10/14/02

Chem 664
Handout #7

Mean Square Radius of Gyration

$$R_g^2 \equiv \frac{\sum M_j \langle R_j^2 \rangle}{\sum_j M_j},$$

M_j : mass of j^{th} mass point

$\langle R_j^2 \rangle$: MS radial vector of j^{th} mass point from the center of mass

If $M_j = M_i$ for i, j from $0 \to N$

$$R_g^2 = \frac{\sum \langle R_j^2 \rangle}{(N+1)},$$

$M_j = M_i = M_0$

$N+1$ mass points with $\underline{r}_i$

If solid objects

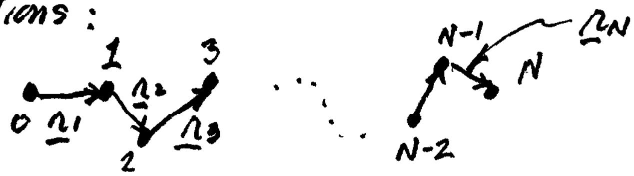
$$R_g^2 = \int_0^\infty \rho(\underline{R}) R^2 d\underline{R} \Big/ \int_0^\infty \rho(\underline{R}) d\underline{R}$$

For deformed objects

$$R_g^2 = \int_0^\infty \rho(\underline{R}) \mathbb{P}(\underline{R}) R^2 d\underline{R} \Big/ \int_0^\infty \rho(\underline{R}) \mathbb{P}(\underline{R}) d\underline{R}$$

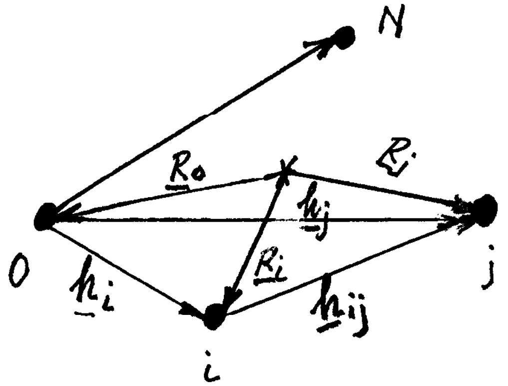
$$= \int_0^\infty \rho(\underline{R}) \mathbb{P}(\underline{R}) R^2 d\underline{R} \Big/ (\text{Mass of object})$$

Definitions:



Bond vector $\underline{r}_i$ connecting $i-1^{th}$ mass pt to i th mass pt

Model: deformable object with $(N+1)$ mass points



$\underline{R}_0$: radial vector from cm to $0^{\underline{th}}$ mass pt.
$\underline{R}_i$: " " to $i^{\underline{th}}$ mass pt.
$\underline{R}_j$: " " to $j^{\underline{th}}$ "
$\underline{h}_i$: vector connecting $0^{\underline{th}}$ to $i^{\underline{th}}$ mass pt.
$\underline{h}_j$: " $0^{\underline{th}}$ to $j^{\underline{th}}$ "
$\underline{h}_{ij}$: " $i^{\underline{th}}$ to $j^{\underline{th}}$ "

$$\underline{R}_i = \underline{R}_0 + \underline{h}_i, \quad \underline{h}_j = \underline{h}_i + \underline{h}_{ij}, \quad \underline{h}_{ij} = \underline{h}_j - \underline{h}_i$$

$$h_{ij}^2 = h_j^2 + h_i^2 - 2\,\underline{h}_i\cdot\underline{h}_j, \quad \underline{h}_i\cdot\underline{h}_j = \tfrac{1}{2}(h_j^2 + h_i^2 - h_{ij}^2)$$

Center of mass definition when all mass points are equal in magnitude,

$$\sum_{i=0}^{N} \underline{R}_i = 0, \quad \sum_{i=0}^{N}(\underline{R}_0 + \underline{h}_i) = (N+1)\underline{R}_0 + \sum_{i=0}^{N}\underline{h}_i$$

$$\underline{R}_0 = -\frac{1}{(N+1)}\sum_{i=0}^{N}\underline{h}_i$$

$$Rg^2 = \frac{1}{2(N+1)^2}\sum_{i=0}^{N}\sum_{j=0}^{N}\langle h_{ij}^2\rangle$$ — general for deformable uniform mass objects

Proof: $$Rg^2 = \frac{1}{N+1}\sum\langle R_i^2\rangle$$

$$\begin{cases} R_i^2 = \underline{R}_i\cdot\underline{R}_i = (\underline{R}_0+\underline{h}_i)\cdot(\underline{R}_0+\underline{h}_i) = R_0^2 + h_i^2 + 2(\underline{R}_0\cdot\underline{h}_i) \\ R_0^2 = \dfrac{1}{(N+1)^2}\left(\sum_{i=0}^{N}\underline{h}_i\right)\cdot\left(\sum_{j=0}^{N}\underline{h}_j\right) = \dfrac{1}{(N+1)^2}\sum_i\sum_j(\underline{h}_i\cdot\underline{h}_j) \\ 2(\underline{R}_0\cdot\underline{h}_i) = 2\left[-\dfrac{1}{N+1}\sum_i\underline{h}_i\right]\cdot\underline{h}_i \end{cases}$$

$$\sum R_i^2 = \sum_i\left[R_0^2 + h_i^2 + 2(\underline{R}_0\cdot\underline{h}_i)\right] = (N+1)R_0^2 + \sum_i h_i^2 - \frac{2}{(N+1)}\left(\sum \underline{h}_i\right)^2$$

$$= \frac{1}{(N+1)}\sum_i\sum_j(\underline{h}_i\cdot\underline{h}_j) + \sum h_i^2 - \frac{2}{(N+1)}\sum_i\sum_j(\underline{h}_i\cdot\underline{h}_j)$$

$$= \sum_i h_i^2 - \frac{1}{(N+1)}\sum_i\sum_j(\underline{h}_i\cdot\underline{h}_j)$$

Note that

$$\underline{h}_i \cdot \underline{h}_j = \frac{1}{2}(h_i^2 + h_j^2 - h_{ij}^2)$$

Thus $\sum_i \sum_j \underline{h}_i \cdot \underline{h}_j = \frac{1}{2}\left(\sum_i \sum_j h_i^2 + \sum_i \sum_j h_j^2 - \sum_i \sum_j h_{ij}^2\right)$

$$= \frac{1}{2}\left[(N+1)\sum_i h_i^2 + (N+1)\sum_j h_j^2 - \sum_i \sum_j h_{ij}^2)\right]$$

So, $\sum_i R_i^2 = \cancel{\sum_i h_i^2} - \cancel{\frac{1}{2}\sum h_i^2} - \frac{1}{2}\sum h_j^2 + \frac{1}{2(N+1)}\sum_i \sum_j h_{ij}^2$

$$= \frac{1}{2(N+1)}\sum_i \sum_j h_{ij}^2$$

Finally, a deformable uniform mass point object,

$$R_g^2 = \frac{1}{(N+1)}\sum \langle R_i^2 \rangle = \underline{\frac{1}{2(N+1)^2}\sum_i \sum_j \langle h_{ij}^2 \rangle}$$

As applied to FJC model

$$\langle h_{ij}^2 \rangle = b^2 |j-i| \quad , \quad 0 \le i, j \le N$$

$$R_g^2 = \frac{b^2}{2(N+1)^2}\sum_{i=0}^{N}\sum_{j=0}^{N} |j-i| = \frac{b^2}{2(N+1)^2} \cdot 2\sum_{j=1}^{N}\sum_{i=0}^{j-1}(j-i)$$

$$= \frac{b^2}{(N+1)^2}\sum_{k=1}^{N} k(N-k+1) = \frac{b^2}{(N+1)^2}\left\{(N+1)\sum_{k=1}^{N} k - \sum_{k=1}^{N} k^2\right\}$$

$$= \frac{b^2}{(N+1)^2}\left\{(N+1) \cdot \frac{N(N+1)}{2} - \frac{N(N+1)(2N+1)}{6}\right\}$$

$$= \frac{b^2}{(N+1)^2} \cdot \frac{N(N+1)(N+2)}{6} = \frac{Nb^2}{6}\left(\frac{N+2}{N+1}\right) \underset{N \gg 1}{\approx} \frac{Nb^2}{6}$$

MS ETE distance

$$\langle R^2 \rangle = N b^2 \quad // \quad \langle R^2 \rangle / R_g^2 = 6$$

$$[\langle R^2 \rangle / R_g^2]^{1/2} =$$