Chain Models

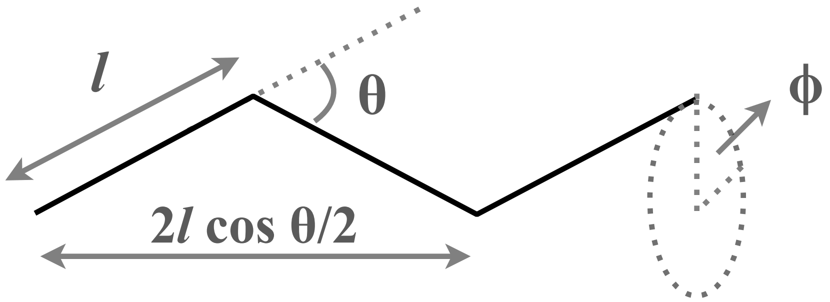
Ideal chain model
Freely jointed chain
Kuhn model
Freely-rotating chain

Today's Lecture

1. Relation of conformational isomerism to macromolecular shape (motivate coil model for flexible polymers)
2. Define the 'size' of a macromolecules
3. Introduce physical models to represent single chains

Ideal Chain Models

- **Assumption:** no interactions between monomers (i.e. polymer melts)
- picture for flexible polymers



l : segment length
θ : bond angle
ϕ : torsional angle

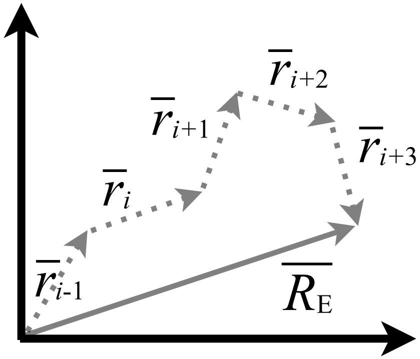
* Note: for C-C "backbones", $\theta = 68°$

- quantity of interest: **$\langle R_E^2 \rangle$**

  → chain end-to-end distance as a junction of **the number of segments (n)** and **the segment length (l)**

Ideal Chain Models

- **Define: chain end-to-end distance $\langle R_E^2\rangle^{1/2}$**



$$\overline{R_E} = \sum_i r_i$$

* Note: $\langle R_E\rangle = 0$ due to random orientation of segments

→ better definition: $\langle R_E^2\rangle^{1/2}$
mean-square end-to-end distance

$$\langle R_E^2\rangle = \langle \sum_i \overline{r_i} \cdot \sum_j \overline{r_j} \rangle = \sum_i \sum_j \langle \overline{r_i} \cdot \overline{r_j} \rangle$$

because $\overline{r_i}, \overline{r_j}$ are independent of each other $|\overline{r_i}| = |\overline{r_j}| = l$

$$\boldsymbol{\langle R_E^2\rangle = l^2 \sum_i \sum_j \langle \cos \theta_{ij} \rangle}$$

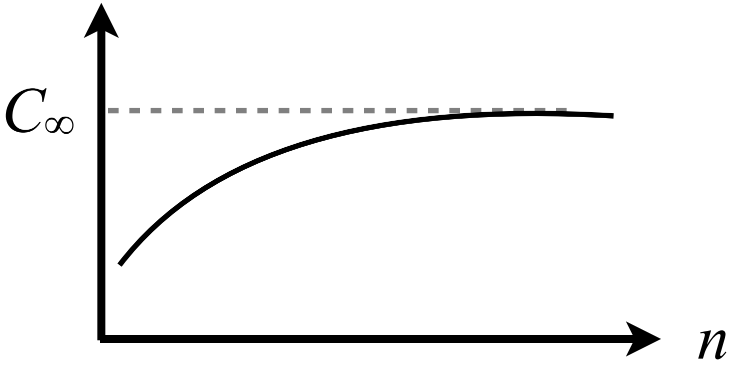
→ we can calculate $\langle R_E^2\rangle$ if l and θ_{ij} is known

Next: different chain models make different assumptions about $\langle \cos \theta_{ij} \rangle$

Freely-Jointed Chain

- **Question:** Account for deviations from ideality without giving up simplicity of freely-jointed chain model
- **Solution (by Flory):** $\sum_i \sum_j < \cos \theta_{ij} >$ converges for any given chain

$$\sum_i \sum_j < \cos \theta_{ij} >$$



For $n \rightarrow \infty$,
C_∞ is Flory expansion ratio

$$\boldsymbol{<R_E^2> = C_\infty\, n \cdot l^2}$$

Ideal chains: $C_\infty = 1$

Reality : $C_\infty = 2 \sim 12$

* Note: accounts for <u>expansion of chains</u> due to implications of fixed chemical bond angles as well as interactions

Kuhn model

- **Idea:** Flexible polymers have universal properties that do not depend on the local architecture. This can be expressed by introducing the equivalent length (***l***).

- **Define:** b = equivalent length
  N_b = number of equivalent segments along the contour length of polymers

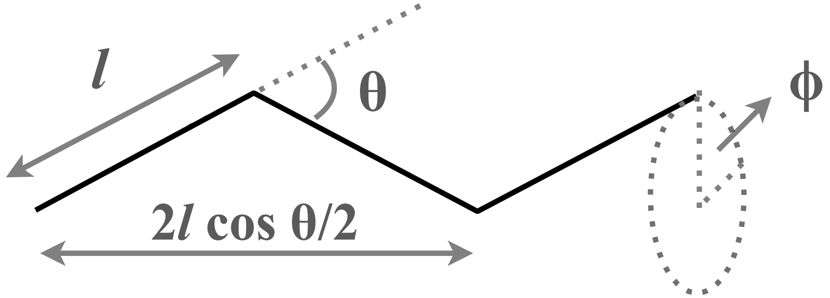
$$\boldsymbol{L = n\,l = N_b\,b}$$

$$\langle R_E^2 \rangle \underset{\substack{\uparrow \\ \text{Flory}}}{=} C_\infty n \cdot l^2 = \boldsymbol{N_b\,b^2}$$

$$N_b = \frac{L^2}{C_\infty n l^2}, \qquad b = \frac{C_\infty n l^2}{L}$$

Freely-Rotating Chain

- **Assumption:** no restrictions on torsion angle (ϕ), but fixed bond angle (θ)



$$\langle R_E^2 \rangle = n \cdot l^2 \ \frac{1 + \cos\theta}{1 - \cos\theta}$$

- **Consider:** all carbon sp^3 polymer backbone

$$\frac{1 + \cos\theta}{1 - \cos\theta} \simeq 2$$

$$\langle R_E^2 \rangle = n \cdot l^2 \ \frac{1 + \cos\theta}{1 - \cos\theta} \ \simeq \overset{C_\infty}{2}\ n \cdot l^2$$

* Note: experimental observation for PE, $C_\infty \simeq 4 \sim 5$

→ effect of restricted torsional angles

→ effect of steric hinderance

Hindered-Rotating Chain

- **Assumption:** fixed bond angle (θ), torsion angle (ϕ) depends on the potential energy of a given conformation

$$<R_E^2> = n \cdot l^2 \; \frac{1 + \cos\theta}{1 - \cos\theta} \; \frac{1 + < \cos\phi >}{1 - < \cos\phi >}$$

$$< \cos\phi > = \frac{\int_0^{2\pi} \cos\phi \bullet e^{-u(\phi)/kT}}{\int_0^{2\pi} e^{-u(\phi)/kT}}$$

* Note: average calculated from Boltzmann distribution

→ computational models for polymer chains

Radius of Gyration $<R_g^2>^{1/2}$

- Average squared distance between monomers in a given conformation from the polymer's center of mass

center of mass $\overline{r_{CM}} = \frac{1}{N}\sum_i \overline{r_i}$

$$<R_g^2> = \frac{1}{N}\sum_i <(\overline{r_i} - \overline{r_{CM}})^2> \simeq \frac{1}{N^2}\sum_i\sum_j <(\overline{r_i} - \overline{r_j})^2>$$

- Relation between $<R_g^2>$ and $<R_E^2>$ depending on geometry of molecule

for random coil-type chains
(~ freely jointed chains) $<R_g^2> = \frac{1}{6}<R_E^2>$

for rodlike (stiff) chains $<R_g^2> = \frac{1}{12}<R_E^2>$

* Note: Experimentally accessible measure of the size of a polymer chain
→ Light, X-ray or neutron scattering

Chain Models

- **End-to-end distance:** geometric measure of the size of a polymer chain

Ideal Chain Models

neglect all interactions between repeat units but different models make different assumptions about the relation of bond angles

Freely-Jointed Chain

all bond/torsion angles are equally likely to occur

$$\left\langle R_E^2 \right\rangle = nl^2$$

Freely-Rotating Chain

bond angles are fixed
torsion angles are free

$$\left\langle R_E^2 \right\rangle = nl^2 \frac{1+\cos\theta}{1-\cos\theta}$$

Hindered-Rotation Models

bond angles are fixed
torsion angles are weighted dependent on energy

$$\left\langle R_E^2 \right\rangle = nl^2 \frac{1+\cos\theta}{1-\cos\theta} \frac{1+\left\langle \cos\phi \right\rangle}{1-\left\langle \cos\phi \right\rangle}$$