Mean Field Flory Huggins Lattice Theory

- **Mean field**: the interactions between molecules are assumed to be due to the interaction of a given molecule and an *average field* due to all the other molecules in the system. To aid in modeling, the solution is imagined to be divided into a set of cells within which molecules or parts of molecules can be placed (lattice theory).

- The total volume, \( V \), is divided into a lattice of \( N_o \) cells, each cell of volume \( v \). The molecules occupy the sites randomly according to a probability based on their respective volume fractions. To model a polymer chain, one occupies \( x_i \) adjacent cells.

\[
N_o = N_1 + N_2 = n_1 x_1 + n_2 x_2
\]

\[
V = N_o v
\]

- Following the standard treatment for small molecules \((x_1 = x_2 = 1)\)

\[
\Omega_{1,2} = \frac{N_0!}{N_1! N_2!}
\]

using Stirling’s approximation: \( \ln M! = M \ln M - M \) for \( M >> 1 \)

\[
\Delta S_m = k(-N_1 \ln \phi_1 - N_2 \ln \phi_2) \quad \phi_1 = ?
\]
The entropic contribution to $\Delta G_m$ is thus seen to always favor mixing if the random mixing approximation is used.

Remember this is for small molecules $x_1 = x_2 = 1$
Enthalpy of Mixing $\Delta H_m$

• Assume lattice has $z$ nearest-neighbor cells.

• To calculate the enthalpic interactions we consider the number of *pairwise* interactions. The probability of finding adjacent cells filled by component $i$, and $j$ is given by assuming the probability that a given cell is occupied by species $i$ is equal to the volume fraction of that species: $\phi_i$. 
$\Delta H_m$ cont’d

$\nu_{ij} = \# \text{ of } i,j \text{ interactions}$

$\nu_{12} = N_1 z \phi_2$

$\nu_{11} = N_1 z \phi_1 / 2$

$\nu_{22} = N_2 z \phi_2 / 2$

Mixed state enthalpic interactions

$H_{1,2} = \nu_{12} \varepsilon_{12} + \nu_{11} \varepsilon_{11} + \nu_{22} \varepsilon_{22}$

$H_{1,2} = z N_1 \phi_2 \varepsilon_{12} + \frac{z}{2} N_1 \phi_1 \varepsilon_{11} + \frac{z}{2} N_2 \phi_2 \varepsilon_{22}$

Pure state enthalpic interactions

$H_1 = \frac{z N_1}{2} \varepsilon_{11}$

$H_2 = \frac{z N_2}{2} \varepsilon_{22}$

$\Delta H_M = z \left[ N_1 \phi_2 \varepsilon_{12} + \frac{N_1 \varepsilon_{11}}{2} (\phi_1 - 1) + \frac{N_2 \varepsilon_{22}}{2} (\phi_2 - 1) \right]$
\( \chi \) Parameter

- Define \( \chi \): 
\[
\chi = \frac{z}{kT} \left[ \varepsilon_{12} - \frac{1}{2} (\varepsilon_{11} + \varepsilon_{22}) \right]
\]

\( \chi \) represents the chemical interaction between the components.

\[
\frac{\Delta H_M}{N_0} = kT \phi_1 \phi_2
\]

Note: \( \Delta H_M \) is symmetric in \( \phi_1 \) and \( \phi_2 \).

- \( \Delta G_M \): 
\[
\Delta G_M = \Delta H_M - T \Delta S_M
\]

\[
\frac{\Delta G_M}{N_0} = kT \chi \phi_1 \phi_2 - kT \left[ -\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2 \right]
\]

\[
\frac{\Delta G_M}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 \right]
\]

Note: \( \Delta G_M \) is symmetric in \( \phi_1 \) and \( \phi_2 \).

This is the Bragg-Williams result for the change in free energy for the mixing of binary metal alloys.
\[ \Delta G_M(T, \phi, \chi) \]

- Flory showed how to pack chains onto a lattice and correctly evaluate \( \Omega_{1,2} \) for polymer-solvent and polymer-polymer systems. Flory made a complex derivation but got a very simple and intuitive result, namely that \( \Delta S_M \) is decreased by factor \( (1/x) \) due to connectivity of \( x \) segments into a single molecule:

\[
\frac{\Delta S_M}{N_0} = -k \left[ \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right] 
\]

For polymers

- **Systems of Interest**

  - solvent – solvent \( x_1 = 1 \quad x_2 = 1 \)
  - solvent – polymer \( x_1 = 1 \quad x_2 = \text{large} \)
  - polymer – polymer \( x_1 = \text{large}, x_2 = \text{large} \)

\[
\frac{\Delta G_M}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right]
\]

Note possible huge asymmetry in \( x_1, x_2 \)

\[
\chi = \frac{z}{kT} \left[ \varepsilon_{12} - \frac{1}{2} (\varepsilon_{11} + \varepsilon_{22}) \right]
\]

Need to examine variation of \( \Delta G_M \) with \( T, \chi, \phi_1 \), and \( x_1 \) to determine phase behavior.
Flory Huggins Theory

- **Many Important Applications**
  1. Phase diagrams
  2. Fractionation by molecular weight, fractionation by composition
  3. $T_m$ depression in a semicrystalline polymer by 2$^{\text{nd}}$ component
  4. Swelling behavior of networks (when combined with the theory of rubber elasticity)

The two parts of free energy per site \[ \frac{\Delta G_M}{N_0 k T} \]

\[ \begin{align*}
\Delta S_M &= -\frac{\phi_1}{x_1} \ln(\phi_1) - \frac{\phi_2}{x_2} \ln(\phi_2) \\
\Delta H_M &= \chi \phi_1 \phi_2
\end{align*} \]

- $\Delta H_M$ can be measured for low molar mass liquids and estimated for nonpolar, noncrystalline polymers by the Hildebrand solubility approach.
Solubility Parameter

• Liquids

\[
\delta = \left( \frac{\Delta E}{V} \right)^{1/2} = \sqrt{\frac{\text{cohesive energy}}{\text{density}}} = \left[ \frac{\Delta H_v - RT}{V_m} \right]^{1/2}
\]

\(\Delta H_v\) = molar enthalpy of vaporization

Hildebrand proposed that compatibility between components 1 and 2 arises as their solubility parameters approach one another \(\delta_1 \rightarrow \delta_2\).

• \(\delta_p\) for polymers

Take \(\delta_p\) as equal to \(\delta\) solvent for which there is:

1. maximum in *intrinsic viscosity* for soluble polymers
2. maximum in swelling of the polymer network
3. calculate an approximate value of \(\delta_p\) by chemical group contributions for a particular monomeric repeat unit.
Estimating the Heat of Mixing

Hildebrand equation:

\[ \Delta H_M = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \geq 0 \]

\( V_m \) = average molar volume of solvent/monomers
\( \delta_1, \delta_2 \) = solubility parameters of components

Inspection of solubility parameters can be used to estimate possible compatibility (miscibility) of solvent-polymer or polymer-polymer pairs. This approach works well for non-polar solvents with non-polar amorphous polymers. Think: usual phase behavior for a pair of polymers?

Note: this approach is not appropriate for systems with specific interactions, for which \( \Delta H_M \) can be negative.
Influence of $\chi$ on Phase Behavior

Assume $kT = 1$ and $x_1 = x_2$

Expect symmetry

At what value of chi does the system go biphasic?

What happens to entropy for a pair of polymers?
Polymer-Solvent Solutions

- **Equilibrium**: Equal Chemical potentials: so need partial molar quantities

\[
\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n,j}
\]

- Pure:

\[
\begin{bmatrix}
\mu_1^0 \\
\mu_2^0
\end{bmatrix}
\]

- Mixed:

\[
\mu_1, \mu_2
\]

\[
\mu_i - \mu_i^0 = RT \ln a_i \quad \text{where } a \text{ is the activity}
\]

\[
\frac{\partial \Delta G_m}{\partial n_i} \left| _{T,P,n,j} \right. = \frac{\partial \Delta G_m}{\partial \phi_i} \frac{\partial \phi_i}{\partial n_i}
\]

and \( \mu_i^0 \) is the chemical potential in the standard state

\[
\begin{align*}
\mu_1 - \mu_1^0 &= RT \left[ \ln \phi_1 + \left(1 - \frac{1}{x_2}\right) \phi_2 + \chi \phi_2^2 \right] \\
\mu_2 - \mu_2^0 &= RT \left[ \ln \phi_2 - (x_2 - 1) \phi_1 + x_2 \chi \phi_1^2 \right]
\end{align*}
\]

Note: For a polydisperse system of chains, use \( x_2 = <x_2> \) the number average

- Recall at equilibrium: \( \mu_{i\alpha} = \mu_{i\beta} \) etc

P.S. #1: For a pure mixed solvent system, use
Construction of Phase Diagrams

\[
\frac{\Delta G_m}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right]
\]

- **Chemical Potential**
  \[ \mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n,j} \]
- **Binodal** - curve denoting the region of 2 distinct coexisting phases
  \[ \mu_1' = \mu_1'' \quad \mu_2' = \mu_2'' \]
  or equivalently
  \[ \mu_1' - \mu_1^0 = \mu_1'' - \mu_1^0 \]
  \[ \mu_2' - \mu_2^0 = \mu_2'' - \mu_2^0 \]
  Phases called prime and double prime

\[ \left[ \frac{\partial \Delta G_m}{\partial n_2} \right]_{T,P} = \Delta \mu_2 \] and since
\[ \left[ \frac{\partial \Delta G_m}{\partial n_2} \right] = \left[ \frac{\partial \Delta G_m}{\partial \phi_2} \right] \left[ \frac{\partial \phi_2}{\partial n_2} \right] \]

Binodal curve is given by finding common tangent to \( \Delta G_m(\phi) \) curve for each \( \phi, T \) combination. Note with lattice model \( (x_1 = x_2) \) (can use volume fraction of component in place of moles of component)
Construction of Phase Diagrams cont’d

- **Spinodal (Inflection Points)**

\[
\left[ \frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right]^{\alpha} = 0 \quad \left[ \frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right]^{\beta} = 0
\]

- **Critical Point**

\[
\chi_c \left[ \frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right] = 0 \quad \text{and} \quad \left[ \frac{\partial^3 \Delta G_m}{\partial \phi_2^3} \right] = 0
\]

\[
\phi_1, c
\]

Figure by MIT OCW.
Dilute Polymer Solution

- # moles of solvent \((n_1) \gg\) polymer \((n_2)\) and \(n_1 \gg n_2x_2\)

\[
\phi_1 = \frac{n_1v_1}{n_1v_1 + n_2x_2v_2} \quad \phi_2 = \frac{n_2x_2v_2}{n_1v_1 + n_2x_2v_2} \sim \frac{n_2x_2}{n_1}
\]

Useful Approximations

\[
\phi_2 = \frac{n_2x_2}{n_1} \sim X_2x_2 \quad \text{Careful…}
\]

\[
\ln(1 + x) \cong x - \frac{x^2}{2} + \frac{x^3}{3} - \ldots
\]

\[
\ln(1 - x) \cong -x - \frac{x^2}{2} - \frac{x^3}{3} - \ldots
\]

- For a dilute solution:

\[
\mu_1 - \mu_1^0 = RT \left[-\frac{\phi_2}{x_2} + \left(\chi - \frac{1}{2}\right)\phi_2^2\right]
\]

Let’s do the math:
Dilute Polymer Solution cont’d

- Recall for an **Ideal Solution** the chemical potential is proportional to the activity which is equal to the mole fraction of the species, $X_i$

  $$\mu_1 - \mu_1^0 = RT \ln X_1 = RT \ln(1 - X_2) \cong -RTX_2 = -RT \frac{\phi_2}{x_2}$$

- Comparing to the $\mu_1 - \mu_1^0$ expression we have for the dilute solution, we see the first term corresponds to that of an ideal solution. The 2nd term is called the **excess chemical potential**

  $$\mu_1 - \mu_1^0 = RT \left[ -\frac{\phi_2}{x_2} + \left( \chi - \frac{1}{2} \right) \phi_2^2 \right]$$

  - This term has 2 parts due to
    - **Contact interactions** (solvent quality) $\chi \phi_2^2 RT$
    - **Chain connectivity** (excluded volume) $-(1/2) \phi_2^2 RT$

- **Notice that for the special case of** $\chi = 1/2$, **the entire 2nd term disappears!**
This implies that in this special situation, the dilute solution acts as an **Ideal solution**.

  The excluded volume effect is precisely compensated by the solvent quality effect.

Previously we called this the **$\theta$ condition**, so $\chi = 1/2$ is also the theta point
F-H Phase Diagram at/near $\theta$ condition

- $x_1 = 1, \ x_2 \gg 1 \ and \ n_1 >> n_2 x_2$

Find:

$$\chi_c = \frac{1}{2} \left( \frac{1}{\sqrt{x_1}} + \frac{1}{\sqrt{x_2}} \right)^2$$

$$\phi_{1,c} = \frac{\sqrt{x_2}}{\sqrt{x_1} + \sqrt{x_2}}$$

Note strong asymmetry!

Symmetric when $x_1 = 1 = x_2$

Figure by MIT OCW.
## Critical Composition & Critical Interaction Parameter

<table>
<thead>
<tr>
<th>Binary System</th>
<th>$\phi_{1,c}$</th>
<th>$\chi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 low molar mass liquids</td>
<td>$x_1 = x_2 = 1$</td>
<td>0.5</td>
</tr>
<tr>
<td>Solvent-polymer</td>
<td>$x_1 = 1$; $x_2 = N$</td>
<td>$\frac{\sqrt{x_2}}{1 + \sqrt{x_2}}$</td>
</tr>
<tr>
<td>Symmetric Polymer-Polymer</td>
<td>$x_1 = x_2 = N$</td>
<td>0.5</td>
</tr>
<tr>
<td>General</td>
<td>$x_1, x_2$</td>
<td>$\frac{\sqrt{x_2}}{\sqrt{x_1} + \sqrt{x_2}}$</td>
</tr>
</tbody>
</table>
Polymer Blends

Good References on Polymer Blends:


- Upper Critical Solution Temperature (UCST) Behavior
  Well accounted for by F-H theory with $\chi = a/T + b$

- Lower Critical Solution Temperature (LCST) Behavior
  FH theory cannot predict LCST behavior. Experimentally find that blend systems displaying hydrogen bonding and/or large thermal expansion factor difference between the respective homopolymers often results in LCST formation.
Phase Diagram for UCST Polymer Blend

Predicted from FH Theory

\[ \chi = \frac{A}{T} + B \]
\[ x_1 = x_2 = N \]

\[ \frac{\partial \Delta G_m}{\partial \phi} = 0 \] binodal

\[ \frac{\partial^2 \Delta G_m}{\partial \phi^2} = 0 \] spinodal

\[ \frac{\partial^3 \Delta G_m}{\partial \phi^3} = 0 \] critical point

A polymer \( x_1 \) segments \( v_1 \approx v_2 \) & \( x_1 \approx x_2 \)
B polymer \( x_2 \) segments

Figure by MIT OCW.
2 Principal Types of Phase Diagrams

Konigsveld, Klentjens, Schoeffeleers

Nishi, Wang, Kwei
Macromolecules, 8, 227 (1995)

Figure by MIT OCW.
Assignment - Reminder

• Problem set #1 is due in class on February 15th.