Introduction to Polymer Science
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Lecture - 23
Polymers in Solution: Flory - Huggins Theory

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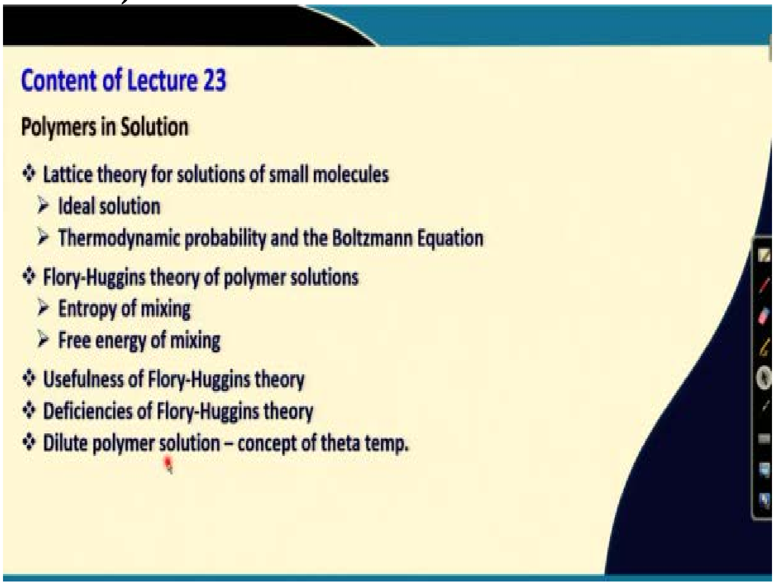

Content of Lecture 23

Polymers in Solution

- Lattice theory for solutions of small molecules
  - Ideal solution
  - Thermodynamic probability and the Boltzmann Equation
- Flory-Huggins theory of polymer solutions
  - Entropy 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. From this lecture onwards we will start a new module on characterization of polymers and in today's lecture the focus will be on polymers in solution.

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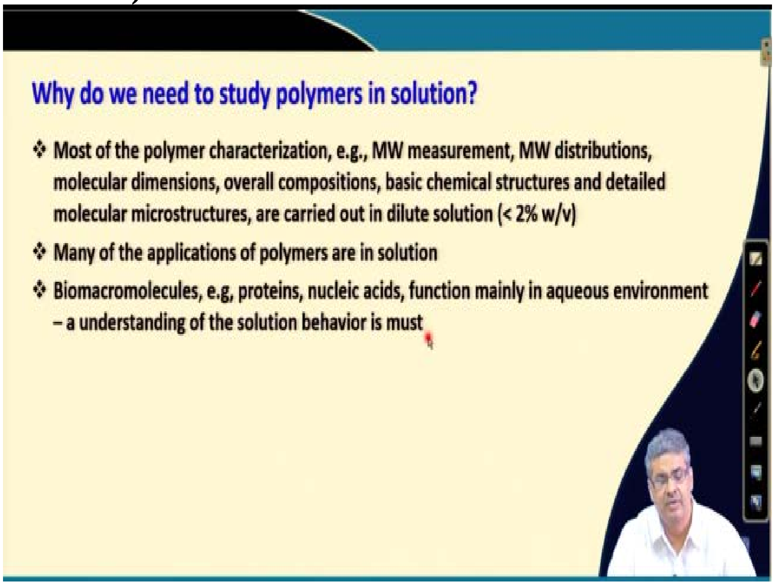

Why do we need to study polymers in solution?

- Most of the polymer characterization, e.g., MW measurement, MW distributions, molecular dimensions, overall compositions, basic chemical structures and detailed molecular microstructures, are carried out in dilute solution (< 2% w/v)
- 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, first question is why do we need to study polymers in solution? Most of the polymer characterization techniques which we will learn in coming lectures, for example, molecular weight measurement, molecular weight distribution, molecular dimensions, overall compositions, basic chemical structure and detailed microstructure, they are mostly carried out in dilute solution. By dilute it means, it is approximately less than 2% weight by volume in the solution. Another reason is that many of the applications of polymers are in solution e.g. biomacromolecules like proteins, nucleic acids function mainly in aqueous environment and understanding of their solution behavior is a must to understand the function of proteins and nucleic acids.

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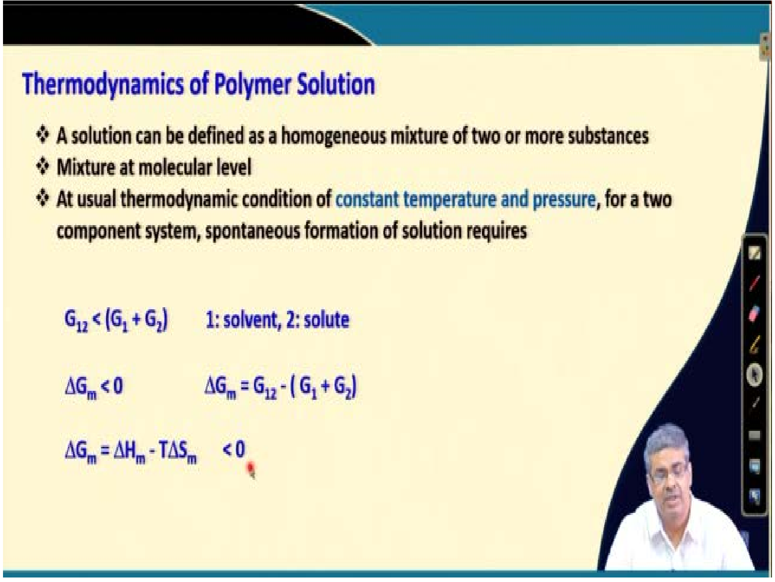

Thermodynamics of Polymer Solution

- 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

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

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

Let me begin with thermodynamics of polymer solution. A solution can be defined as a homogeneous mixture of 2 or more substances and a homogeneous mixture means mixtures at molecular level, i.e. if I collect a sample from different parts of the solution, the molecular composition of different parts will be same. At usual thermodynamic conditions of constant temperature and pressure for a 2 component system, for example, a solute and a solvent, the spontaneous formation of solution requires that the Gibbs free energy of the system after mixing which is represented as G_{12} should be less than the summation of Gibbs free energy of the individual components. Now, going forward, 1 will generally represent the solvent component and 2, the solute component. In the solution, the Gibbs free energy of mixing at constant temperature and pressure should be less than 0. From our basic knowledge of thermodynamics at constant temperature and pressure, we can represent Gibbs free energy of mixing as,

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where, ΔH_m is enthalpy of mixing, ΔS_m is entropy of mixing and ΔG_m must be less than 0 to form the solution spontaneously.

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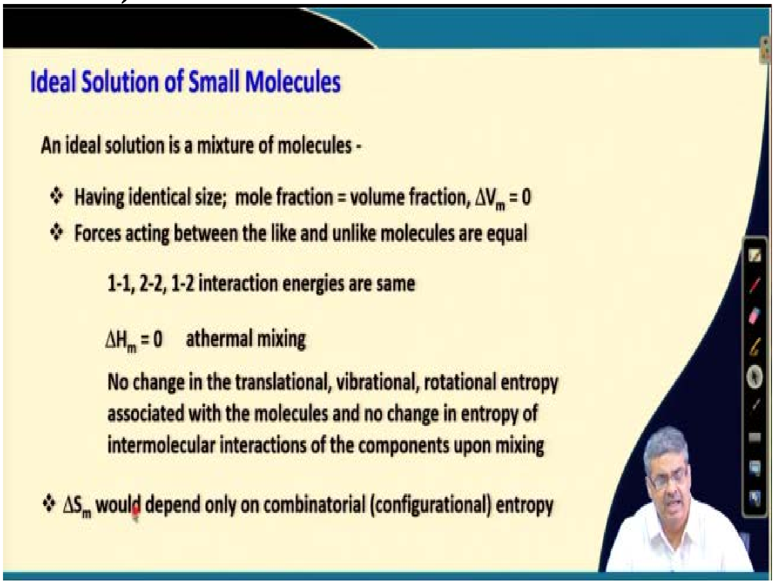

Ideal Solution of Small Molecules

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

  $\Delta H_m = 0$ athermal mixing

  No change in the translational, vibrational, rotational entropy associated with the molecules and no change in entropy of intermolecular interactions of the components upon mixing

- ΔS_m would depend only on combinatorial (configurational) entropy

Now, let us begin with the ideal solution of small molecules. An ideal solution is a mixture of molecules having identical size, which means, mole fraction is equal to the volume fraction and delta V_m, which is the change in volume on mixing, is zero. That means, whatever the volume was before mixing is same after mixing, and the forces acting between the two like molecules are same as forces acting between the unlike molecules which means here the forces between solute molecules are same as the forces between solvent molecules. i.e., 1-1 interactions are of same energies as 2-2 and 1-2. In effect this means that enthalpy of mixing is zero or we call this as athermal mixing and hence there is no change in translational, vibrational, rotational entropy associated with the molecules as well as there is no change in entropy of intermolecular interactions of the components upon mixing. The entropy of mixing comes only from the combinatorial part of the entropy, we also call this as configurational entropy in some text. So, in Gibbs free energy of mixing, the ΔS_m, in case of ideal solution of small molecules comes only from the combinatorial entropy.

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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

k is the Boltzmann constant

Now, let us discuss how to calculate this combinatorial entropy for small molecules leading to ideal solutions and for that lattice theory was proposed earlier and combinatorial entropy of the system is given by the number of possible distinguishable spatial arrangements. For a given state we know the Boltzmann equation, which is given by this expression, S is entropy, k is Boltzmann constant and W, sometimes expressed as omega (ϖ), is the number of possible distinguishable degenerate (states of equal energy) arrangements in this case.

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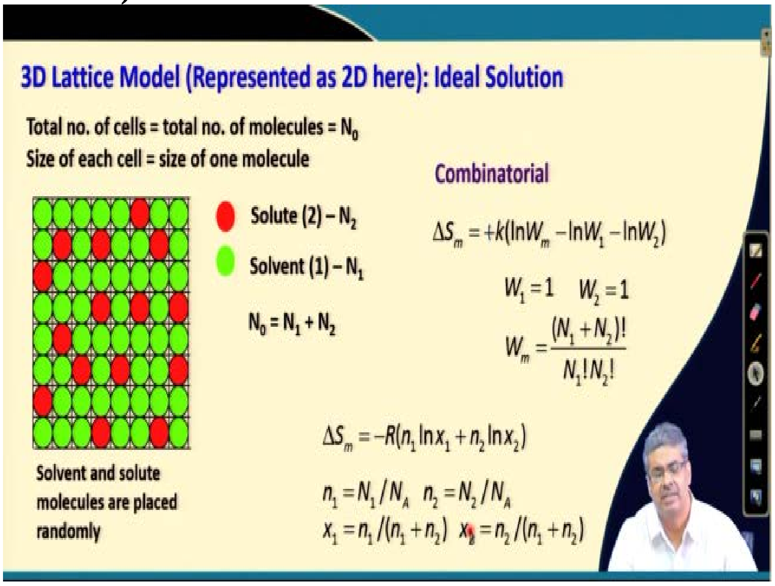

3D Lattice Model (Represented as 2D here): Ideal Solution

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

Combinatorial

$$\Delta S_m = +k(\ln W_m - \ln W_1 - \ln W_2)$$

$$W_1 = 1 \quad W_2 = 1$$

$$W_m = \frac{(N_1 + N_2)!}{N_1! N_2!}$$

$$\Delta S_m = -R(n_1 \ln x_1 + n_2 \ln x_2)$$

$$n_1 = N_1 / N_A \quad n_2 = N_2 / N_A$$
$$x_1 = n_1 / (n_1 + n_2) \quad x_2 = n_2 / (n_1 + n_2)$$

In the 3D lattice model for ideal solution we have a 3D matrix, though in this screen it has been represented as 2D but you can imagine that there are cells coming out of this computer screen as well as there are cells behind the screen forming a 3D structure. For simplicity, it is shown as 2D structure here. Now, the total number of cells in this lattice is the total number of molecules, which is represented as N_0, and size of each cell is equal to the size of 1 molecule of the solvent or solute, and since we have considered ideal solution, they are same. Now, when we have this lattice filled up with two components, the one shown here with the red circles are for solutes. We generally represent solutes by the number 2, and this green ones as solvent molecules, the number of solute molecules are given by N_2 and number of solvent molecules given by N_1. So, total number of molecules is capital $N_1 + N_2$. N_0 is the total number of cells in this lattice. As there is no preference, or preferred interaction between solvent and solute molecules, we can place the solvent and solute molecules randomly in these cells. So, the combinatorial entropy will be given by the entropy after mixing which is given by klnW. The entropy before mixing is given by $k\ln W_1 + k\ln W_2$ corresponding to solvent molecules and the solute molecules respectively. If this lattice was filled up with only solute molecules, with only red circles, then how many different distinguishable ways we can arrange these circles? It would be only 1, since no matter how many interchanges between these circles you make, you will always land up with the same arrangement because they are all red circles. So, W_2 would be equals to 1. Similarly, if this lattice is filled up with only solvent molecules or green circles, then also we will have W_1 is equals to 1 because we will have only 1 distinguishable arrangement irrespective of how many number of exchanges or interchanges we do between these circles within this lattice. So, W_1 would be also equals to 1 and W_2 also will be equals to 1. So, W_m would be given by the number of ways we can arrange these $N_1 + N_2$ molecules, and we can remove the arrangements which are done by interchange between the similar molecules. We get the number of distinguishable arrangements that can be possible from N_1 solvent molecules and N_2 solute molecules, will be given by this expression. The combinatorial entropy for this mixture is given by this expression where n_1 is the number of moles of solvent molecules, which is given by number of molecules divided by Avogadro's number, n_2 is the number of moles of solute molecules, and x_1 is nothing but mole fraction of solvent molecules and x_2 is the mole fraction of solute molecules.

$$\Delta S_m = k(\ln W_m - \ln W_1 - \ln W_2)$$

$$W_1 = 1 \qquad W_2 = 1$$

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

$$\Delta S_m = -R(n_1 \ln x_1 + n_2 \ln x_2)$$

$$n_1 = N_1/N_A \qquad n_2 = N_2/N_A$$

$$x_1 = n_1/(n_1 + n_2) \qquad x_2 = n_2/(n_1 + n_2)$$

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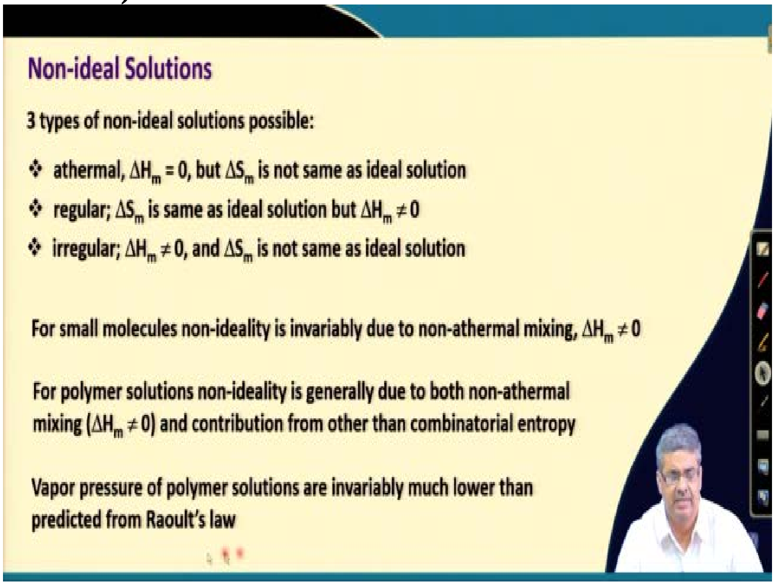

Non-ideal Solutions

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 to 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, that was in the case of ideal solution. Most of the solutions are non-ideal and there could be 3 types of non-ideal solutions possible, one is athermal where ΔH_m or enthalpy of mixing is 0, but entropy of mixing is not same as ideal solution; second possibility is just a reverse, where ΔS is mixing is same as ideal solution, but enthalpy of mixing is not equals to 0. And the third is irregular where both are not same as ideal solution. Now, most of the cases of small molecules, they differ from ideality because of non athermal mixing or in another way that enthalpy of mixing is not equals to 0. For example, if we mix water with ethanol we will get non-ideal behavior because of ΔH_m not equals to 0. In case of polymer solutions, non-ideality is generally due to both non-athermal mixing i.e. ΔH not equals to 0 and contribution to entropy by other than combinatorial effect. So, basically there could be other entropies which will also contribute in ΔS_m for polymer solutions. Vapor pressures of polymer solutions are invariably much lower than what is predicted from Raoult's law.

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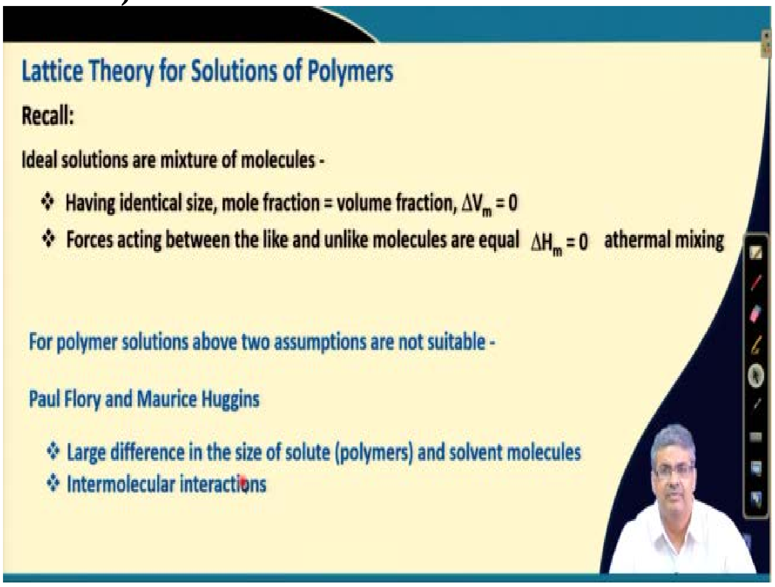

Lattice Theory for Solutions of Polymers

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 molecules
- Intermolecular interactions

Let us now discuss the lattice theory for solutions of polymers. We must recall that for ideal solutions for small molecules, we had identical size of the components and there was no preference of interaction between like and unlike molecules. So, we had ΔV_m is 0 and ΔH_m is 0 as well. Now, in case of polymers solutions, these two assumptions are not accurate. These two scientists, Paul Flory and Maurice Huggins actually deduced a theory for thermodynamics of polymers solutions, considering the large differences in the size of solutes e.g. polymers in this case, and solvent molecules in a polymer solution, and also the existence of intermolecular interactions between the polymer molecules and the solvent molecules. So, they basically considered these two non-ideal situations and derived an equation for polymers solution.

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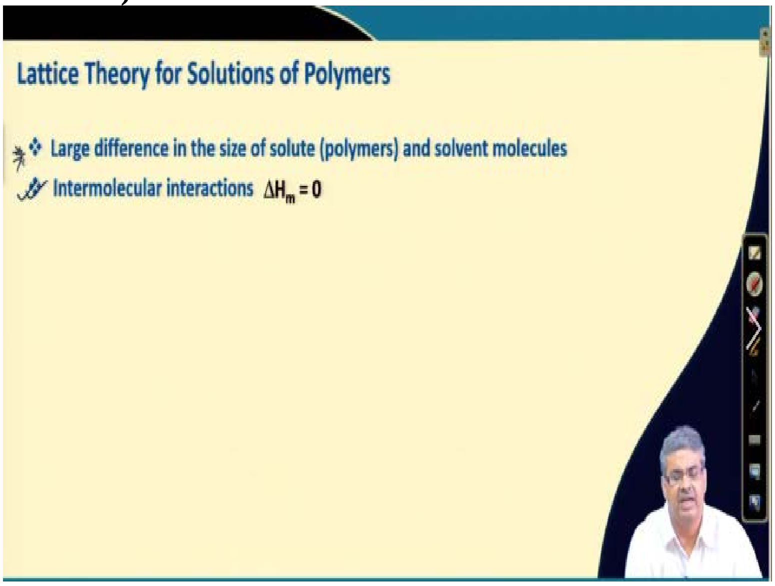

Lattice Theory for Solutions of Polymers

- Large difference in the size of solute (polymers) and solvent molecules
- Intermolecular interactions $\Delta H_m = 0$

These are the two possible reasons for deviation from ideality for polymers solution. So, in first case, we will consider that, this is ok, that for the polymer solution, ΔH, you know, it does not contribute anything on ΔH_m. We will only first consider the effect of large differences in the size of solute, in this case polymer and solvent molecules.

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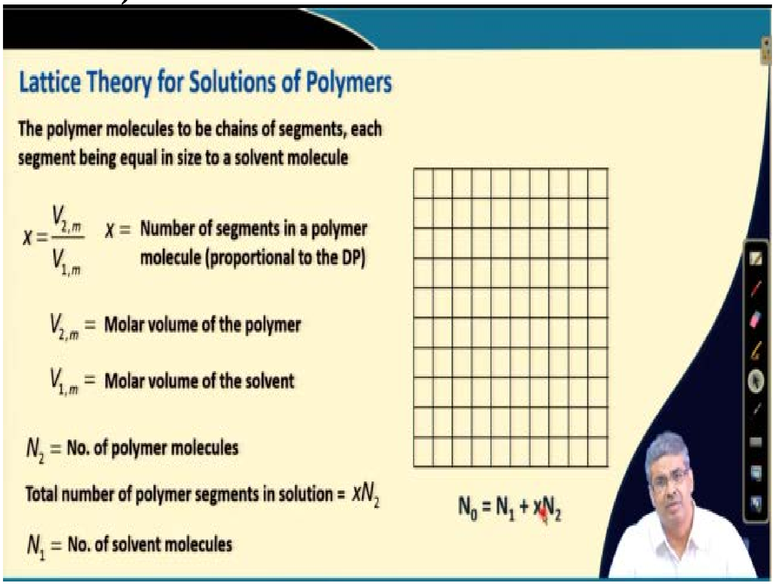

Lattice Theory for Solutions of Polymers

The polymer molecules to be chains of segments, each segment being equal in size to a solvent molecule

$x = \frac{V_{2,m}}{V_{1,m}}$ x = Number of segments in a polymer molecule (proportional to the DP)

$V_{2,m}$ = Molar volume of the polymer

$V_{1,m}$ = Molar volume of the solvent

N_2 = No. of polymer molecules

Total number of polymer segments in solution = xN_2

N_1 = No. of solvent molecules

$N_0 = N_1 + xN_2$

Flory and Huggins considered the polymer molecules to be chains of segments and each segment being equal in size to the solvent molecule. They considered that a polymer chain consists of several segments of equal length and each segment have same volume as the volume of a solvent molecule. So, the number of segment in one polymer molecule is given by $x=V_{2,m}/V_{1,m}$ where $V_{2,m}$ and $V_{1,m}$ are molar volume of polymer and molar volume of solvent respectively So, x is proportional to the degree of polymerization, but not necessarily equal to the degree of polymerization for that particular polymer. Now, if N_2 is the number of polymer molecules, then the total number of polymer segments present in the solution is given by xN_2, x is the number of segments for one polymer and N_2 is the total number of polymer molecules. Now, if I have N_1 number of solvent molecules, then I need to construct a lattice with a total number of these many cells plus N_1 cells, then we can fill all the cells with either solvent molecules or a polymer segment. So, we can construct a 3D lattice having N_0 numbers of cells, and each of these cells will be filled with either a solvent molecule or a polymer segment. So, the total number of cells in this 3D lattice will be given by N_1 number of solvent molecules plus total number of polymer segments present in this solution.

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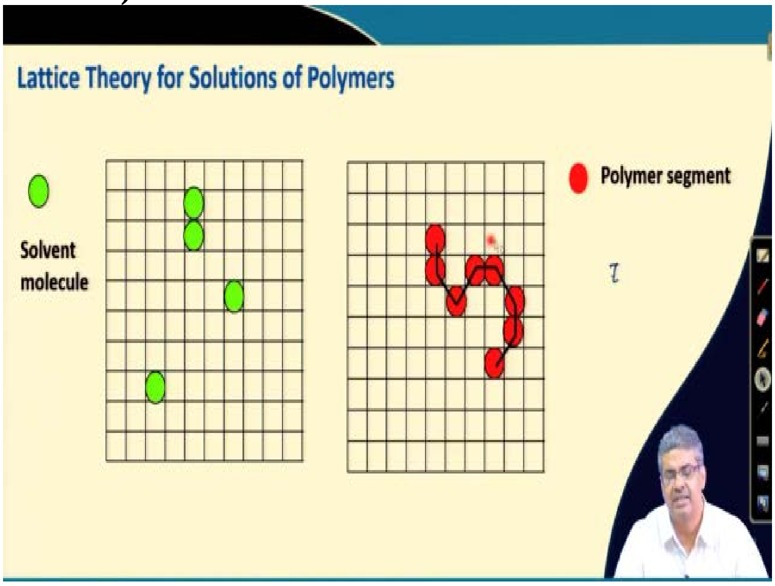

Lattice Theory for Solutions of Polymers

If we have a solvent molecule in this lattice, next solvent molecule I can place anywhere, evene next to the existing solvent molecule. So, the number of ways I can place this second solvent molecule depends on the number of free cells present in this lattice, there is no bias that it has to be placed in a particular area in these 3D cells. However, in case of polymer, if I have a segment placed in this particular cell, then the next segment can only be placed in the second cell in the neighborhood, as the next segment is covalently connected with the first segment. The number of neighboring cells is given by the coordination number in this particular case and we generally represent the coordination number as z. So, this second segment can only be placed among the available cells, which is in the neighborhood of the first segment and the third can be placed in the vicinity of the second and so on.

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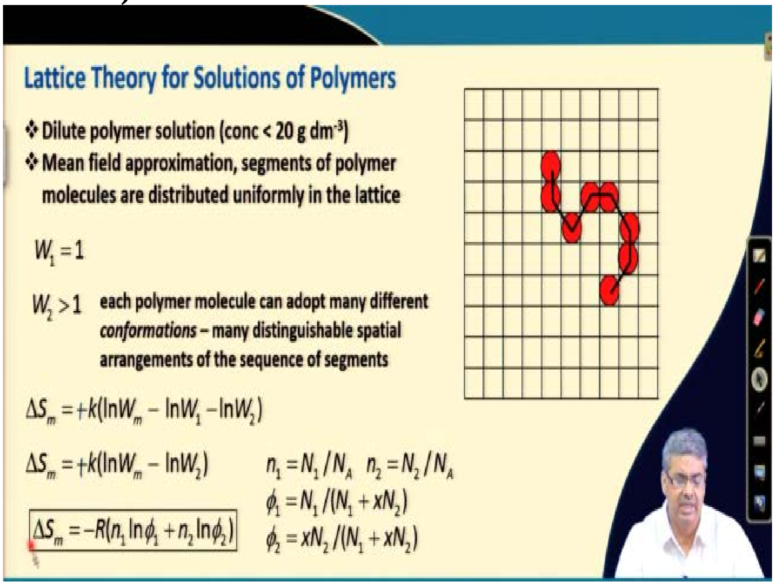

Lattice Theory for Solutions of Polymers

- Dilute polymer solution (conc < 20 g dm^{-3})
- Mean field approximation, segments of polymer molecules are distributed uniformly in the lattice

$W_1 = 1$

$W_2 > 1$ each polymer molecule can adopt many different *conformations* – many distinguishable spatial arrangements of the sequence of segments

$\Delta S_m = +k(\ln W_m - \ln W_1 - \ln W_2)$

$\Delta S_m = +k(\ln W_m - \ln W_2)$ $n_1 = N_1 / N_A$ $n_2 = N_2 / N_A$

$\phi_1 = N_1 / (N_1 + xN_2)$

$\boxed{\Delta S_m = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2)}$ $\phi_2 = xN_2 / (N_1 + xN_2)$

We must understand that there are two assumptions that the polymer solutions are dilute in nature (concentration < 20 g dm^{-3}) and another approximation, called mean field approximation, where it is assumed that the segments of polymer molecules which are already present in the lattice, they are distributed uniformly in the lattice, not localized in any part of the lattice. So, if we consider these two assumptions, then we can deduce the expression for the entropy of mixing for a polymer solution. Now, again for the solvent molecules, because they are of identical molecules, W_1 is 1 as we discussed earlier, but for polymer molecules W_2 is greater than 1, because each polymer molecule can adopt many different confirmations. As a result, we can have many distinguishable spatial arrangements of the sequence of segments. Hence, W_2 is not equals to 1 in this case, but it is much larger than 1. So, when we consider the entropy of mixing, in this case W_1 is 1, so entropy term is 0. So, we will have the expression

$\Delta S_m = k(\ln W_m - \ln W_2)$.

Now, in this case, the model is derived by Flory Huggins in such a way that they found out the number of ways each polymer segment can be introduced in the lattice where the lattice was partially filled with some of the polymer molecules. Then, if this segment has to be placed, then it has to be placed in the vicinity of this segment. Number of cells totally available is z, but out of that z number of neighboring cells, some are already occupied with existing polymer segments now, so, it can be only placed in the free neighborhood cells and that free neighborhood cells will be given by z - 2, one this side and another the other side multiplied by the volume fraction of the polymer molecules present in the system. So, when a fresh segment is introduced in the cell, the number of ways it can be introduced within the cell is proportional to z - 2 multiplied by the volume fraction of the polymer molecule. Now, I am not going in the details of derivation of Flory Huggins equation, but I am straight going to the expression they have derived for entropy of mixing which is given by this expression.

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

$$\text{Where} \quad \phi_1 = N_1/(N_1 + xN_2)$$

$$\phi_2 = xN_2/(N_1 + xN_2)$$

In case of small molecules, we had mole fraction. Now, in this polymer solution, instead of mole fraction, we have volume fraction. So, ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer molecules, respectively, in this solution. So, n_1 is the number of moles of solvent molecules, n_2 is the number of moles of polymer molecules and ϕ_1 is the volume fraction of solvent and ϕ_2 is the volume fraction of the polymer molecules. So, this is the expression for the combinatorial entropy for a polymer solution derived by Flory and Huggins. Why this is combinatorial? Remember, till now we are assuming that ΔH_m or enthalpy of mixing is 0. That means, the only contribution to this entropy of mixing comes from combinatorial entropy.

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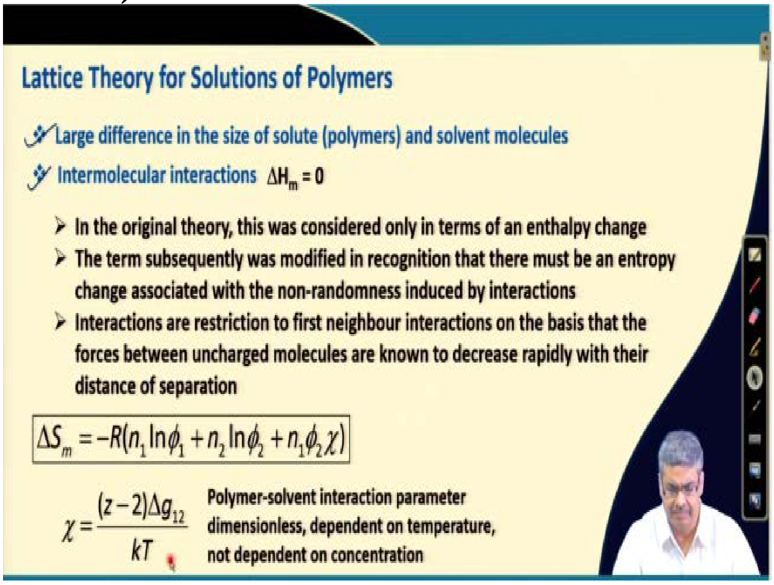

Lattice Theory for Solutions of Polymers

- Large difference in the size of solute (polymers) and solvent molecules
- Intermolecular interactions $\Delta H_m = 0$
  - In the original theory, this was considered only in terms of an enthalpy change
  - The term subsequently was modified in recognition that there must be an entropy change associated with the non-randomness induced by interactions
  - Interactions are restriction to first neighbour interactions on the basis that the forces between uncharged molecules are known to decrease rapidly with their distance of separation

$$\boxed{\Delta S_m = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi)}$$

$$\chi = \frac{(z-2)\Delta g_{12}}{kT}$$

Polymer-solvent interaction parameter dimensionless, dependent on temperature, not dependent on concentration

We have considered the first factor till now, we need to consider the other factor as well. Because ΔH_m is not equals to 0, this will not only contribute to the value for enthalpy of mixing in Gibbs free energy but, because of intermolecular interaction, there will be some contribution in the entropy of mixing as well.

Now, in the original theory by Flory and Huggins, it was only considered in terms of enthalpy change, but later it was modified in recognition that there must be an entropy change associated with the non-randomness induced by the interaction between polymer and solvent molecules. We also considered the interactions only among the first neighborhood molecules, only on the basis that the forces between uncharged molecules are known to decrease rapidly with their distance of separation. Again without going into the derivation part, the entropy of mixing is represented by this expression where χ is polymer-solvent interaction parameter, a dimensional temperature dependent parameter which is not dependent on concentration, z is the coordination number and Δg_{12} is the change in contact Gibbs free energy as a result of contact between solvent and polymer molecules. This is Boltzmann constant and this is absolute temperature.

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

$$\chi = \frac{(z-2)\Delta g_{12}}{kT}$$

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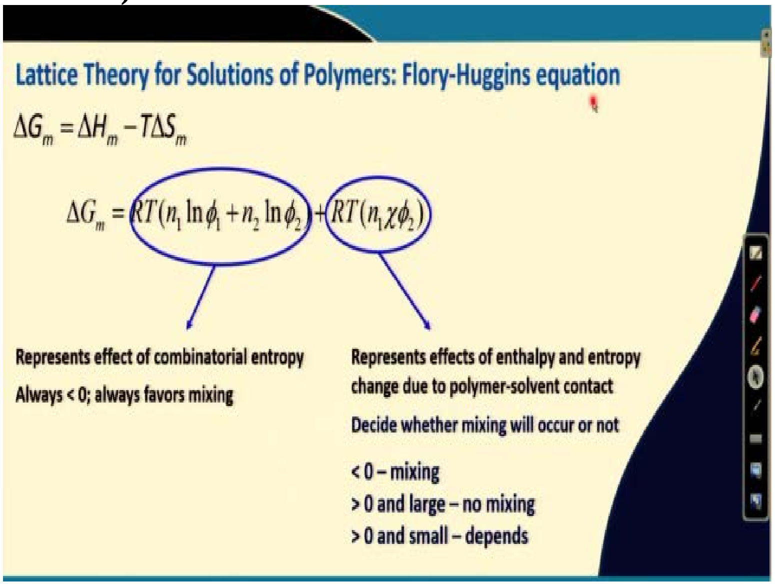

Lattice Theory for Solutions of Polymers: Flory-Huggins equation

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

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

Represents effect of combinatorial entropy

Always < 0; always favors mixing

Represents effects of enthalpy and entropy change due to polymer-solvent contact

Decide whether mixing will occur or not

< 0 – mixing

> 0 and large – no mixing

> 0 and small – depends

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

This is the equation for ΔG_m at constant temperature. The first part represents the effect of combinatorial entropy which is always negative, as these are volume fractions. So, this term is negative, which means that this term always favors mixing which is expected because mixing always increases the number of ways two molecules can be arranged in a mixture. The second term represent the effect of enthalpy and entropy change due to polymer solvent contacts and these basically decide whether the polymer and solvent will mix to form a solution or not? If it is less than zero, obviously, then it will form a solution. If it is positive and very high value then there will be no mixing as it will make ΔG_m a positive term. If it is positive and small, then obviously, it will depend on the value of the second part. So, this is the term the value of which will determine whether a polymer solvent will mix to form a polymer solution. In the next class we will discuss the utility or usefulness of this Flory Huggins equation as well as deficiency of Flory Huggins equations, and some derivation of thermodynamic quantities will be done.