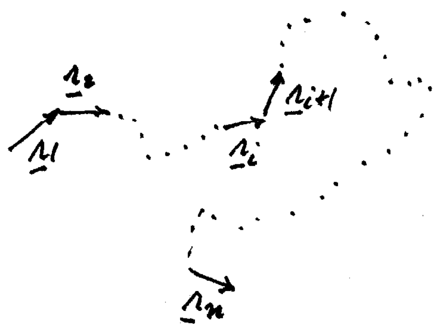
Linear Dimensions of Ideal Model Chains

A. Freely-jointed Chain:



$$\underline{R}_n = \sum_{i=1}^{n} \underline{\ell}_i \quad , \quad |\underline{\ell}_i| = \ell \quad i=1,\cdots,n$$

$$\langle R^2 \rangle = \langle (\sum_i \underline{\ell}_i)\cdot(\sum_j \underline{\ell}_j) \rangle$$

MS ETE distance

$$= \sum_i \ell_i^2 + 2 \sum\sum_{i<j} \langle \underline{\ell}_i \cdot \underline{\ell}_j \rangle$$

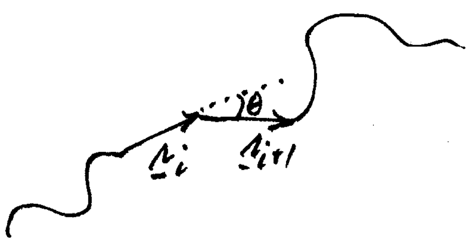
$$= n\ell^2 + 2 \sum\sum_{i<j} \ell^2 \langle \cos\theta_{ij} \rangle$$

$$= n\ell^2$$

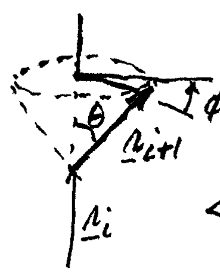
for $\langle \cos\theta_{ij} \rangle = 0$

$$\int_0^{2\pi} \cos\theta_{ij} \sin\theta_{ij} \, d\theta_{ij} = 0$$

B. Freely-rotating Chain:



θ is the supplement of bond angle



$\angle\theta$ is fixed

$0 \le \phi \le 2\pi$ freely rotating

$$\langle \underline{\ell}_i \cdot \underline{\ell}_{i+1} \rangle = \ell^2 \cos\theta$$

$$\langle \underline{\ell}_i \cdot \underline{\ell}_{i+2} \rangle = \ell^2 \cos^2\theta$$

$$\vdots$$

$$\langle \underline{\ell}_1 \cdot \underline{\ell}_n \rangle = \ell^2 \cos^{n-1}\theta$$

$$\langle R^2 \rangle = \sum \ell_i^2 + 2 \sum\sum_{i<j} \langle \underline{\ell}_i \cdot \underline{\ell}_j \rangle$$

$$= n\ell^2 + 2\ell^2 \left[\sum_{k=1}^{n-1} (n-k)\cos^k\theta \right]$$

$$\left.\begin{array}{l} \begin{pmatrix} 11 & 12 & 13 & \cdots & 1n \\ 21 & 22 & 23 & \cdots & 2n \\ \vdots & & & & \\ n1 & n2 & n3 & \cdots & nn \end{pmatrix} \end{array} \begin{array}{l} \cos^{n-1}\theta \\ \vdots \\ (n-2)\cos^2\theta \\ (n-1)\cos\theta \\ n(\cos\theta)^0 \end{array} \right\} \quad n\ell^2 + 2\ell^2 \left[(n-1)\cos\theta + (n-2)\cos^2\theta + (n-3)\cos^3\theta + \cdots + \cos^{n-1}\theta \right]$$

Let $\cos\theta \equiv \alpha$, then

$$\langle R^2\rangle = nl^2 + 2l^2\left[\sum_{k=1}^{n-1} n\alpha^k - \sum_{k=1}^{n-1} k\alpha^k\right]$$

$$\sum_k \alpha^k \equiv S, \qquad \frac{1}{1-\alpha} = 1 + \underbrace{\alpha + \alpha^2 + \cdots + \alpha^{n-1}} + \alpha^n(1+\alpha+\alpha^2+\cdots)$$

$$= 1 + S + \alpha^n \frac{1}{(1-\alpha)}$$

$$\therefore S = \frac{\alpha - \alpha^n}{1-\alpha}$$

$$\sum_k k\alpha^k = \alpha\frac{d}{d\alpha}\left(\sum_k \alpha^k\right) = \alpha\frac{d}{d\alpha}\left(\frac{\alpha-\alpha^n}{1-\alpha}\right)$$

$$= \alpha\,\frac{(1-n\alpha^{n-1})(1-\alpha) - (\alpha-\alpha^n)(-1)}{(1-\alpha)^2} = \frac{\alpha(1-\alpha^n)}{(1-\alpha)^2} - \frac{n\alpha^n}{(1-\alpha)}$$

Thus, the 2nd term in the bracket is

$$\sum_{k=1}^{n-1}(n-k)\alpha^k = \frac{n\alpha}{(1-\alpha)} - \frac{\alpha(1-\alpha^n)}{(1-\alpha)^2}$$

$$\langle R^2\rangle = nl^2 + 2l^2\left[\frac{n\alpha}{(1-\alpha)} - \frac{\alpha(1-\alpha^n)}{(1-\alpha)^2}\right]$$

$$= nl^2\left[\frac{1-\alpha}{1-\alpha} + \frac{2\alpha}{(1-\alpha)} - \frac{2\alpha}{n}\frac{(1-\alpha^n)}{(1-\alpha)^2}\right]$$

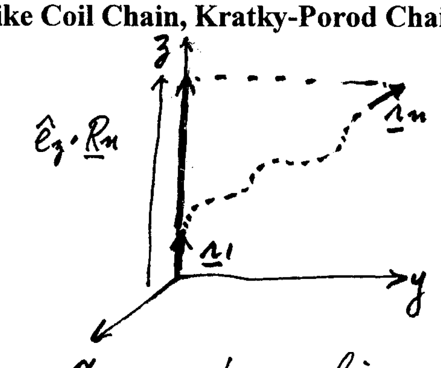
$$\underline{\langle R^2\rangle = nl^2\left[\frac{1+\alpha}{1-\alpha} - \frac{2\alpha}{n}\frac{(1-\alpha^n)}{(1-\alpha)^2}\right]}$$

$$\lim_{n\to\infty}\langle R^2\rangle_{f.r.c} = nl^2\left(\frac{1+\alpha}{1-\alpha}\right)$$

For tetrahedral bonding with $\theta = 70°32'$, $\cos\theta = \frac{1}{3}$

$$\langle R^2\rangle_{f.r.c} = nl^2\frac{4/3}{2/3} = 2nl^2, \qquad C_\infty(f.r.c.) = 2 \text{ for } \cos\theta = \tfrac{1}{3}$$

B-1 Wormlike Coil Chain, Kratky-Porod Chain:



$$\left\langle\left(\frac{\underline{r}_1}{l}\right)\cdot \underline{R}_n\right\rangle = \frac{1}{l}\left\langle \underline{r}_1 \cdot \sum_{i=1}^{n} \underline{r}_i\right\rangle$$

$\uparrow$ $\hat{e}_z$

$$= \frac{1}{l}l^2(1+\alpha+\alpha^2+\cdots\alpha^{n-1})$$

$$= l\left(\frac{1-\alpha^n}{1-\alpha}\right)$$

Thus, $\lim_{n\to\infty}\langle \hat{e}_z\cdot \underline{R}_n\rangle = l\cdot\lim_{n\to\infty}\left(\frac{1-\alpha^n}{1-\alpha}\right) = \frac{l}{1-\alpha}$, since $\alpha \lesssim 1$

which is the definition of <u>persistence length, l_p</u>

Persistence Segment $s_p \equiv l_p/l$

$\alpha = e^{-1/s_p}$, $\ln\alpha = -\frac{1}{s_p}$, $s_p = -\frac{1}{\ln\alpha} \cong \frac{2}{\theta^2}$

$l_p \equiv s_p \cdot l = l\frac{2}{\theta^2}$

$C_\infty = \frac{1+\alpha}{1-\alpha} \cong \frac{1+1-\frac{\theta^2}{2}}{1-1+\frac{\theta^2}{2}} = \frac{2-\theta^2/2}{\theta^2/2} \cong \frac{4}{\theta^2}$

Kuhn length $b = l\cdot\frac{C_\infty}{\cos\theta/2} \cong l\frac{4}{\theta^2} = 2l_p$

$\ln\cos\theta \cong -\theta^2/2$

$\cos\theta \cong 1-\theta^2/2$

$\ln(1-x) \cong -x$ ← if $x \ll 1$

$R_{max} = Nb$, $\langle R^2\rangle = Nb^2 = b R_{max} = C_\infty n l^2$
$= b \cdot n l \cos(\theta/2)$

$l\cos(\theta/2)$, $R_{max} = nl\cos(\theta/2)$, contour length

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Wormlike Coil Chain is a model of stiff chain defined as the limiting continuous case of freely-rotating chain by letting $l \to 0$ and $\alpha \to 1$ under the constraint that $\left(\frac{l}{1-\alpha}\right)$ remains constant.

$\frac{l}{1-\alpha} \equiv l_p$, $l/l_p = 1-\alpha$, $\alpha = 1 - l/l_p \underset{\substack{l_p = const \\ l \to 0}}{\simeq} e^{-l/l_p}$

$\alpha^n = e^{-nl/l_p} = e^{-R_{max}/l_p}$

1. $\langle R_{n,z}\rangle = \langle \underline{R}_n \cdot \hat{e}_z\rangle = \frac{l(1-\alpha^n)}{1-\alpha} = l_p \cdot (1-e^{-R_{max}/l_p})$

2. $\langle R^2\rangle = nl^2\left[\frac{1+\alpha}{1-\alpha} - \frac{2\alpha}{n}\frac{(1-\alpha^n)}{(1-\alpha)^2}\right]$

$= nl \cdot \frac{l}{1-\alpha}(1+\alpha) - 2\alpha \cdot \frac{l^2}{(1-\alpha)^2}(1-\alpha^n)$

$\cong R_{max} l_p (1+\alpha) - 2\alpha \cdot l_p^2 (1-e^{-R_{max}/l_p})$

$= 2l_p R_{max} - 2l_p^2(1-e^{-R_{max}/l_p})$

$= \underbrace{L/\lambda - \frac{1}{2\lambda^2}(1-e^{-2\lambda L})}_{\text{in the literature}}$, $1/2\lambda \equiv l_p$, $1/\lambda \equiv b$, $R_{max} \equiv L$

3. Limiting cases

a) $\frac{R_{max}}{l_p} \to 0$, $\quad R_{max} << l_p$

$$\langle R^2 \rangle = 2l_p R_{max} - 2l_p^2 \left[1 - \left(1 - \frac{R_{max}}{l_p} + \frac{R_{max}^2}{2l_p^2} - \frac{R_{max}^3}{6l_p^3} + \cdots \right) \right]$$
$$= 2l_p \cdot R_{max} - 2l_p^2 \left[\frac{R_{max}}{l_p} - \frac{R_{max}^2}{2l_p^2} + O(R_{max}^3/l_p^3) \right]$$
$$= R_{max}^2 - 2l_p^2 \cdot O(R_{max}^3/l_p^3) \cong R_{max}^2 = n^2 l^2 \text{ (rod limit)}$$

b) $\frac{R_{max}}{l_p} >> 1$

$$\langle R^2 \rangle \cong 2l_p R_{max} - 2l_p^2 = 2l_p(nl) - 2l_p^2 = 2l_p(nl - l_p)$$
$$\cong n(2l_p \cdot l) = C_\infty \cdot nl^2 \text{ (Coil limit)}$$
$$C_\infty = 2l_p = b$$