Distribution of ϕ

- ❑ **Distribution (probability) of ϕ is determined by**
  - ■ Boltzmann distribution
  - ■ Frequency of occurrence depends on exp[-E/kT]

  - ■ $P(\phi)d\phi = U/Z = \exp[-E(\phi)/kT]d\phi \, / \int \exp[-E(\phi)/kT]d\phi$

    - » $U(\phi)$ ~ statistical weight ~ relative probability ~ = exp[-E(ϕ)/kT]
    - » Z ~ rotational partition function ~ Σ U(ϕ)
    - » for *n*-butane at 400 K
      - ◆ U(T) = 1 ← E(T) = 0
      - ◆ U(G) = U(G′) = exp[-E(G)/kT] = exp[-2.1/3.3] ~ .5
      - ◆ E(cis,eclipsed) >> kT → U ~ 0
      - ◆ Leaves 3 RIS of T, G, G′
      - ◆ Z = U(T) + U(G) + U(G′) = 1+.5+.5 = 2
      - ◆ P(G) = U(G)/Z = .5/1+.5+.5 = .25
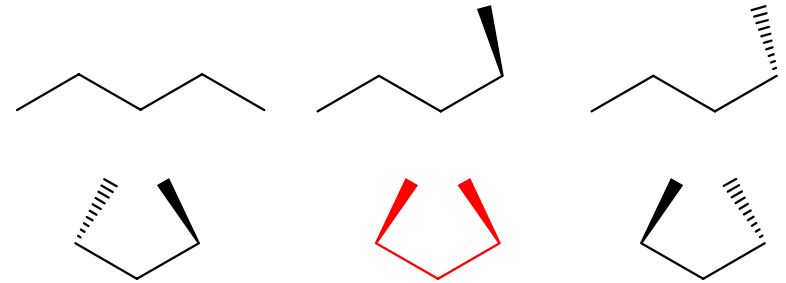
» for n-pentane at 400 K

- ◆ E(TT) = 0
- ◆ E(TG, GT, TG′, G′T) = 2.1
- ◆ E(GG, G′G′) = 4.2
- ◆ E(GG′,G′G) = 14.5
  - – U(GG′) = exp[-14.5/kT] = .01
  - – P(GG′) = .01/Z ~ 0 ~ prohibited

❑ short-range interaction (2nd-order interaction)

- ▪ common in chain molecules (not only in alkanes or PE)
- ▪ ϕ_i depends on ϕ_{i+1} ~ interdependent ϕ
- ▪ Bond rotation must be considered pairwise.
- ▪ higher-order interactions?
  - » Higher energy conformations like GGG′G must have at least one GG′ or G′G.
  - » pairwise potential is enough

Conformational energy

❑ **conformational energy of a chain**

$$E\{\phi\} = \sum_{i=2}^{n-1} E_i(\phi_{i-1}, \phi_i) = \sum_{i=2}^{n-1} E_{\zeta\eta;i} \quad (2.35)$$

$\zeta \sim$ state of a bond i-1
$\eta \sim$ state of a bond i

$$E_{\zeta T} = 0 \text{ for } \zeta = T, G, G'$$

$$E_{TG} = E_{TG'} = E_{GG} = E_{G'G'} = 2.1 \text{ kJ mol}^{-1}$$

$$E_{GG'} = E_{G'G} = 12.4 \text{ kJ mol}^{-1}$$

tentatively putting bond i+1 trans
(considered at the next term)

■ **for n-pentane (for bond 2 and 3), E{ϕ}**

$$E = \sum_{i=2}^{3} E_{\zeta\eta;i} = E_{\eta,2} + E_{\zeta\eta,3}$$

TT: $E = E_{T,2} + E_{T,3} = 0 + 0 = 0$

TG: $E = E_{T,2} + E_{TG,3} = 0 + 2.1 = 2.1$

TG': $E = E_{T,2} + E_{TG',3} = 0 + 2.1 = 2.1$

GG: $E = E_{G,2} + E_{GG,3} = 2.1 + 2.1 = 4.2$

G'G': $E = E_{G',2} + E_{G'G',3} = 2.1 + 2.1 = 4.2$

GG': $E = E_{G,2} + E_{GG',3} = 2.1 + 12.4 = 14.5$

Statistical weight

$$u_{\zeta\eta,i} = \exp(-E_{\zeta\eta,i}/RT) \qquad (2.36)$$

$E_{\zeta\eta}$ not E{ϕ}

- ❑ statistical weight matrix, **U**

$$\mathbf{U}_i = [u_{\zeta\eta}]_i \qquad (2.37)$$

$E_{\zeta T} = 0$ for $\zeta = T, G, G'$

$E_{TG} = E_{TG'} = E_{GG} = E_{G'G'} = 2.1$ kJ mol^{-1}

$E_{GG'} = E_{G'G} = 12.4$ kJ mol^{-1}

  - ▪ for *n*-alkane

η (bond i-1)

$$U = \begin{array}{c} \\ T \\ G \\ G' \end{array} \begin{array}{ccc} T & G & G' \\ \left[\begin{array}{ccc} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{array}\right] \end{array}$$

← η (bond i)

$\sigma = \exp[-E_{TG,TG', GG, G'G'}/kT] = .5$

$\exp[-E_{GG', G'G}/kT] \sim 0$

$\exp[-E_{\zeta T}/kT] = 1$

- **U** generalized for 3-fold, symmetric chain
  - » 3-fold ~ T, G, G′ → 3x3 matrix
  - » symmetric ~ no asymmetric carbon ~ $U_G = U_{G'}$
    - ◆ PE, POM are symmetric
    - ◆ vinyl polymers are asymmetric

$$U = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix}$$

where $\sigma\psi$ describes the GG (or G′G′) interaction and $\sigma\omega$ describes the GG′ (or G′G) interaction. The symmetry of the chain requires that:

$$u_{12} = u_{13}; \; u_{21} = u_{31}; \; u_{22} = u_{33}; \; u_{23} = u_{32}$$

- Stat wt for a certain conformation (combination of ϕ's)

$$\Omega_{\{\phi\}} = \prod_{i=2}^{n-1} u_{\zeta\eta;i} \qquad (2.40)$$

- partition function for a chain (all possible conformations)

$$Z = \sum_{\{\phi\}} \Omega_{\{\phi\}} = \sum_{\{\phi\}} \prod_{i=2}^{n-1} u_{\zeta\eta;i} \qquad (2.41)$$

Homework #1 (Due on 25 Sept 06)

Q1. For TGTG′G′TG′TTG conformation of n-$C_{13}H_{28}$ with bond angle of 120° and bond length of 1 cm,

(1) Find the end-to-end distance.

(2) C?

Q2. Using the energy values given so far, estimate the probability of GG′ conformations in n-pentane at 350 K

(1) for independent ϕ's

(2) for interdependent ϕ's

Q3. For n-octane,

(1) how many conformations?

(2) Express the probability of TTTTT.

(3) Express the probability of TGG′TG.

Calculation of Z

❑ **matrix expression**

- chain with 2-fold RIS, α and β
- U for 2nd bond ~ $U(\alpha)$, $U(\beta)$
- U for 3rd, --- ~ $U(\alpha\alpha)$, $U(\alpha\beta)$, $U(\beta\alpha)$, $U(\beta\beta)$
- for n=4
  - » $Z = U(\alpha)U(\alpha\alpha) + U(\alpha)U(\alpha\beta) + U(\beta)U(\beta\alpha) + U(\beta)\,U(\beta\beta)$
  - » $\quad$ = sum of the elements of $\mathbf{U_2U}$
- for n=5, Z = sum of the elements of $\mathbf{U_2UU}$
- for n=n,

$$Z = [1,\ 1]U_2 U^{n-3}\begin{bmatrix} I \\ I \end{bmatrix} \qquad (2.44)$$

$$U_2 = \begin{bmatrix} u_\alpha & 0 \\ 0 & u_\beta \end{bmatrix}$$

$$U = \begin{bmatrix} u_{\alpha\alpha} & u_{\alpha\beta} \\ u_{\beta\alpha} & u_{\beta\beta} \end{bmatrix}$$

The same result is obtained if **U** is rewritten as

$$U_2 = \begin{bmatrix} u_\alpha & u_\beta \\ 0 & 0 \end{bmatrix} \qquad (2.45)$$

and

$$Z = [1,\ 0]U_2 U^{n-3}\begin{bmatrix} I \\ I \end{bmatrix} \qquad (2.46)$$

- Simplifying by $\mathbf{U}_2 = \mathbf{U}$

$$Z = [1,\ 0]\mathbf{U}^{n-2}\begin{bmatrix} 1 \\ \mathbf{I} \end{bmatrix}$$

- general form

$$Z = \mathbf{J}^{*}\left[\prod_{i=2}^{n-1} \mathbf{U}_i\right]\mathbf{J} \qquad (2.48)$$

$$\mathbf{J}^{*} = [\mathbf{I} \quad 0 \quad \ldots \quad 0] \text{ and } \mathbf{J} = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ \mathbf{I} \end{bmatrix} \qquad (2.49)$$

- for simple chain (symmetric and with one type of bond like PE)

$$Z = \mathbf{J}^{*}\mathbf{U}^{n-2}\mathbf{J} \qquad (2.50)$$

- for PE

  » $Z = [1\ 0\ 0]\begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix}^{n-2}\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$

❑ algebraic expression

- simplify by transforming **U** to a diagonal tensor with eigenvalues λ_η of **U** as elements

$$\mathbf{A}^{-1}\mathbf{U}\mathbf{A} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix} \equiv \Lambda = \mathbf{BUA} \qquad \mathbf{B}=\mathbf{A}^{-1} \qquad \mathbf{AB} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \equiv \mathbf{E}$$

If eq. (2.52) is premultiplied by **A**:

$$\mathbf{ABUA} = \mathbf{AA}$$
$$\mathbf{EUA} = \mathbf{AA} \qquad (2.54)$$
$$\mathbf{UA} = \mathbf{AA}$$

The latter can be separated into three vector equations:

$$\mathbf{UA}_k = \mathbf{A}_k \lambda_k \qquad k = 1, 2, 3 \qquad (2.55)$$

where $\mathbf{A}_k$ are the column eigenvectors of **U**:

$$\mathbf{A}_k = \begin{bmatrix} A_{1k} \\ A_{2k} \\ A_{3k} \end{bmatrix} \qquad k = 1, 2, 3 \qquad (2.56)$$

If eq. (2.52) is postmultiplied by $\mathbf{B}$:

$$\mathbf{BUAB} = \mathbf{\Lambda B}$$

$$\mathbf{BUE} = \mathbf{\Lambda B} \qquad (2.57)$$

$$\mathbf{BU} = \mathbf{\Lambda B}$$

which can be written in the form

$$\mathbf{B}_k^* \mathbf{U} = \lambda_k \mathbf{B}_k^* \qquad (2.58)$$

where $\mathbf{B}_k^* = [B_{k1}, B_{k2}, B_{k3}]$ are the eigenrows of $\mathbf{U}$.

Since $\mathbf{AB} = \mathbf{E}$, we can write:

$$\mathbf{B}_j^* \mathbf{A}_k = \delta_{jk} \qquad (2.59)$$

where δ_{jk} is the Kronecker delta (equal to 1 for $j = k$ and equal to 0 for $j \neq k$). Equation (2.55) can be rewritten as:

$$(\mathbf{U} - \lambda_k \mathbf{E})\mathbf{A}_k = 0 \qquad (2.60)$$

which has solution

$$|\mathbf{U} - \lambda_k \mathbf{E}| = 0 \qquad (2.61)$$

- using $\mathbf{U} = \mathbf{A}\Lambda\mathbf{B}$

$$Z = \Gamma\Lambda\Lambda^{n} {}^{2}\mathbf{B}J$$

or

$$Z = [A_{11}\lambda_1^{n-2} \quad A_{12}\lambda_2^{n-2} \quad \cdots \quad A_{1v}\lambda_v^{n-2}] \begin{bmatrix} \sum_{\eta=1}^{v} B_{1\eta} \\ \vdots \\ \sum_{\eta=1}^{v} B_{v\eta} \end{bmatrix} \quad (2.62)$$

$$\mathbf{BUA} = \Lambda$$
$$\mathbf{ABUABU} = \mathbf{A}\Lambda\mathbf{B}$$
$$\mathbf{EUE} = \mathbf{A}\Lambda\mathbf{B}$$
$$\mathbf{U} = \mathbf{A}\Lambda\mathbf{B}$$

← for v-fold RIS
for 3-fold, to $A_{13}\lambda_3^{n-2}$ and B_{33}

The partition function can be written:

$$Z = \sum_{\zeta=1}^{v} \Gamma_\zeta \lambda_\zeta^{n-2}$$

where   (2.63)

$$\Gamma_\zeta = A_{1\zeta} \sum_{\zeta=1}^{v} B_{\zeta\eta}$$

which for large values of n can be approximated by

$$Z \cong \Gamma_1 \lambda_1^{n-2} \quad (2.64)$$

where λ_1 is the largest eigenvalue.
At even larger n values, eq. (2.64) simplifies to:

$$Z \cong \lambda_1^{n-2} \quad (2.65)$$

- **for simple, 3-fold, symmetric chain like PE**

$$|\mathbf{U} - \lambda_k \mathbf{E}| = 0 \quad \text{with} \quad \mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \quad \text{gives}$$

$$\lambda_{1,2} = \tfrac{1}{2}\big[1 + \sigma(\psi + \omega) \pm \sqrt{[1 - \sigma(\psi + \omega)]^2 + 8\sigma}\big]$$
$$\lambda_3 = \sigma(\psi - \omega)$$

$\approx \sigma=.5,\ \psi=1,\ \omega=.01$ at 400 K $\rightarrow \lambda_1, \lambda_2, \lambda_3$

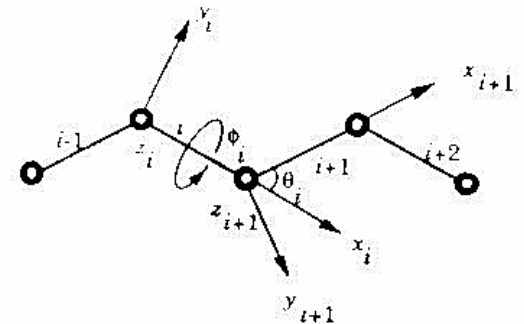» P(G) = U(G)/Z = .18 at 400 K ~ with interdependent ϕ

» compared with P(G) with independent ϕ of .25

Size of RIS chain

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

- $\mathbf{r}_i = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ in coordinate i, $\mathbf{r}_j = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ in coordinate j

- $\mathbf{r}_i \mathbf{r}_i = (1, 0, 0) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \mathbf{r}_i^{\mathsf{T}} \mathbf{r}_i$ if in the same coordinate

- if NOT, $\mathbf{r}_i \mathbf{r}_i = \mathbf{r}_i^{\mathsf{T}} \mathbf{T} \mathbf{r}_i$ ~ needs coordinate transformation
- transformation matrix, T_i (i+1 → i)

$$T_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi_i & -\cos\theta_i \cos\phi_i & \sin\phi_i \\ \sin\theta_i \sin\phi_i & -\cos\theta_i \sin\phi_i & -\cos\phi_i \end{bmatrix} \quad (2.21)$$

$$\bar{\mathbf{r}}_i \bar{\mathbf{r}}_j = \bar{\mathbf{r}}_i^T (\mathbf{T}_i \dots \mathbf{T}_{j-1}) \bar{\mathbf{r}}_j \qquad \bar{\mathbf{r}}_i^T = (1, 0, 0) \qquad \bar{\mathbf{r}}_j = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\bar{\mathbf{r}}_i \bar{\mathbf{r}}_j = l^2 (\mathbf{T}_i \dots \mathbf{T}_{j-1})_{11}$$

$$\langle \bar{\mathbf{r}}_i \bar{\mathbf{r}}_j \rangle = l^2 \langle (\mathbf{T}_i \dots \mathbf{T}_{j-1})_{11} \rangle$$

- for simple chain with independent ϕ, $<\mathbf{T}_i \text{----} \mathbf{T}_{j-1}> = <\mathbf{T}>^{j-i}$

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

$$= nl^2 + 2l^2 (1, 0, 0) \left[\sum_{k=1}^{n-1} (n-k) T_i^k \right] \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

(2.26)

$$= nl^2 \left[\frac{\mathbf{E} + \langle \mathbf{T} \rangle}{\mathbf{E} - \langle \mathbf{T} \rangle} \right]_{11} \qquad \mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- for FRC, $\langle\cos\phi_i\rangle = \langle\sin\phi_i\rangle = 0$

$$T_i^* = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\bar{r}_i\bar{r}_j = l^2(T_i^* \ldots T_{j-1}^*)_{11} = l^2(\cos\theta)^{j-i}$$

- for FJC, $\langle\cos\phi_i\rangle = \langle\sin\phi_i\rangle = \langle\cos\theta_i\rangle = \langle\sin\theta_i\rangle = 0$

  $\mathbf{T} = \mathbf{O}$

$$\langle r^2 \rangle = nl^2$$

- for simple symmetric chain with hindered rotation

$\langle \sin\phi_i \rangle = 0$ ← G and G′ are of the same population.

$$T_i =$$

$$\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\langle\cos\phi\rangle & -\cos\theta\langle\cos\phi\rangle & 0 \\ 0 & 0 & -\langle\cos\phi\rangle \end{bmatrix}$$

$$(2.25)$$

$$\langle r^2 \rangle = nl^2 \left[\frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right] \left[\frac{1 + \langle\cos\phi\rangle}{1 - \langle\cos\phi\rangle} \right]$$

$$(2.29)$$

- for, *n*-alkane (PE)

$$\langle \cos \phi \rangle = \frac{\sum_{\eta} u_{\eta} \cos \phi_{\eta}}{z} = \frac{1 + \sigma \cos(120°) + \sigma \cos(-120°)}{1 + \sigma + \sigma} = \frac{1 - \sigma}{1 + 2\sigma}$$

$$\langle r^2 \rangle = nl^2 \left[\frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right] \left[\frac{2 + \sigma}{3\sigma} \right] \quad (2.34)$$

$\sigma = U(G) = \exp[-2.1/3.3] \sim .5$ at 400 K

$$\langle r^2 \rangle = nl^2 \times 2 \times \frac{2 + 0.54}{3 \times 0.54} = 3.4nl^2$$

» exp'tal C = 6.7; difference due to
  - wrong E(G)?
    – For C=3.4, E(G) be 4.5 kJ/mol (too high)
  - wrong ϕ(G)?
    – Actual ϕ(G)~110 → not that much different
  - interdependent ϕ ~ major contributor

Size of RIS chain with interdependent φ

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

$$\langle \vec{r}_i \vec{r}_j \rangle = l^2 \langle (T_i \ldots T_{j-1})_{11} \rangle$$

- with independent φ, $\langle T_i \text{----} T_{j-1} \rangle = \langle T \rangle^{j-i}$
- with interdependent φ, $\langle T_i \text{----} T_{j-1} \rangle = \langle T^{j-i} \rangle$ Flory Chpater 4

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

$$= 2 \, Z^{-1} \, J^* \, G^n \, J$$

Size of chain

❑ $<r^2> = C(\mathbf{U})\, nl^2$

- $C(U) \rightarrow C_\infty$ as $n \rightarrow \infty$

- $C_\infty = 1$ for FJC

- $C_\infty = 2\text{-}3$ for FRC due to q

- $C_\infty = 4\text{-}10$ for RIS chain due to short range interaction

- C_∞ for different polymers?
  - » measure of chain stiffness
  - » in unperturbed state (Θ condition), melt, bulk