Chapter 2

Chain Conformations
Structure of polymers

- **Chemical Structure**
  - atomic structure
  - isomers ~ configurations
  - architecture

- **Physical Structure**
  - single chain structure ~ conformations
  - aggregation structure
    - amorphous state
    - semicrystalline state
Single chain structure ~ Conformation

- Configuration ~ breaking single bond
  - isomers, copolymers, branches

Conformation ~ rotation about single bond
  - syn-anti, trans-gauche, staggered-eclipsed

- Misnomers by Flory
  - spatial configuration
  - rotational isomers

Ch 2 #3
A polymer chain

- $n + 1$ atoms
- $n$ bonds (length $l$)
- $n - 1$ bond angles ($\tau = 180 - \theta$)
- $n - 2$ rotational angles (angle $\phi$)
Degree of freedom of a polymer chain

- $n + 1$ atoms $\Rightarrow$ $3(n+1)$ DOF
  - restricted by bonding $\Rightarrow$ $- n$ DOF
  - restricted by bond angle $\Rightarrow$ $- (n - 1)$ DOF
  - remaining DOF $= n + 4$

- $n + 4$ DOF of a polymer chain
  - 3 translational DOF $\sim$ position of CG
  - 3 orientational DOF
  - $n - 2$ rotational DOF $\sim$ $n - 2 \phi$’s
Size of a chain

- end-to-end distance, $r$
  - distance between the two chain ends

$$\bar{r} = \sum_{i=1}^{n} \bar{r}_i$$

(2.11)\

$$r = (\mathbf{r} \cdot \mathbf{r})^{1/2}$$

$$r^2 = \sum_{i=1}^{n} \bar{r}_i^2 + \sum_{j=1}^{n} \bar{r}_j^2 = \sum_{i=1}^{n} \bar{r}_i^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \bar{r}_i \bar{r}_j$$

(2.12)  \[ \sim \text{for } 1 \text{ conform'n} \]

$$\langle r^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \bar{r}_i^2 = \sum_{i=1}^{n} \langle \bar{r}_i^2 \rangle + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \bar{r}_i \bar{r}_j \rangle$$

~ avg of N conform'ns

\[
\begin{bmatrix}
    \langle \bar{r}_1 \bar{r}_1 \rangle + \langle \bar{r}_1 \bar{r}_2 \rangle + \cdots + \langle \bar{r}_1 \bar{r}_n \rangle + \\
    \langle \bar{r}_2 \bar{r}_1 \rangle + \langle \bar{r}_2 \bar{r}_2 \rangle + \cdots + \langle \bar{r}_2 \bar{r}_n \rangle + \\
    \cdots \cdots \cdots \cdots \cdots \cdots \cdots + \\
    \langle \bar{r}_n \bar{r}_1 \rangle + \langle \bar{r}_n \bar{r}_2 \rangle + \cdots + \langle \bar{r}_n \bar{r}_n \rangle
\end{bmatrix}
\]

(2.13)
Size of a chain (2)

- end-to-end distance (cont’d)

\[ \langle r^2 \rangle = n l^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle r_i r_j \rangle \]

- \( \langle r^2 \rangle^{1/2} \sim \) root-mean-square end-to-end distance
  » a measure of chain dimension
Size of a chain (3)

- radius of gyration, $s$
  - another measure of chain dimension
  - $\langle s^2 \rangle^{1/2} \sim$ root-mean-square distance to the atoms from CG
- $\langle r^2 \rangle_{(0)} = \langle s^2 \rangle_{(0)} / 6$
  - for (infinitely) long chain (very large $n$)
  - in unperturbed state (0)

See Appendix A of Flory
Exp’tal determ’n of chain dimension

- size depends on solvent
  - good or poor solvent
  - theta solvent (theta condition) ~ unperturbed state

📖 Fig 2.7

- in dilute soln
  - viscometry
  - light scattering

- in conc. solution, melt, or solid state
  - SANS
Parameters expressing chain characteristics

- **characteristic ratio**
  - $C_{(\infty)} = \frac{\langle r^2 \rangle_{(0)}}{n l^2} \sim \text{definition}$
  - a measure of chain stiffness
  - Table 2.1

- **temperature coefficient**
  - $\frac{d[\ln \langle r^2 \rangle_0]}{dT}$ (thermal expansion)
  - change in chain dimension with increasing temp due to conformational change
  - Table 2.2
Modeling of polymer chain

- from artificial to real chain
- with reducing artificiality
  - Freely jointed chain (l fixed)
  - Freely rotating chain (l, \( \theta \) fixed)
  - Chain with hindered rotation (l, \( \theta \) fixed; \( \phi \) restricted)
  - Chain with excluded volume effect
  - Gaussian chain or ‘random coil’
Freely Jointed Chain

- bond length \((l)\) only fixed
- chain dimension

\[
\langle \mathbf{r}^2 \rangle = n l^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \mathbf{r}_i \mathbf{r}_j \rangle
\]

\[
\langle \mathbf{r}_i \mathbf{r}_j \rangle = l^2 \langle \cos \theta_{ij} \rangle
\]

\[
\langle \mathbf{r}^2 \rangle = n l^2 + 2 l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos \theta_{ij} \rangle
\]

- For FJC, \(\langle \cos \theta_{ij} \rangle = 0\) for \(i \neq j\)
  - random disposition of bond vectors
  - For every \(\cos \theta\), there is \(\cos (\theta+\pi) = -\cos \theta\).
- MS e-t-e distance, \(\langle \mathbf{r}^2 \rangle = n l^2\)
- \(C_\infty = 1\)
**Freely Rotating Chain**

- bond length \((l)\) and bond angle \((\tau = 180 - \theta)\) fixed
  - reduced artificiality from FJC

- chain dimension

\[
\langle \mathbf{r}^2 \rangle = nl^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \mathbf{r}_i, \mathbf{r}_j \rangle
\]

\[
\langle \mathbf{r}_i, \mathbf{r}_{i+1} \rangle = l^2 \cos(180 - \tau)
\]

\[
\langle \mathbf{r}_i, \mathbf{r}_{i+2} \rangle = l^2 \cos^2(180 - \tau)
\]

\[
\langle \mathbf{r}_i, \mathbf{r}_j \rangle = l^2 |\cos(180 - \tau)|^{j-i}
\]

\[
\langle \mathbf{r}^2 \rangle = nl^2 + 2l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} |\cos(180 - \tau)|^{j-i}
\]

\[
\text{j - i = k and } \cos(180 - \tau) = \alpha
\]

\[
\langle \mathbf{r}^2 \rangle = nl^2 \left[ 1 + \frac{2}{n} \sum_{k=1}^{n-1} (n - k) x^k \right] \quad (2.18)
\]
FRC (2)

\[
\langle r^2 \rangle = n l^2 \left[ 1 + \frac{2}{n} \sum_{k=1}^{n-1} (n-k) x^k \right]
\]

\[
= n l^2 \left[ 1 + 2 \sum_{k=1}^{n-1} x^k - \frac{2}{n} \sum_{k=1}^{n-1} k x^k \right]
\]

\[
= n l^2 \left[ 1 + \frac{2(x - x^n)}{1-x} - \frac{2}{n} \left( \frac{x(1-x)^n}{(1-x)^2} - 1-x \right) \right]
\]

\[
= n l^2 \left[ 1 + \frac{2x}{1-x} - \frac{2x(1-x)^n}{n(1-x)^2} \right]
\]

For infinitely long chains \((n = \infty)\):

\[
\langle r^2 \rangle = n l^2 \left[ 1 + \frac{2x}{1-x} \right] = n l^2 \left[ \frac{1+x}{1-x} \right]
\]

\[
= n l^2 \left[ \frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right]
\]

\((2.19)\)

\(\square\) For \(\tau = 110^\circ\), \(\langle r^2 \rangle \approx 2n l^2\)

\(\square\) For \(\tau > 90^\circ\), \(C_{\infty,FRC} > C_{\infty,FJC}\).
Chain with Hindered Rotations

- Bond length and bond angle fixed
- Not all rotational angles between $0^\circ < \phi < 360^\circ$ are allowed.
- Only some discrete states are allowed
  $\rightarrow$ rotational isomeric states (RIS)
- Due to the interactions
  - intrinsic rotational potential $\sim$ eclipsed-staggered
  - non-bonded interaction (dispersion) $\sim$ trans-gauche
  - dipole interaction $\sim$ when dipoles present
Conformational energy map for ethane

- E(eclipsed) ~ 11.8 kJ/mol
- thermal E at RT ~ kT ~ 8.314 x 300 J/mol ~ 2.5 kJ/mol
- Only staggered conform’n stable (present)
Energy map for \( n \)-butane

- \( E(\text{gauche}) \sim 2.1 \text{ kJ/mol} \)
- Thermal energy at RT \( \sim 2.5 \text{ kJ/mol} \)
- Only T, G, and G’ conformers stable (present)
for \( n \)-alkane (PE) chains

- At very high temperatures
  - All \( \phi \) allowed \( \rightarrow \) FRC

- At lower temperatures
  - Only 0, 120, and -120 are allowed for each bond.
  - T, G, and G’ are the three discrete rotational isomeric states (RIS).

- For a PE chain with \( n \) bonds,
  - \( n-2 \) \( \phi \)’s \( \rightarrow \) \( 3^{n-2} \) RIS (conform’ns)
  - actually, fewer conform’ns allowed
Short-range interaction

- for \( n \)-pentane
  - 2 \( \phi \)’s \( \rightarrow \) 9 RIS; 6 distinguishable
  - TT, TG, TG’, GG, GG’, G’G’
  - GG’ is of high E (~ 14 kJ/mol)
    - GG’ not likely present
    - ‘pentane interaction’
    - ‘pentane effect’
    - ‘2nd-order interaction’
    - ‘shot-range interaction’
  - common in chain molecules
  - reduces the # of conformations
  - must be considered in analysis