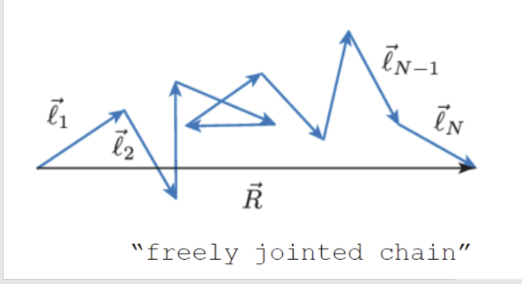
The Ideal chain model



- end to end vector : $\vec{R} = \sum_{i=1}^{N} \vec{l}_i$

- $\langle \vec{l}_i \rangle = 0 \Rightarrow \langle \vec{R} \rangle = 0$

- $\langle \vec{l}_i \cdot \vec{l}_j \rangle = \langle |\vec{l}|^2 \rangle \delta_{ij} \Rightarrow \langle |\vec{R}|^2 \rangle = \sum_{i,j} \langle \vec{l}_i \cdot \vec{l}_j \rangle$

$$= \sum_{i=1}^{N} l_K^2$$

MSD end-to-end distance of an ideal polymer chain

$$\boxed{\langle |\vec{R}|^2 \rangle = \underbrace{l_K}_{\text{Kuhn length}}^2 N}$$

Kuhn length (twice the persistence length of a polymer)

- **RMSD end-to-end distance**

RMSD : $R_0 = \left(\langle |\vec{R}|^2 \rangle \right)^{1/2} = l_K N^{1/2}$

$\Rightarrow$ $\boxed{R_0 = l_K N^{\nu}, \text{ with } \nu = 1/2 \text{ for ideal chains}}$

- Probability of an ideal chain having end-to-end distance 'R', given 'N' monomers in the chain: (in d-dimensions)

$$\boxed{P(\vec{R},N) = \underbrace{\left(\frac{1}{2\pi R_0^2/d}\right)^{d/2}}_{\text{normalization factor.}} \underbrace{e^{-\frac{dR^2}{2R_0^2}}}_{\text{gaussian centered at } 0 \ (\because \langle R\rangle = 0)}}$$

* valid for large N (central limit theorem?)

* similar to expression of particle diffusing a Random distance R in time t ($P(\vec{R},t)$), but the time is replaced by number of steps.

$N \rightarrow \frac{t}{\Delta t}$

- $P(\vec{R},N) = \frac{\Omega(\vec{R},N)}{\int d^d R \, \Omega(\vec{R},N)}$

\# of microstates when the polymer chain has an end-to-end distance $\vec{R}$.

$\Rightarrow S = k_B \ln \Omega$

$\therefore$ change in entropy in stretching the polymer chain from an end-to-end distance of 0 to $\vec{R}$:

$$\Delta S(\vec{R}, N) = S(\vec{R}, N) - S(0, N)$$

$$= k_B \left[\ln \Omega(\vec{R}, N) - \ln \Omega(0, N) \right]$$

use

$$\Omega(\vec{R}, N) = P(\vec{R}, N) \int d^d R \, \Omega(\vec{R}, N)$$

⋮

$$\boxed{\Delta S(\vec{R}, N) = -\frac{k_B d}{2 R_0^2} R^2}$$

⇒ negative entropy → by stretching the chain we reduce the number of available microstates.

* in stretching a polymer, we do work

⇒ in eqb^m free energy of the system is minimized.

$$F = U - TS$$

↳ 0 for ideal chain.

$$\Rightarrow \Delta F = -T \Delta S$$

use ΔS from above

$$\Rightarrow \boxed{\Delta F = \frac{k_B T d}{2 R_0^2} R^2}$$

$\Rightarrow$ force : $$f = -\frac{dF}{dx} = \overbrace{-\underbrace{\left(\frac{k_B T d}{R_0^2}\right)}_{\text{stiffness of ideal chain}} R}^{\text{hookean spring behavior } (f_{hooke} = -kx)}$$

→ stiffness reflects the fluctuation of the polymer (R_0 in denominator)

↳ tells us how stiffness in polymer depends on the fluctuation

→ rubber band get stiffer when heated.

Legend

≤ : spoken verbatim, in the lecture

Flory argument

- The idea :
  * A self avoiding random walk will swell faster.
    ⇒ the end to end distance is expanding.

$$F = \underbrace{U}_{\text{energy cost (from the interaction of monomers within the polymer)}} - \underbrace{TS}_{\text{controls the swelling of the polymer}}$$

energy cost (from the interaction of monomers within the polymer)

controls the swelling of the polymer

(≤ because by expanding the polymer, according to Flory's arguments, we reduce the entropy)

- for a self avoiding walk
  - ↳ the swelling is limited by the entropy term
  - ↳ the tendency of polymer to be compact (opposite of swelling) is controlled by the energy cost U.

* Preferred size of the polymer will be given by the balance b/w two terms.

- $-TS = \dfrac{k_B T\, d}{2 R_0^2} R^2$ } → entropy of the ideal chain.

Mean field within the polymer is the avg. density of the monomers.

- $\dfrac{U}{k_B T} \propto$ monomer density

  $\propto$ no. of monomers

$\Rightarrow \dfrac{U}{k_B T} = v \, \underbrace{n_{mon}}_{\text{monomer density}} N$

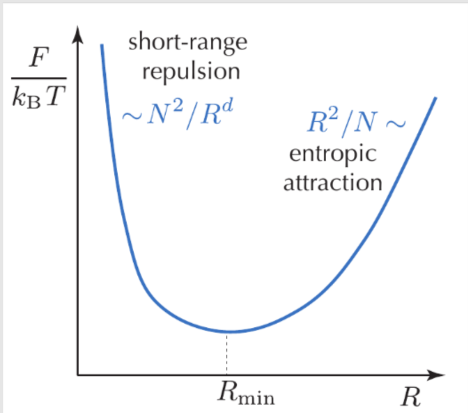
v → prefactor that depends on the interaction strength b/w the monomers (excluded volume parameter)

$\Rightarrow n_{mon} = \dfrac{N}{R^d}$] volume

* # of monomers in a chain N, is some times referred to as degree of poly-merization in this course

$\therefore$ the Flory free energy is given by:

$$\boxed{\frac{F}{k_B T} = \frac{v N^2}{R^d} + \frac{d R^2}{2 \underbrace{N l_k^2}_{R_0^2}}}$$



to solve for minima:

$$\frac{dF}{dR} = 0 \Rightarrow R = (v\, l_k^2 N^3)^{1/d+2}$$

$$\boxed{\sim N^{3/d+2}}$$

$$\Rightarrow \boxed{\nu_{Flory} = \frac{3}{d+2}}$$

Works very well, even though this
is a “mean field” theory.
Both entropy and repulsive interactions are
actually overestimated in Flory’s argument
but they happen to cancel out