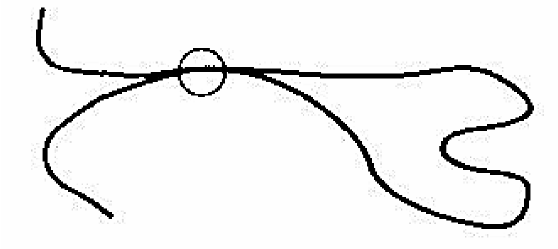
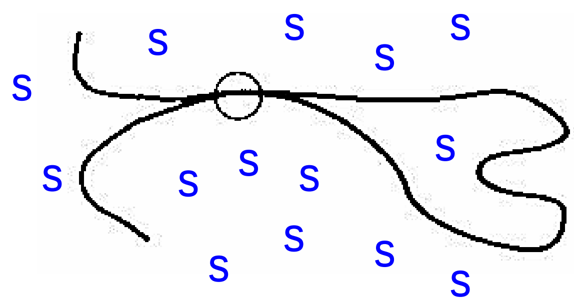
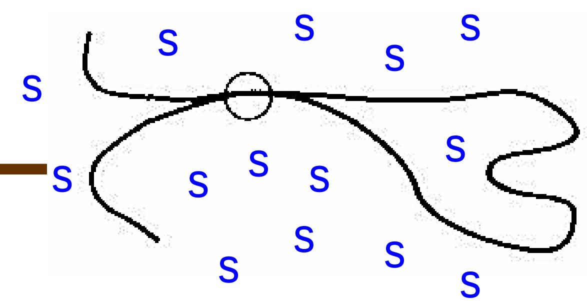
Excluded volume effect



- intrachain volume exclusion
  - 'long-range interaction'
  - gives larger dimension



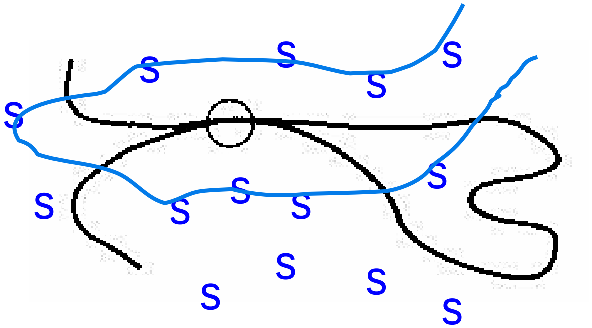
- $\langle r^2 \rangle_{EV} = \alpha^2 \langle r^2 \rangle_{RIS}$
  - in good solvent
    - » Repulsion(polymer-polymer) > Repulsion(polymer-solvent)
    - » chain expands, $\alpha > 1$
    - » by Flory-Krigbaum, $\alpha^5 - \alpha^3 = C\, n^{1/2}\, \psi\, (1 - \theta/T)$
      - – C ~ const, ψ ~ entropy factor, θ ~ theta temp
      - ◆ $\alpha^5 >> \alpha^3 \rightarrow \alpha \propto n^{0.1}$; $\langle r^2 \rangle_{RIS} = C_\infty\, n\, l^2$
      - ◆ $\langle r^2 \rangle_{EV} \propto n^{0.6}$ (exp't $\langle r^2 \rangle \propto n^{0.59}$)



- $<r^2>_{EV} = \alpha^2 <r^2>_{RIS}$
  - in poor solvent
    - » Repulsion(polymer-polymer) < Repulsion(polymer-solvent)
    - » chain shrinks, $\alpha < 1$
  - in a condition between good and poor solvent
    - » where $\alpha = 1$
    - » Repulsion(polymer-polymer) = Repulsion(polymer-solvent)
    - » chain neither expands nor shrinks
    - » ‘phantom’ or ‘ghost’ chain
    - » ‘theta (Θ) condition’
      - in a theta solvent/temperature
    - » polymer is in ‘unperturbed state’
      - unperturbed by environment (solvent)
    - » $<r^2>_{EV} = <r^2>_{RIS} = <r^2>_0$
    - » in Flory-Krigbaum eqn, $\alpha = 1 \rightarrow <r^2> \propto n^{0.5}$

Real chain in bulk ~ ‘random coil’

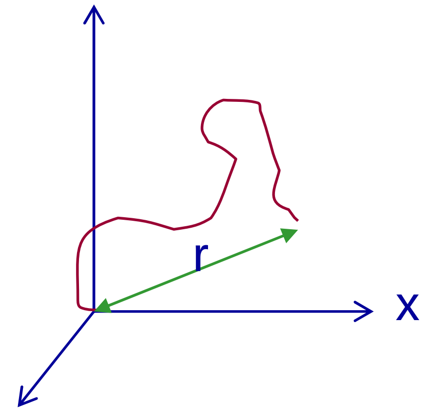
- In bulk amorphous state
  - polymer chain instead of solvent
  - Repulsion(polymer-polymer, intra)
    = Repulsion(polymer-polymer, inter)
  - Chains are in unperturbed state
  - $\langle r^2 \rangle = \langle r^2 \rangle_0 = r_\theta^2 = \langle r^2 \rangle_{RIS}$
  - proposed by Flory; proved by SANS exp’t
  - also in the melt state
  - also in the semicrystalline state (dimension)



- RIS model describes the state of single chain in bulk (melt, amorphous, semicrystalline).
  - crystal structure ~ conformation with the lowest energy

Distribution of r

- r, e-t-e distance
  - average = $<r^2>^{1/2}$
  - distribution? probability of finding the chain end
- random-flight analysis
  - random flight (3-D) → random walk (2-D)



$$P(l_x)dl_x = \frac{2\pi l(\sin\psi)l\,d\psi}{2\pi l^2} = \sin\psi\,d\psi \qquad (2.77)$$

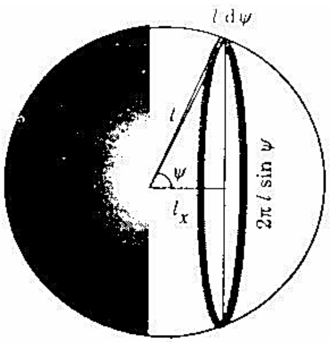
$$= \left(\frac{1}{2}\right)^{2k}\frac{(2k)!}{k!k!}$$

$$\langle l_x^2\rangle = \int_0^l l_x^2 P(l_x)dl_x = \int_0^{\pi/2} l^2\cos^2\psi\,\sin\psi\,d\psi \qquad (2.78)$$

By substitution in eq. (2.78) of $t = \cos\psi$ and $dt = -\sin\psi\,d\psi$

$$\langle l_x^2\rangle = l^2\int_0^{-1} -t^2\,dt = \frac{l^2}{3}$$

$$(\langle l_x^2\rangle)^{1/2} = \frac{l}{\sqrt{3}} \qquad (2.79)$$



- distance walked along x-axis

$$x = (n_+ - n_-)\frac{l}{\sqrt{3}} = (l/\sqrt{3})\ m \qquad m = n_+ - n_-$$

- probability of a (n_+/n_-)

$$P(n_+, n_-) = \left(\frac{1}{2}\right)^n \frac{n!}{n_+!\,n_-!} \qquad P(n, m) = \left(\frac{1}{2}\right)^n \frac{n!}{\left(\frac{n+m}{2}\right)!\left(\frac{n-m}{2}\right)!} \qquad (2.82)$$

- Stirling's approximation
  - » for large n, n>>m, m/n<<1
  - » $N! = N^N e^N (2\pi x)^{½}$ and following (2.83) through (2.88)
  - » or using $\ln N! = N \ln N - N + ½ \ln 2\pi + ½ \ln N$

$$P(n, m) = \sqrt{\frac{2}{\pi n}} \exp(-m^2/2n) \qquad (2.89)$$

- P(m,n) → P(x)Δx ~ probability of x betw x and x+dx
  - » m = (√3/l)x
  - » m changes by 2 → x changes by 2 l/√3 → Δx = 2 l/√3

$$P(x)dx = \sqrt{\frac{3}{2\pi}}\left(\frac{1}{\sqrt{n}\,l}\right)\exp(-3x^2/2nl^2)dx \quad (2.90)$$

~ Gaussian distribution

- for 3-D, probability of finding the chain end in dxdydz (vol)

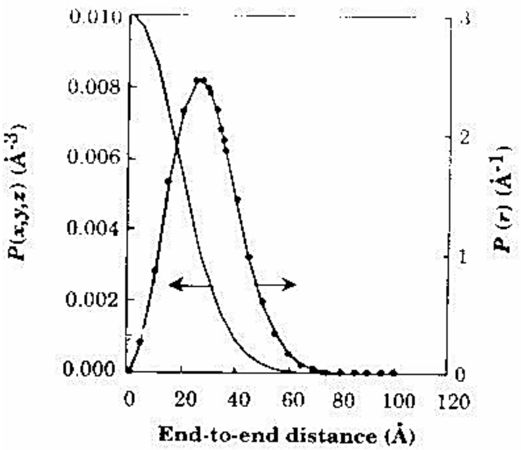
$$P(x,y,z)dx\,dy\,dz = \left(\frac{3}{2\pi n l^2}\right)^{3/2}\exp(-3(x^2+y^2+z^2)/2nl^2)dx\,dy\,dz$$

$$P(x,y,z)dx\,dy\,dz = \left(\frac{3}{2\pi n l^2}\right)^{3/2}\exp(-3r^2/2nl^2)dx\,dy\,dz$$

$$P(x,y,z)dx\,dy\,dz = \left(\frac{3}{2\pi\langle r^2\rangle_0}\right)^{3/2}\exp(-3r^2/2\langle r^2\rangle_0)dx\,dy\,dz$$

» $\langle r^2\rangle = n\,l^2$ for FJC or Kuhn chain

- $P(x,y,z)$
  - » P_{max} at the origin ← random flight
  - » fast decreasing



- $P(x,y,z)$ → $P(r)$ ~ prob of r betw r and r+dr
  - » radial distribution of r

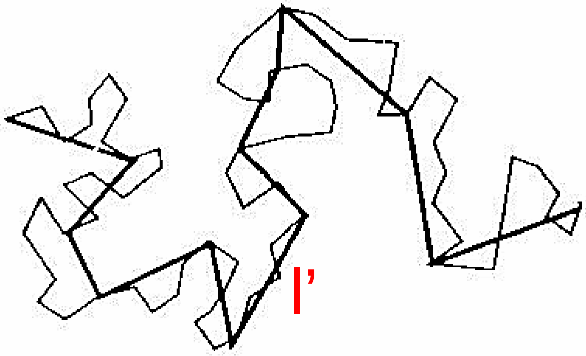
$$P(r)dr = P(x,y,z)dx\,dy\,dz\left(\frac{4\pi r^2\,dr}{dx\,dy\,dz}\right) = 4\pi r^2\left(\frac{3}{2\pi\langle r^2\rangle_0}\right)^{3/2}\exp(-3r^2/2\langle r^2\rangle_0)dr$$

  - » P_{max} not at the origin
  - » P_{max} at $r = (2/3)^{½} n\,l^2 = .82\langle r^2\rangle^{½}$ (of FJC or Kuhn chain)

- $\langle r^2\rangle = \int r^2 P(r)dr \,/\, \int P(r)dr = n\,l^2$

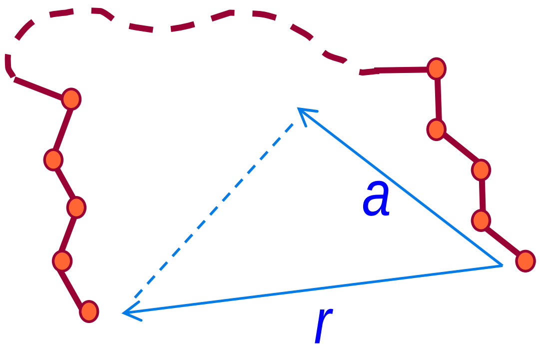
Kuhn chain

- Kuhn chain = statistical segment
  = (statistically) equivalent (freely jointed) chain
- Kuhn (chain) length, l'
  - $n' l'^2 = \langle r^2 \rangle_0 = r_\theta^2 = C_\infty n l^2$
  - $n' l' = r_{max}$ (max or contour length) $= f nl$
  - $l' = r_\theta^2 / r_{max} = (C_\infty/f) l$
  - a measure of axial correlation length
  - for PE
    - » $C_\infty = 6.7$, $r_{max} = (\cos 35)\, n\, l = .83\, n\, l$
    - » $l' = 8.2\, l$, $n' = 0.1\, n$



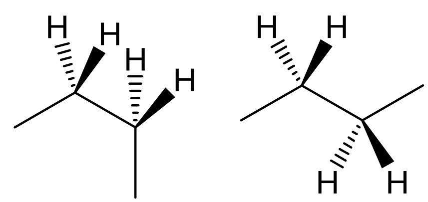
Persistence length

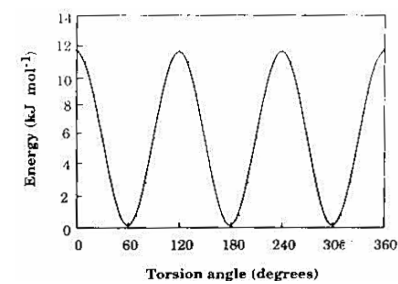
- Persistence length, a
  - average projection of r to a bond
  - length over the chain persists in one direction
    - » $a = <(\mathbf{r}_i/l) \Sigma \mathbf{r}_j>$
    - » $<r^2>_0 = n l^2 + 2 < \Sigma \Sigma \mathbf{r}_i \mathbf{r}_j > = C_\infty n l^2$
    - » $a = (C_\infty + 1) l / 2$
  - a measure of axial correlation length also
  - for PE, a ~ 4 l



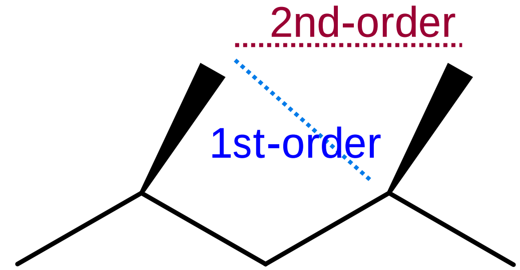
RIS Application to polymers

- interactions
  - conformation-dependent interactions
    → potential (conformational) energies → structure, size
  - inherent torsional potential
    - » ecliped – staggered
    - » $E_{tor} = (E^0/2)\,(1 - \cos 3\phi)$
      - ◆ E^0 for eclipsed





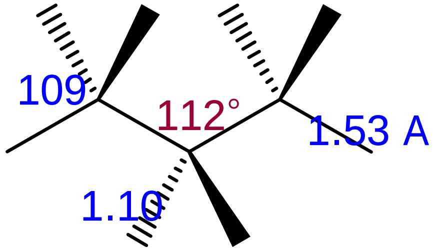
  - nonbonded interaction
    - » London dispersion force
    - » Lennard-Jones potential
      - ◆ $E_{kl} = a_{kl} \exp[-b\ r_{kl}] - c_{kl}/r_{k}^{l6}$



  - dipole interaction
    - » $E_d = e^{-1}[\Sigma q_i q_j / r_{ij}]$
  - $E_{\{\phi\}} = \Sigma\, E_{tor} + \Sigma\, E_{kl} + \Sigma\, E_d$

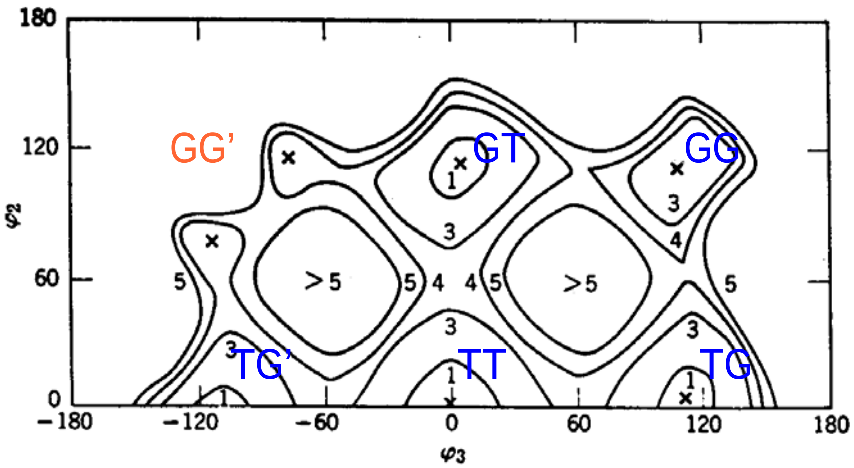
Polyethylene

1. geometric parameters
   - from exp't with model comp'd (*n*-alkane)
   - WAXS, ED, etc
2. choose interaction parameters
   - r(HH), r(CH), r(CC)
   - a(HH), a(CH), a(CC)
   - E^0
   - to give best fit to exp't results of model comp'd

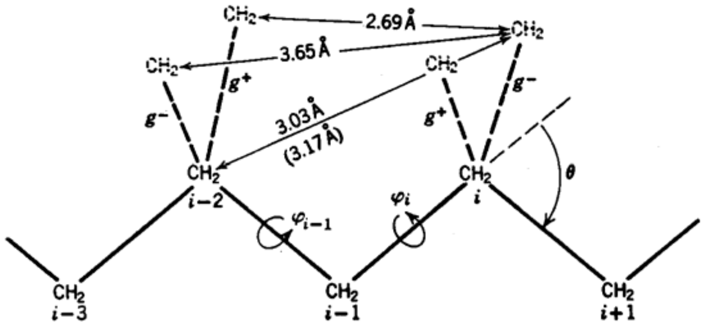


PE (2)

3. draw conformational energy map
   - for n-butane ~ 1st-order interaction
   - for n-pentane ~ 2nd-order interaction



4. establish chain molecule
   - ϕ(T) ~ 0°, ϕ(TG) ~ 4°
   - ϕ(G) ~ 112°, ϕ(GG) ~ 110°



PE (3)

5. determine statistical weights
   - 1st-order interaction, **D**
   - 2nd-order interaction, **V**
   - **U** = **V D**

$$\mathbf{D} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{bmatrix} \qquad \mathbf{V} = \begin{bmatrix} 1 & 1 & 1 \\ 0 & \psi & \omega \\ 0 & \omega & \psi \end{bmatrix}$$

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 0 & \sigma\psi & \sigma\omega \\ 0 & \sigma\omega & \sigma\psi \end{bmatrix} = \begin{bmatrix} 1 & \sigma & \sigma \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{bmatrix} \quad (\psi \sim 1,\ \omega \sim 0)$$

6. do RIS calculation
   - $\langle r^2 \rangle_0 = 2\, \mathbf{Z}^{-1}\, \mathcal{J}^{*}\, \mathbf{G}^n\, \mathcal{J}$
   - with **U**, l, θ, ϕ

7. adjust **U** to fit exp'tal values of $\langle r^2 \rangle_0$ and $d[\ln \langle r^2 \rangle_0]/dT$
   - with E^0, a, c, ϕ

PE (4)

- results
  - $\langle r^2 \rangle_0 = 6.7\, n\, l^2$ at 400 K

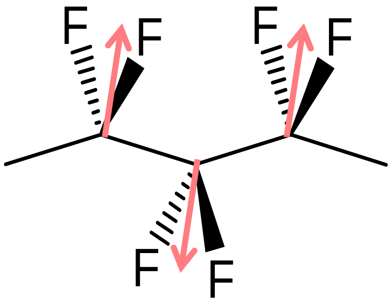
    $\sigma = u(G)/u(T) = 0.5$, $\omega = u(GG')/u(TT) = 0.01$

    $P(T) = 0.62$, $P(G) = P(G') = 0.19$
  - temperature coefficient

    $d[\ln \langle r^2 \rangle_o] / dT < 0$

- preferred conformation
  - all-trans ~ TTTTTTTT---
  - of the lowest energy
  - planar zigzag in crystal

PTFE



- geometry and interaction
  - R(F) > R(H) → a(FF) > a(HH)
  - do have dipole ~ $E_d > 0$
- conf map and stat wt
  - ϕ(T) ~ +17° and -17° with very shallow barrier
  - ϕ(G) = ϕ(G') ~ 120° with high E(G) → low σ ~ .2
- RIS
  - 4 RIS with T, T', G, G' → C_∞ ~ 30
    - » closer to exp't and explain helix inversion
  - 3 RIS with T, G, G' → C_∞ ~ 11
  - much stiffer than PE ~ high melting, high viscosity