POLYMER PHYSICS:

THERMODYNAMICS OF POLYMER SOLUTIONS

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CONTENT

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_{Av}: Avogadro constant (~6.022×10^{23} mol^{-1})

k_{B}: Boltzmann constant (~1.3806×10^{23} J K^{-1})

R: Universal gas constant (~8.314 J mol^{-1} K^{-1})

H_i: Enthalpy of component i

S_i: Entropy of component i

G_i: Gibbs free energy of component i

ΔH_{m}: Enthalpy change of mixing

ΔS_{m}: Entropy change of mixing

ΔG_{m}: Gibbs free energy change of mixing

T: Temperature

x: Number of segments per polymer molecule

THERMODYNAMICS OF IDEAL SOLUTION

Ideal Solution: The components are of the same size and have identical interactions

$$\Delta H_{\mathrm{m}} = 0 \qquad \Delta V_{\mathrm{m}} = 0$$

$$\Delta G_{\mathrm{m}} = \Delta H_{\mathrm{m}} - T\Delta S_{\mathrm{m}} = -T\Delta S_{\mathrm{m}}$$

Entropy Change: $\Delta S_{\mathrm{m}} = S_{12} - (S_1 + S_2)$

Boltzmann's Entropy Expression: Definition of entropy from statistical mechanics

$$S = k_B \ln \Omega$$

Ω: Total number of **distinguishable** equal energy arrangements of molecules

$$S_1 = k_B \ln \Omega_1 \qquad S_2 = k_B \ln \Omega_2 \qquad S_{12} = k_B \ln \Omega_{12}$$

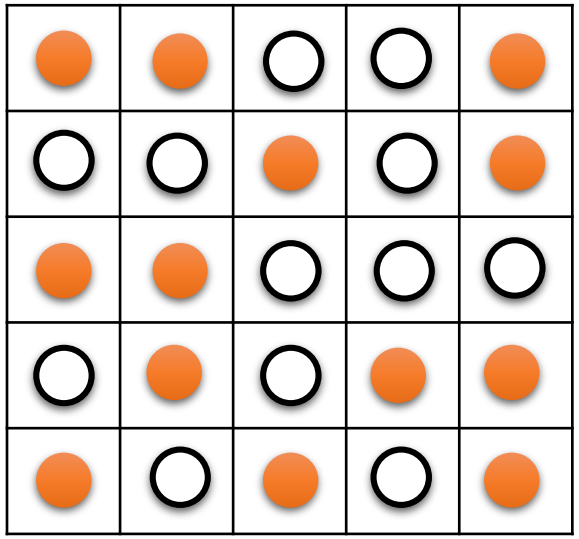
THERMODYNAMICS OF IDEAL SOLUTION

Entropy Change:

$$\Delta S_{\mathrm{m}} = S_{12} - (S_1 + S_2) = k_B[\ln \Omega_{12} - (\ln \Omega_1 + \ln \Omega_2)\,] = k_B \ln\left(\frac{\Omega_{12}}{\Omega_1 \Omega_2}\right)$$

Ω_1: Number of ways of placing N_1 **indistinguishable** ● particles/molecules of solvent in N_1 lattice sites

Ω_2: Number of ways of placing N_2 **indistinguishable** ○ particles/molecules of solute in N_2 lattice sites



Ω_{12}: Number of ways of placing $N_1 + N_2$ particles/molecules in $N_1 + N_2$ lattice sites

$$\Omega_1 = 1 \qquad \Omega_2 = 1 \qquad \Omega_{12} = \frac{(N_1 + N_2)!}{N_1!\, N_2!}$$

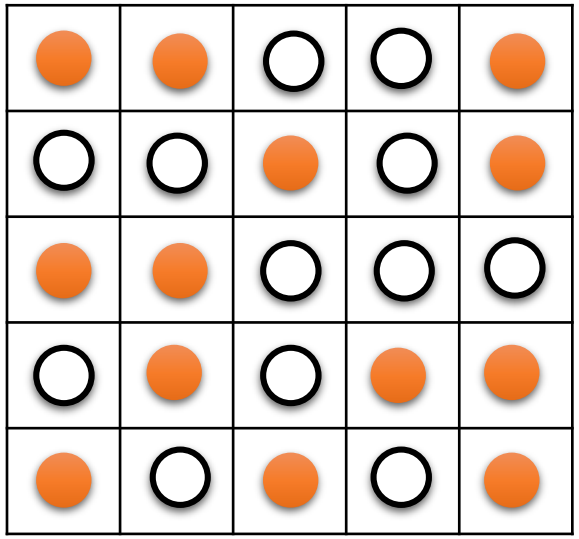
THERMODYNAMICS OF IDEAL SOLUTION

Entropy Change:

$$\Delta S_{\mathrm{m}} = S_{12} - (S_1 + S_2) = k_B[\ln \Omega_{12} - (\ln \Omega_1 + \ln \Omega_2)\,] = k_B \ln\left(\frac{\Omega_{12}}{\Omega_1 \Omega_2}\right)$$

Ω_1: Number of ways of placing N_1 **indistinguishable** particles/molecules of solvent in N_1 lattice sites

Ω_2: Number of ways of placing N_2 **indistinguishable** particles/molecules of solute in N_2 lattice sites

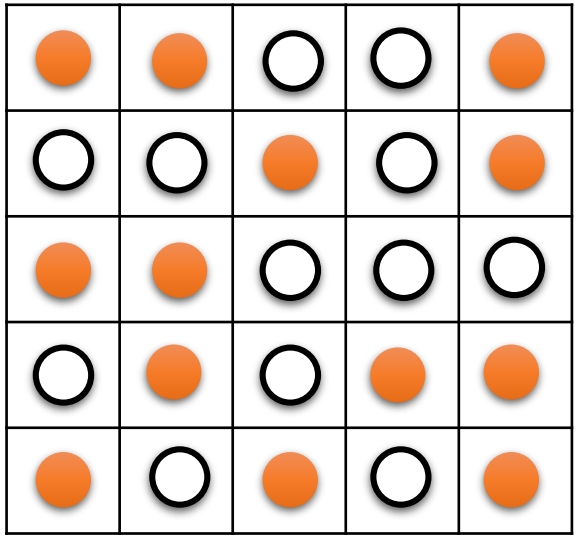


Ω_{12}: Number of ways of placing $N_1 + N_2$ particles/molecules in $N_1 + N_2$ lattice sites

$$\Omega_1 = 1 \qquad \Omega_2 = 1 \qquad \Omega_{12} = \frac{(N_1 + N_2)!}{N_1!\, N_2!}$$

$$\Delta S_{\mathrm{m}} = k_B \ln\left(\frac{\Omega_{12}}{\Omega_1 \Omega_2}\right) = k_B \ln\left[\frac{(N_1 + N_2)!}{N_1!\, N_2!}\right] = k_B[\ln(N_1 + N_2)! - \ln N_1! - \ln N_2!]$$

THERMODYNAMICS OF IDEAL SOLUTION



Stirling's Approximation (valid for large N):

$$\ln N! = N \ln N - N$$

$$\Delta S_{\mathrm{m}} = k_B[\ln (N_1 + N_2)! - \ln N_1! - \ln N_2!\ ]$$

Applying Stirling's approximation:

$$\Delta S_{\mathrm{m}} = k_B[(N_1 + N_2)\ln (N_1 + N_2) - (N_1 + N_2) - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2]$$

$$\Delta S_{\mathrm{m}} = k_B[(N_1 + N_2)\ln (N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2]$$

$$\Delta S_{\mathrm{m}} = -k_B[N_1 \ln N_1 - N_1 \ln (N_1 + N_2) + N_2 \ln N_2 - N_2 \ln (N_1 + N_2)]$$

$$\Delta S_{\mathrm{m}} = -k_B\left[N_1 \ln\left(\frac{N_1}{N_1 + N_2}\right) + N_2 \ln\left(\frac{N_2}{N_1 + N_2}\right)\right] = -k_B[N_1 \ln X_1 + N_2 \ln X_2]$$

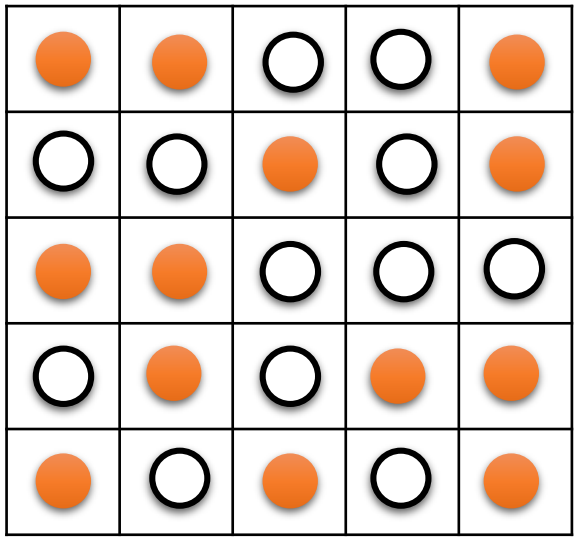
THERMODYNAMICS OF IDEAL SOLUTION

$$\Delta S_{\mathrm{m}} = -k_B[N_1 \ln X_1 + N_2 \ln X_2] = -k_B N_{\mathrm{Av}}[n_1 \ln X_1 + n_2 \ln X_2]$$

$$\boxed{\Delta S_{\mathrm{m}} = -R[n_1 \ln X_1 + n_2 \ln X_2]}$$

(as $R = k_B N_{\mathrm{Av}}$)

$$\boxed{\Delta G_{\mathrm{m}} = -T\Delta S_{\mathrm{m}} = RT[n_1 \ln X_1 + n_2 \ln X_2]}$$

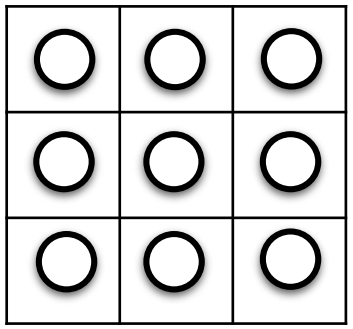


As the mole fractions (X_i) are less than 1, $\ln X_i < 0$. Therefore,

$$\Delta S_{\mathrm{m}} > 0$$

$$\Delta G_{\mathrm{m}} < 0$$

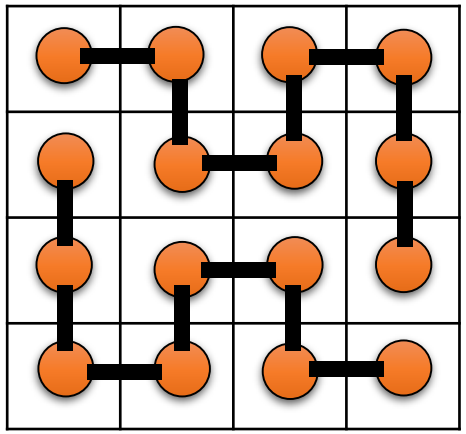
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY



Component 1: Solvent
(N_1 molecules)

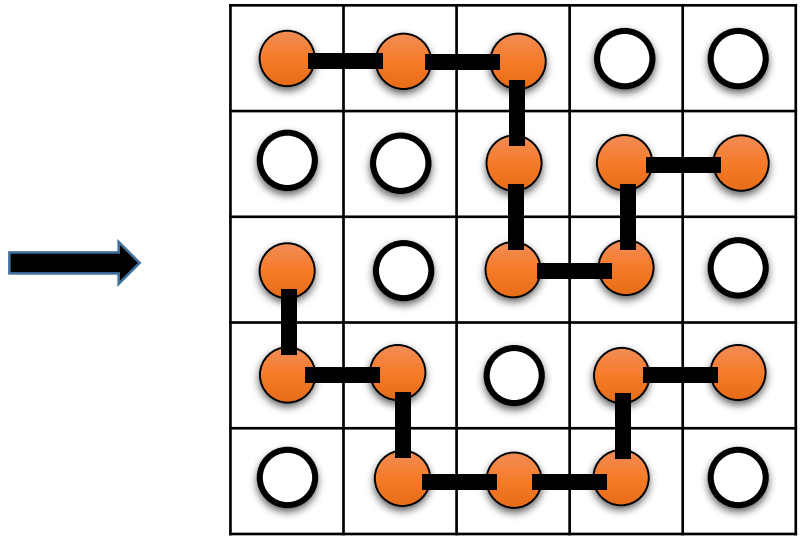
$\Omega_1 = 1$

+



Component 2: Polymer
(N_2 molecules)
(x segments per molecule)

$\Omega_2 = ?$

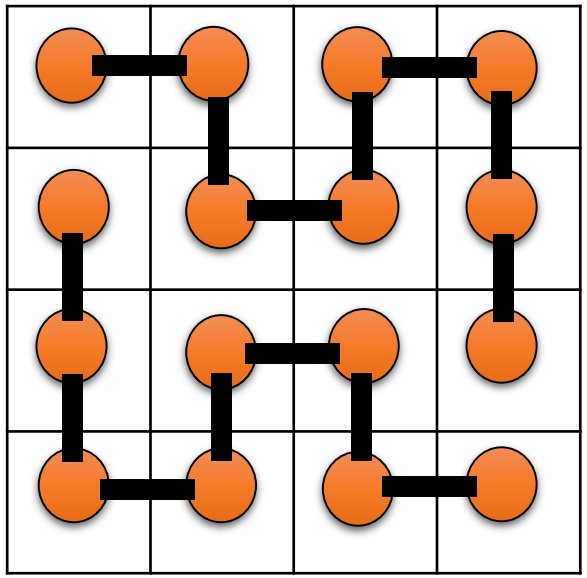


Polymer Solution
($N_1 + N_2$ molecules)
($N = N_1 + xN_2$ lattice cells)

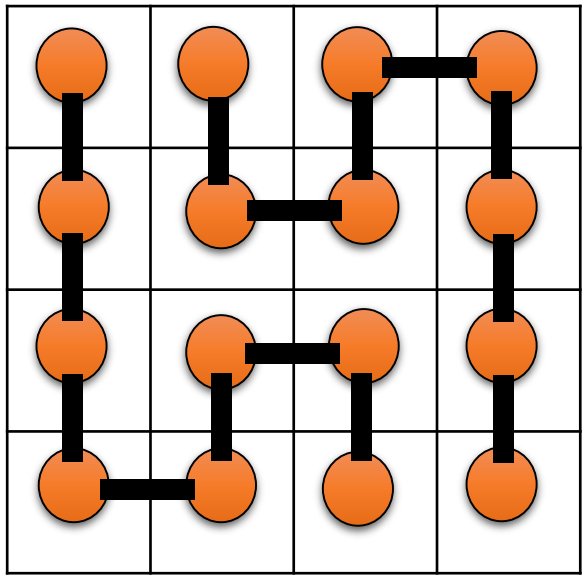
$\Omega_{12} = ?$

Due to long chain nature of polymer molecules, Ω_2 and Ω_{12} are large.

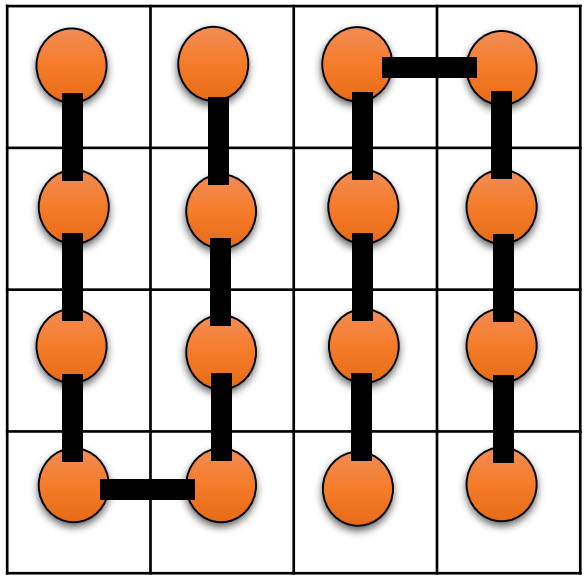
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY



THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY



THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY



$$\Omega_2 \gg 1$$

$$\Omega_{12} \gg 1$$

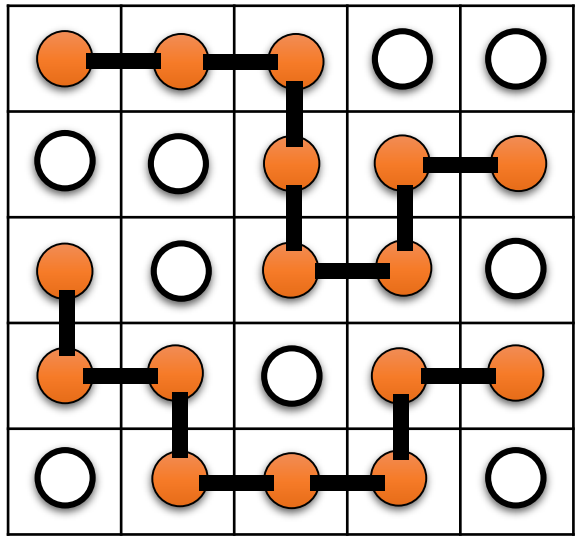
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

System: **Polymer Solution**

$N_1 + N_2$ molecules

x segments per polymer molecule; xN_2 polymer segments

$N = N_1 + xN_2$ lattice cells



$\Omega_{12} = ?$

To calculate Ω_{12}, consider the addition of N_2 polymer molecules one by one, followed by the addition of N_1 solvent molecules

- For the first polymer molecule, its first segment can be placed anywhere
- Remaining $x - 1$ segments can only be placed in empty cells adjacent to previous segment due to chain connectivity
- Individual number of possible placements calculated for each segment of a chain
- Number of possible conformations of a polymer chain, ν, calculated by multiplying together the number of possible placements of all segments in a chain
- Calculation is carried out for each polymer molecule added successively
- N_1 solvent molecules are added in the N_1 empty cells after all polymer chains are added. Only one distinguishable spatial arrangement as solvent molecules are identical.

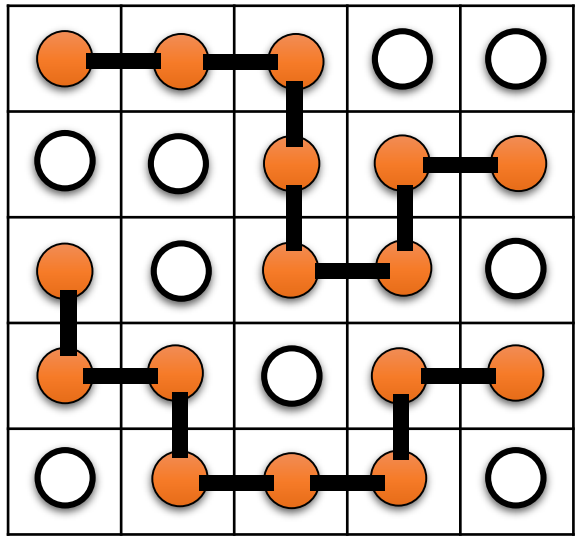
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

System: **Polymer Solution**

$N_1 + N_2$ molecules

x segments per polymer molecule; xN_2 polymer segments

$N = N_1 + xN_2$ lattice cells



$\Omega_{12} = ?$

$$\Omega_{12} = \frac{1}{N_2!}\prod_{\zeta=1}^{N_2} \nu_\zeta$$

$$\nu_\zeta = [N - x(\zeta - 1)]\left\{z\frac{[N - x(\zeta - 1)]}{N}\right\}\left\{(z-1)\frac{[N - x(\zeta - 1)]}{N}\right\}^{x-2}$$

z: Coordination number of lattice

$$\nu_\zeta = z(z-1)^{x-2}N^{1-x}[N - x(\zeta - 1)]^x$$

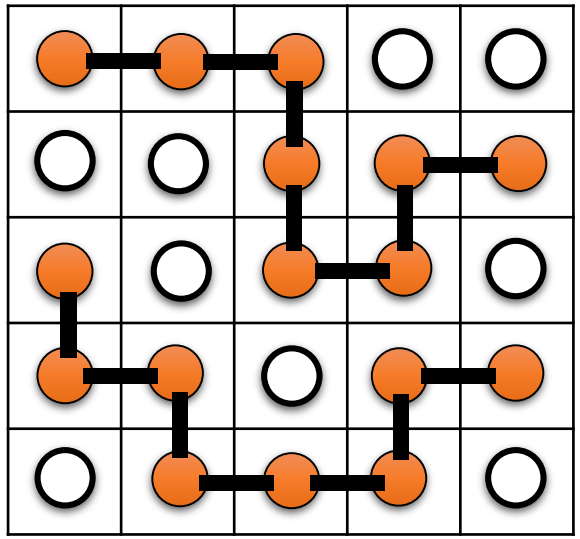
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

System: **Polymer Solution**

$N_1 + N_2$ molecules

x segments per polymer molecule; xN_2 polymer segments

$N_1 + xN_2$ lattice cells



$$\Omega_{12} = \frac{1}{N_2!}\prod_{\zeta=1}^{N_2} \nu_\zeta \qquad \nu_\zeta = z(z-1)^{x-2}N^{1-x}[N - x(\zeta - 1)]^x \qquad \Omega_{12} = ?$$

$$\Omega_{12} = \frac{1}{N_2!}\prod_{\zeta=1}^{N_2} z(z-1)^{x-2}N^{1-x}[N - x(\zeta - 1)]^x$$

$$\Omega_{12} = \frac{1}{N_2!}\{z(z-1)^{x-2}N^{1-x}\}^{N_2}\prod_{\zeta=1}^{N_2}[N - x(\zeta - 1)]^x$$

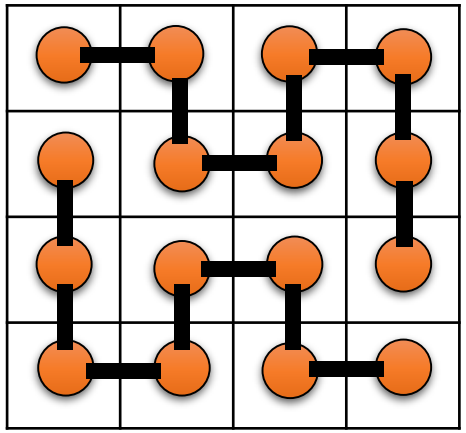
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

System: **Polymer**

N_2 molecules

x segments per polymer molecule; xN_2 polymer segments

xN_2 lattice cells



$$\Omega_{12} = \frac{1}{N_2!}\{z(z-1)^{x-2}N^{1-x}\}^{N_2}\prod_{\zeta=1}^{N_2}[N-x(\zeta-1)]^x$$

$\Omega_2 = ?$

For pure polymer, Ω_2 corresponds to the different arrangements of xN_2 polymer segments in xN_2 lattice cells. Replacing N in expression for Ω_{12} with xN_2, we get

$$\Omega_2 = \frac{1}{N_2!}\{z(z-1)^{x-2}(xN_2)^{1-x}\}^{N_2}\prod_{\zeta=1}^{N_2}[xN_2-x(\zeta-1)]^x$$

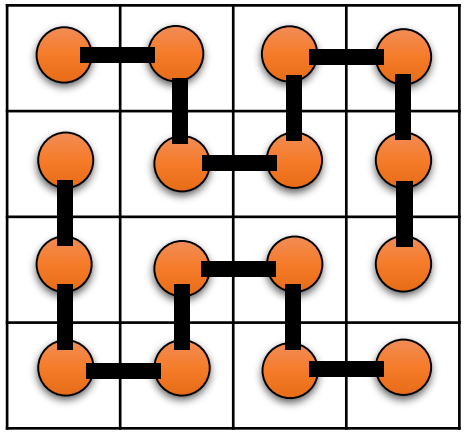
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

System: **Polymer**

N_2 molecules

x segments per polymer molecule; xN_2 polymer segments

xN_2 lattice cells



$\Omega_2 = ?$

$$\Omega_2 = \frac{1}{N_2!}\{z(z-1)^{x-2}(xN_2)^{1-x}\}^{N_2}\prod_{\zeta=1}^{N_2}[xN_2 - x(\zeta-1)]^x$$

$$\Omega_2 = [z(z-1)^{x-2}]^{N_2}\left\{\frac{1}{N_2!}(xN_2)^{(1-x)N_2}\prod_{\zeta=1}^{N_2}[xN_2 - x(\zeta-1)]^x\right\}$$

$$\frac{1}{N_2!}(xN_2)^{(1-x)N_2}\prod_{\zeta=1}^{N_2}[xN_2 - x(\zeta-1)]^x = \frac{1}{N_2!}(xN_2)^{(1-x)N_2}x^{xN_2}(N_2!)^x = {N_2}^{(1-x)N_2}x^{N_2}(N_2!)^{x-1}$$

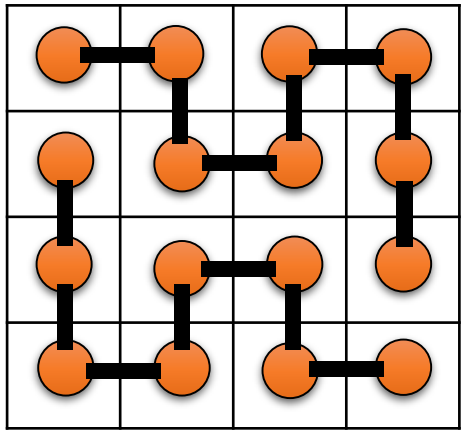
THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

System: **Polymer**

N_2 molecules

x segments per polymer molecule; xN_2 polymer segments

xN_2 lattice cells



$$\frac{1}{N_2!}(xN_2)^{(1-x)N_2}\prod_{\zeta=1}^{N_2}[xN_2 - x(\zeta-1)]^x = {N_2}^{(1-x)N_2}x^{N_2}(N_2!)^{x-1}$$

$\Omega_2 = ?$

Taking natural logarithm and applying Stirling's approximation, it can be shown that

$${N_2}^{(1-x)N_2}x^{N_2}(N_2!)^{x-1} = \left[\frac{x}{e^{x-1}}\right]^{N_2}$$

$$\Omega_2 = \left[z(z-1)^{x-2}\right]^{N_2}\left\{\frac{1}{N_2!}(xN_2)^{(1-x)N_2}\prod_{\zeta=1}^{N_2}[xN_2 - x(\zeta-1)]^x\right\} = \left[z(z-1)^{x-2}\right]^{N_2}\left[\frac{x}{e^{x-1}}\right]^{N_2}$$

THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

$$\Omega_2 = \left[z(z-1)^{x-2}\right]^{N_2} \left[\frac{x}{e^{x-1}}\right]^{N_2} \qquad \Omega_1 = 1$$

$$\Omega_{12} = \Omega_2 \left[\left(\frac{N}{xN_2}\right)^{N_2} \left(\frac{N}{N_1}\right)^{N_1}\right]$$

$$\Delta S_m^{comb} = k_B \ln\left(\frac{\Omega_{12}}{\Omega_1 \Omega_2}\right) = k_B \ln\left[\left(\frac{N}{xN_2}\right)^{N_2} \left(\frac{N}{N_1}\right)^{N_1}\right]$$

$$\Delta S_m^{comb} = k_B \left[N_2 \ln\left(\frac{N}{xN_2}\right) + N_1 \ln\left(\frac{N}{N_1}\right)\right] = -k_B \left[N_1 \ln\left(\frac{N_1}{N}\right) + N_2 \ln\left(\frac{xN_2}{N}\right)\right]$$

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

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

ϕ_1: Volume fraction of solvent

ϕ_2: Volume fraction of polymer