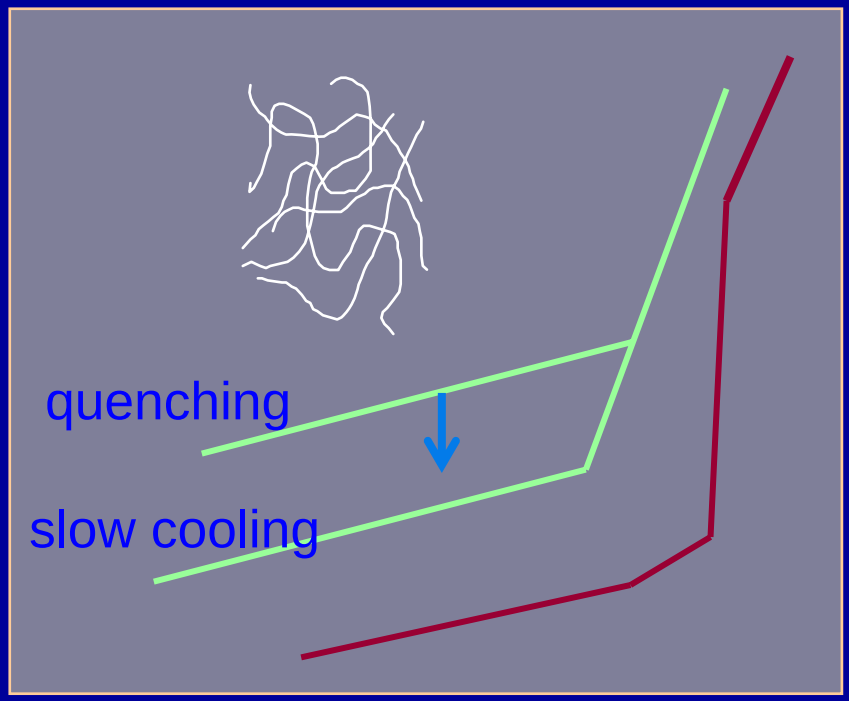
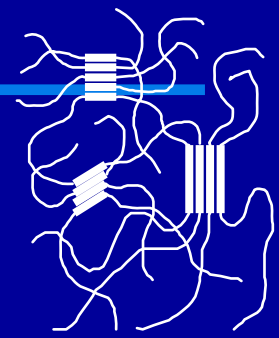
Chapter 5
Amorphous State

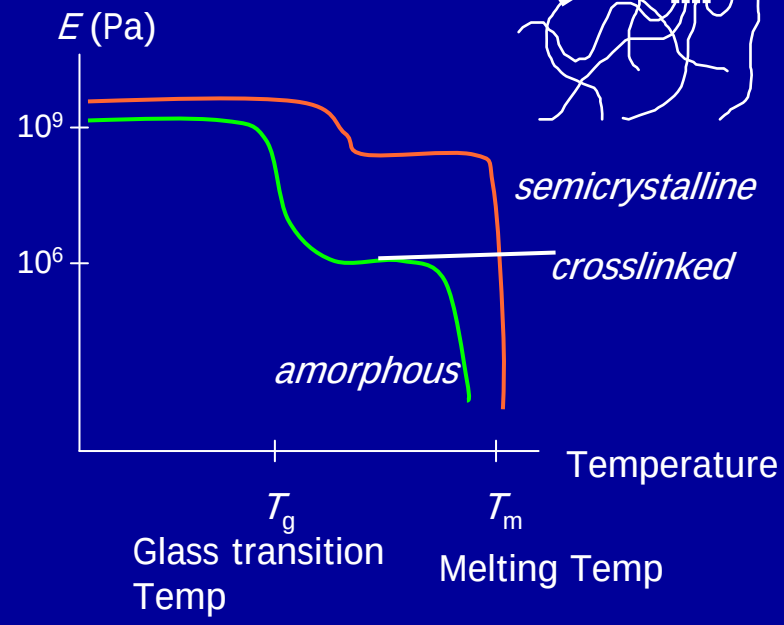
Structure of polymers

- 화학적 구조
  - 반복단위 구조 atomic structure
  - 이성질체 isomers
  - 연결 구조 sequence structure
- 물리적 구조
  - 한 사슬의 구조 single chain structure
  - 사슬 모임의 구조 aggregation structure
    - » 무정형 구조 amorphous state
    - » 반결정성 구조 semicrystalline state

Polymers upon cooling







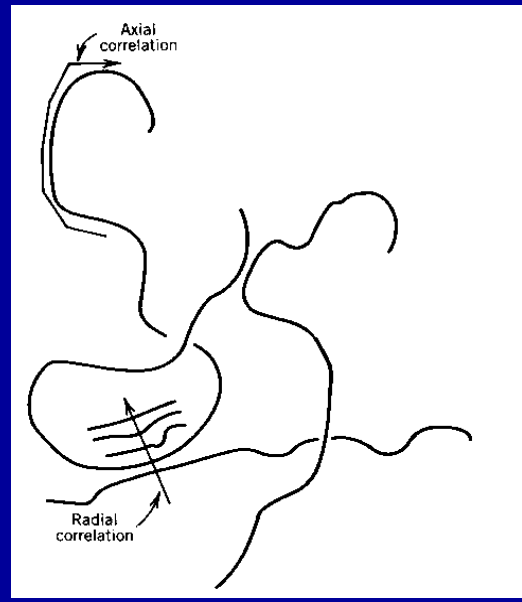
- amorphous vs. semicrystalline
- glass transition, aging, melting, crystallization

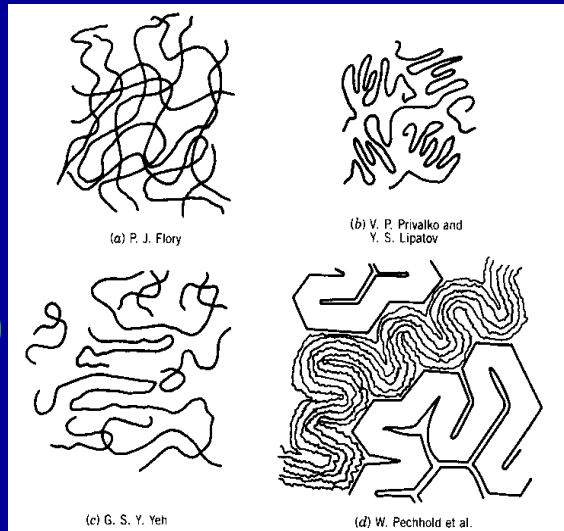
Amorphous vs Semicrystalline state

- governing factors
  - chain regularity → crystallizability
  - cooling rate → time for crystallization
- regular chain structure
  - » main-chain polymer (PE, nylon, PEster etc)
    isotactic or syndiotactic vinyl polymers
  - » semicrystalline when slow-cooled; amorphous upon quenching
- irregular chain structure
  - » atactic vinyl polymers
    branched polymers
  - » amorphous upon quenching; aged amorphous upon slow-cooling
    - crystallizable when side group is small or crystallizable itself

1&2. Is amorphous completely disordered?

- Arguing partial order ~ parallelization
  - intuition ~ spaghetti ~ space-filing
  - high density (90% of crystal)
  - nodules in electron microscopy
  - lateral (radial) order in ED and WAXS
- Arguing complete disorder ~ random
  - unperturbed dimension by SANS – random coil
  - vanishing radial correlation in WAXS
  - little change in birefringence
  - rubber elasticity works
- Order should be local, if any.
- Short-range order only: No long-range order
- See discussions 📖p198-210 (only the results) 📖Table 5.6, 📖p214-216, and 📖Fig 5.5





3. Single chain structure ~ Conformation

- configuration - breaking single bond
  - isomers, copolymers, sequences

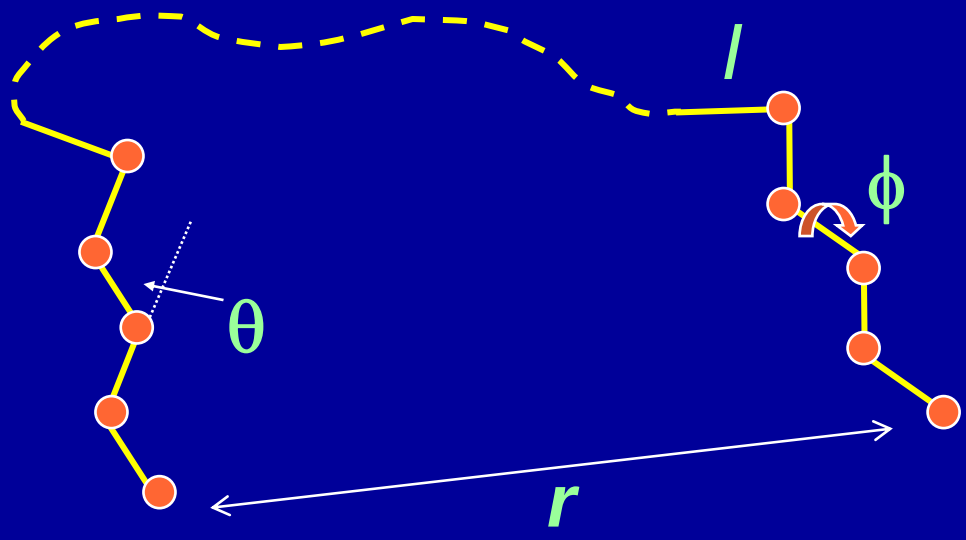
  conformation - rotation about single bond
  - rotational isomers (conformer, actually)

- Modeling of single chain

  - from *artificial* to *real* chain
  - freely jointed
  - freely rotating
  - restricted rotation
  - excluded volume effect
  - ‘Random Coil’

A Polymer Chain

- *n* + *1* atoms
- *n* bonds (length *l*)
- *n* - *1* bond angles (angle 180 - θ)
- *n* - *2* rotational angles (angle ϕ)



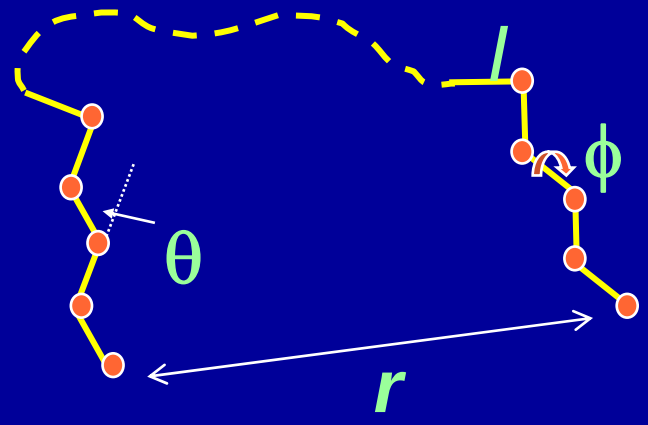
📖Fig 5.4 p211

- end-to-end distance, *r*

Freely Jointed Chain

- Bond length only fixed
- Gaussian coil, 'ideal chain'
- mean square end-to-end distance
  - a measure of chain dimension

    $\langle r^2 \rangle = n l^2$ for FJC



- characteristic ratio
  - a measure of chain stiffness

    $C_\infty = \langle r^2 \rangle / n l^2$ ~ definition 📖 Eqn (5.14) p212

    $C_\infty = 1$ for FJC

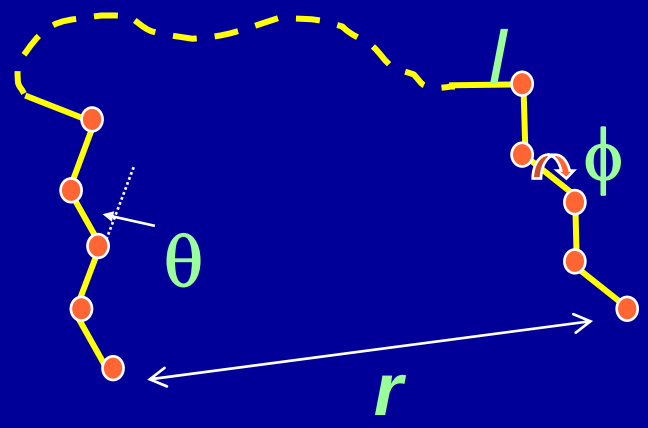
    $C_\infty > 1$ for *real* chains

Freely Rotating Chain

- Bond length and bond angle fixed
  - reduced artificiality
- $\langle r^2 \rangle = n l^2 [(1 + \cos\theta) / (1 - \cos\theta)]$
- For FRC with sp^3 atoms ($\theta = 70^o$)

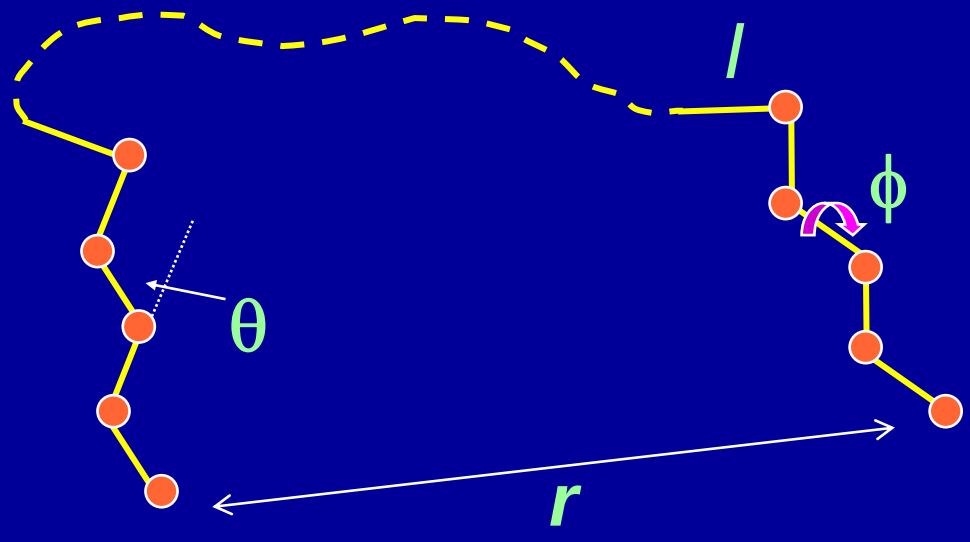
  $\langle r^2 \rangle = 2 n l^2$

  $C_\infty = \langle r^2 \rangle / n l^2 = 2$
- FRC is stiffer than FJC, if $\theta < 90^o$.



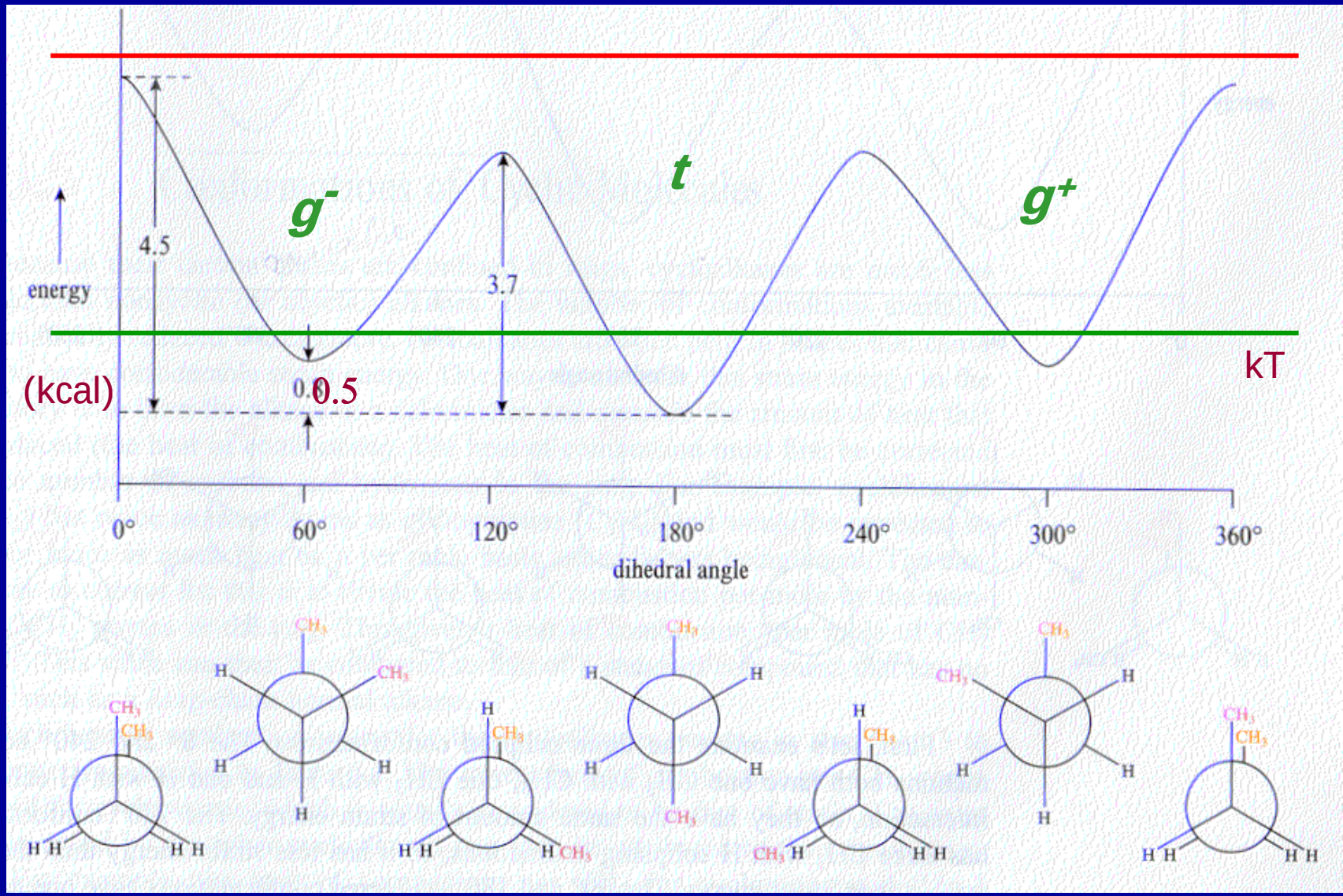
Chain with Restricted Rotations

- Bond length and bond angle fixed
- Not all rotational angles between $0^o < \phi < 360^o$ allowed.
- Only some discrete states allowed
  $\rightarrow$ rotational isomeric states (RIS)



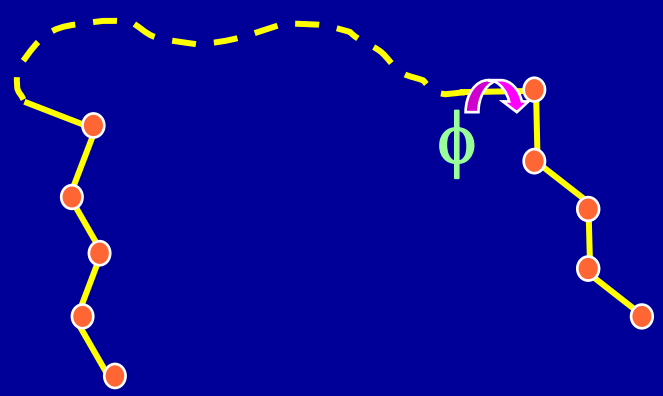
Energy map for *n*-butane

📖Fig 2.11 p49



RIS Calculation 1

- 3 RIS (t, g^+, g^-) for every bond (except for the first and the last) of the chain



- For a chain with n bonds, (n - 2) ϕ gives 3^{n-2} conformations.

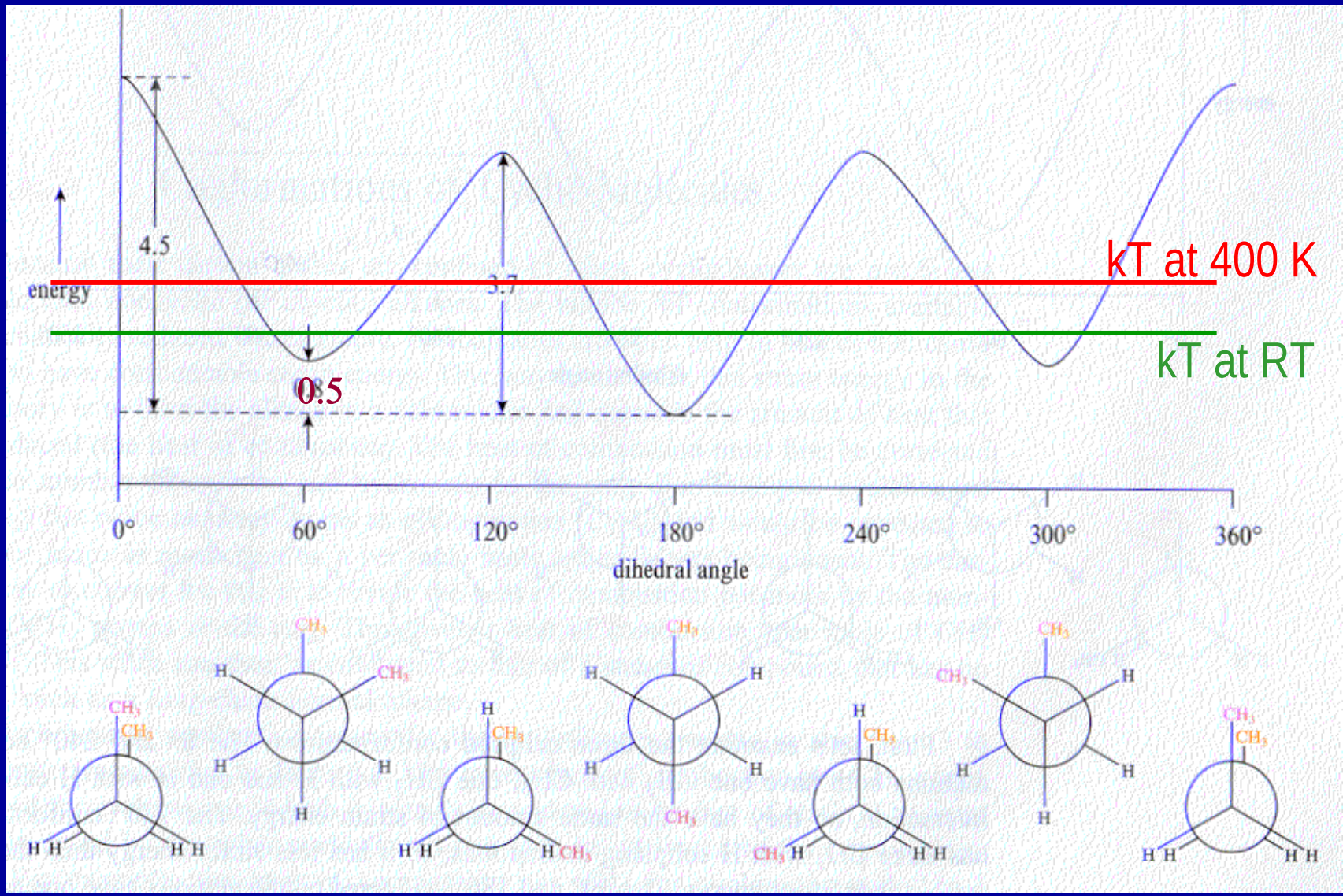
- Statistical weights for the bonds are determined by Boltzmann distribution (energy difference between t, g^+, and g^-; temperature).

$$u = exp\,[-E / kT]$$

$u(t)$, $u(g^+)$, $u(g^-)$

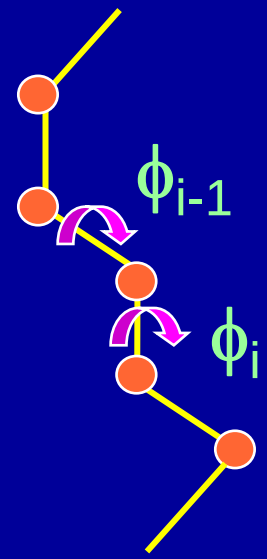
$u(g^+) = \exp [-E(g^+)/kT]$
$= \exp [-0.5/0.8] = .53$ at 400 K

Energy map for *n*-butane



RIS Calculation 2

- Interactions governing energy
  - non-bonded interaction (dispersion)
  - dipole interaction
  - intrinsic rotational potential
- Pairwise potential
  - 1st-order interaction
    - » 1-bond rotation ~ 3-bond interaction
    - » t, g^+, g^-
  - 2nd-order interaction
    - » 2-bond rotation ~ 4-bond interaction
    - » tt, tg^+, tg^-, g^+g^+, g^-g^-, g^+g^-
    - » pentane interaction, short-range interaction
    - » Bond rotations should be considered pairwise.



RIS Calculation 3

- By taking 2nd moment (average size) of all the conformations, the chain dimension is calculated.

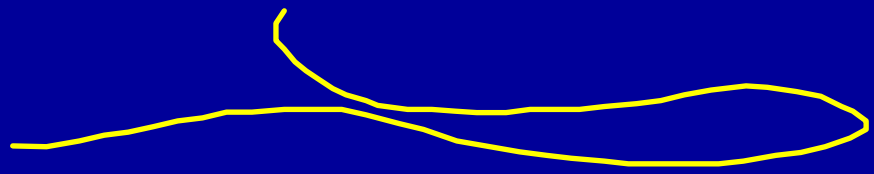
- $C_\infty = \langle r^2 \rangle / n l^2 = 5 - 10$ for chains with restricted rotation

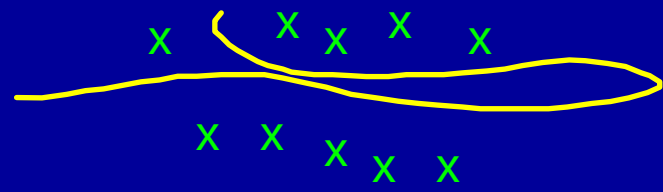
📖Table 5.7 p212

📖 Eqn (5.13) is totally wrong.
1. $\langle \cos \phi \rangle = \Sigma u \cos \phi / \Sigma u$
2. 2nd order interaction not considered

- Compare with the experimental results (viscosity, light scattering, SANS, etc.) and adjust parameters

Excluded Volume Effect





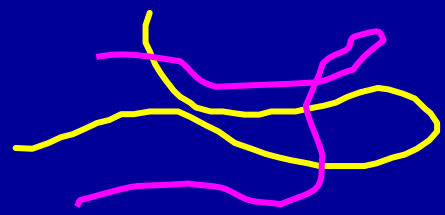
- Intrachain volume exclusion
  - long-range interaction
  - gives larger dimension
- $\langle r^2 \rangle_{EV} = \alpha \langle r^2 \rangle_0$
  - in good solvent, $\alpha > 1$
    - » Repulsion(p-p) > Repulsion(p-s)
  - in poor solvent, $\alpha < 1$
    - » Repulsion(p-p) < Repulsion(p-s)
  - in theta (Θ) condition, $\alpha = 1$ ~ unperturbed ($_0$)
    - » Repulsion(p-p) = Repulsion(p-s)

$\alpha^5 - \alpha^3 = C\, n^{1/2}\, \psi\, (1 - \theta/T)$

📖Eqn (3.29) p84

Real Chain in Bulk – 'random coil'

- In bulk amorphous state
  - Repulsion(p-p, intra) = Repulsion(p-p, inter)
  - unperturbed state ($\alpha = 1$)
  - 'phantom' or 'ghost' chain
  - $\langle r^2 \rangle = \langle r^2 \rangle_0 = r_\theta^2 = \langle r^2 \rangle_{RIS}$
  - proposed by Flory; proved by SANS expt
    - also in the melt state
    - *probably* also in the semicrystalline state

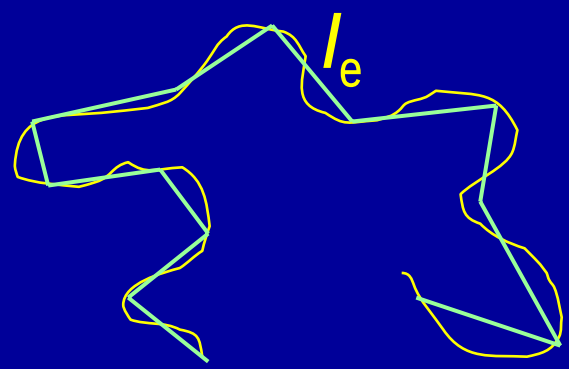


- RIS model describes the state of single chain in bulk (amorphous, semicrystalline)
  - crystal structure ~ conformation with the lowest energy

a = l (C + 1)/2 = le / 2 확인

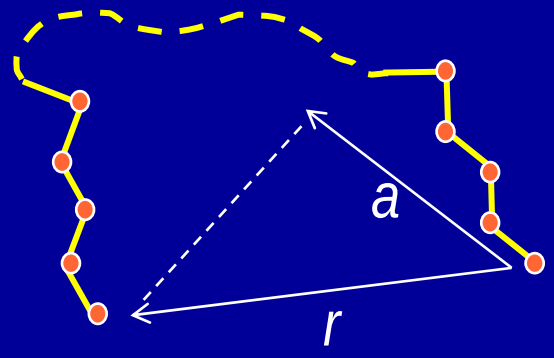
Kuhn chain and Persistence length

- Kuhn chain = (Statistically) equivalent (freely jointed) chain
- Kuhn (chain) length, l_e
  - $n_e l_e^2 = \langle r^2 \rangle_0 = r_\theta^2 = C_\infty n l^2$
  - $n_e l_e = L$ (contour length)
  - $l_e = r_\theta^2 / L$ 📖 Eqn (5.15) p213
  - A measure of axial correlation length
  - For PE, $l_e = 8\,l$, $n_e = 0.1\,n$



📖 Fig 5.1 p201

- Persistence length, a
  - Projection of r to a bond
  - A measure of axial correlation length also
  - For PE, $a \sim 4\,l$



Examples of RIS Application 1

- Polyethylene
  - $\langle r^2 \rangle_o = 6.8\, n\, l^2$ at 400 K

    $\sigma = u(g^+)/u(t) = 0.5$, $\omega = u(g^+g^-)/u(tt) = 0.05$

    $P(t) = 0.62$, $P(g^+) = P(g^-) = 0.19$
  - temperature coefficient

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

    all-*trans* (with the lowest energy)

    planar zigzag in crystal structure

Examples of RIS Application 2

- Polyoxymethylene
  - $\langle r^2 \rangle_o = 8\, n\, l^2$

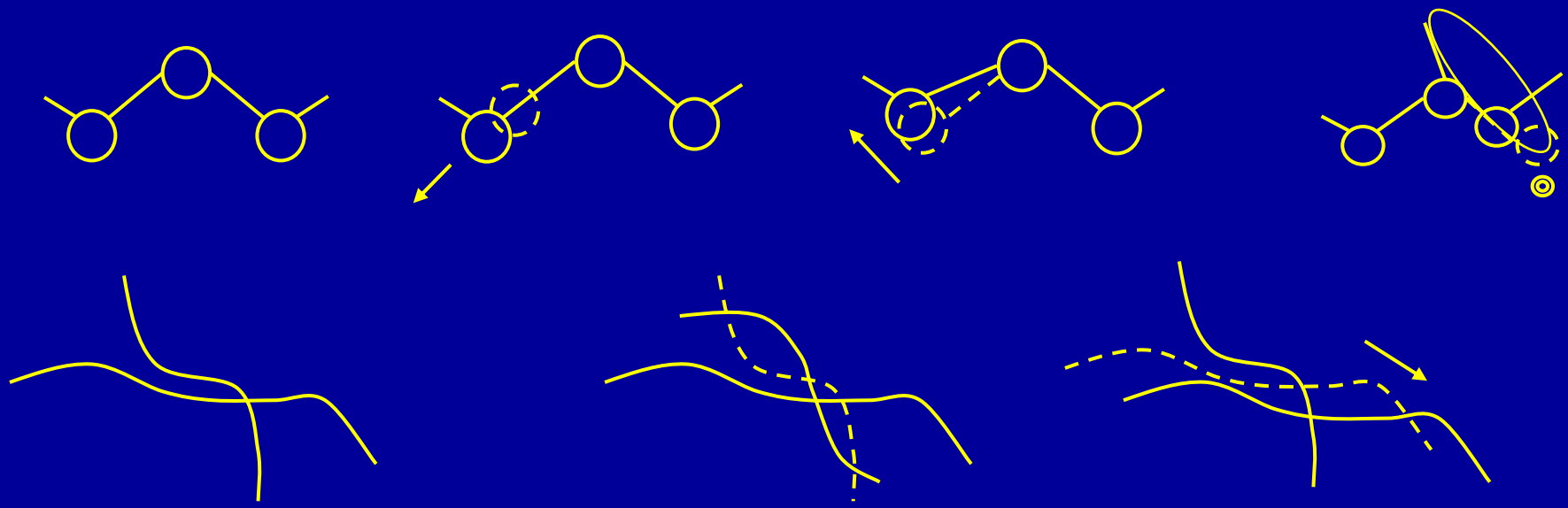
    $\sigma = 10$, $\omega = 0.05$
  - $d[\ln \langle r^2 \rangle_o] / dT > 0$
  - preferred conformation

    $g^+g^+g^+ \ldots$ or $g^-g^-g^- \ldots$

    2_1 helix in crystal structure

4. Macromolecular Dynamics

- Motions in polymers
  - Defomation in bond angle and length ~ elastic
  - Change in conformation ~ segmental motion ~ viscoelastic
  - Translational motion ~ viscous



Models for macromolecular dynamics

- Rouse (– Bueche – Zimm) model 🕮 Fig 5.6
  - Bead and spring
  - Single chain, dilute solution
- Reptation (de Gennes (– Doi – Edward)) model 🕮 Fig 5.7
  - Effect of entanglements
  - Chain in a tube 🕮 Fig 5.9
  - Conc. solution, bulk
  - $\eta = K M^3$
  - Effect of branch 🕮 Fig 5.10