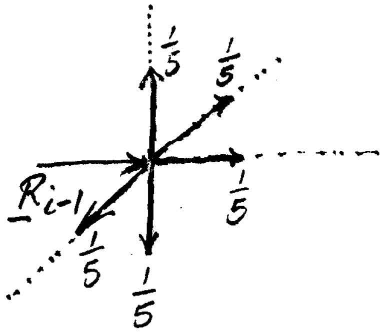
Solutions to Problem #4
due 10/14/02

A (2.7) (i) Cubic lattice with no probability for reverse step,



$$\langle \underline{r}_{i-1} \cdot \underline{r}_i \rangle = l^2\left[\tfrac{4}{5}\cos\tfrac{\pi}{2} + \tfrac{1}{5}\cos 0\right]$$
$$= l^2/5 = l^2\cos\theta$$

Hence, in analogy with the FRC model,

$$N \to \infty, \quad \langle R^2 \rangle = Nl^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right)$$
$$= Nl^2\left(\frac{1+\frac{1}{5}}{1-\frac{1}{5}}\right) = \frac{3}{2}Nl^2$$

(ii) $C_\infty = \dfrac{\langle R^2 \rangle}{Nl^2} = \dfrac{3}{2}$

B (2.11)
$$C^* = \frac{M}{N_{AV} \cdot V} \approx \frac{M}{N_{AV} \cdot \frac{4\pi R_g^3}{3}} = \frac{3 \cdot 10^7 \text{ g/mol}}{6.02 \cdot 10^{23} \frac{\text{molec}}{\text{mol}} \cdot \frac{4\pi}{3}(1.01 \cdot 10^{-5} \text{cm})^3/\text{molec}}$$

pervaded volume

$$= 1.15 \cdot 10^{-2} \text{ g/cm}^3 = 11.5 \text{ mg/mL} \approx 1\% \text{ solution}$$

Note that $30 \cdot 10^6$ g/mol PS is very easily shear-cleaved by stirring

C (2.12)
(i) $R_0^2 = Nb^2$
(ii) $R_{max} = Nb$
(iii) $R_g^2 = Nb^2/6$
(iv) $C^* = \dfrac{M}{N_{AV} \cdot V} \approx \dfrac{M}{N_{AV} \cdot 4\pi R_g^3/3}$
(v) $C^* \sim N/N^{3/2} = 1/N^{1/2}, \quad C^* \sim 1/\sqrt{N}$
(vi) $R_{max}/R_0 = bN/b\sqrt{N} = \sqrt{N} = 10$
(vii) $C^* \approx M/N_{AV} \cdot 4\pi R_g^3/3 \cong 5.8 \cdot 10^{-2} \text{ g/cm}^3 \cong 6\%$ solution

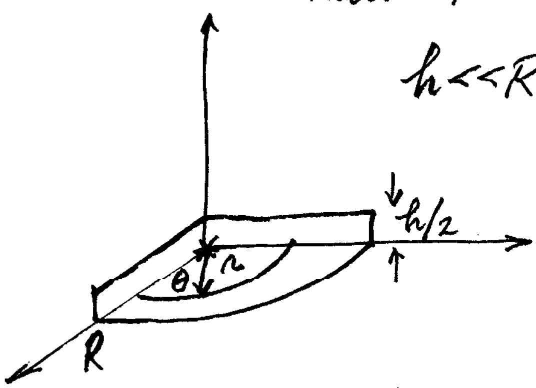
D (2.15)
$$R_g^2 \equiv \frac{\sum M_i \langle R_i^2 \rangle}{\sum M_i} = \int_{-L/2}^{L/2} x^2 \rho_0 \, dx \Big/ \int_{-L/2}^{L/2} \rho_0 \, dx = \frac{1}{3}\left[\left(\tfrac{L}{2}\right)^3 + \left(\tfrac{L}{2}\right)^3\right]/L$$
$$= L^2/12$$

ρ_0 = linear mass density

E (2.16), Radius of gyration of a disk with negligible thickness & radius R

vol element in the cylindrical element:

$h \ll R$, $\quad h\,r\,dr\,d\theta$, $\quad 0 \le r \le R$, $\quad 0 \le \theta \le 2\pi$



$$R_g^2 = \frac{\int_0^R \int_0^{2\pi} \rho_0 (h\,r\,dr\,d\theta)\, r^2}{\int_0^R \int_0^{2\pi} \rho_0\, h\,r\,dr\,d\theta} = \frac{R^4/4}{R^2/2} = \underline{\underline{R^2/2}}$$

ρ_0 : mass density of unit area slab with height h

More generally with a cylinder of height h and radius R,

Cylindrical coordinate, vol element

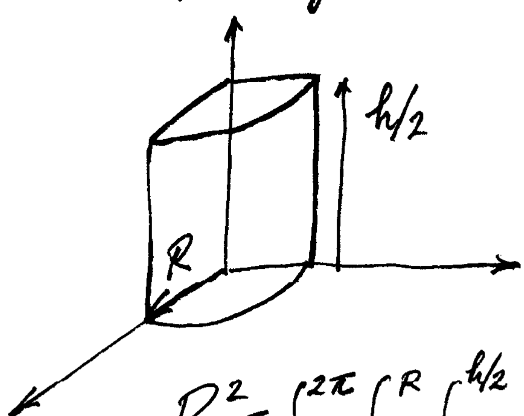
$dV = l\,d\theta\,dl\,dz$

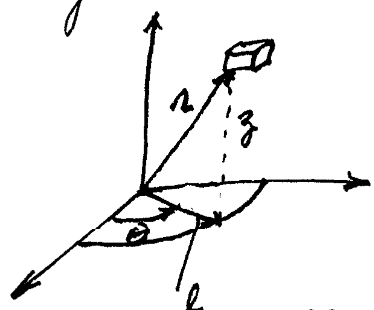
$-\frac{h}{2} \le z \le \frac{h}{2}$

$0 \le l \le R$

$0 \le \theta \le 2\pi$

$r^2 = l^2 + z^2$





$$R_g^2 = \int_0^{2\pi}\int_0^R\int_{-h/2}^{h/2} \rho_0\, r^2 \cdot l\,d\theta\,dl\,dz \Big/ \int_0^{2\pi}\int_0^R\int_{-h/2}^{h/2} \rho_0\, l\,d\theta\,dl\,dz$$

$$= \frac{1}{\pi R^2 h}\left\{2\pi h \int_0^R l^3\,dl + \frac{R^2}{2}\cdot 2\pi \int_{-h/2}^{h/2} z^2\,dz\right\}$$

$$= \frac{1}{\pi R^2 h}\left\{2\pi h \cdot \frac{R^4}{4} + R^2 \cdot \frac{\pi}{3}\left(h^3/8 + h^3/8\right)\right\}$$

$$= \frac{R^2}{2} + \frac{h^2}{12} = \frac{h^2}{12}\left(1 + 6\frac{R^2}{h^2}\right)$$

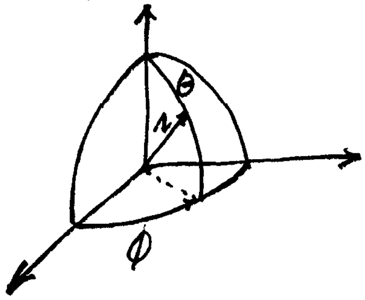
Two limits: $\lim_{R/h \to 0} R_g^2 = h^2/12$ Rod limit (skinny cylinder)

$\lim_{R/h \to \infty} R_g^2 = R^2/2$ Disk limit (flat cylinder)

F(2.1)

Radius of gyration of a sphere with radius R & uniform density

Vol element in spherical coordinate $r^2 dr \sin\theta d\theta d\phi$



ϱ_o : mass density

$$R_g^2 = \frac{\varrho_o \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^R r^4 dr}{\varrho_o \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^R r^2 dr} = \frac{\frac{1}{5}R^5}{\frac{1}{3}R^3} = \underline{\underline{\frac{3}{5}R^2}}$$

G(2.20), For $N \gg 1$, $R_g^2 = \frac{1}{2N^2}\sum_{i=0}^{N}\sum_{j=0}^{N} \langle h_{ij}^2 \rangle$

l_p: persistence length, $\langle h_{ij}^2 \rangle = 2l_p(|j-i|b) - 2l_p^2(1 - e^{-|j-i|b/l_p})$

for a wormlike chain with a contour length $|j-i|b$

Let $u \equiv jb$, $v \equiv ib$, $R_{max} = Nb$

$$R_g^2 \approx \frac{1}{N^2b^2}\int_0^{Nb}\int_0^{u}[2l_p(u-v) - 2l_p^2(1 - e^{-(u-v)/l_p})]\,du\,dv$$

$$\int_0^u 2l_p(u-v)dv = 2l_p(u\cdot u - \tfrac{1}{2}u^2) = l_p u^2$$

$$-2l_p^2\int_0^u (1 - e^{-(u-v)/l_p})dv = -2l_p^2\{u - e^{-u/l_p}(l_p e^{u/l_p} - l_p)\}$$
$$= -2l_p^2[u - l_p(1 - e^{-u/l_p})]$$

$$R_g^2 \approx \frac{1}{R_{max}^2}\cdot\int_0^{R_{max}}\{l_p u^2 - 2l_p^2[u - l_p(1 - e^{-u/l_p})]\}du$$

$$= \frac{1}{R_{max}^2}\{l_p \tfrac{1}{3}R_{max}^3 - 2l_p^2 \tfrac{1}{2}R_{max}^2 + 2l_p^3[R_{max} + l_p(e^{-R_{max}/l_p} - 1)]\}$$

$$= \underline{\underline{\frac{l_p R_{max}}{3} - l_p^2 + \frac{2l_p^3}{R_{max}} - \frac{2l_p^4}{R_{max}^2}(1 - e^{-R_{max}/l_p})}}$$

Note $b = 2l_p$ (Kuhn length), $L = R_{max} = Nb$ (contour length)
$= M/M_L$

M_L = mass per unit length

$$R_g^2 = \frac{bL}{6} - \frac{b^2}{4} + \frac{b^3}{4L} - \frac{b^4}{8L^2}(1 - e^{-2L/b})$$

Two limits: $L \gg b$, $R_g^2 \approx \frac{bL}{6} = \frac{Nb^2}{6}$ (Coil lim)

$L \ll b$, $R_g^2 \approx L^2/12 \ldots$ (Rod limit)

upon expansion of $e^{-2L/b}$