

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

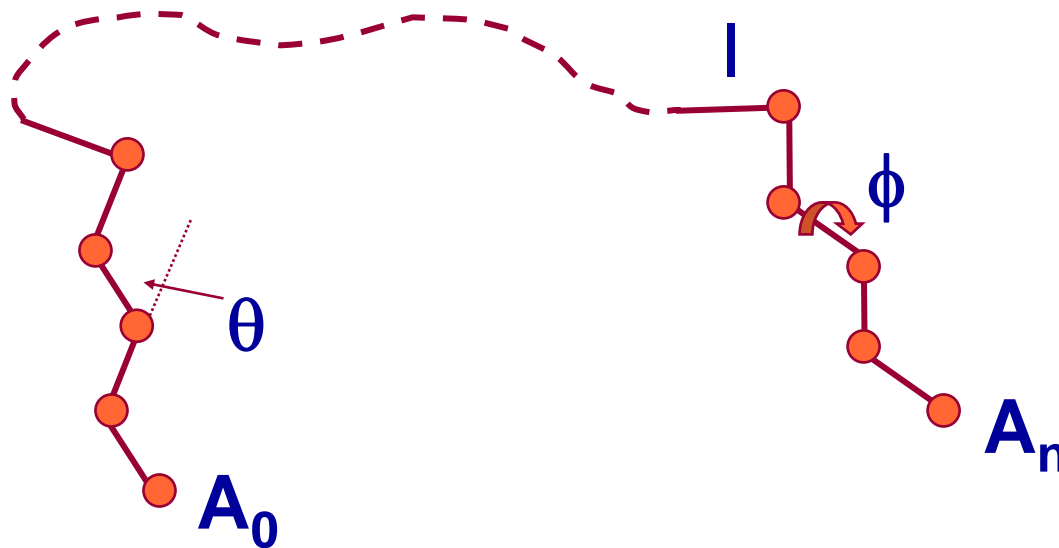
- syn-anti, trans-gauche, staggered-eclipsed

- Misnomers by Flory

- spatial configuration
- rotational isomers

A polymer chain

- $n + 1$ atoms
- n bonds (length l)
- $n - 1$ bond angles ($\tau = 180 - \theta$)
- $n - 2$ rotational angles (angle ϕ)



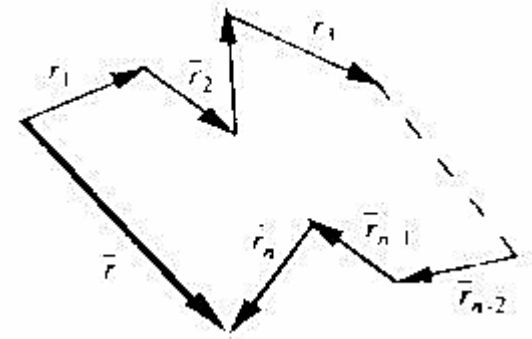
Degree of freedom of a polymer chain

- $n + 1$ 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 $\sim n - 2$ ϕ 's

Size of a chain

- end-to-end distance, r
 - distance betw the two chain ends



$$\bar{\mathbf{r}} = \sum_{i=1}^n \bar{\mathbf{r}}_i \quad (2.11)$$

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

$$r^2 = \sum_{i=1}^n \bar{\mathbf{r}}_i \cdot \sum_{j=1}^n \bar{\mathbf{r}}_j = \sum_{i=1}^n \bar{\mathbf{r}}_i^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^n \bar{\mathbf{r}}_i \cdot \bar{\mathbf{r}}_j \quad (2.12) \quad \sim \text{for 1 conform'n}$$

$$\langle r^2 \rangle = \frac{1}{N} \sum_{k=1}^N \bar{\mathbf{r}}_k^2 = \sum_{i=1}^n \langle \bar{\mathbf{r}}_i^2 \rangle + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^n \langle \bar{\mathbf{r}}_i \cdot \bar{\mathbf{r}}_j \rangle \quad \sim \text{avg of N conform'ns}$$

$$= \begin{bmatrix} \langle \bar{\mathbf{r}}_1 \bar{\mathbf{r}}_1 \rangle + \langle \bar{\mathbf{r}}_1 \bar{\mathbf{r}}_2 \rangle + \cdots + \langle \bar{\mathbf{r}}_1 \bar{\mathbf{r}}_n \rangle + \\ \langle \bar{\mathbf{r}}_2 \bar{\mathbf{r}}_1 \rangle + \langle \bar{\mathbf{r}}_2 \bar{\mathbf{r}}_2 \rangle + \cdots + \langle \bar{\mathbf{r}}_2 \bar{\mathbf{r}}_n \rangle + \\ \cdots \cdots \cdots \cdots \cdots \cdots + \\ \cdots \cdots \cdots \cdots \cdots \cdots + \\ \langle \bar{\mathbf{r}}_n \bar{\mathbf{r}}_1 \rangle + \langle \bar{\mathbf{r}}_n \bar{\mathbf{r}}_2 \rangle + \cdots + \langle \bar{\mathbf{r}}_n \bar{\mathbf{r}}_n \rangle \end{bmatrix} \quad (2.13)$$

Size of a chain (2)

□ end-to-end distance (cont'd)

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

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

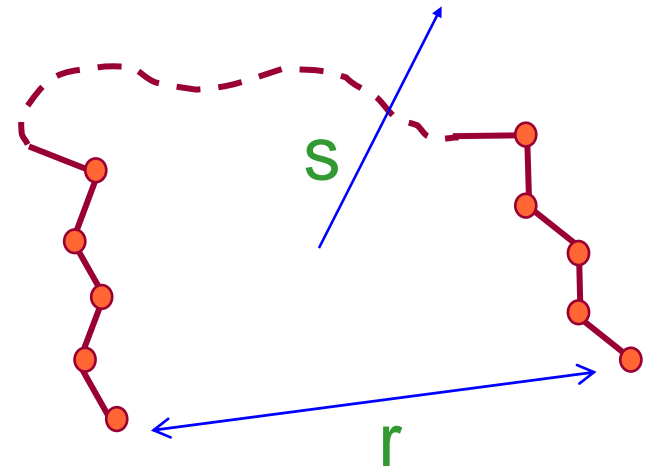
Size of a chain (3)

□ 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

- $C_{(\infty)} = \langle r^2 \rangle_{(0)} / n l^2 \sim \text{definition}$
- a measure of chain stiffness

 Table 2.1

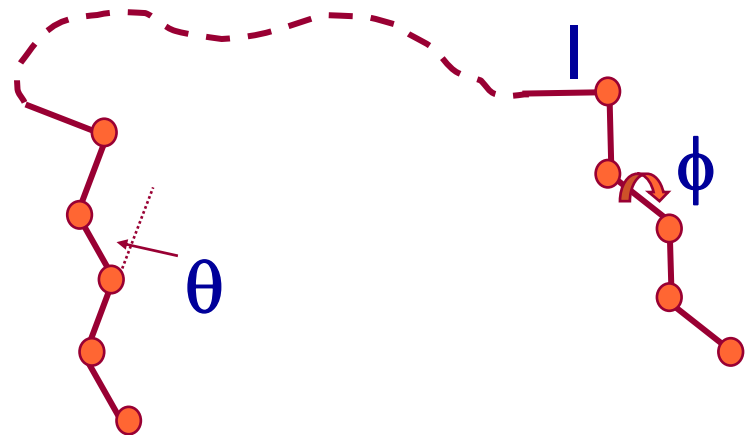
□ temperature coefficient

- $d[\ln \langle r^2 \rangle_0] / dT$ (– 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 , θ fixed)
- Chain with hindered rotation (l , θ fixed; ϕ restricted)
- Chain with excluded volume effect
- Gaussian chain or 'random coil'



Freely Jointed Chain

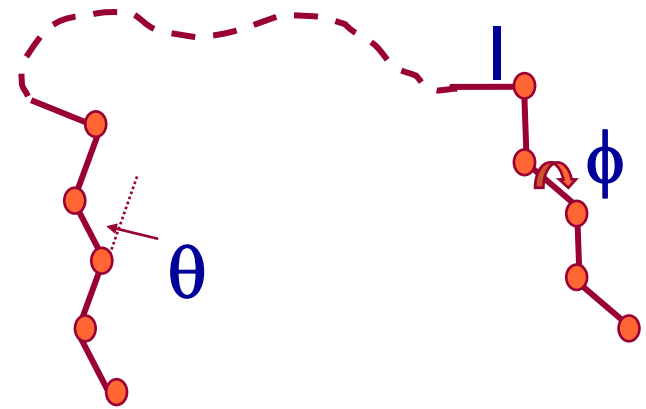
- bond length (l) only fixed
- chain dimension

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

$$\langle \bar{r}_i \bar{r}_j \rangle = l^2 \langle \cos \theta_{ij} \rangle$$

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

- 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, $\langle r^2 \rangle = nl^2$
- $C_\infty = 1$



Freely Rotating Chain

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

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

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

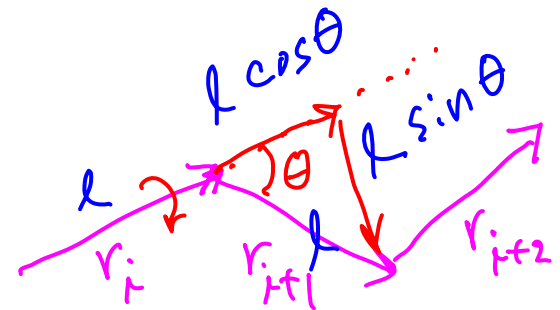
$$\langle \bar{\mathbf{r}}_i, \bar{\mathbf{r}}_{i+2} \rangle = l^2 \cos^2(180 - \tau)$$

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

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

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

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



FRC (2)

$$\begin{aligned}
 \langle r^2 \rangle &= nl^2 \left[1 + \frac{2}{n} \sum_{k=1}^{n-1} (n-k)\alpha^k \right] \\
 &= nl^2 \left[1 + 2 \sum_{k=1}^{n-1} \alpha^k - \frac{2}{n} \sum_{k=1}^{n-1} k\alpha^k \right] \\
 &= nl^2 \left[1 + \frac{2(\alpha - \alpha^n)}{1 - \alpha} - \frac{2}{n} \left(\frac{\alpha(1 - \alpha)^n}{(1 - \alpha)^2} - \frac{n\alpha^n}{1 - \alpha} \right) \right] \\
 &= nl^2 \left[1 + \frac{2\alpha}{1 - \alpha} - \frac{2\alpha(1 - \alpha)^n}{n(1 - \alpha)^2} \right]
 \end{aligned}$$

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

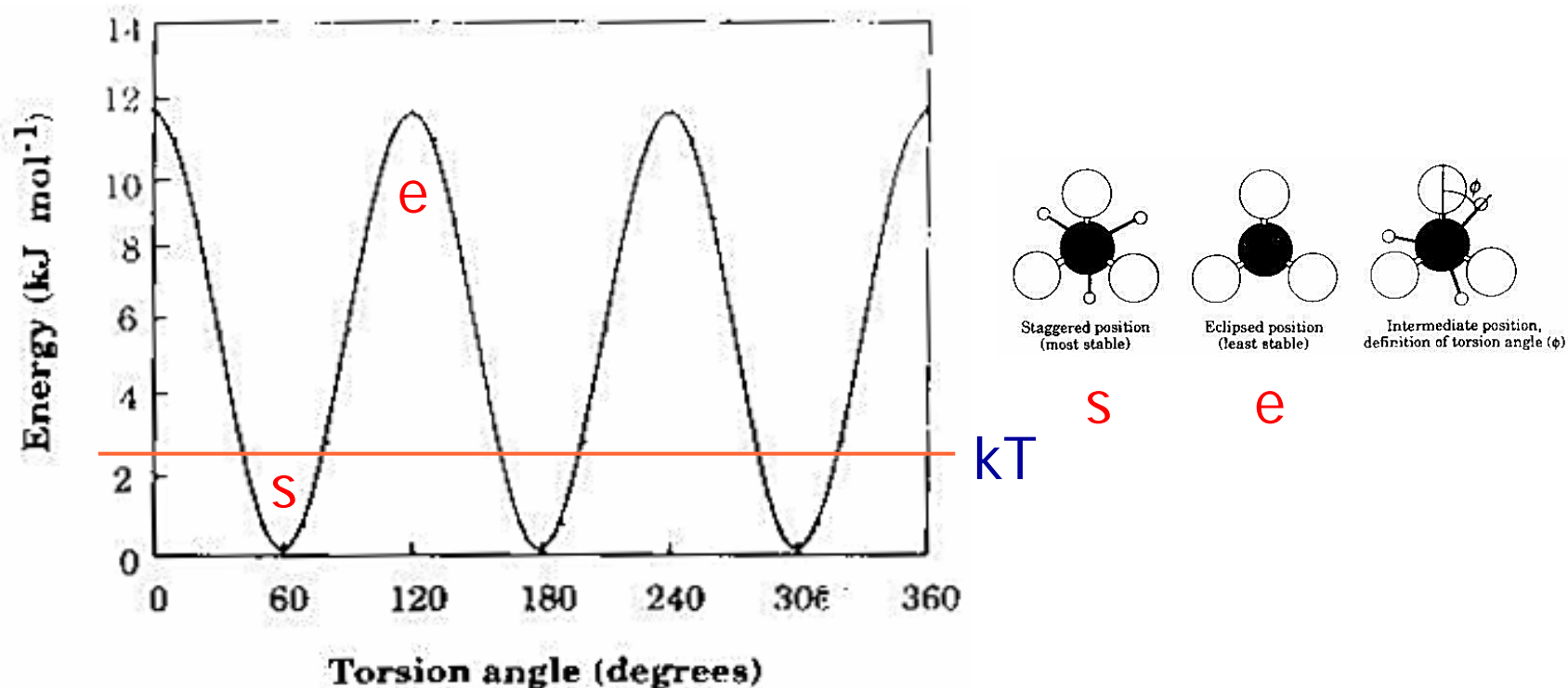
$$\begin{aligned}
 \langle r^2 \rangle &= nl^2 \left[1 + \frac{2\alpha}{1 - \alpha} \right] = nl^2 \left[\frac{1 + \alpha}{1 - \alpha} \right] \\
 &= nl^2 \left[\frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right] \quad (2.19)
 \end{aligned}$$

- For $\tau = 110^\circ$, $\langle r^2 \rangle \approx 2nl^2$
- For $\tau > 90^\circ$, $C_{\infty, \text{FRC}} > C_{\infty, \text{FJC}}$.

Chain with Hindered Rotations

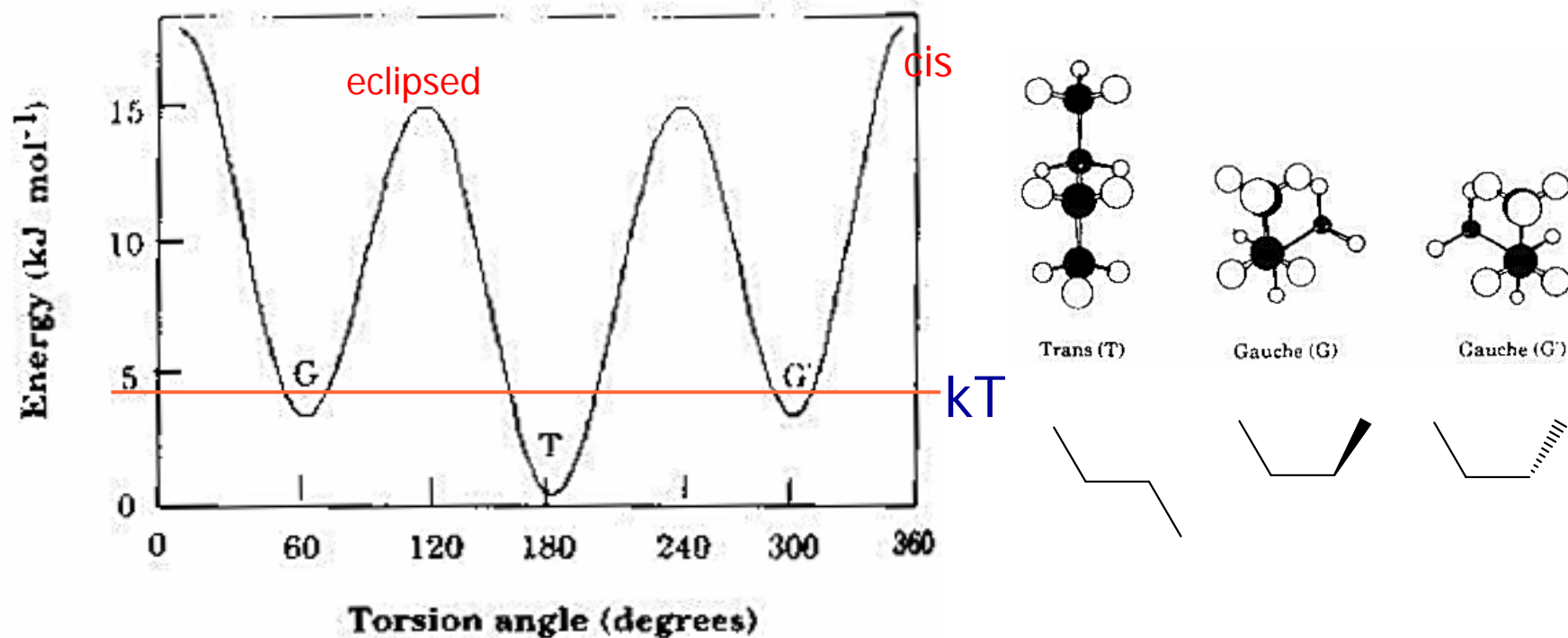
- Bond length and bond angle fixed
- Not all rotational angles between $0^\circ < \phi < 360^\circ$ are allowed.
- Only some discrete states are allowed
→ rotational isomeric states (RIS)
- Due to the interactions
 - intrinsic rotational potential ~ eclipsed-staggered
 - non-bonded interaction (dispersion)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

Conformational energy map for ethane



- $E(\text{eclipsed}) \sim 11.8 \text{ kJ/mol}$
- thermal E at $RT \sim kT \sim 8.314 \times 300 \text{ J/mol} \sim 2.5 \text{ kJ/mol}$
- Only staggered conform'n stable (present)

Energy map for *n*-butane



- $E(\text{gauche}) \sim 2.1 \text{ kJ/mol}$
- thermal E at RT $\sim 2.5 \text{ kJ/mol}$
- Only T, G, and G' conform'ns stable (present)

for *n*-alkane (PE) chains

- At very high temperatures
 - All ϕ 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,
 - $n-2$ ϕ 's $\rightarrow 3^{n-2}$ RIS (conform'ns)
 - actually, fewer conform'ns allowed

Short-range interaction

□ for *n*-pentane

- 2 ϕ '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'
 - » 'short-range interaction'
 - » common in chain molecules
 - » reduces the # of conformations
 - » must be considered in analysis

