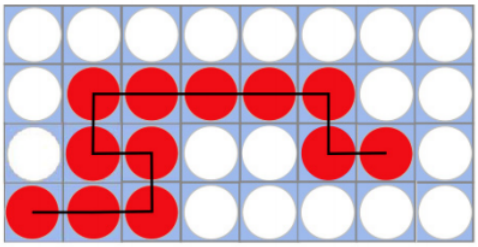
8.4: Flory–Huggins Model of Polymer Solutions



Let's being by defining the variables for the lattice:

- M: total number of lattice cells
- N_P: number of polymer molecules
- n: number of beads per polymer
- N_S: number of solvent cells
- nN_P = total number of polymer beads

The total number of lattice sites is then composed of the fraction of sites occupied by polymer beads and the remaining sites, which we consider occupied by solvent:

$$M = nN_P + N_S$$

Volume fractions of solvent and polymer:

$$\phi_S = \frac{N_S}{M} \quad \phi_P = \frac{nN_P}{M} \quad \phi_S + \phi_P = 1$$

The mole fraction of polymer:

$$x_P = \frac{N_P}{N_S + N_P}$$

x_P is small even if the volume fraction is high.

Excluded Volume for Single Polymer Chain

Generally, excluded volume is difficult to account for if you don't want to elaborate configurations explicitly, as in self-avoiding walks. However, there is a mean field approach we can use to account for excluded volume.

A better estimate for chain configurations that partially accounts for excluded volume:

$$\Omega_P = M\left[z\left(\frac{M-1}{M}\right)\right]\left[(z-1)\left(\frac{M-2}{M}\right)\right]\cdots\left[(z-1)\frac{(M-n+1)}{M}\right]$$

1st bead; 3rd bead; nth bead

Second bead on reduced lattice space counting only fraction of empty cells

Large n:

$$\Omega_P \approx \frac{(z-1)^{n-1}}{M}\frac{M!}{(M-n)!}$$

Entropy of Multiple Polymer Chains

For N_P chains, we count growth of chains by adding beads one at a time to all growing chains simultaneously.

1) First bead. The number of ways for placing the 1^{st} bead for all chains:

$$\nu^{(1)} = M(M-1)(M-2)\cdots(M-(N_P-1)) = \frac{M!}{(M-N_P)!}$$

1st bead 1st chain; 1st bead 2nd chain; 1st bead on N_Pth chain

2) Place the second bead on all chains. We assume the solution is dilute and neglect collisions between chains.

$$\nu^{(2)} = \left[z\left(\frac{M-N_P}{M}\right)\right]\left[z\left(\frac{M-N_P-1}{M}\right)\right]\cdots\left[z\left(\frac{M-2N_P+1}{M}\right)\right]$$

Ways of placing 2nd bead on 1st chain with a volume reduced by the number of beads present from the 1st beads. Volume fraction excluded: $(M-N_P)/M$

$$= \frac{(z)^{N_P}}{M}\left(\frac{(M-N_P)!}{(M-2N_P)!}\right)$$

3) For placing the n^{th} bead on N_P growing chains. Here we neglect collisions between site i and sites $>(i+4)$, which is the smallest separation that one can clash on a cubic lattice.

$$V^{(n)} = \left(\frac{z-1}{M}\right)^{N_P(N-1)} \frac{(M-N_P)!}{(M-n\cdot N_P)!}$$

4) Total number of configurations of N_P chains with n beads:

$$\Omega_P = \frac{\nu^{(1)}\nu^{(n)}}{N_P!}$$ ← indistinguishablity of polymer chains

$$\Omega_P = \left(\frac{z-1}{M}\right)^{N_P(n-1)} \frac{M!}{(M-nN_P)!N_P!}$$

$N_S!$

Entropy of Polymer Solution

Entropy of polymer/solvent mixture:

$$S_{\text{mix}} = k_B \ln \Omega_P$$

Calculate entropy of mixing:

$$\Delta S_{\text{mix}} = S_{\text{mix}} - S^0_{\text{solvent}} - S^0_{\text{polymer}}$$

pure solvent; pure polymer

$$S^0_{\text{solvent}} = 0 \text{ since } \Omega_{\text{solvent}} = 1$$

The pure polymer has many possible entangled configurations Ω^0_P, and therefore a lot of configurational entropy: S^0_{polymer}. But we can calculate Ω^0_P just by using the formula for Ω_P with the number of cells set to the number of polymer beads $M = nN_P$.

$$\Omega^0_P = \left(\frac{z-1}{N_P\cdot n}\right)^{N_P(n-1)} \frac{(N_P\cdot n)!}{N_P!}$$

$$\frac{\Omega_P}{\Omega^0_P} = \left(\frac{N_P\cdot n}{M}\right)^{N_P(n-1)} \frac{M!}{N_S!(N_P\cdot n)!} \tag{8.4.1}$$

Since $\Delta S_{\text{mix}} = k_B \ln \dfrac{\Omega_P}{\Omega^0_P}$

$$\begin{aligned}\Delta S_{\text{mix}} &= -k_B N_S \ln\left(\frac{N_S}{M}\right) - k_B N_P \ln\left(\frac{N_P\cdot n}{M}\right) \\ &= -Mk_B\left(\phi_S \ln\phi_S + \frac{\phi_P}{n}\ln\phi_P\right)\end{aligned}$$

where the volume fractions are:

$$\phi_S = \frac{N_S}{M} \qquad \phi_P = \frac{nN_P}{M} = 1 - \phi_S$$

Note for $n = 1$, we have original lattice model of fluid.
