Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 9 - Flory-Huggins Model for Polymer Solutions

February 5, 2001

Read Sperling, Chapter 4

Objectives

■ To develop the classical **Flory-Huggins** theory for the free energy of mixing of polymer solutions based on a statistical approach on a regular lattice.

■ To describe the criteria for phase stability and illustrate typical phase diagrams for polymer blends and solutions.

Outline

- **Lattice Theory for Solutions of Small Molecules**
  - Thermodynamic probability and the Boltzmann Equation
  - Ideal solution
- **Flory-Huggins Theory of Polymer Solutions**
  - Placement of a new polymer molecule on a partially filled lattice
  - Entropy of mixing
  - Enthalpy of mixing (for dispersive or dipole-dipole interactions)
  - Cohesive energy density and solubility parameter
  - Free energy of mixing

Lattice Theory for Solutions of Small Molecules

Assume that a **solution** may be formed by distributing the pure components on the sites of a regular **lattice**. Further assume that there are N_1 molecules of Type 1, N_2 molecules of Type 2, and that Type 1 and Type 2 molecules are indistinguishable but identical in size and interaction energy.
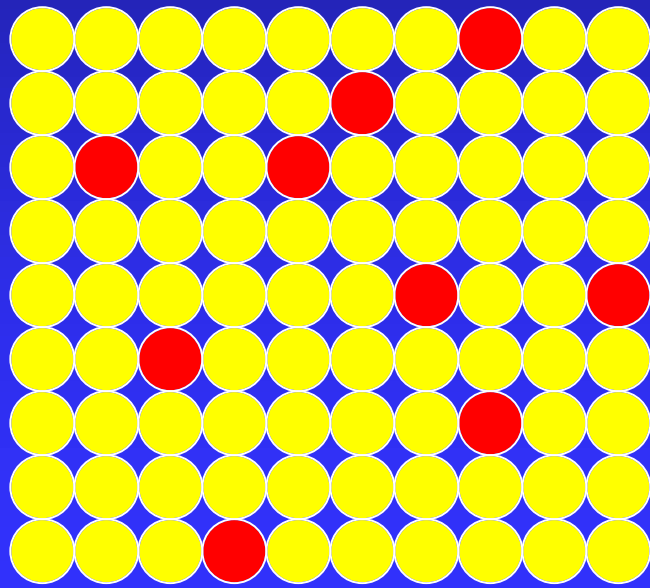
Small molecule of Type 1 (e.g. solvent)

Small molecule of Type 2 (e.g. solute)

Thermodynamic Probability

Place the molecules on the $N = N_1 + N_2$ sites of a three-dimensional lattice.

Total number of arrangements of N molecules

Total no. different ways of arranging molecules of Types 1 and 2 on the lattice

$$\equiv \quad \Omega = \frac{N!}{N_1! N_2!}$$

Interchanging the 1's or 2's makes no difference.

Ω is the **thermodynamic probability**, which counts the number of ways that a particular state can come about.

Boltzmann Equation

The **thermodynamic probability** (or the number of ways that the system may come about)may be related to the **entropy** of the system through a fundamental equation from statistical thermodynamics that is known as the **Boltzmann Equation**.

$$S = k \ln \Omega$$

Configurational Entropy

Apply the Boltzmann Equation to the mixing process:

$$\Delta S = S_2 - S_1 = k \ln\left(\frac{\Omega_2}{\Omega_1}\right)$$

$$\Omega_2 > \Omega_1 \implies \Delta S > 0$$

$$\Omega_2 < \Omega_1 \implies \Delta S < 0$$

Consider the entropy of the mixture:

$$S_{mix} = k \ln \Omega = k\left(\ln N! - \ln N_1! - \ln N_2!\right)$$

$$N \equiv N_A$$

Stirling's approximation: $\ln y! \cong y \ln y - y$

$$S_{mix} = -k\left[N_1 \ln\left(\frac{N_1}{N}\right) + N_2 \ln\left(\frac{N_2}{N}\right)\right]$$

Multiply r.h.s. by $\dfrac{N_A}{N_A}$

$$S_{mix} = -R\left(x_1 \ln x_1 + x_2 \ln x_2\right)$$

$$\Delta S_m = S_{mix} - S_1 - S_2 = -R\sum x_i \ln x_i$$

$$S_{mix} = \Delta S_m$$

S_{mix} is that part of the total entropy of the mixture arising from the mixing process itself. This is the **configurational entropy**.

Ideal Solution of Small Molecules

What entropy effects can you envision other than the configurational entropy?

$$\Delta S_m = -R \sum x_i \ln x_i$$

If the 1-1, 2-2, and 1-2 interactions are equal, then

$$\Delta H_m = 0$$

(athermal mixing)

If the solute and the solvent molecules are the same size,
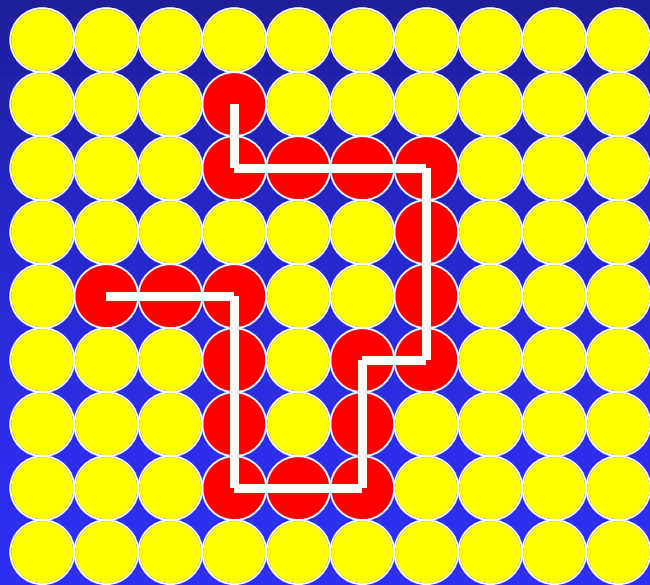
$$\Delta V_m = 0$$

The thermodynamics of mixing will be governed by the Gibbs free energy of mixing.
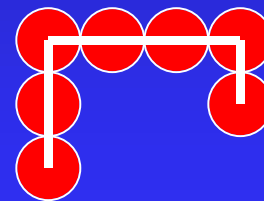
$$\Delta G_m = -RT \sum x_i \ln x_i$$

Do you expect a polymer solution to be ideal?

Lattice Approach to Polymer Solutions

To place a macromolecule on a lattice, it is necessary that the polymer segments, which do not necessarily correspond to a single repeat unit, are situated in a contiguous string.

Small molecule of Type 1 (solvent)

Macromolecule of Type 2 (solute)

Flory-Huggins Theory of Polymer Solutions

Assume (for now) that the polymer-solvent system shows **athermal** mixing. Let the system consist of N_1 **solvent** molecules, each occupying a **single site** and N_2 **polymer** molecules, each occupying **n lattice sites**.

$$N_1 + nN_2 = N$$

What assumption about molecular weight distribution is implicit in the system chosen?

Placement of a New Polymer Molecule on a Partially Filled Lattice

Let **(i) polymer molecules be initially placed** on an empty lattice and determine the number of ways that the **(i + 1)st polymer molecule** can be placed on the lattice.
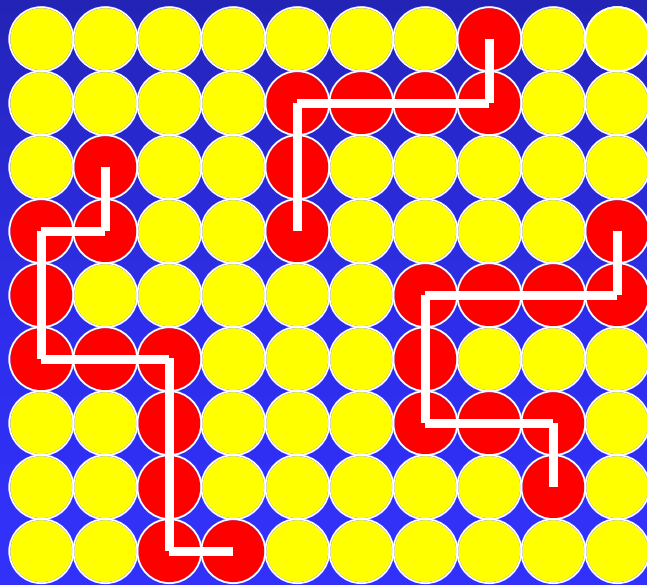
How can we get the (i+1)st molecule to fit on the lattice?
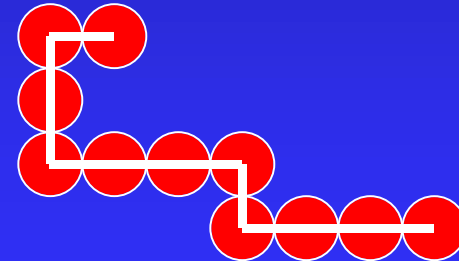
Placement of Polymer Segments on a Lattice

Placement of first segment of polymer (i + 1):

$$N - ni =$$

Number of remaining sites

Number of ways to add segment 1

Number of sites occupied
by initial i polymer molecules

Placement of second segment of polymer (i + 1):

Let Z = coordination number of the lattice

$$Z\left(\frac{N - ni}{N}\right) =$$

Number of ways to add segment 2

Number of lattice
sites adjacent to the
first segment

Average fraction of vacant sites on
the lattice as a whole (When is this
most valid?)

Probability of Placement of the (i)th Molecule

Placement of third segment (and all others) of polymer (i + 1):

$$(Z - 1)\left(\frac{N - ni}{N}\right) =$$ Number of ways to add segment 3

One site on the coordination sphere is occupied by the second segment

Ignore contributions to the average site vacancy due to segments of molecule (i + 1)

Thus, the (i + 1)st polymer molecule may be placed on a lattice already containing (i) molecules in ω_{i+1} ways.

$$\omega_{i+1} = (N - ni)Z\left(\frac{N - ni}{N}\right)\left[(Z - 1)\left(\frac{N - ni}{N}\right)\right]^{n-2}$$

$$\omega_{i+1} = Z(Z - 1)^{n-2} N\left(\frac{N - ni}{N}\right)^{n}$$

For the (i)th molecule:

$$\omega_i = Z(Z - 1)^{n-2} N\left(\frac{N - n(i - 1)}{N}\right)^{n}$$

Total Number of Ways of Placing N_2 Polymer Molecules on a Lattice

$$\Omega = \frac{\omega_1 \omega_2 \sqcup \omega_i \sqcup \omega_{N_2}}{N_2!} = \frac{1}{N_2!} \prod_{i=1}^{N_2} \omega_i$$

Apply Boltzmann's Equation: $S_{mix} = k \ln \left(\frac{1}{N_2!} \prod_{i=1}^{N_2} \omega_i \right)$

Substitute for ω_i to obtain:

$$\Omega = \frac{Z^{N_2} (Z-1)^{N_2(n-2)}}{N_2! \, N^{N_2(n-1)}} \prod_{i=1}^{N_2} \left[N - n(i-1) \right]^n$$

Examine the product:

$$\frac{nN}{n} = N$$

$$\prod_{i=1}^{N_2} \left[N - n(i-1) \right]^n = n^{nN_2} \prod_{i=1}^{N_2} \left(\frac{N}{n} + 1 - i \right)^n$$

Entropy of the Mixture

Write out several terms in the product expression:

$$\prod = \left(\frac{N}{n} + 1 - 1\right)^n \left(\frac{N}{n} + 1 - 2\right)^n \left(\frac{N}{n} + 1 - 3\right)^n \llcorner \left(\frac{N}{n} + 1 - N_2\right)^n$$

Note that:
$$\frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n} - N_2\right)!} = \frac{(1)(2)(3)\llcorner\left(\frac{N}{n} - N_2\right)\left(\frac{N}{n} - N_2 + 1\right)\llcorner\left(\frac{N}{n}\right)}{(1)(2)(3)\llcorner\left(\frac{N}{n} - N_2\right)}$$

Thus

$$\prod = \left[\frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n} - N_2\right)!}\right]^n \qquad \Omega = \frac{Z^{N_2}(Z-1)^{N_2(n-2)} n^{nN_2}}{N_2! N^{N_2(n-1)}} \left[\frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n} - N_2\right)!}\right]^n$$

Apply Stirling's approximation to obtain:

$$\frac{S_{mix}}{k} = -N_2 \ln\left(\frac{nN_2}{N}\right) - N_1 \ln\left(\frac{N_1}{N}\right)$$
$$+ N_2\left[\ln Z + (n-2)\ln(Z-1) + (1-n) + \ln n\right]$$

Flory-Huggins Entropy of Mixing

Calculate entropy of pure solvent and pure polymer:

Pure solvent: $N_2 = 0$ $S_1 = 0$

Pure polymer: $N_1 = 0$ Entropy of the disordered polymer when it fills the lattice

$$S_2 = kN_2\left[\ln Z + (n-2)\ln(Z-1) + (1-n) + \ln n\right]$$

$$\Delta S_m = S_{mix} - S_2 - S_1 \qquad \Delta S_m = -k\left[N_1\ln\left(\frac{N_1}{N}\right) + N_2\ln\left(\frac{nN_2}{N}\right)\right]$$

Multiply and divide r.h.s. by N_1+N_2 and assume $N_1+N_2=N_A$

Calculate entropy of mixing:

$$\Delta S_m = -R\left[x_1\ln\left(\frac{N_1}{N}\right) + x_2\ln\left(\frac{nN_2}{N}\right)\right] \qquad \frac{N_1}{N} = \varphi_1 \qquad \frac{nN_2}{N} = \varphi_2$$

Flory-Huggins Theory for an Athermal Solution

Entropy of mixing:

$$\Delta S_m = -R\left[x_1 \ln\varphi_1 + x_2 \ln\varphi_2\right]$$

Enthalpy of mixing:

$$\Delta H_m = 0$$

Gibbs free energy of mixing:

$$\Delta G_m = -RT\left[x_1 \ln\varphi_1 + x_2 \ln\varphi_2\right]$$

Concentration Conversions

$$\frac{\varphi_2}{\varphi_1} = \frac{nN_2}{N_1}$$

$$\frac{N_2}{N_1} = \frac{1}{n}\left(\frac{\varphi_2}{\varphi_1}\right)$$

$$x_2 = \frac{N_2}{N_1 + N_2} = \frac{\dfrac{N_2}{N_1}}{1 + \dfrac{N_2}{N_1}} = \frac{\dfrac{1}{n}\left(\dfrac{\varphi_2}{\varphi_1}\right)}{1 + \dfrac{1}{n}\left(\dfrac{\varphi_2}{\varphi_1}\right)}$$

$$x_1 + x_2 = 1 \qquad \varphi_1 + \varphi_2 = 1$$

$$x_2 = \frac{\left(\dfrac{1}{n}\right)\left(\dfrac{\varphi_2}{1 - \varphi_2}\right)}{1 + \left(\dfrac{1}{n}\right)\left(\dfrac{\varphi_2}{1 - \varphi_2}\right)}$$

$$\varphi_2 = \frac{x_2}{\left(\dfrac{1}{n}\right) + x_2\left(1 - \left(\dfrac{1}{n}\right)\right)}$$

Flory-Huggins Enthalpy of Mixing

Use the same lattice model as for the entropy of mixing, and consider a **quasi-chemical reaction**:

$$(1,1) + (2,2) \longrightarrow 2(1,2)$$

1 represents a solvent and 2 represents a polymer repeat unit

The **interaction energy** is then given by:

$$\Delta w = 2w_{12} - w_{11} - w_{22}$$

$$\frac{\Delta w}{2} =$$ Change in interaction energy per (1,2) pair

Define the system to be a filled lattice with Z nearest neighbors. Each polymer segment is then surrounded by $Z\varphi_2$ polymer segments and $Z\varphi_1$ solvent molecules.

Contributions to the Interaction Energy

Contributions of polymer segments

Interaction of a polymer segment with its neighbors yields

$$Z\varphi_2 w_{22} + Z\varphi_1 w_{12}$$

The total contribution is

$$\left(\frac{1}{2}\right) Z\varphi_2 N\left[(1-\varphi_1)w_{22} + \varphi_1 w_{12}\right]$$

Remove double counting

Contributions of solvent molecules

Each solvent molecule is surrounded by $Z\varphi_2$ polymer segments and $Z\varphi_1$ solvent molecules. Interaction of the solvent with its neighbors then yields

$$Z\varphi_2 w_{12} + Z\varphi_1 w_{11}$$

The total contribution is

$$\left(\frac{1}{2}\right) Z\varphi_1 N\left[\varphi_2 w_{12} + (1-\varphi_2)w_{11}\right]$$

Remove double counting

Flory-Huggins Enthalpy of Mixing

$$\Delta H_m = \left(\frac{1}{2}\right) ZN \left(2\varphi_1\varphi_2 w_{12} - \varphi_1\varphi_2 w_{11} - \varphi_1\varphi_2 w_{22}\right)$$

$$\Delta H_m = \left(\frac{1}{2}\right) ZN \varphi_1\varphi_2 \Delta w$$

Let $\quad \left(\frac{1}{2}\right) Z\Delta w = \chi RT$

Flory-Huggins interaction parameter (the "chi" parameter)

$\chi = 0$ For athermal mixtures

$\chi > 0$ For endothermic mixing

$\chi < 0$ For exothermic mixing

$$\Delta H_m = N\varphi_1\varphi_2 \chi RT = N_1\varphi_2 \chi RT$$

Flory-Huggins Free Energy of Mixing: General Case

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

$$\Delta H_m = N\varphi_1\varphi_2\chi RT$$

$$\Delta S_m = -R\left[x_1 \ln \phi_1 + x_2 \ln \phi_2\right]$$

$$\Delta G_m = RT\left[N\varphi_1\varphi_2\chi + \left(x_1 \ln \varphi_1 + x_2 \ln \varphi_2\right)\right]$$

>0
0
<0

<0