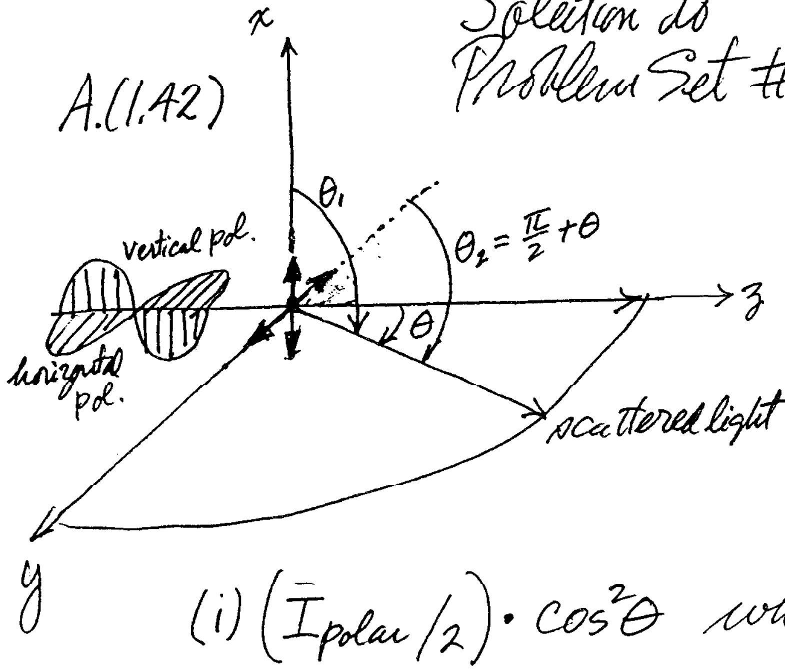
Solution to Problem Set #3 Chem 664

A.(1.42)



(i) $\left(\bar{I}_{polar}/2\right) \cdot \cos^2\theta$ where θ is the scattering angle

$$I_{polar} = I_i \frac{16\pi^4 \alpha^2 \sin^2\theta_i}{\lambda^4 r^2}$$

where θ_i is the angle between the induced dipole oscillation direction & scattering direction

Horizontal polarization

$$\sin^2\theta_2 = \sin^2\left(\frac{\pi}{2} + \theta\right) = \Big[\sin\left(\tfrac{\pi}{2}\right)\cos\theta + \sin\theta \underbrace{\cos\tfrac{\pi}{2}}_{=0}\Big]^2$$
$$= \cos^2\theta$$

$$\bar{I}_{polar} = \frac{I_i}{2}\left(\frac{16\pi^4\alpha^2}{\lambda^4 r^2}\right)\cos^2\theta$$

(ii) $$\bar{I}_{unpolarized} = \bar{I}_x + \bar{I}_y = \left[\frac{\cancel{4}\pi^2 n_0^2}{\lambda^4 r^2}\left(\frac{\partial n}{\partial c}\right)_T^2 \frac{cM}{N_{AV}}\frac{I_i}{\cancel{2}}\right]^2 \times \left(\sin^2\theta_1 + \sin^2\theta_2\right)$$
$$= \left[\quad\right]\left(1 + \cos^2\theta\right)$$

(iii) $$R_\theta^{unp} = \frac{\bar{I}_{unp}\, r^2}{I_i} = \left[\frac{2\pi^2 n_0^2}{\lambda^4}\left(\frac{\partial n}{\partial c}\right)_T^2 \frac{CM}{N_{AV}}\right](1+\cos^2\theta)$$
$$= KCM\left(\frac{1+\cos^2\theta}{2}\right) \text{ where } K = \frac{4\pi^2 n_0^2}{\lambda^4 N_{AV}}\left(\frac{\partial n}{\partial c}\right)_T^2$$

B.(1.43)

$$\tau = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, \frac{r^2 \bar{\bar{I}}_{unpol}}{I_i} = \int_0^{2\pi} d\phi \int_0^{\pi} KCM \frac{(1+\cos^2\theta)}{2} \sin\theta\, d\theta$$

$$= KCM \cdot 2\pi \int_{-1}^{1} \left(\frac{1+\cos^2\theta}{2}\right) d(\cos\theta)$$

$\sin\theta\, d\theta = -d(\cos\theta)$

$$= KCM \cdot 2\pi \cdot \frac{1}{2} \int_{-1}^{1} (1+x^2)\, dx = KCM \cdot \pi \left(2 + \frac{1}{3} 2\right)$$

$$= \frac{8\pi}{3} KCM$$

C.(2.2)

PS, $dp = 100$, 200 backbone bonds

$$\langle R^2 \rangle = C_\infty n l^2 = 9.5 \cdot 200 (1.5 Å)^2$$

$$= 4275 Å^2$$

$$\langle R^2 \rangle^{1/2} = 65.4 Å$$

$M = 10{,}400$ g/mol

D.(2.3) PE w/ $M = 10^7$ g/mol, $C_\infty = 7.4$, $n = \frac{M}{M_0} \cdot 2 = \frac{10^7 \cdot 2}{28} = 7.14 \cdot 10^5$

$$\langle R^2 \rangle^{1/2} = (C_\infty n l^2)^{1/2} = (7.4 \cdot 7.14 \cdot 10^5)^{1/2} \cdot 1.5 Å$$

$$= 3.45 \cdot 10^3 Å = 345\, nm$$

$$R_{max}(\text{contour length}) = nl(\cos[\theta/2]) = 7.14 \cdot 10^5 \cdot 1.5 Å \cos\left(\frac{70.5}{2}\right)$$

$$= 7.14 \cdot 1.5 \cdot 0.817 \cdot 10^5 Å$$

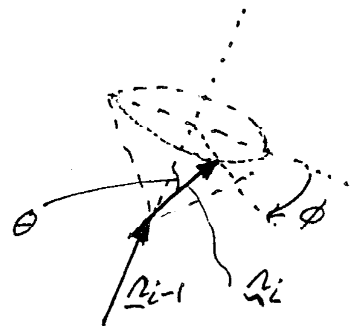
$$= 8.75 \cdot 10^5 Å = 87.5\, \mu m$$

E. (2.4)

$$\langle R^2\rangle = \sum_{i=1}^{n} r_i^2 + 2\sum_{1\le i<j\le n}\langle \underset{\sim}{r_i}\cdot \underset{\sim}{r_j}\rangle$$

$$\langle \underset{\sim}{r_i}\cdot \underset{\sim}{r_{i+1}}\rangle = l\cdot l\cos\theta$$

Model: n bond vectors with the supplement of bond angle θ for any adjacent pair with equally probable ϕ without any preference, so it is freely-rotating



$$\langle \underset{\sim}{r_i}\cdot \underset{\sim}{r_j}\rangle = l^2[\cos\theta]^{|i-j|}$$

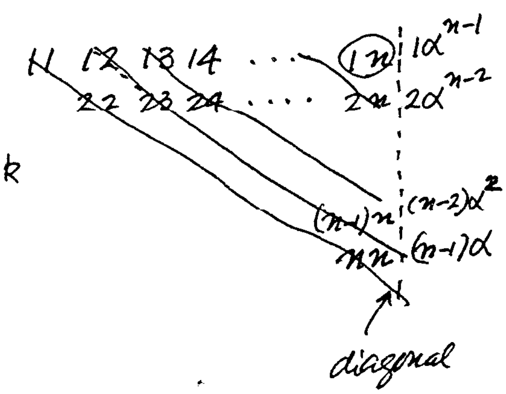
$$= l^2(\cos\theta)^{j-i}$$

if $j>i$

$$\langle R^2\rangle = nl^2 + 2l^2\sum_{k=1}^{n-1}(n-k)\alpha^k$$

$\alpha \equiv \cos\theta$

$$= nl^2 + 2l^2 n\sum_{k=1}^{n-1}\alpha^k - 2l^2\sum_{k=1}^{n-1}k\alpha^k$$



Note that $\sum_{k=1}^{n-1}\alpha^k \equiv S$

Since $\alpha<1$

$$\frac{1}{1-\alpha} = 1 + \underbrace{\alpha+\alpha^2+\alpha^3+\cdots+\alpha^{n-1}}_{S} + \alpha^n\cdot(1+\alpha+\alpha^2+\cdots)$$

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

$$\sum_{k=1}^{n-1}k\alpha^k = \alpha\frac{d}{d\alpha}\underbrace{\sum_{k=1}^{n-1}\alpha^k}_{S} = \alpha\frac{dS}{d\alpha} = \alpha\frac{(1-n\alpha^{n-1})(1-\alpha)}{(1-\alpha)^2}$$

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

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

$$-2l^2\sum_{k=1}^{n-1}k\alpha^k = 2l^2\left[\frac{n\alpha^n}{(1-\alpha)} - \frac{\alpha(1-\alpha^n)}{(1-\alpha)^2}\right]$$

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

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

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

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

$$C_\infty = \frac{1+\alpha}{1-\alpha} = 2 \quad \text{if } \alpha = \tfrac{1}{3} \text{ (Tetrahedral angle)}$$

$$C_n/C_\infty = 1 - \frac{2}{n}\frac{\alpha(1-\alpha^n)}{(1-\alpha^2)}$$

$$\alpha = \cos\theta = \cos 70.5^\circ = \tfrac{1}{3}$$

$$= \cos 10^\circ = 0.985$$

Plots are in the next two pages

F.(2.5) b – Kuhn segment length

$$\cos^2(\theta/2) - \sin^2(\theta/2) = 2\cos^2(\theta/2) - 1$$

$$b = \frac{C_\infty nl^2}{R_{max}} = \frac{\cancel{n}l^2}{\cancel{n}l\cos(\theta/2)}\left(\frac{1+\cos\theta}{1-\cos\theta}\right)$$

$$= \frac{l(1+2\cos^2(\theta/2)-1)}{\cos(\theta/2)(1-\cos\theta)} = 2l\frac{\cos(\theta/2)}{(1-\cos\theta)}$$

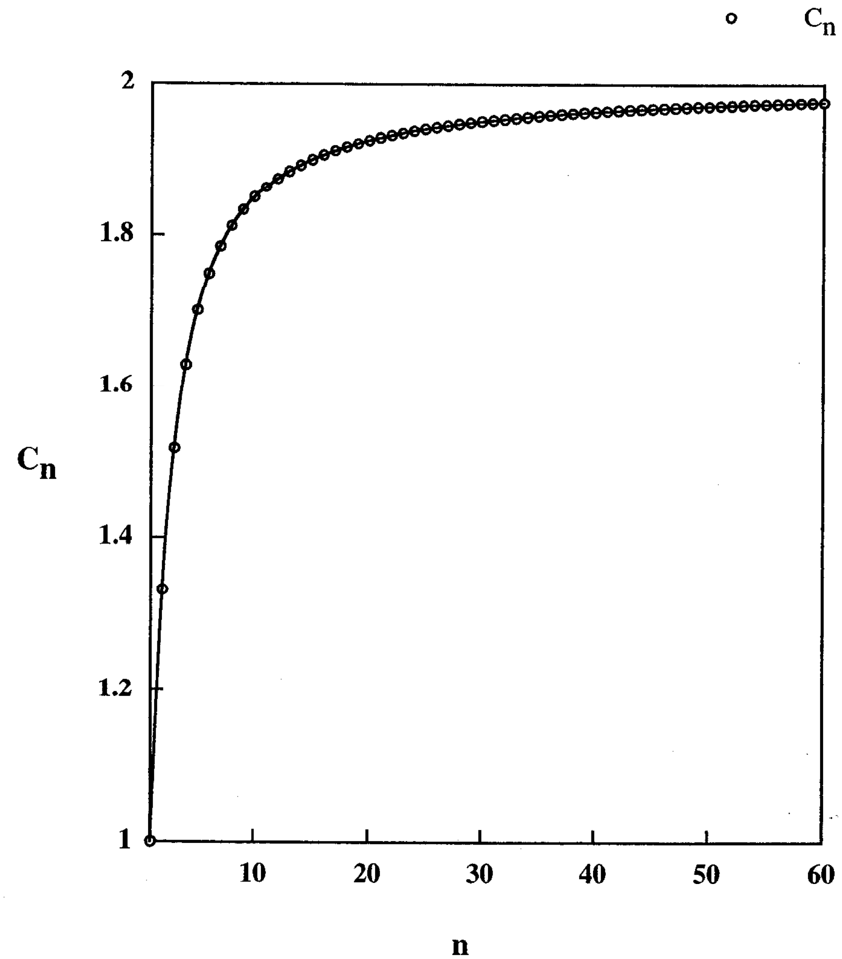
$$= 2\cdot 1.52\cdot\frac{0.817}{4/3} = 3.1\,\mathring{A}$$

$$N = \frac{R^2_{max}}{C_\infty nl^2} = \frac{n^2\cancel{l}^2\cos^2(\theta/2)}{\left(\frac{1+\cos\theta}{1-\cos\theta}\right)n\cancel{l}^2} = \frac{n}{2}(1-\cos\theta)$$

$$= n/3$$

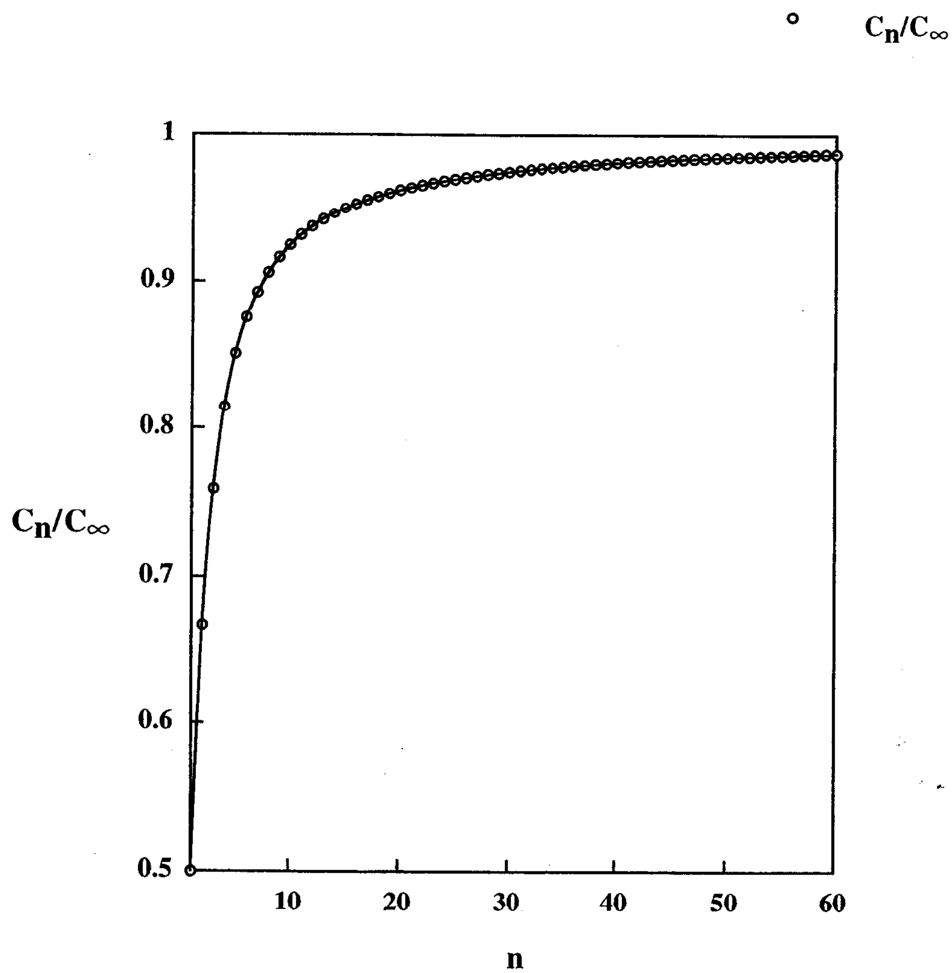
SPS3/5

Characteristic Ratio vs. Bond Vector Number
for a freely rotating chain with cosθ=1/3



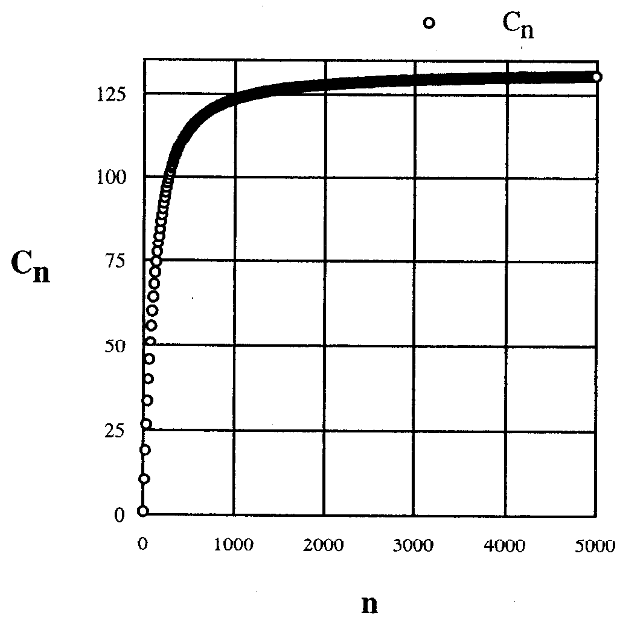
SPS3/6

Relative characteristic ratio with cosθ=1/3

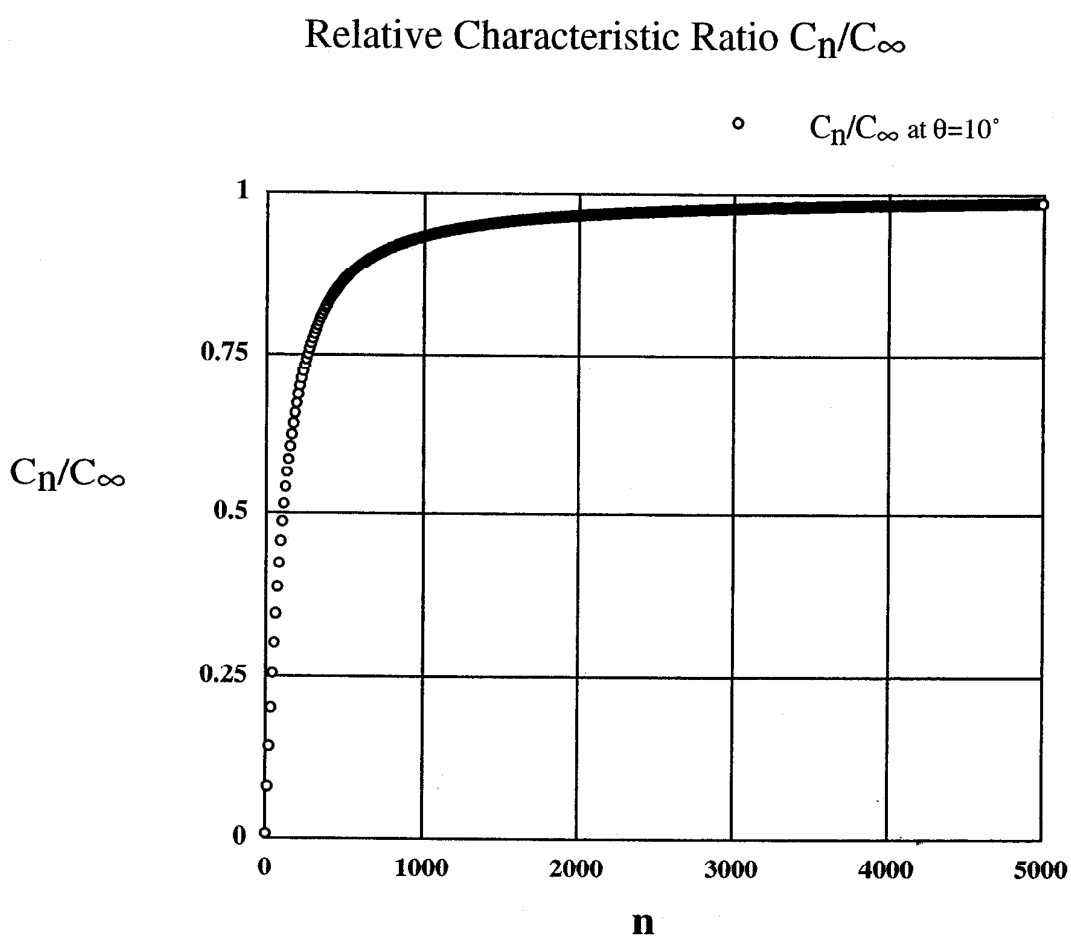


SPS3/7

Characteristic Ratio of a Freely Rotating Chain with θ=10°

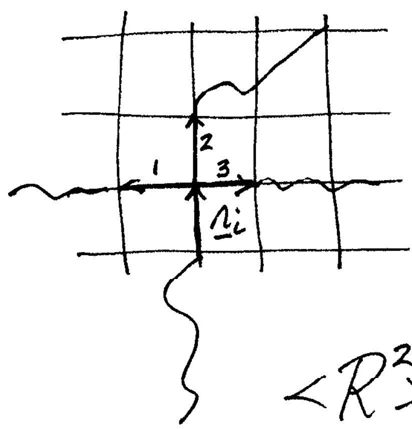


SPS3/8



Relative Characteristic Ratio C_n/C_∞
C_n/C_∞ at θ=10°
C_n/C_∞
1
0.75
0.5
0.25
0
0
1000
2000
3000
4000
5000
n

G.(2.6) / 2D Square lattice Random Walk w/o reverse step



$$\underline{l}_{i+1}^{(1)} \cdot \underline{l}_i = l^2 \cdot \cos\frac{\pi}{2} = 0$$

$$\underline{l}_{i+1}^{(2)} \cdot \underline{l}_i = l^2 \cdot \cos 0 = l^2$$

$$\underline{l}_{i+1}^{(3)} \cdot \underline{l}_i = l^2 \cdot \cos\frac{\pi}{2} = 0$$

$$\langle \underline{l}_{i+1} \cdot \underline{l}_i \rangle = \frac{1}{3}0 + \frac{1}{3}l^2 + \frac{1}{3}0 = \frac{1}{3}l^2$$

$$\langle R^2 \rangle = \langle (\sum \underline{l}_i) \cdot (\sum \underline{l}_j) \rangle$$

$$= \sum_{i=1}^{n} l_i^2 + 2 \sum_{i<j} \langle \underline{l}_i \cdot \underline{l}_j \rangle$$

$$= nl^2 + 2l^2 \sum_{k=1}^{n-1} (n-k)(\tfrac{1}{3})^k$$

$$= nl^2 \left[\frac{1+\frac{1}{3}}{1-\frac{1}{3}} - \frac{2}{n} \frac{\frac{1}{3}(1-\frac{1}{3^n})}{(1-\frac{1}{3})^2} \right]$$

$$= nl^2 \left[2 - \frac{3}{2n}(1-\frac{1}{3^n}) \right]$$ – Exactly the same as tetrahedral bonding case in 3D

$$C_\infty = \frac{1}{nl^2} \lim_{n\to\infty} \langle R^2 \rangle = 2$$