7.2: Excluded Volume Effects

Excluded Volume Effects

In real polymers, the chance of colliding with another part of the chain increases with chain length.

$$\langle R^2 \rangle = n\ell^2 + \sum_{i \neq j} \langle \vec{\ell_i} \cdot \vec{\ell_j} \rangle$$

$$\langle \vec{\ell_i} \cdot \vec{\ell_j} \rangle = g(s) = \langle \vec{\ell_i} \cdot \vec{\ell_{i+s}} \rangle \quad s = |i-j|$$

$g(s)$ gives the orientational correlations between polymer segments.

Flory, statistical mechanics of chain molecules

- If correlations are purely based on bond angles and rotational potential, then $g(s)$ decays exponentially with s. There is no excluded volume.
- With excluded volume, $g(s)$ does not vanish for large k. There are "long-range" interactions within the chain. "
  - "Long range" means along long distance along contour, but short range in space.
- Excluded volume depends on chain + solvent and temperature.

Virial expansion

At low densities, thermodynamic functions can be expanded in a power series in the number of particles per unit volume: $n = N/V$ (density).

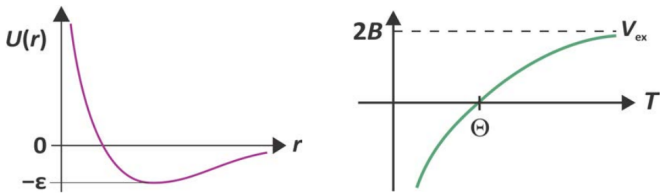
$$\begin{aligned} F &= F^0 + F_{\text{int}} \\ F_{\text{int}} &= N_p k_B T (nB + n^2 C + \dots) \end{aligned}$$

- F^0 refers to ideal chain
- N_p is # of polymer molecules
- B: units of volume

Excluded volume (repulsion) and attractive interactions are related to the second virial coefficient B. The excluded volume (or volume correlation relative to ideal behavior) for interacting beads of a polymer chain is calculated from

$$V_{\text{ex}} = \int d^3 r (1 - \exp[-U(r)/k_B T])$$

$U(r)$ is the interaction potential. In the high temperature limit $V_{\text{ex}} = 2B$. So $2B$ can be associated with the excluded volume associated with one segment (bead) of the chain.



Temperature dependence

- At hight T ($k_B T \gg \varepsilon$)
  The attractive part of potential is negligible, and repulsions result in excluded volume. In this limit $2B \approx V_{\text{ex}}$.
- As $T \to 0$, the attractive part of potential matters more and more, resulting in collapse relative to ideal chain.
- Cross over: Theta point $T = \Theta$
  Near Θ $2B \sim V_{\text{ex}} \left(\dfrac{T - \Theta}{\Theta} \right)$
  $T > \Theta$ High T. Repulsion dominates. Polymer swells (good solvent)
  $T < \Theta$ Low T. Attractions dominate. Polymer collapses (globule, poor solvent)

Polymer swelling

At high temperatures $(T \gg \Theta)$, the free energy of a coil can be expressed in terms interaction potential, which is dominated by repulsions that expand the chain, and the entropic elasticity that opposes it (see next chapter).

$$F = U - TS = nk_BTB\frac{3n}{4\pi R^3} + k_BT\frac{3R^2}{2n\ell^2} + const.$$

By minimizing F with respect to the end-to-end distance, R, and solving for R, we can find how the R scales with polymer size:

$$R \propto (B\ell^2)^{3/5}n^{3/5}$$

We see that the end-to-end distance of the chain with excluded volume scales with monomer number (n) with a slightly larger exponent than an ideal chain: $n^{3/5}$ rather than $n^{1/2}$. Generally, the relationship between R and n is expressed in terms of the Flory exponent, ν, which is related to several physical properties of polymer chains:

$$R \propto n^V$$