

INTRODUCTION TO  
**POLYMER PHYSICS:**  
**THERMODYNAMICS OF POLYMER SOLUTIONS**

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## Thermodynamics of Polymer Solution: Flory-Huggins Theory

- Combinatorial Term:  $\Delta S_m^{\text{comb}}$
- Contact Term:  $\Delta G_m^{\text{contact}}$
- Flory-Huggins Interaction Parameter,  $\chi$
- Flory-Huggins Equation for Gibbs Free Energy of Mixing
- Partial Molar Properties: Chemical Potential

# NOMENCLATURE

$X_i$ : Mole fraction of component  $i$

$N_i$ : Number of molecules of component  $i$

$N$ : Total number of lattice cells

$n_i$ : Number of moles of component  $i$

$m_i$ : Mass of component  $i$

$n$ : Total mass (of all components)

$N_{\text{Av}}$ : Avogadro constant ( $\sim 6.022 \times 10^{23} \text{ mol}^{-1}$ )

$k_{\text{B}}$ : Boltzmann constant ( $\sim 1.3806 \times 10^{-23} \text{ J K}^{-1}$ )

$R$ : Universal gas constant ( $\sim 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$H_i$ : Enthalpy of component  $i$

$S_i$ : Entropy of component  $i$

$G_i$ : Gibbs free energy of component  $i$

$\Delta H_{\text{m}}$ : Enthalpy change of mixing

$\Delta S_{\text{m}}$ : Entropy change of mixing

$\Delta G_{\text{m}}$ : Gibbs free energy change of mixing

$T$ : Temperature

$x$ : Number of segments per polymer molecule

# FLORY-HUGGINS THEORY: ASSUMPTIONS

## Flory-Huggins Theory:

Combinatorial Term

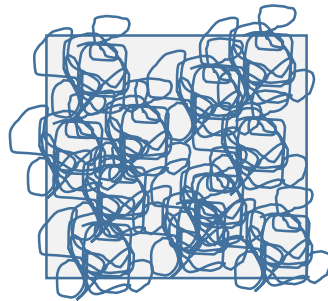
Contact Term

Flory-Huggins  
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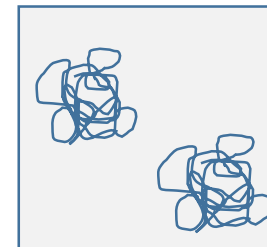
Flory-Huggins  
Equation

Chemical Potential

- Same lattice describes the solvent, the polymer and the solution
- There is no volume change of mixing
- All polymer molecules contain the same number of segments
- Self-intersections within polymer chain is allowed
- The volume occupied by one polymer segment is equal to that occupied by one solvent molecule
- **Mean Field Approximation:** The segments are uniformly distributed on the lattice. Poor assumption for dilute solutions.



Concentrated Solution



Dilute Solution

# FLORY-HUGGINS THEORY: COMBINATORIAL TERM

Consider Athermal Mixing First:  $\Delta H_m = 0$

$$\Delta S_m^{\text{comb}} = -k_B [N_1 \ln \phi_1 + N_2 \ln \phi_2] = -R [n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

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

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

$\phi_1$ : Volume fraction of solvent

$\phi_2$ : Volume fraction of polymer (solute)

Compare with Ideal Solution Expression (when  $x = 1$ ):

$$\Delta S_m^{\text{ideal}} = -k_B [N_1 \ln X_1 + N_2 \ln X_2] = -R [n_1 \ln X_1 + n_2 \ln X_2]$$

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# FLORY-HUGGINS THEORY: COMBINATORIAL TERM

$$\Delta S_m^{\text{comb}} = -k_B [N_1 \ln \phi_1 + N_2 \ln \phi_2] = -R [n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

Even at very low mole fraction, the volume fraction of polymer chains can be considerable.

Example:

Consider a system with 98 solvent molecules and 2 polymer molecules ( $N_1 = 98, N_2 = 2$ ).  
Let each polymer molecule contain 100 segments ( $x = 100$ )

$$X_1 = \frac{N_1}{N_1 + N_2} = \frac{98}{98 + 2} = 0.98$$

$$X_2 = 1 - X_1 = 0.02$$

$$\phi_1 = \frac{N_1}{N} = \frac{N_1}{N_1 + xN_2} = \frac{98}{98 + 2 \times 100} \cong 0.33$$

$$\phi_2 = 1 - \phi_1 \cong 0.67$$

$$\Delta S_m^{\text{ideal}} = -k_B [N_1 \ln X_1 + N_2 \ln X_2] = 9.8k_B$$



$$[\Delta S_m^{\text{comb}}]_{\text{FH}} = -k_B [N_1 \ln \phi_1 + N_2 \ln \phi_2] = 109.45k_B$$



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# FLORY-HUGGINS THEORY: CONTACT TERM

## Next Step: Incorporate Effects of Intermolecular Interactions

- Enthalpy Change
- Entropy Change (ordering induced by interactions)

Both effects are considered together as contact Gibbs free energy change  $\Delta G_m^{\text{contact}}$

Assumption: Only first neighbour interactions are considered

Types of Contact:

Gibbs free energies of interaction

- Solvent-Solvent Contact  $\longrightarrow g_{11}$
- Segment-Segment Contact  $\longrightarrow g_{22}$
- Solvent-Segment Contact  $\longrightarrow g_{12}$

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# FLORY-HUGGINS THEORY: CONTACT TERM

To form two solvent-segment contacts, one solvent-solvent and one segment-segment contact are broken.



Pure Solvent   Polymer Solution   Pure Polymer

So, the Gibbs free energy change for the formation of a single solvent-segment contact is:

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

If the number of solvent-segment contacts in the solution is  $p_{12}$ , we have

$$\Delta G_m^{\text{contact}} = p_{12} \Delta g_{12}$$

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# FLORY-HUGGINS THEORY: CONTACT TERM

Number of lattice cells adjacent to each polymer molecule:

$$(z - 2) \times (x - 2) + (z - 1) \times 2 = (z - 2)x + 2 \cong (z - 2)x$$

Segments NOT  
at chain ends

Segments  
at chain ends

For large  $x$

Total number of lattice cells adjacent to all polymer molecules in the solution:  $N_2(z - 2)x$

Number of solvent-segment contacts in the solution,  $p_{12} = N_2(z - 2)x\phi_1$

(Mean-field Approximation)

$$N_2x\phi_1 = (xN_2)\frac{N_1}{N_1 + xN_2} = N_1\frac{xN_2}{N_1 + xN_2} = N_1\phi_2$$

$$p_{12} = N_2(z - 2)x\phi_1 = (z - 2)N_1\phi_2$$

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# FLORY-HUGGINS INTERACTION PARAMETER, $\chi$

$$\Delta G_m^{\text{contact}} = p_{12} \Delta g_{12}$$

$$p_{12} = (z - 2)N_1\phi_2$$

$$\Delta G_m^{\text{contact}} = (z - 2)N_1\phi_2 \Delta g_{12}$$

Define Flory-Huggins Polymer-Solvent Interaction parameter,  $\chi$ :

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

$$\Delta G_m^{\text{contact}} = k_B T N_1 \phi_2 \chi = RT n_1 \phi_2 \chi$$

$$\chi = a + \frac{b}{T} \quad (a, b \text{ are independent of temperature}) \quad \chi = \chi_H + \chi_S$$

$$\chi_H = -T \left( \frac{\partial \chi}{\partial T} \right) = \frac{b}{T} \quad \chi_S = \frac{\partial (T\chi)}{\partial T} = a$$

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# FLORY-HUGGINS EQUATION

Combinatorial contribution to change in Gibbs free energy:

$$-T\Delta S_m^{\text{comb}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

Change in Gibbs free energy due to interaction:

$$\Delta G_m^{\text{contact}} = RTn_1\phi_2\chi$$

**Gibbs Free Energy of Mixing:**

$$\Delta G_m = \Delta G_m^{\text{contact}} - T\Delta S_m^{\text{comb}} = RTn_1\phi_2\chi + RT[n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi]$$

**Flory-Huggins Equation for the Gibbs Free Energy of Mixing**

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# FLORY-HUGGINS EQUATION

$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi]$$

Flory-Huggins equation can qualitatively describe:

- Equilibrium thermodynamic properties of polymer solutions
- Phase separation and fractionation behavior
- Swelling of network polymers

Limitations:

- Trends are predicted but quantitative agreement not achieved
- Self intersections of polymer chains allowed: physically unrealistic
- Mean-field approximation: Not satisfactory for dilute solutions
- $\chi$  is not a simple parameter

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# PARTIAL MOLAR PROPERTY AND CHEMICAL POTENTIAL

Partial Molar Property:  $\bar{Z}_i = \left( \frac{\partial Z}{\partial n_i} \right)_{T,P,n_{j \neq i}}$

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Chemical Potential,  $\mu_i$ , is the Partial Molar Gibbs Free Energy

$$\mu_i = \bar{G}_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

Activity,  $a_i$ , is related to the chemical potential by:

$$\mu_i - \mu_i^0 = RT \ln a_i$$

$\mu_i^0$ : Chemical potential of component  $i$  in its standard state

# FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

$$\mu_i - \mu_i^0 = \overline{\Delta G}_i = \left( \frac{\partial \Delta G}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

## Flory-Huggins Theory:

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Using Flory-Huggins equation:

$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi]$$

For the solvent (component 1):

$$\mu_1 - \mu_1^0 = \left( \frac{\partial \Delta G_m}{\partial n_1} \right)_{T,P,n_2} = RT \left[ \frac{\partial}{\partial n_1} \{n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi\} \right]_{T,P,n_2}$$

$$\frac{\mu_1 - \mu_1^0}{RT} = n_1 \left[ \frac{\partial (\ln \phi_1)}{\partial n_1} \right]_{T,P,n_2} + \ln \phi_1 + n_2 \left[ \frac{\partial (\ln \phi_2)}{\partial n_1} \right]_{T,P,n_2} + \phi_2 \chi + n_1 \chi \left[ \frac{\partial (\phi_2)}{\partial n_1} \right]_{T,P,n_2}$$

# FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

$$\frac{\mu_1 - \mu_1^0}{RT} = n_1 \left[ \frac{\partial(\ln\phi_1)}{\partial n_1} \right]_{T,P,n_2} + \ln\phi_1 + n_2 \left[ \frac{\partial(\ln\phi_2)}{\partial n_1} \right]_{T,P,n_2} + \phi_2\chi + n_1\chi \left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2}$$

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$$\left[ \frac{\partial(\ln\phi_1)}{\partial n_1} \right]_{T,P,n_2} = \left[ \frac{\partial(\ln\phi_1)}{\partial \phi_1} \right]_{T,P,n_2} \left[ \frac{\partial(\phi_1)}{\partial n_1} \right]_{T,P,n_2} = \frac{1}{\phi_1} \left[ \frac{\partial(\phi_1)}{\partial n_1} \right]_{T,P,n_2}$$

$$\phi_1 = \frac{N_1}{N_1 + xN_2} = \frac{n_1}{n_1 + xn_2}$$

$$\left[ \frac{\partial(\phi_1)}{\partial n_1} \right]_{T,P,n_2} = \frac{1}{n_1 + xn_2} - \frac{n_1}{(n_1 + xn_2)^2} = \frac{xn_2}{(n_1 + xn_2)^2}$$

$$\left[ \frac{\partial(\ln\phi_1)}{\partial n_1} \right]_{T,P,n_2} = \frac{xn_2}{\phi_1(n_1 + xn_2)^2} = \frac{xn_2}{n_1(n_1 + xn_2)} = \frac{\phi_2}{n_1}$$

# FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

$$\frac{\mu_1 - \mu_1^0}{RT} = n_1 \left[ \frac{\partial(\ln\phi_1)}{\partial n_1} \right]_{T,P,n_2} + \ln\phi_1 + n_2 \left[ \frac{\partial(\ln\phi_2)}{\partial n_1} \right]_{T,P,n_2} + \phi_2\chi + n_1\chi \left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2}$$

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$$\left[ \frac{\partial(\ln\phi_2)}{\partial n_1} \right]_{T,P,n_2} = \left[ \frac{\partial(\ln\phi_2)}{\partial \phi_2} \right]_{T,P,n_2} \left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2} = \frac{1}{\phi_2} \left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2}$$

$$\phi_2 = \frac{xN_2}{N_1 + xN_2} = \frac{xn_2}{n_1 + xn_2}$$

$$\left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2} = -\frac{xn_2}{(n_1 + xn_2)^2} = -\frac{\phi_2}{n_1 + xn_2}$$

$$\left[ \frac{\partial(\ln\phi_2)}{\partial n_1} \right]_{T,P,n_2} = \frac{1}{\phi_2} \left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2} = -\frac{1}{n_1 + xn_2}$$



# FLORY-HUGGINS THEORY: CHEMICAL POTENTIAL

$$\frac{\mu_1 - \mu_1^0}{RT} = n_1 \left[ \frac{\partial(\ln\phi_1)}{\partial n_1} \right]_{T,P,n_2} + \ln\phi_1 + n_2 \left[ \frac{\partial(\ln\phi_2)}{\partial n_1} \right]_{T,P,n_2} + \phi_2\chi + n_1\chi \left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2}$$

$$\left[ \frac{\partial(\ln\phi_1)}{\partial n_1} \right]_{T,P,n_2} = \frac{\phi_2}{n_1} \quad \left[ \frac{\partial(\ln\phi_2)}{\partial n_1} \right]_{T,P,n_2} = -\frac{1}{n_1 + xn_2} \quad \left[ \frac{\partial(\phi_2)}{\partial n_1} \right]_{T,P,n_2} = -\frac{\phi_2}{n_1 + xn_2}$$

$$\frac{\mu_1 - \mu_1^0}{RT} = n_1 \left( \frac{\phi_2}{n_1} \right) + \ln\phi_1 - \frac{n_2}{n_1 + xn_2} + \phi_2\chi - \frac{n_1\chi\phi_2}{n_1 + xn_2}$$

$$\frac{\mu_1 - \mu_1^0}{RT} = \phi_2 + \ln\phi_1 - \frac{\phi_2}{x} + \phi_2\chi - \phi_1\chi\phi_2 = \ln\phi_1 + \phi_2 \left( 1 - \frac{1}{x} \right) + \phi_2\chi(1 - \phi_1)$$

$$\mu_1 - \mu_1^0 = RT \left[ \ln\phi_1 + \phi_2 \left( 1 - \frac{1}{x} \right) + \chi\phi_2^2 \right]$$

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# CHEMICAL POTENTIAL AND ACTIVITY

**For Solvent:** 
$$\mu_1 - \mu_1^0 = RT \left[ \ln \phi_1 + \phi_2 \left( 1 - \frac{1}{x} \right) + \chi \phi_2^2 \right]$$

( $\gamma_i$ : Activity Coefficient)

$$\ln a_1 = \ln(\gamma_1 X_1) = \frac{\mu_1 - \mu_1^0}{RT} = \ln \phi_1 + \phi_2 \left( 1 - \frac{1}{x} \right) + \chi \phi_2^2$$

**For Polymer:** 
$$\mu_2 - \mu_2^0 = RT [\ln \phi_2 + \phi_1 (x - 1) + x \chi \phi_1^2]$$

$$\ln a_2 = \ln(\gamma_2 X_2) = \frac{\mu_2 - \mu_2^0}{RT} = \ln \phi_2 + \phi_1 (x - 1) + x \chi \phi_1^2$$

**Per Segment:** 
$$\mu_s - \mu_s^0 = \frac{\mu_2 - \mu_2^0}{x} = RT \left[ \frac{\ln \phi_2}{x} + \phi_1 \left( 1 - \frac{1}{x} \right) + \chi \phi_1^2 \right]$$

For polydisperse sample, number-average value of  $x$  should be used: 
$$\bar{x}_n = \frac{\sum_i x_i n_i}{\sum_i n_i} = \frac{\sum_i x_i n_i}{n_2}$$

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