Polymer Chemistry
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Lecture - 26
Polymer Solutions (Contd.)

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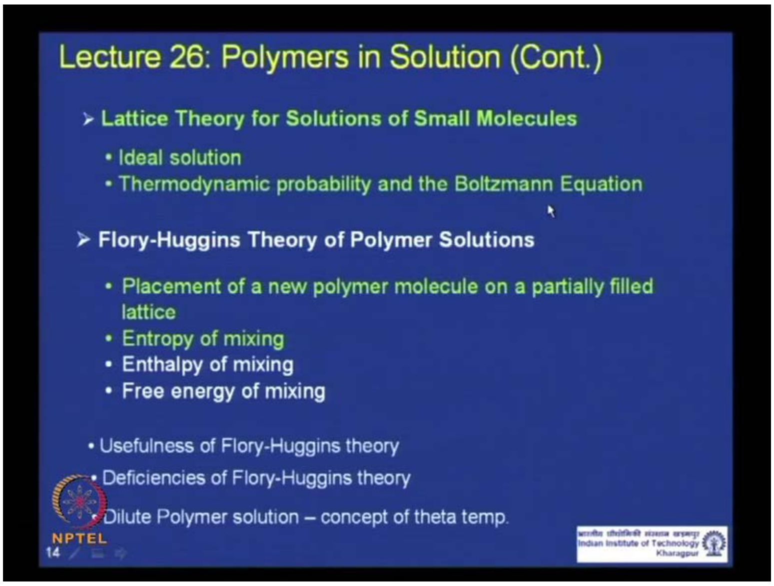

Lecture 26: Polymers in Solution (Cont.)

- 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
- Usefulness of Flory-Huggins theory
- Deficiencies of Flory-Huggins theory
- Dilute Polymer solution – concept of theta temp.

Welcome back to this course on polymer chemistry. We will continue in this lecture our discussion which we are having the last lecture on polymers in solution. In last lecture, we started lattice theory of solutions of small molecules and then, we introduced the thermodynamic probability and Boltzmann equation, how to get this combinatorial entropy from number of distinguishable this degenerate arrangements of a system. Then, we started our discussion on Flory-Huggins theory on polymer solution. In this case, if you can recollect that polymer molecules, because their size was quite different from the solvent molecules, each polymer molecules were divided into x segments, where each segment was having same size with the size of a solvent. Then with this total segments and the solvent molecules were placed in the 3D lattice like the small molecules.

First we introduced the polymer molecules one by one in case of each polymer molecule, segment by segment and then once all the polymers molecules were introduced in the lattice, then we added all the solvents. In that process, we calculated how many different ways, how many distinguishable ways we can introduce all the polymer segments. Then, we got the entropy of the mixture from the Boltzmann expression and then, we deduce or deducted the entropies of the polymer molecules, pure polymer molecules and the solvent molecules to reach the value for the entropy of mixing for polymer solvent system or polymer solution.

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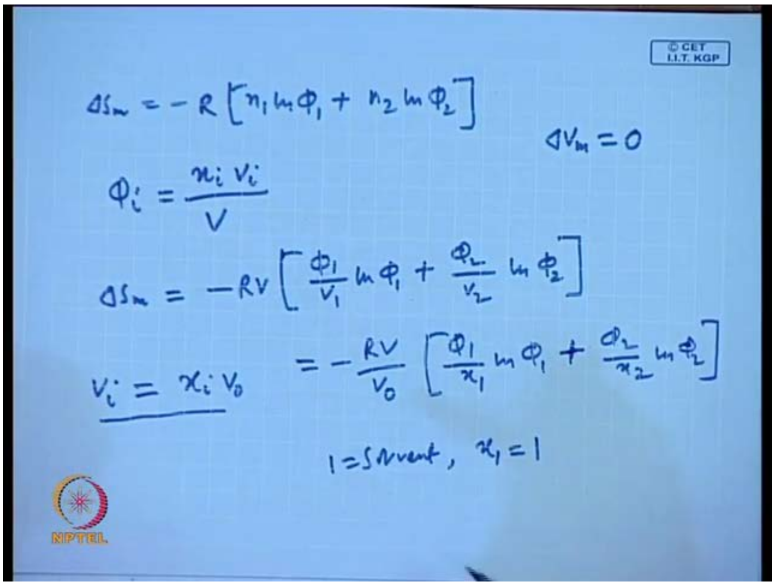

$$\Delta S_m = -R\left[n_1 \ln \phi_1 + n_2 \ln \phi_2\right]$$

$$\Delta V_m = 0$$

$$\phi_i = \frac{n_i V_i}{V}$$

$$\Delta S_m = -RV\left[\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2\right]$$

$$\underline{V_i = x_i V_0} \qquad = -\frac{RV}{V_0}\left[\frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2\right]$$

$1 = \text{Solvent}, \; x_1 = 1$

What we got, this is the final expression, we have received. So, in this lecture, what we will do, we will get the expression for enthalpy of mixing. So, once we get the enthalpy of mixing, we have to get the Gibbs free energy of mixing and once we get the final expression of the Gibbs free energy mixing, then we will look at the usefulness of the Flory-Huggins theory and what are the limitations or deficiencies in the Flory-Huggins theory and then, try to apply this Flory-Huggins theory in the dilute polymer solutions and get the concept of theta temperature.

Now, before we start getting the expression for enthalpy of mixing, just one point just to highlight that this is the expression we received or deduced for entropy of mixing for a polymer solvent. Then phi i, which is the polymer fraction of the solvent molecule can be obtained from the number of moles. This is the molar volume and this is total volume. This is for the ith components. So, we can write delta s m minus r v phi 1. We also know for ideal solution, in this polymer solution, we assume that the volume of mixture, there is no change in the volume compared to the original volume. Now, what we trying here is to find out if there is, to define the size of polymers, which will have more solubility for a given solvent or if there are, if it is not a solvent, it is two polymers or two different size molecules, then how the entropy of mixing varies with the size of the molecules.

Now, we can divide each molecule, which is represented as i into the segments and one volume; this is reference volume, which is the size of the individual cells in the 3D lattice. Now, in case of solvent molecules, x i is 1, so v i is the size of the solvent molecule. For polymer, what we discussed is, x i is the number of polymer segment. See, in this case, we are not mentioning solvent time now. We are just, to make it general, we are using this expression. So, we get from this delta s m equals to minus r v v 0.

For if, say one was solvent, obviously x 1 is your 1. So, you will get back the same expression. Now, what does this expression says that, if the size, if the size x 2, the value of x 2, if the value of x 2 goes up or the values of x goes up, then the size of the molecules is going up. If the size goes up, the entropy of mixing comes down. Now, what is the sign of this entropy of mixing of these things? This is the fraction. Obviously, this is the negative term and there is a negative sign here, so this is a positive term.

Obviously, mixing has former general knowledge and general understanding that any mixing generally gives in increase in entropy. So this entropy mixing is always positive. Now, if the value of this x 1 or x 2 goes up, the value of entropy mixing goes down. Which means that, a polymer having larger size, it will be, which will give less entropy of mixing compared to a polymer having a lower size for a given solvent in given condition.

So, for same temperature and pressure and same solvent, if you mix a polymer having same size, it will give lower entropy of mixing than a polymer which is having a lower size. This is what it does. So, solubilising larger size polymers are always difficult compared to lower size polymers at a given condition. This is what it does. Now, we will move on and try to find out the value of entropy of mixing.

Now, entropy, sorry, enthalpy of mixing. Now, enthalpy of mixing is, as you see that, unlike one, where the ideal solution where this interaction, the solvent solvent, solute solute and the solute solvent interactions were having same interaction energy. In this case, they could be different. So, what we are writing this as, this is interaction energy psi 1 1 epsilon 2 2 and this is epsilon 1 2.

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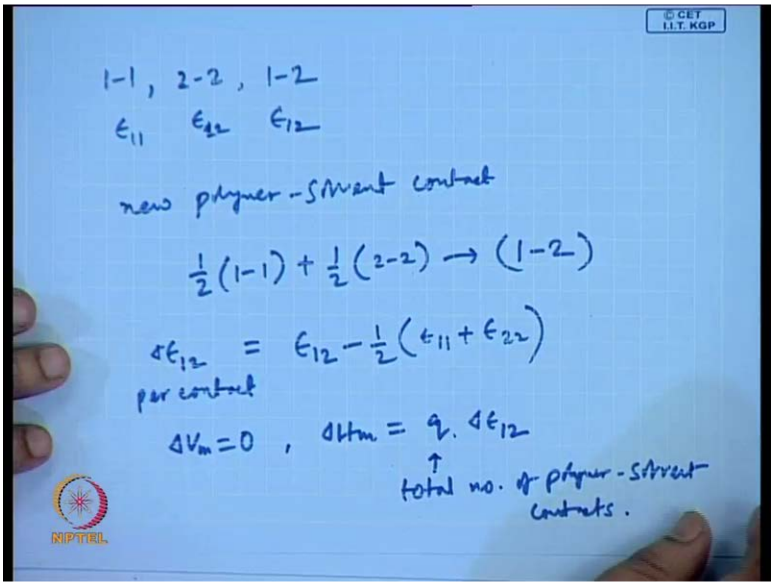

1-1, 2-2, 1-2

ϵ_{11} ϵ_{22} ϵ_{12}

new polymer - solvent contact

$$\frac{1}{2}(1-1) + \frac{1}{2}(2-2) \rightarrow (1-2)$$

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

per contact

$$\Delta V_m = 0, \quad \Delta H_m = \underset{\substack{\uparrow \\ \text{total no. of polymer - solvent contacts.}}}{q} . \Delta\epsilon_{12}$$

When a polymer, new polymer, new polymer solvent contact is found, due to polymer getting dissolved in solvent, obviously it comes at the expense of solvent solvent contact and polymer polymer or segment segment contact. So, we can write a expression like a chemical, pseudo-chemical energy, where half solvent solvent contact and half segment segment contact give 1 polymer solvent contact and we can also write the interaction energy power contact is the interaction energy for polymer solvent minus half of the interaction energy for the solvent solvent plus interaction energy for the segment segment.

Now, we know that del v m is 0, so del h m will be given by q 1 2. This is the interaction energy power contact and q is the total number of polymer solvent contacts. So, if q is the total number of polymer solvent contacts, then enthalpy of mixing will be given q multiplied by the interaction energy for each contact.

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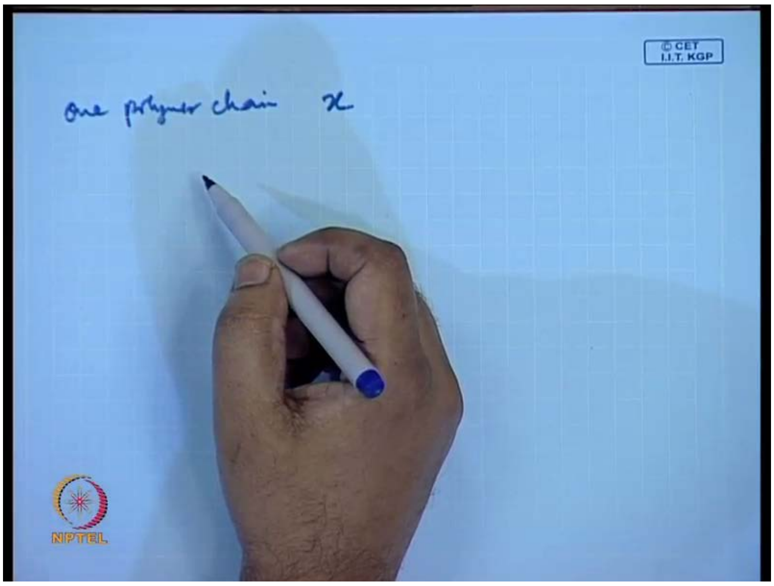
One polymer chain x

Now, one polymer has how many segments? One polymer chain has x segments and each segment is in, how many contacts solvent molecules?

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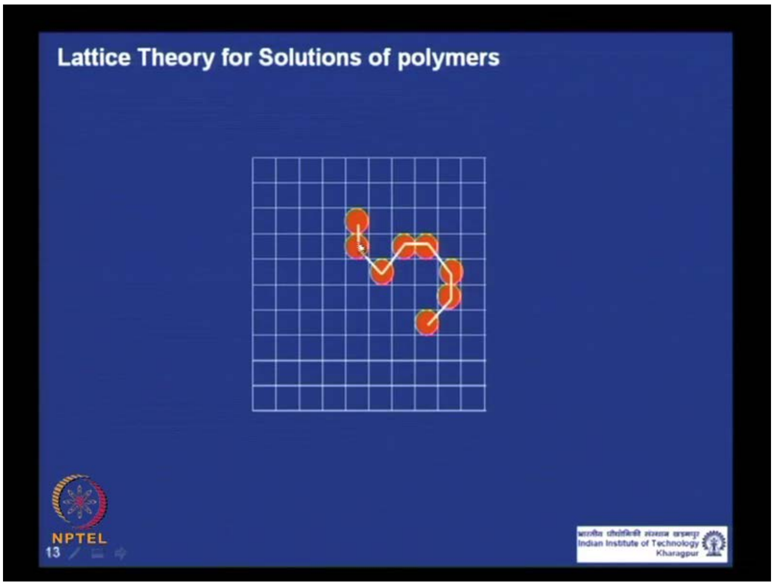
Lattice Theory for Solutions of polymers

If you go back here, each polymer segment, if all of these are, say for argument, all these neighboring cells has solvent molecules, and then it will have z contacts. One segment will have z polymer contacts; next one will have z minus 1 contacts; next one also z minus 1 contact. So, except the two ends, each segment have z minus 1 contact. So, each segment have z minus 1 contact. Now, what is the chance that each of this vacant cells is a solvent molecule or each of this contacts is giving a polymer solvent contact, which is again given by the volume fraction of the solvent molecule because, its segment size and the size of a solvent molecule is same. So, this would be given by the volume fraction.

So, the volume fraction of the solvent would be that, forbidding that, each segment or each neighborhood has a solvent molecule. So, that is, what is the chance that each segment would be giving up a polymer solvent contact. Now, this is any, just this is not 1. Each segment’s intermediate actually has z minus 2, one this side and one this side. So, they have z minus 2 contact. Each segment has z minus two 2, with a neighboring cell other than a polymer. So, if you consider this segment, it has z minus 2 contacts with other than polymer.

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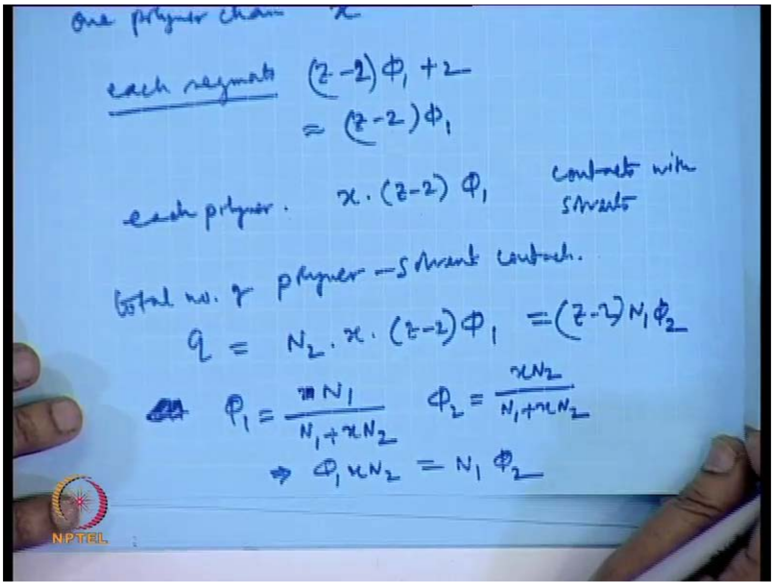

One polymer chain x

each segment $(z-2)\phi_1 + 2$

$= (z-2)\phi_1$

each polymer. $x\cdot(z-2)\phi_1$ contacts with solvents

total no. of polymer-solvent contacts.

$q = N_2\cdot x\cdot(z-2)\phi_1 = (z-2)N_1\phi_2$

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

$\Rightarrow \phi_1 x N_2 = N_1\phi_2$

Now, what is the chance that the other cells are solvent molecules? These have to be multiplied by solvent mono-fraction. You can add 2 extra for the two ends, which is z being high, I can just write, we can ignore the two ends and write this. So, this is each segment having this many polymer solvent contact. Each polymer has x segment. So, each polymer has how many contacts? x z minus 2. So, each polymer has these many contacts with solvents. So, total number of polymer solvent contacts, q would be, n 2 is the number of molecules, polymer molecules x, z minus 2 phi 1. So, now let us do some maths. phi 1 is given by n 1 n 1 plus x n 2. Phi 2 is given by x n 2 n 1 plus x n 2. This gives phi 1 x n 2 is n 1 phi 2. So, I can write this q, instead of phi 1 x n 2 phi 1 x n 2, I can write z minus 2 n 1 phi 2. So, this gives the total number of contacts q.

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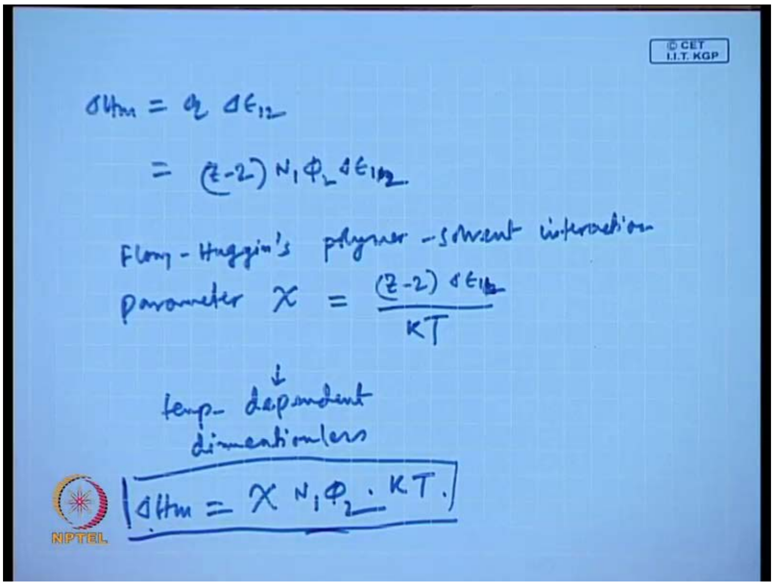

$$\Delta H_m = q\,\Delta\epsilon_{12}$$

$$= (z-2)\,N_1\phi_2\,\Delta\epsilon_{12}$$

Flory-Huggin's polymer-solvent interaction parameter $\chi = \frac{(z-2)\,\Delta\epsilon_{12}}{kT}$

↓

temp- dependent dimentionless

$$\boxed{\Delta H_m = \chi\, N_1 \phi_2 \cdot kT.}$$

So, what will be del h mixture? It will be q multiplied by 1 2. This should be z minus 2 n 1 phi 2. Now, to remove these terms, which is a little abstract, is the number of coordination number in the lattice. We already defined a term interaction, Flory-Huggins polymer solvent interaction, parameter chi was defined as z minus 2 k T. k is the Boltzmann constant and t is the absolute temperature. This chi is a temperature dependent dimensionless quantity, which is just defined like this to remove all the information from the lattice. So, we can write del h m is chi n 1 phi 2 into k T. So, this is the expression for the (()). We will come back and look at little more deep on the polymer solvent interaction. Parameter is basically gives you the difference when a solvent molecule is taken out from a solvent environment and put in a polymer environment.

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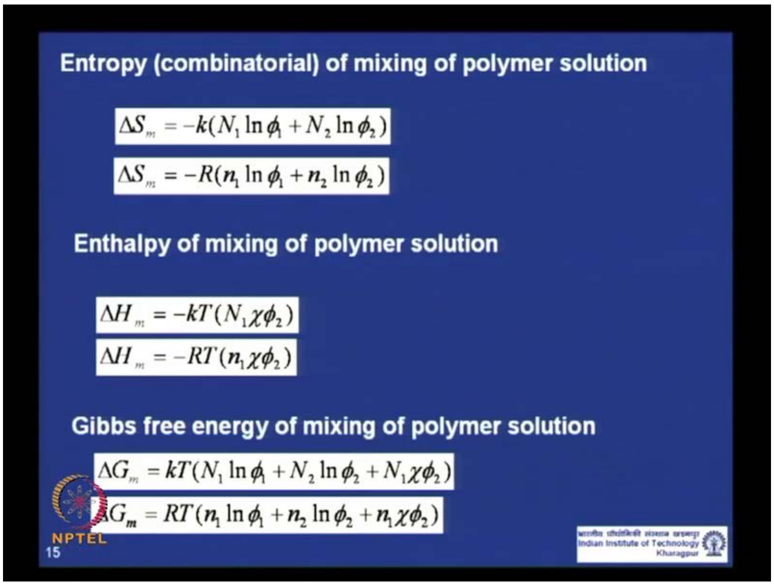

Entropy (combinatorial) of mixing of polymer solution

$$\Delta S_m = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2)$$

$$\Delta S_m = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2)$$

Enthalpy of mixing of polymer solution

$$\Delta H_m = -kT(N_1 \chi \phi_2)$$

$$\Delta H_m = -RT(n_1 \chi \phi_2)$$

Gibbs free energy of mixing of polymer solution

$$\Delta G_m = kT(N_1 \ln \phi_1 + N_2 \ln \phi_2 + N_1 \chi \phi_2)$$

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \chi \phi_2)$$

So, that is the, I guess the interaction energy between a polymer and a solvent and we named as a Flory-Huggins polymer solvent interaction parameter. So, that gives our enthalpy of mixing. So, if we just go back and see what we have seen, now we know the entropy of mixing of a polymer solution and polymer plus solvent is truly, now in this case, the entropy is truly a combinatorial entropy. Remember, we have only calculated this entropy and the number of ways you can arrange the polymer in the three lattice. So, it is a only configuration or combinatorial entropy. No other entropy is involved in this case. Now, we calculated the entropy or the enthalpy of mixing as k t, this is mentioned here and you can replace like this also. So, you can write Gibbs free energy mixing of polymer solution by this. This is given.

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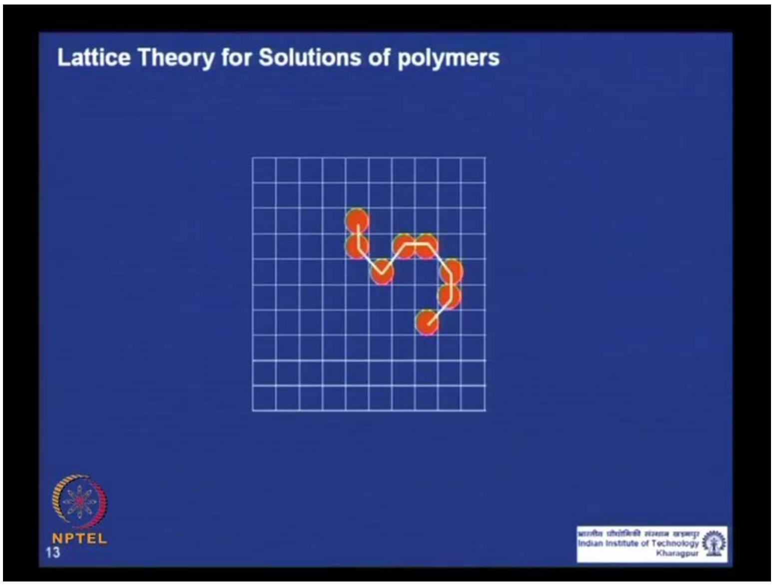

Lattice Theory for Solutions of polymers

Now, one thing you must ask wondering that, why should you use a lattice like this. Is this justifiable? In case of a pure liquid or a pure solvent or pure solution, the molecules are very regular, you know, quite regular, so that, we can use such a 3D lattice. As we have seen that or you know the place of the molecules in the first neighbor, in a solution or in a liquid is quite established, whereas the place of the second neighbor and third neighbor and so on, it will become uncertain. As we have seen that, in deriving this expression or against expression, only we are interested in the first neighbor. So, this type of model, 3D lattice model is quite justifiable. So, this expression is which we derived using 3D lattice model should be quite justifiable. Now, this is known as Flory-Huggins equation as you might have known by now. So, just rewrite this. I am breaking into two terms. This term, as we, this is again.