8.5: Polymer–Solvent Interactions

- Use same strategy as lattice model of a fluid.
- Considering polymer (P) and solvent (S) cells:

$$U = m_{SS}\omega_{SS} + m_{PP}\omega_{PP} + m_{SP}\omega_{SP}$$

ω_{ij} = interaction energy between cells i and j

m_{ij} = Number of contacts between i and j cells

- Number of solvent cell contacts:

$$zN_S = 2m_{SS} + m_{SP}$$

- Number of polymer cell contacts:

$$\approx (z-2)\cdot N_P \cdot n \approx z \cdot N_P n = 2m_{PP} + m_{SP}$$

each bead connects to 2 other beads

- Mean field approximation: Substitute the average number of solvent/polymer contacts.

$$m_{SP} \approx \frac{zN_S N_P \cdot n}{M} = \langle m_{SP} \rangle$$

$$U_{\text{mix}} = k_B T\left\{\frac{z\omega_{SS}}{2k_B T}N_S + \frac{z\omega_{PP}}{2k_B T}N_P n + \chi_{SP}\frac{N_S N_P}{M}n\right\}$$

$$\chi_{SP} = \frac{z}{k_B T}\left(\omega_{SP} - \frac{\omega_{SS}+\omega_{PP}}{2}\right)$$ solvent-polymer bead exchange parameter

$$\vdots$$

$$F_{\text{mix}} = N_S k_B T \ln\phi_S + N_P k_B T \ln\phi_P + \frac{z}{2}\left(\omega_{SS}N_S + \omega_{PP}N_P\right) + \chi_{SP}\frac{N_S N_P n}{M}$$

- Polymers expand in good solvents, collapse in bad solvents, retain Gaussian random coil behavior in neutral solvents (θ solvents).

Good solvents	$\chi < 0.5$	$\sqrt{\langle r^2 \rangle} \sim N^{3/5} \sim R_0 N^{3/5}$
Bad solvents (collapse)	$\chi > 0.5$	$R \sim R_0 N^{1/3}$
Theta solvents	$\chi = 0.5$	$\sqrt{\langle r^2 \rangle} \sim \dfrac{2N\ell^2}{3} = R_0$