Lecture # 24

11/9/05

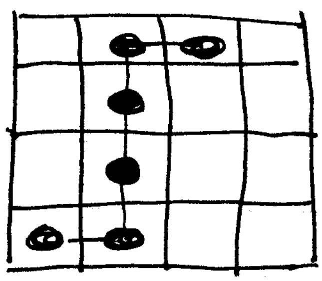
Polymers (see attached figures)

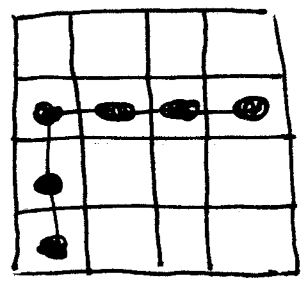
N = # of repeat units

Simple polymer :

repeat unit (monomer) -

Polymers have configurational entropy





M total sites

How many ways to put chain on lattice

$1^{st} \Rightarrow M$ sites

$2^{nd} \Rightarrow z$ sites (must go next to 1^{st})

$3^{rd} \Rightarrow z-1$ sites

Total configurations $\nu_1 = M(z-1)^{N-1}$ ← see text

or more correctly, if you avoid occupied sites

$$\nu_1 = \left(\frac{z-1}{M}\right)^{N-1} \left(\frac{M!}{(M-N)!}\right)$$

See pages 596-598 in DB for derivation

Can calculate entropy from adding up all possible configurations of all chains on lattice ⇒ derive entropy of mixing

We define the volume fraction of polymer on the lattice as $\phi_p = \frac{N n_p}{M}$ ← total # of polymer chains on lattice

Then the entropy of mixing per lattice site is

$$\frac{\Delta S_{mix}}{MK} = -\frac{\phi_P}{N}\ln\phi_P - (1-\phi_P)\ln(1-\phi_P)$$

NOTE THAT IF $N=1$ this reverts to regular solution theory

$$\frac{\Delta S_{mix}}{MK} = -X_A \ln X_A - (1-X_A)\ln(1-X_A)$$

IF you have two polymers

$$\frac{\Delta S_{mix}}{MK} = -\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B$$

Using analysis similar to that for regular solution theory, we can calculate free energy

Eqn 31.19 $$\frac{\Delta A_{mix}}{MKT} = \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \frac{zW_{AA}}{2KT}\phi_A + \frac{zw_{BB}}{2KT}\phi_B + \chi_{AB}\phi_A\phi_B$$

Compare mixing of 2 polymers to mixing of their monomers ⇒ entropic effects

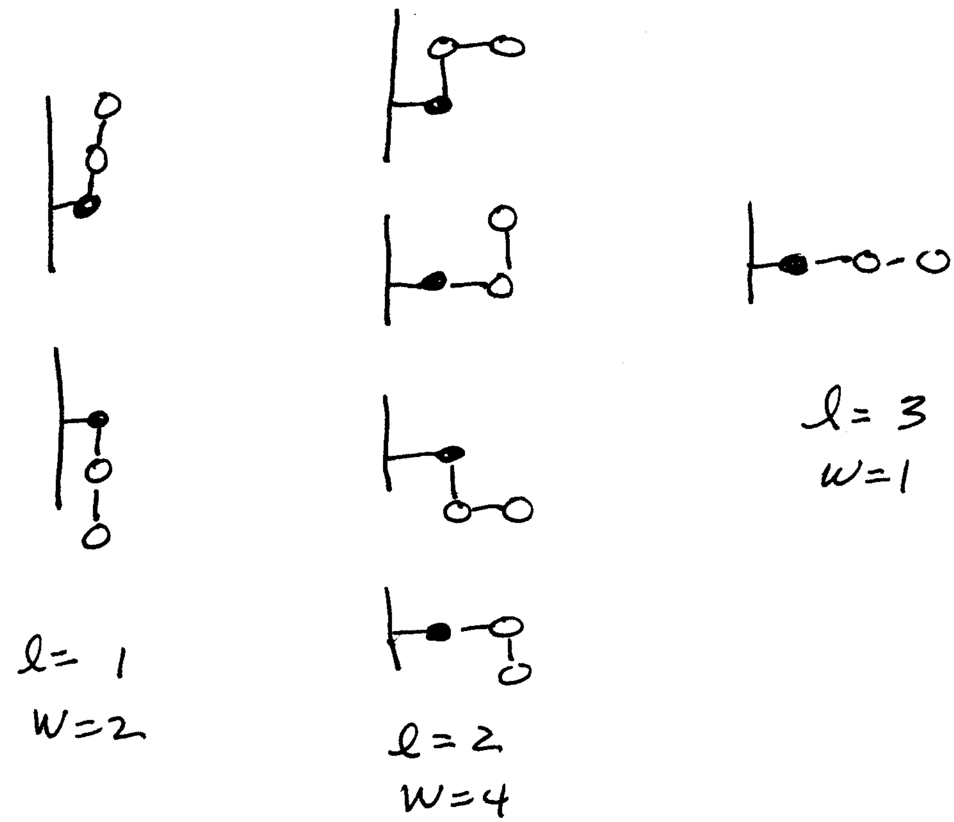
For small molecule $X_A = X_B = 0.5$

$$\frac{\Delta S_{mix}}{MK} = -0.5\ln 0.5 - 0.5\ln 0.5 = 0.69$$

For Polymer $N_A = N_B = 10{,}000$, $\phi_A = \phi_B = 0.5 = X_A = X_B$

$$\frac{\Delta S_{mix}}{MK} = -\left[\frac{0.5}{10{,}000}\ln .5 + \frac{0.5}{10{,}000}\ln .5\right] = 6.9\times 10^{-5}$$

Polymer chain conformation & size



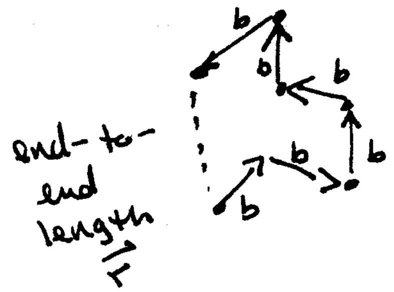
Most probable configuration is not stretched or squished.

Simple model of polymer chain configuration
Consider polyethylene glycol (PEG)

$$-(CH_2 - CH_2 - O)_n- \quad \text{flexible!}$$

treat each bond as a ~~sep~~ vector

$\vec{l}$ magnitude of vector $= b$



freely jointed PEG chain

contour length $L = Nb$

end-to-end length

$$\vec{r} = \sum_{i=1}^{N} l_i$$

We prefer a scalar quantity

a) project on to x-axis

$$r_x = \sum_{i=1}^{N} x_i = \sum_{i=1}^{N} b\cos\theta_i = b\sum_{i=1}^{N}\cos\theta_i$$

but

$$\langle r_x \rangle = \langle b\cos\theta_i \rangle = b\sum_{i=1}^{N}\langle\cos\theta_i\rangle = 0$$

$$= \langle r_y \rangle$$

$$= \langle r_z \rangle$$

better measure = square of end-to end

$$\langle r^2 \rangle = \vec{r}\cdot\vec{r} = \left(\sum_{i=1}^{N} l_i\right)^2 = l_1 l_1 + l_1 l_2 \cdots$$

self term $\langle l_i \cdot l_i \rangle = b^2$

cross term $\langle l_i \cdot l_j \rangle = b\langle\cos\theta_i\rangle = 0$

N "self terms" so

$$\boxed{\langle r^2 \rangle = N b^2}$$

measure of coil size