

# Structure of polymers

- chemical structure
  - atomic structure (of repeat unit)
  - isomers ~ **configuration**
    - cis-trans isomer
      - 1,2-, cis-1,4-, trans-1,4-PBD
    - tacticity **Chapt 15**
      - isotactic/syndiotactic/atactic
- skeletal structure
  - linear
  - branched
  - crosslinked

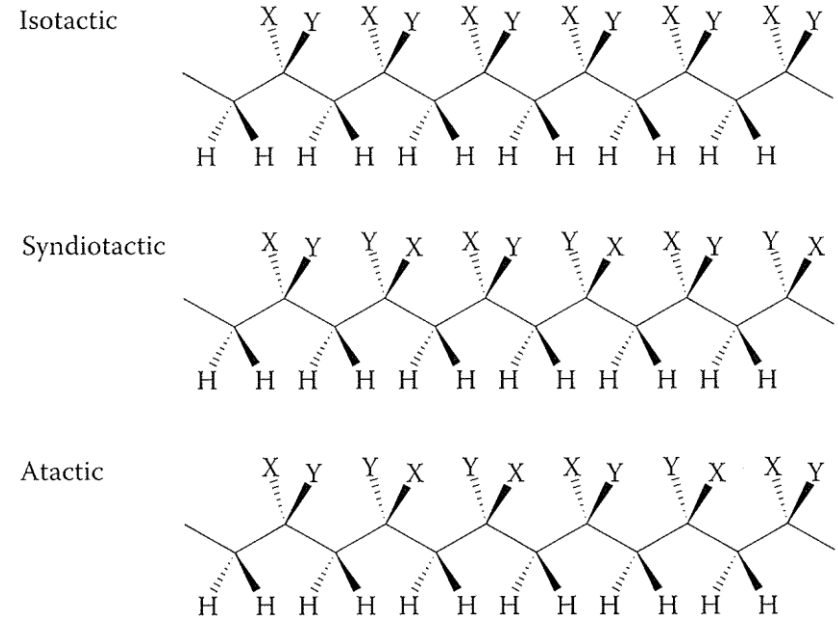


Fig 6.1 p148

- physical structure

- single-chain structure

- conformation

- size and shape of single chain



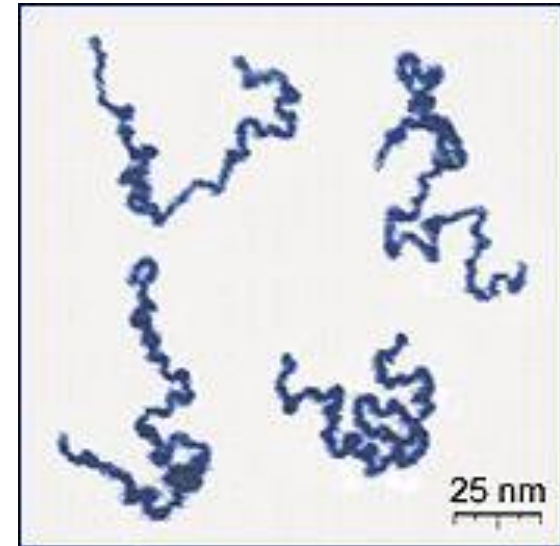
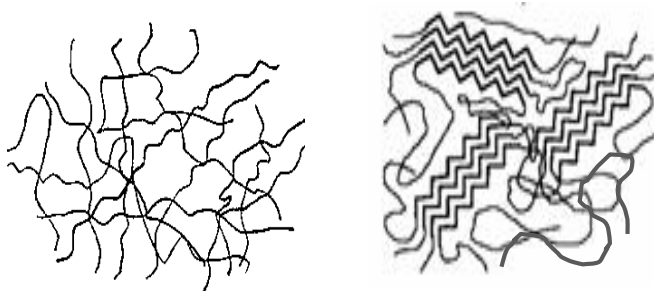
- aggregation structure

- amorphous state [Chapt 16](#)

- ← unperturbed-state conformation

- semicrystalline state [Chapt 17](#)

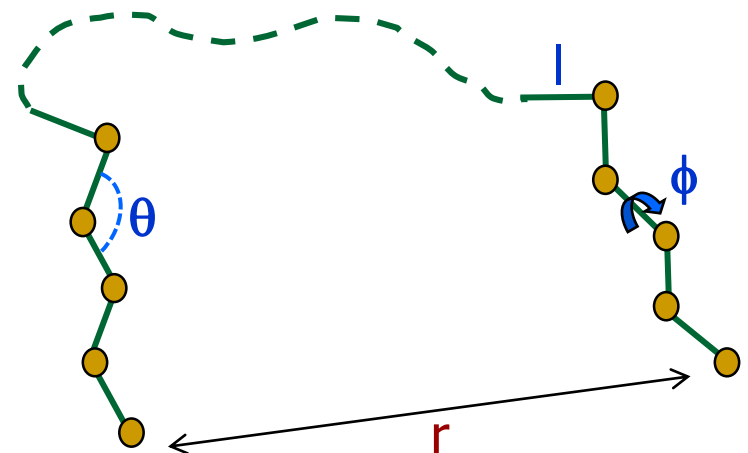
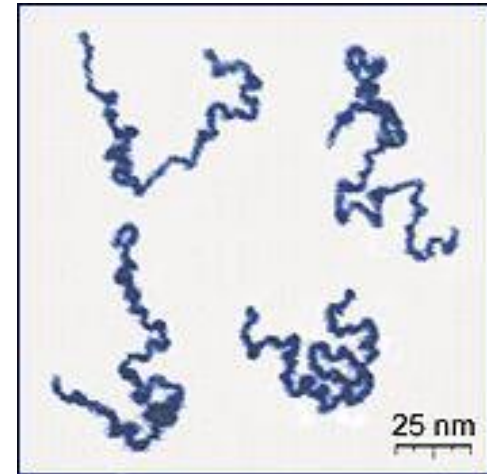
- ← preferred conformation



can be  
 a chain in different times,  
 a chain at different Temp's,  
 different chains in the bulk,  
 or  
 different polymers  
 (different chain stiffness)

# Modeling a polymer chain

- chain dimension  $\leftarrow$  stiffness  $\leftarrow$  structure
  - comparison of modeling and experiments
- a polymer chain with
  - $n$  bonds of length  $l$
  - $n-1$  bond angles  $\theta$
  - $n-2$  rotational angles  $\phi$
  - **end-to-end distance**  $r$  = a measure of dimension
    - contour length  $nl$  does not reflect structure
- modeling
  - freely jointed chain  $\sim l$  only fixed
  - freely rotating chain  $\sim l$  and  $\theta$  fixed
  - chain with hindered rotation  $\sim l, \theta$  fixed;  $\phi$  restricted



# Freely jointed chain

- bond length only fixed
- random-flight analysis (← random-walk)
  - probability finding the end at  $(x,y,z)$   $r$  away from  $O$

$$W(x, y, z) = \left( \frac{\beta}{\pi^{1/2}} \right)^3 \exp[-\beta^2(x^2 + y^2 + z^2)] = \left( \frac{\beta}{\pi^{1/2}} \right)^3 \exp[-\beta^2 r^2]$$

$$\beta = [3/(2nl^2)]^{1/2}$$

- a **Gaussian** distribution function → 'Gaussian chain' 'random coil'
- highest at 0

- probability finding the end at distance  $r$

$$W(r)dr = W(x, y, z) \times 4\pi r^2 dr = 4\pi \left( \frac{\beta}{\pi^{1/2}} \right)^3 r^2 \exp(-\beta^2 r^2)$$

- max not at 0, but at  $r = (2/3)^{1/2} n^{1/2} l = 0.82 \langle r^2 \rangle^{1/2}$

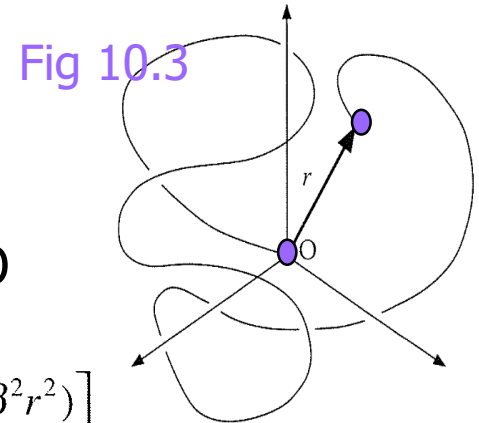


Fig 10.3

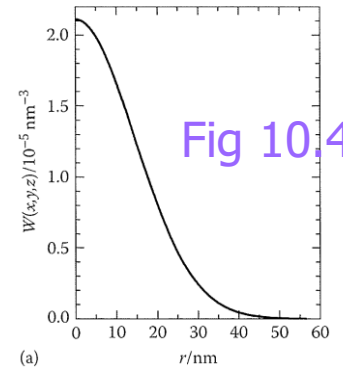
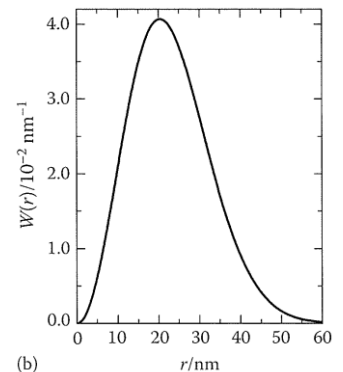


Fig 10.4



## □ random-flight analysis (cont'd)

$$\square \langle r^2 \rangle = \int_0^\infty r^2 W(r) dr = nl^2$$

< > average (over time or chains)

$$\square \langle r^2 \rangle_f^{1/2} = n^{1/2} l$$

■ root-mean-square (RMS) end-to-end distance

■  $n^{1/2}$  smaller than contour length [if  $n = 10^4$ , 1/100 smaller]

## □ vector analysis

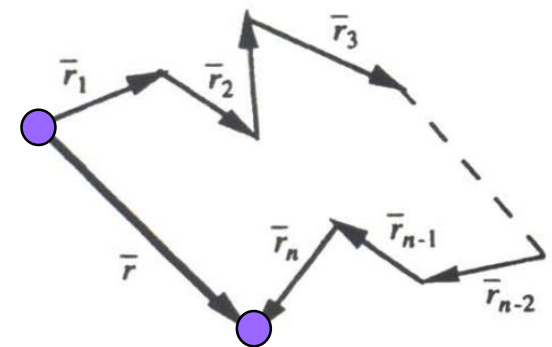
$$\square \text{ e-to-e vector } \quad \bar{\mathbf{r}} = \sum_{i=1}^n \bar{\mathbf{r}}_i$$

$$\square \text{ scalar magnitude of } \check{\mathbf{r}}, \quad r = (\check{\mathbf{r}} \cdot \check{\mathbf{r}})^{1/2}$$

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

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

0 ← random disposition of bond vectors



# Freely rotating chain

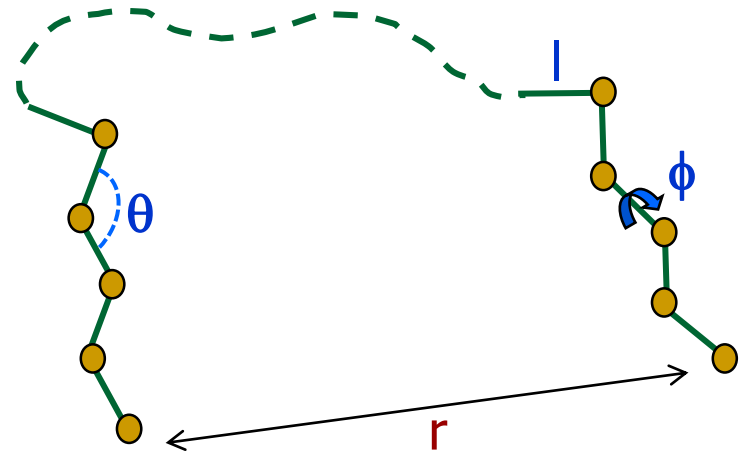
- bond length and bond angle fixed
  - 'valence angle model'
  - reduced artificiality from FJC
- chain dimension

$$\langle r^2 \rangle_{fa} = nl^2 \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right)$$

- FRC with  $sp^3$  atoms [ $\theta=110^\circ$ ]

$$\langle r^2 \rangle_{fa} = 2nl^2$$

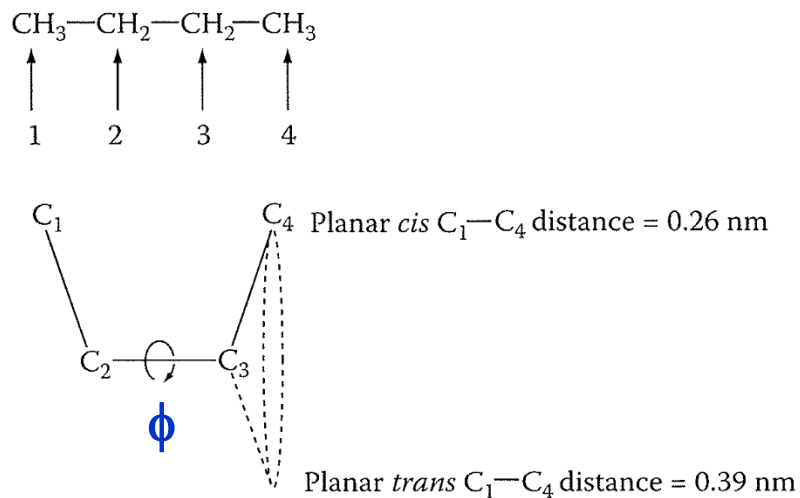
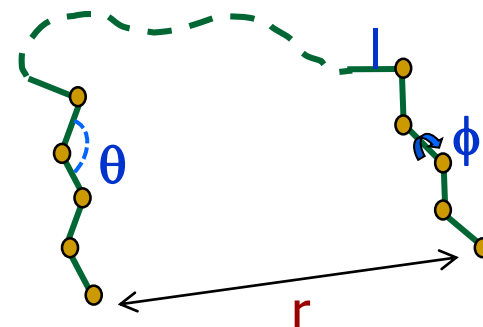
- FRC is  $2^{1/2}$  times larger than FJC.



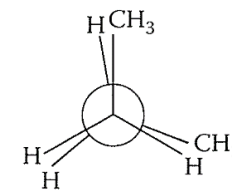
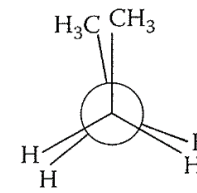
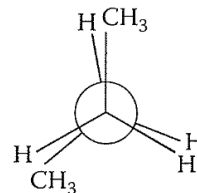
For PE with 10000 bonds,  
 $n = 10^4$ ,  $l = .15$  nm  
contour length  $nl = 1500$  nm  
or  $nl \cos 35^\circ = 1230$  nm  
 $r_{FJC} = 15$  nm  
 $r_{FRC} = 21$  nm

# Chain with restricted rotation

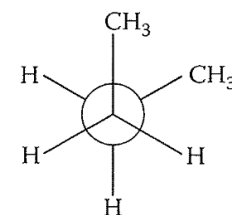
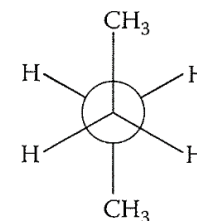
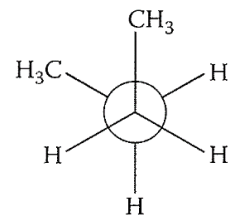
- $l$  and  $\theta$  fixed, and not all rotational angles allowed
  - only some **discrete states** allowed.
  - **rotational isomeric state [RIS]** model
- for butane



Eclipsed conformations



Staggered conformations



*gauche*<sup>-</sup>

*trans*

*gauche*<sup>+</sup>

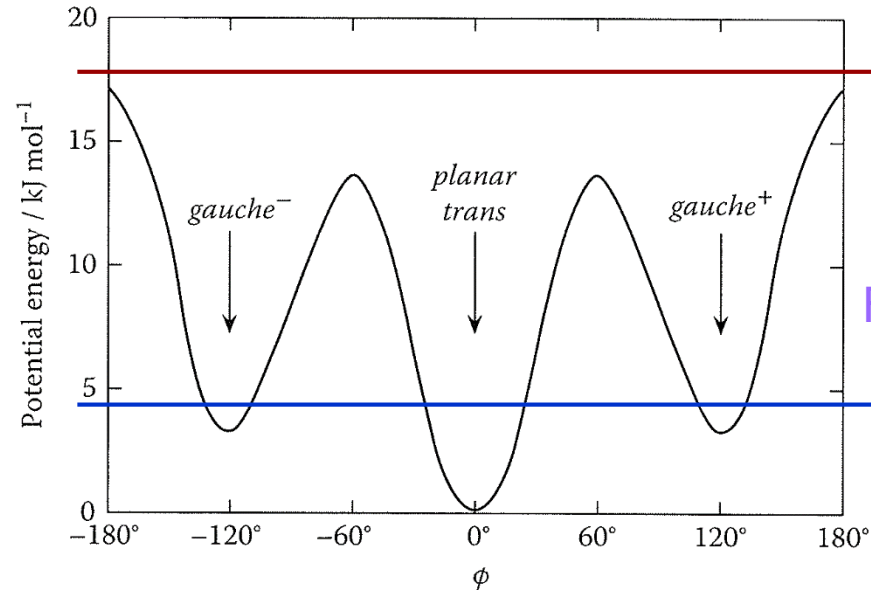
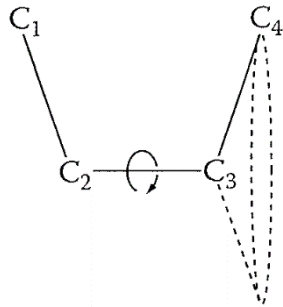
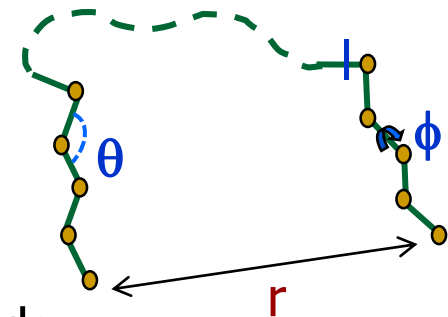


Fig 10.6

- ❑ at **high temp**, all  $\phi$  allowed  $\rightarrow$  FRC
- ❑ at **lower temp**, only  $-120^\circ$ ,  $0^\circ$ , and  $120^\circ$  allowed
  - due to **first-order [3-bond] interaction**
  - $g^-$ ,  $t$ , and  $g^+$  are the three discrete RIS's
- ❑ for polymer [PE] chain, 3 RIS's for each of  $n-2$  bonds





## □ Dimension of chain with 1st-order interaction

$$\langle r^2 \rangle_0 = nl^2 \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right) \left( \frac{1 + \overline{\cos \phi}}{1 - \overline{\cos \phi}} \right)$$

$$\overline{\cos \phi} = \frac{u(t) \cos 0^\circ + u(g^+) \cos (120^\circ) + u(g^-) \cos (-120^\circ)}{u(t) + u(g^+) + u(g^-)}$$

$$u(\phi) = \exp [-E(\phi)/kT]$$

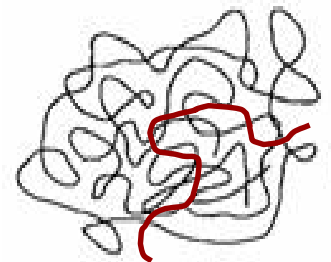
### □ for PE at 400 K

- $u(t) = 1, u(g) = .5 \rightarrow \overline{\cos \phi} = .25 \rightarrow \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right) \left( \frac{1 + \overline{\cos \phi}}{1 - \overline{\cos \phi}} \right) = 3.4$

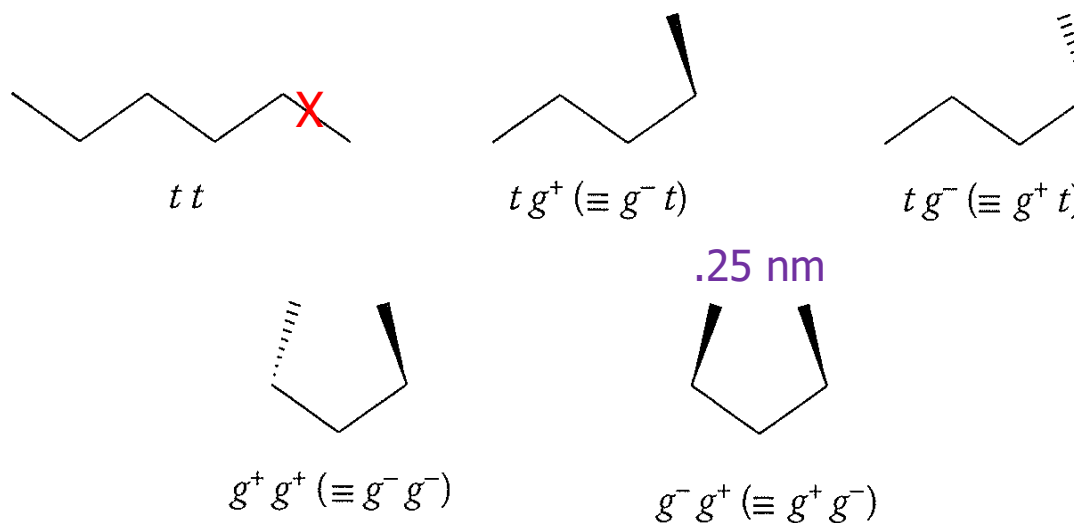
- experiments (light scattering, neutron scattering)  $\rightarrow 6.8$

- for  $n = 10^4$ ,  $r_{\text{measured}} = 55 \text{ nm}$  not 27 nm

- why the difference?



- 2nd-order [4-bond] interaction
  - for pentane, 2-bond rotation
  - 9 RIS's
  - $g^-g^+$  and  $g^+g^-$  are not allowed (due to very high energy)
  - pentane interaction, 'short-range interaction'
  - Bond rotation should be considered pairwise.



## □ RIS calculation Nobel prize 1974

### □ taking pairwise potential

- $u(\phi_i, \phi_{i+1})$  not  $u(\phi)$

### □ tensor transformation and calculation

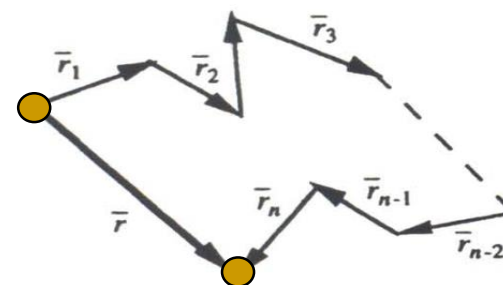
$$\square \langle r^2 \rangle_0 = \sigma^2 n l^2 \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right) = \sigma^2 \langle r^2 \rangle_{\text{FRC}}$$

- $\sigma$  = steric parameter  $\sim$  rarely used

$$\square \langle r^2 \rangle_0 = C_\infty n l^2 \quad C_\infty = \frac{\langle r^2 \rangle_0}{n l^2} = \langle r^2 \rangle / \langle r^2 \rangle_{\text{FJC}}$$

- $C_\infty$  = characteristic ratio  $\sim$  a measure of chain stiffness  $\leftarrow$  structure

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



Polymer	Temperature / °C	$\sigma$	$C_\infty$
Polyethylene	140	1.8	6.8
Isotactic polypropylene	140	1.6	5.2
Poly(vinyl chloride)	25	1.8	6.7
Polystyrene	25	2.3	10.8
Polystyrene	70	2.1	9.2

$$C_\infty = 5 - 10$$

$$C_\infty^{1/2} = 2 - 3$$

Table 10.3

# Quantities characterizing chain

## dimension

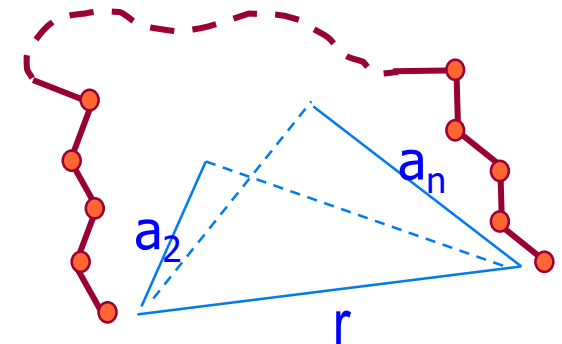
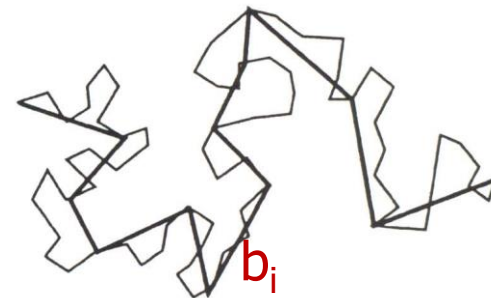
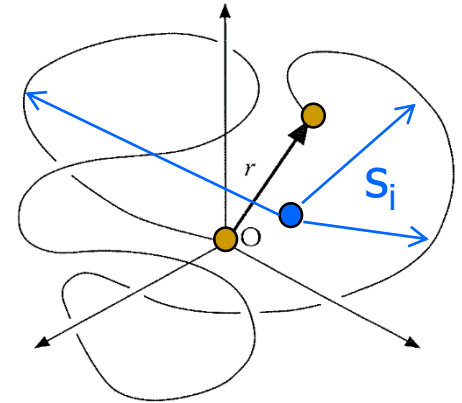
- RMS end-to-end distance,  $\langle r^2 \rangle^{1/2}$
- RMS radius of gyration,  $\langle s^2 \rangle^{1/2}$ 
  - RMS distance from center of mass

$$\langle r^2 \rangle^{1/2} = \frac{\langle s^2 \rangle^{1/2}}{6^{1/2}}$$

- contour length
  - $nl$  or  $nl \sin(\theta/2)$

## stiffness

- characteristic ratio,  $C_\infty$
- Kuhn length,  $b = C_\infty l$  or  $C_\infty l / \sin(\theta/2)$ 
  - Kuhn chain = statistically equivalent FJC
- persistence length,  $a = [(C_\infty + 1)/2] l$



# Chain with excluded volume

- intrachain volume exclusion

  - = 'long-range interaction'

  - makes chain larger

- $\langle r^2 \rangle^{1/2} = \alpha_r \langle r^2 \rangle_0^{1/2}$

  - $\alpha \sim$  expansion parameter

  - in a good solvent

    - repulsion(polymer-polymer) > repulsion(polymer-solvent)

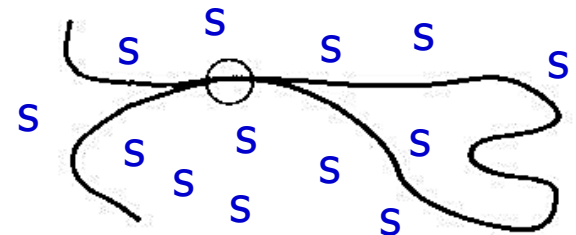
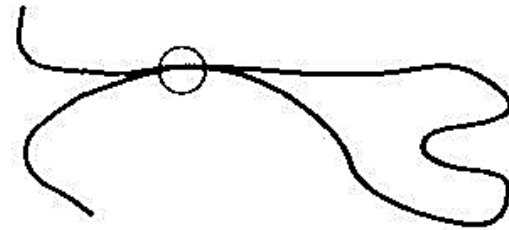
    - chain expands,  $\alpha > 1$

  - in a poor solvent

    - repulsion(polymer-polymer) < repulsion(polymer-solvent)

    - chain shrinks,  $\alpha < 1$

    - Actually,  $\alpha \approx 1$  and chain precipitates.



$$\square \langle r^2 \rangle^{1/2} = \alpha_r \langle r^2 \rangle_0^{1/2} \quad (\text{cont'd})$$

□ in a certain poor solvent with  $\alpha = 1$

■ repulsion(polymer-polymer) = repulsion(polymer-solvent)

■ polymer = solvent; solution behaves ideally

■ Chain neither expands nor shrinks.

■ 'phantom' or 'ghost' chain

■ **theta [ $\Theta$ ] condition**

■ in a theta solvent/temperature

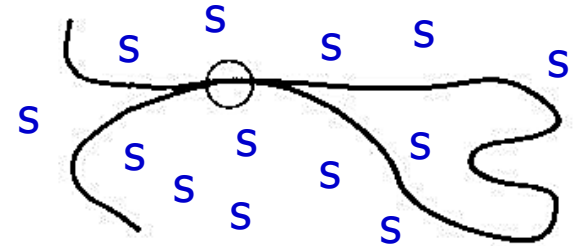
$$\square \beta_e = C_e \left[ \left( \frac{\theta}{T} \right) - 1 \right] = 0$$

■  $\beta_e$  = excluded volume integral = volume excluded by segment

■ 'unperturbed state' or unperturbed dimension [ $\langle r^2 \rangle_0$ ]

■ unperturbed by environment [solvent] or EV effect

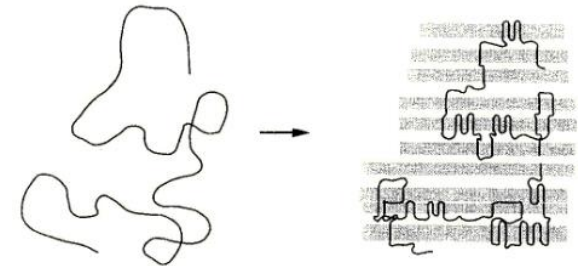
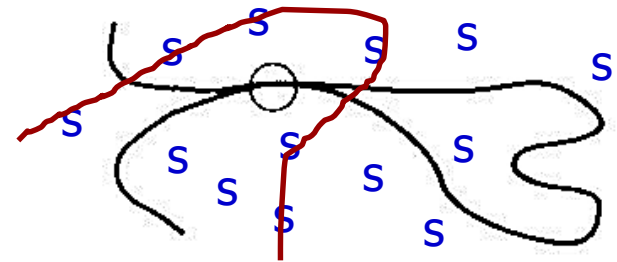
■  $\langle r^2 \rangle = \langle r^2 \rangle_{EV} = \langle r^2 \rangle_{RIS} = \langle r^2 \rangle_0$  at theta [ $\Theta$ ] condition



# Real chain in bulk

## □ in bulk amorphous state

- The neighbor is the polymer chain with the same type.
  - instead of solvent
- repulsion(polymer-polymer, **intra**)  
= repulsion(polymer-polymer, **inter**)
- Chains are in **unperturbed** states.
- proposed by Flory
- proved by SANS exp't later
- valid for melt and semicrystalline states



## □ RIS model describes the state of single chain in bulk (melt, amorphous, semicrystalline).

- chain in crystal  $\sim$  conformation with the lowest energy