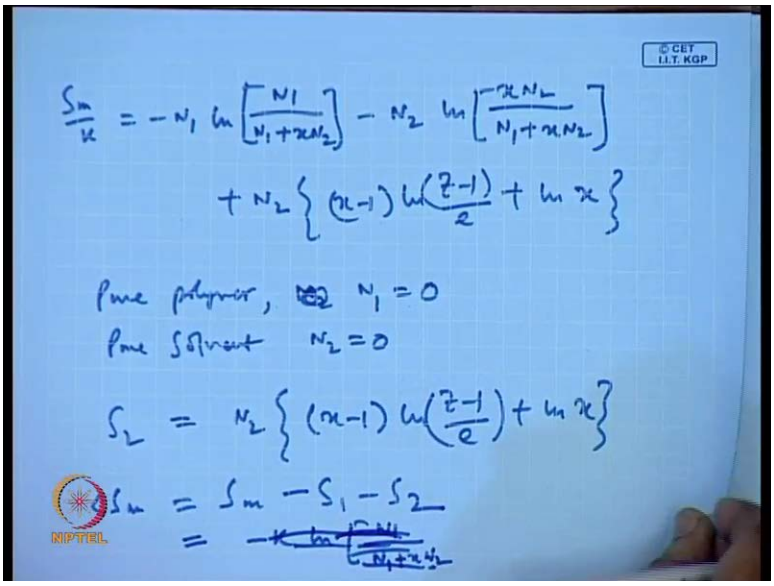

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$$\frac{S_m}{k} = -N_1 \ln\left[\frac{N_1}{N_1+xN_2}\right] - N_2 \ln\left[\frac{xN_2}{N_1+xN_2}\right]$$
$$+ N_2\left\{(x-1)\ln\left(\frac{z-1}{e}\right) + \ln x\right\}$$

Pure polymer, $N_1 = 0$

Pure solvent $N_2 = 0$

$$S_2 = N_2\left\{(x-1)\ln\left(\frac{z-1}{e}\right) + \ln x\right\}$$

$$\Delta S_m = S_m - S_1 - S_2$$
$$= \cancel{-k \ln\left[\frac{N_1}{N_1+xN_2}\right]}$$

S m by k is minus N 1; these are simple mathematical step, I am not explaining which you can do yourself. So, for pure polymer N 1 is 0 and for solvent N 2 is 0. So, S 2 for the pure polymer we can get from this expression just by putting N 1 is 0. It should be N 2 x minus 1 and then z minus 1 e plus ln x. So, delta S m which is mixture minus S 1 minus S 2 would be given by minus k. This is the term same term. So, it would be given by k ln N 1 N 1 plus x N 2. So, let us do it in the next page.

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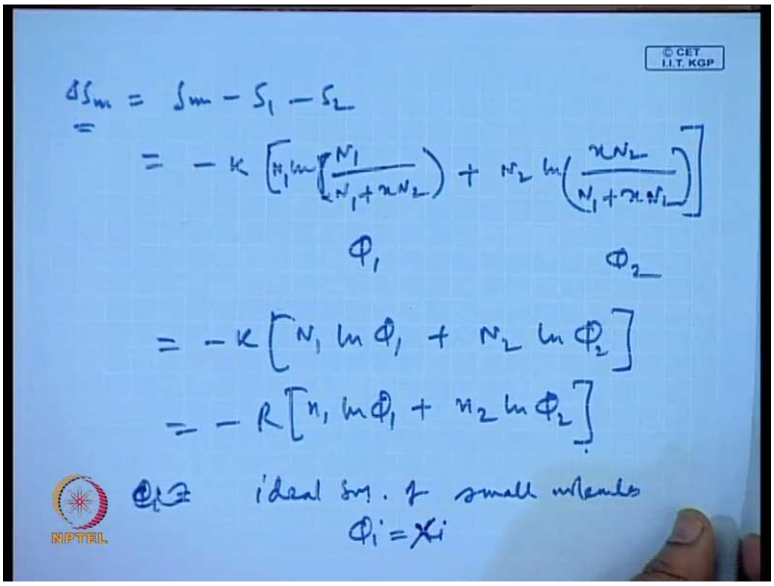

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$$\Delta S_m = S_m - S_1 - S_2$$
$$= -k\left[N_1 \ln\left(\frac{N_1}{N_1+xN_2}\right) + N_2 \ln\left(\frac{xN_2}{N_1+xN_1}\right)\right]$$
$$\qquad \Phi_1 \qquad\qquad\qquad \Phi_2$$
$$= -k\left[N_1 \ln \Phi_1 + N_2 \ln \Phi_2\right]$$
$$= -R\left[n_1 \ln \Phi_1 + n_2 \ln \Phi_2\right]$$

~~$\Phi_i =$~~ ideal sol. of small molecules

$$\Phi_i = x_i$$

Now N 1 by N 1 plus x N 2 we can write this as phi 1 is the volume of fraction. This is the total number of segment, N 1 is the total number of molecules and we knew that the volume or size of a segment is same as the size of a solvent molecule. So, this would the mole volume of fraction of the solvent and this would be the volume fraction of the polymer. So, we can write this N 1 ln phi 1 plus N 2 ln phi 2 or we can write this. So, after all this exercise we got this entropy of mixing for the polymers; for the polymers in a solution is give by this expression and this expression is same as the ideal solution of small molecules. Because in case of ideal solution, we knew that phi i for ideal solution of small molecules phi i was equal to the mole fraction; volume of fraction was equals to mole fraction.

So, you can replace by the mole fraction this number it gives the same number. So, what is this expression? What we will do; we will just come back in the next lecture and by now we understood that by Flory Huggins approach we can find out the entropy of mixing for a polymer and a solvent. So, we need to find out the delta h mixing or enthalpy of mixing for the polymer solvent so that we can get the free energy of mixing for the polymer solvent mixture So in next lecture, we will first get the enthalpy of mixing and then proceed from there to get the total Gibbs free energy of mixing for a polymer solvent system.