Chapter 26 - **RADIUS OF GYRATION CALCULATIONS**

The radius of gyration is a measure of the size of an object of arbitrary shape. It can be obtained directly from the Guinier plot [ln(I(Q)] *vs* Q^2] for SANS data. The radius of gyration squared R_g^2 is the second moment in 3D.

1. SIMPLE SHAPES

First consider some simple shape objects.

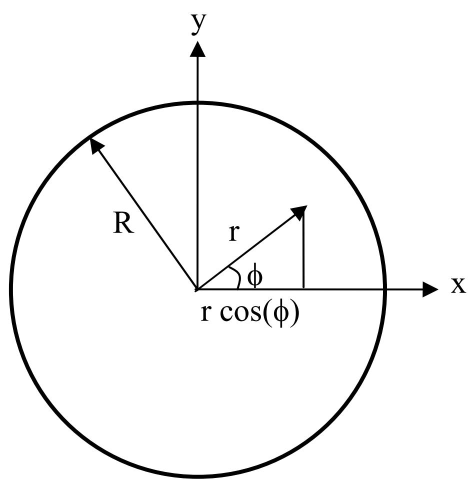

Figure 1: Representation of the polar coordinate system for a disk.

For an infinitely thin disk of radius R, R_g^2 is given by the following integral using polar coordinates.

$$R_{gx}^2 = \frac{\int_0^{2\pi}\int_0^{R_1} r^2\cos^2(\phi)\, r\,dr\,d\phi}{\int_0^{2\pi}\int_0^{R_1} r\,dr\,d\phi} = \frac{\int_0^{R_1} r^3 dr \int_0^{2\pi}\cos^2(\phi)\,d\phi}{\int_0^{R_1} r\,dr \int_0^{2\pi} d\phi} = \frac{R^2}{4}\ . \qquad (1)$$

Similarly for $R_{gy}^2 = \frac{R^2}{4}$. For an infinitely thin disk $R_g^2 = R_{gx}^2 + R_{gy}^2 = \frac{R^2}{2}$.

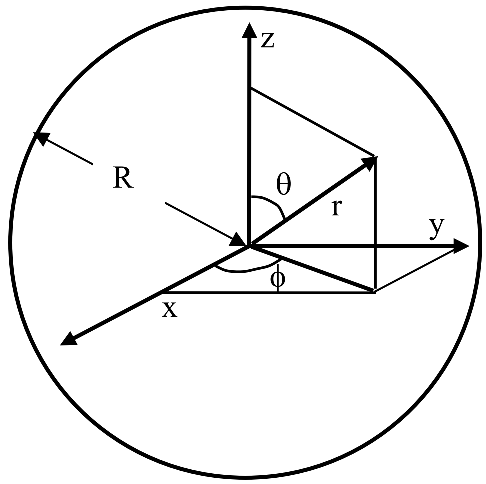

Figure 2: Representation of the spherical coordinate system for a sphere.

In the case of a full sphere, the integration is performed with spherical coordinates.

$$R_g^2 = \frac{\int_0^\pi \sin(\theta)d\theta \int_0^R r^2 dr\, r^2}{\int_0^\pi \sin(\theta)d\theta \int_0^R r^2 dr} = \frac{3R^2}{5}. \qquad (2)$$

The radius of gyration (squared) for the spherical shell of radii R_1 and R_2 is given by:

$$R_g^2 = \frac{3}{4\pi(R_2^3 - R_1^3)} \int_{R_1}^{R_2} 4\pi r^4 dr \qquad (3)$$

$$= \frac{3}{5} \frac{(R_2^5 - R_1^5)}{(R_2^3 - R_1^3)}.$$

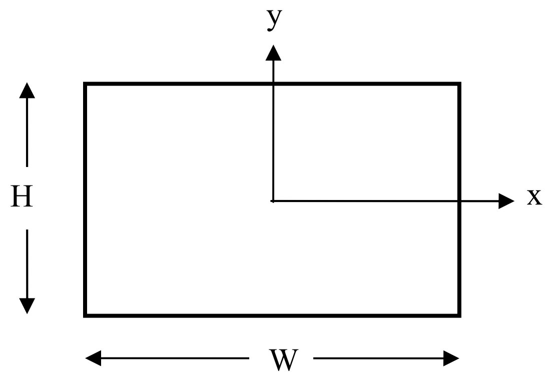

Figure 3: Representation of the Cartesian coordinate system for a rectangular plate.

For an infinitely thin rectangular object of sides W and H, the integration is performed in Cartesian coordinates.

$$R_{gx}^{2} = \frac{\int_{-W/2}^{W/2} dx\, x^{2}}{\int_{-W/2}^{W/2} dx} = \frac{1}{3}\left(\frac{W}{2}\right)^{2}. \tag{4}$$

Similarly for $R_{gy}^{2} = \frac{1}{3}\left(\frac{H}{2}\right)^{2}$. The sum gives $R_{g}^{2} = \frac{1}{3}\left[\left(\frac{W}{2}\right)^{2} + \left(\frac{H}{2}\right)^{2}\right]$.

Note that the moment of inertia I for a plate of width W, height H and mass M is also given by the second moment.

$$I = I_{xx} + I_{yy} = \frac{M}{3}\left[\left(\frac{W}{2}\right)^{2} + \left(\frac{H}{2}\right)^{2}\right]. \tag{5}$$

2. CIRCULAR ROD AND RECTANGULAR BEAM

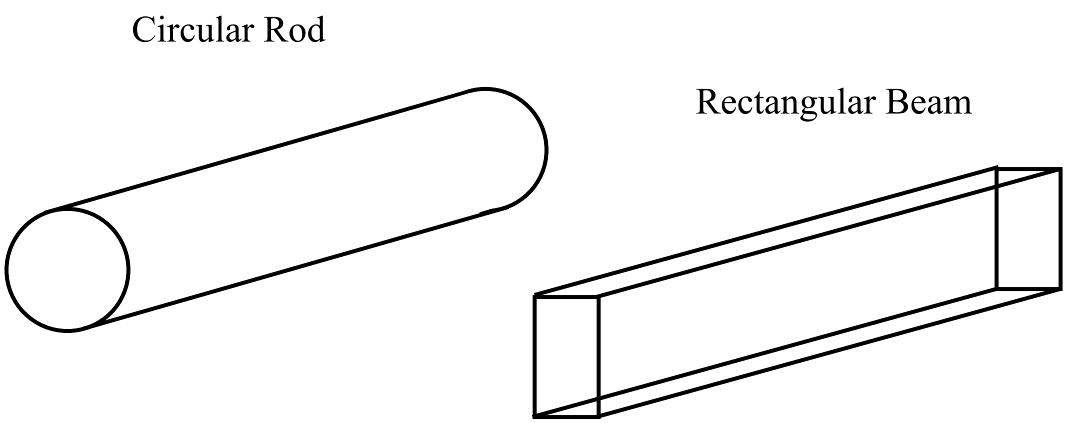

Figure 4: Representation of the cylindrical rod and rectangular beam.

The radius of gyration for a cylindrical rod of length L and radius R is given by:

$$R_g^2 = \frac{R^2}{2} + \frac{1}{3}\left(\frac{L}{2}\right)^2 = \frac{R^2}{2} + \frac{L^2}{12}. \qquad (6)$$

The radius of gyration for a rectangular beam of width W, height H and length L is given by:

$$R_g^2 = \frac{1}{3}\left[\left(\frac{W}{2}\right)^2 + \left(\frac{H}{2}\right)^2 + \left(\frac{L}{2}\right)^2\right]. \qquad (7)$$

This formula holds for a straight "ribbon" where W<H<<L.

The value of R_g^2 for a cylindrical rod with radius R = 10 (diameter D = 20) and length L = 10 is $R_g^2 = 58.3$. This value is to be compared with the case of a rectangular beam with sides W = L = 20 and length L = 10 for which $R_g^2 = 75$.

3. COMMENTS

The radius of gyration squared can be calculated for other more complicated shapes as the second moment for each of the symmetry direction.

Note that R_{gx}^2 for a horizontal strip is the same as that for the whole square plate $R_{gx}^2 = \frac{1}{3}\left(\frac{W}{2}\right)^2$. R_{gx}^2 is independent of the height of the object. Of course R_{gy}^2 depends of the height but not on the width.

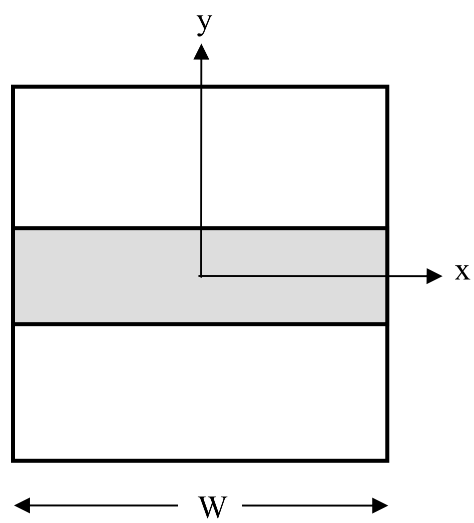

Figure 5: Case of a horizontal flat strip.

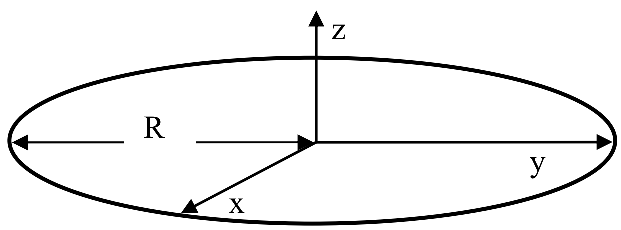

Figure 6: Case of a circular ring.

The radius of gyration for an infinitely thin circular ring of radius R is $R_{gz}^2 = R^2$. This is obtained by spinning the ring in the horizontal plane (around the z-axis). Note that it is the same value for an infinitely thin spherical shell of radius R.

4. TWISTED RIBBON

The radius of gyration for rigid twisted shape objects are worked out here. Consider the simple case of a rigid helical wire, then the case of a rigid twisted ribbon with finite size thickness.

Helical Wire

Consider a very thin helically twisted wire aligned along the vertical z axis. Choose the origin of the Cartesian coordinate system at the center-of mass of the twisted wire. The helix has a radius R and a height L so that $-L/2 \leq z \leq L/2$. The parametric equation of the helix is:

$$X = R\cos(\phi) \qquad (8)$$
$$Y = R\sin(\phi)$$
$$Z = p\phi/2\pi.$$

Here p is the helix pitch and ϕ is the azimuthal angle in the horizontal plane. The wire position along the helix is represented by the vector $\vec{r}(\phi)$. Note that by definition of the center-of-mass, the average of this vector is null, $<\vec{r}(\phi)> = 0$.

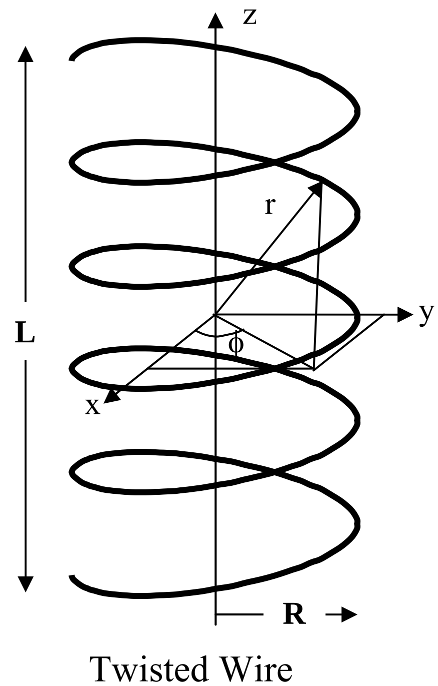

Figure 7: Schematic representation of the twisted wire.

The radius of gyration (squared) R_g^2 is defined as follows:

$$R_g^2 = <r^2(\phi)> = \frac{\int d\phi r^2(\phi)}{\int d\phi}. \qquad (9)$$

Here $r^2(\phi) = X^2+Y^2+Z^2 = R^2 + (p\phi/2\pi)^2$. The azimuthal angle ϕ varies in the range: $-\pi L/p \leq \phi \leq \pi L/p$.

The ϕ integration is readily performed to give:

$$R_g^2 = R^2 + \frac{1}{3}\left(\frac{L}{2}\right)^2. \qquad (10)$$

Note that this is the same result as for a cylindrical shell of radius R and height L. This is not surprising since a cylinder could be built by a number of twisted wires stacked vertically.

Thin Twisted Ribbon

The case of a thin twisted helical ribbon of width W can be worked out similarly using a two-variable parametric notation $r^2(\phi,z)$ where ϕ is the azimuthal angle and z is the vertical ribbon width with $-W/2 \leq z \leq W/2$.

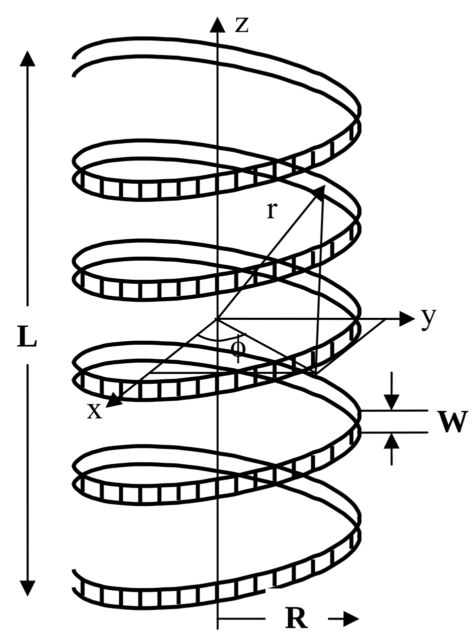

Figure 8: Schematic representation of the thin twisted ribbon.

Here, the variable Z is replaced by Z+z. The radius of gyration (squared) is therefore given by:

$$R_g^2 = <r^2(\phi,z)> = \frac{\int d\phi \int dz\, r^2(\phi,z)}{\int d\phi \int dz} \qquad (11)$$

$r^2(\phi,z)$ is now given by $r^2(\phi,z) = R^2 + \left(\frac{p\phi}{2\pi} + z\right)^2$. The integrations can here also be readily performed to give:

$$R_g^2 = R^2 + \frac{1}{3}\left(\frac{L}{2}\right)^2 + \frac{1}{3}\left(\frac{W}{2}\right)^2. \qquad (12)$$

These involve contributions from $\langle Z^2 \rangle$ and $\langle z^2 \rangle$. The cross term gives no contribution because it involves the null average $\langle z \rangle = 0$.

Thick Twisted Ribbon

For the case of a twisted ribbon of horizontal thickness T, the variable R is replaced by $R+\rho$ where $-T/2 \le \rho \le T$.

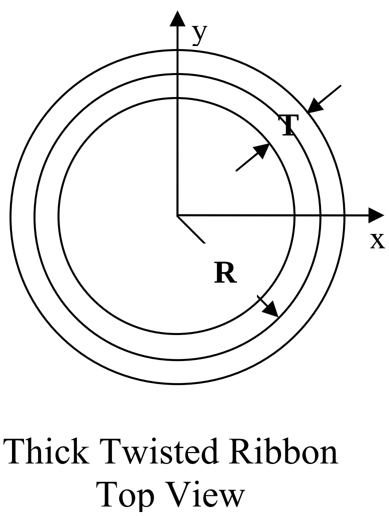

Figure 9: Top view of a thick twisted ribbon.

The calculation of the second moment proceeds as before:

$$\begin{aligned} X &= \rho \cos(\phi) \\ Y &= \rho \sin(\phi) \\ Z &= p\phi/2\pi. \end{aligned} \qquad (13)$$

Here ρ is the polar coordinate variable in the horizontal plane with limits: $R\text{-}T/2 \le \rho \le R\text{+}T/2$. In this case $r^2(Z,z,\rho) = \rho^2 + (Z+z)^2$ where z is the same parameter as before. $R_g^2 = \langle \rho^2 \rangle + \langle (Z+z)^2 \rangle$ involves two averages. The first average is:

$$\langle \rho^2 \rangle = \frac{\int_0^{2\pi} d\phi \int_{R-T/2}^{R+T/2} \rho d\rho\, \rho^2}{\int_0^{2\pi} d\phi \int_{R-T/2}^{R+T/2} \rho d\rho} = \frac{\frac{1}{4}\left[\left(R+\frac{T}{2}\right)^4 - \left(R-\frac{T}{2}\right)^4\right]}{\frac{1}{2}\left[\left(R+\frac{T}{2}\right)^2 - \left(R-\frac{T}{2}\right)^2\right]} = R^2 + \left(\frac{T}{2}\right)^2.$$

(14)

The final result involving both (horizontal and vertical) averages is:

$$R_g^2 = R^2 + \left(\frac{T}{2}\right)^2 + \frac{1}{3}\left(\frac{L}{2}\right)^2 + \frac{1}{3}\left(\frac{W}{2}\right)^2. \qquad (15)$$

Note that all terms add up in quadrature since all cross terms (first moments) average to zero.

5. GAUSSIAN POLYMER COIL

The radius of gyration (squared) for a polymer coil is defined as:

$$R_g^2 = \frac{1}{n}\sum_i^n < S_i^2 >. \qquad (16)$$

S_i refers to the position of monomer i with respect to the center-of-mass of the polymer coil and n is the total number of monomers per coil. The inter-distance vector between two monomers within the same macromolecule is defined as $\vec{S}_{ij} = \vec{S}_j - \vec{S}_i$. Consider the following relation:

$$\sum_{i,j}^n \vec{S}_{ij}^2 = n\sum_i^n \vec{S}_i^2 + n\sum_j^n \vec{S}_j^2 - 2\sum_{i,j}^n \vec{S}_i.\vec{S}_j . \qquad (17)$$

The last summation is null $\sum_{i,j}^n \vec{S}_i.\vec{S}_j = \sum_i^n \vec{S}_i.\sum_j^n \vec{S}_j = 0$ since by definition of the center-of-mass $\sum_i^n \vec{S}_i = 0$. The radius of gyration (squared) is therefore simplified as:

$$R_g^2 = \frac{1}{2n^2}\sum_{i,j}^n < S_{ij}^2 > = \frac{1}{2n^2}\sum_{i,j}^n < r_{ij}^2 >. \qquad (18)$$

The vectorial notation has been dropped for simplicity.

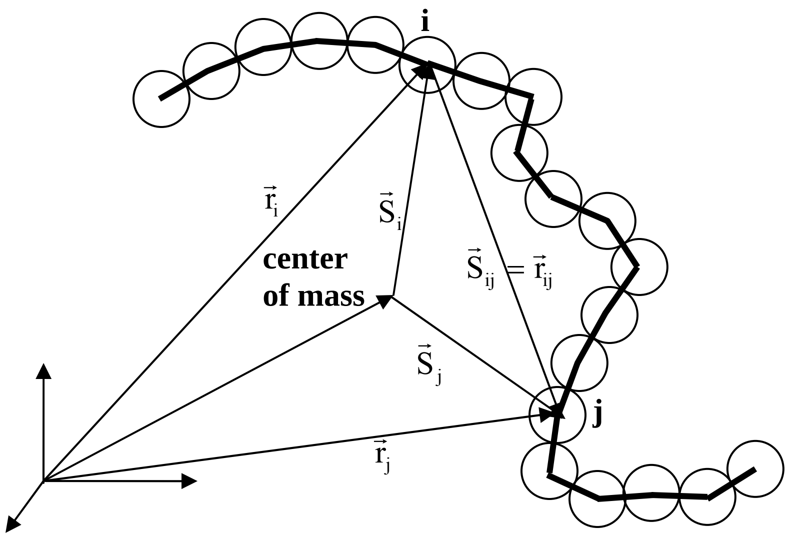

Figure 10: Schematic representation of a Gaussian coil showing monomers i and j and their inter-distance r_{ij}. Note that $\vec{S}_{ij} = \vec{r}_{ij}$ in the notation used.

$$<S_{ij}^2> = a^2 \,|i - j|. \tag{19}$$

Here a is the statistical segment length, and <…> is an average over monomers. The following formulae for the summation of arithmetic progressions are used:

$$\sum_{k=1}^{n} k = \frac{n(n+1)}{2} \tag{20}$$
$$\sum_{k=1}^{n} k^2 = \frac{n(n+1)(2n+1)}{6}.$$

The radius of gyration squared becomes:

$$R_g^{\,2} = \frac{a^2}{2n^2}\sum_{i,j}^{n} |i-j| = \frac{a^2}{n}\sum_{k}^{n}\left(1-\frac{k}{n}\right)k \tag{21}$$
$$= \frac{a^2}{6}\frac{(n^2-1)}{n} \cong \frac{a^2 n}{6} \quad \text{for } n >> 1.$$

Note that taking the n >> 1 limit early on allows us to replace the summations by integrations. Using the variable x = k/n, one obtains:

$$R_g^{\,2} = a^2 n \int_0^1 dx(1-x)x = a^2 n\left(\frac{1}{2}-\frac{1}{3}\right) = \frac{a^2 n}{6}. \tag{22}$$

Similarly, the end-to-end distance squared R_{1n}^2 for a Gaussian polymer coil is given by:

$$R_{1n}^{2} = a^{2} n \quad \text{for } n >> 1. \tag{23}$$

These results are for Gaussian coils that follow random walk statistics (Flory, 1969).

6. THE EXCLUDED VOLUME PARAMETER APPROACH

The Flory mean field theory of polymer solutions describes chain statistics as a random walk process along chain segments. For Gaussian chain statistics, the monomer-monomer inter-distance is proportional to the number of steps:

$$< S_{ij}^{2} >= a^{2} \, | i - j |^{2\nu}. \tag{24}$$

Here a is the statistical segment length, ν is the excluded volume parameter, S_{ij} represents an inter-segment distance and <…> is an average over monomers. The radius of gyration squared for Gaussian chains is expressed as:

$$R_{g}^{2} = \frac{1}{2n^{2}} \sum_{i,j}^{n} < S_{ij}^{2} > = \frac{a^{2}}{2n^{2}} \sum_{i,j}^{n} | i - j |^{2\nu} \tag{25}$$

$$= \frac{a^{2}}{n} \sum_{k}^{n} (1 - \frac{k}{n}) \, k^{2\nu} = \frac{a^{2}}{(2\nu + 1)(2\nu + 2)} n^{2\nu}.$$

i and j are a pair of monomers and n is the number of chain segments per chain. Three cases are relevant:

(1) Self-avoiding walk corresponds to swollen chains with ν = 3/5, for which
$R_{g}^{2} = \frac{25}{176} a^{2} n^{6/5}$.
(2) Pure random walk corresponds to chains in theta conditions (where solvent-solvent, monomer-monomer and solvent-monomer interactions are equivalent) with ν = ½, for which $R_{g}^{2} = \frac{1}{2} a^{2} n$.
(3) Self attracting walk corresponds to collapsed chains with ν = 1/3, for which
$R_{g}^{2} = \frac{9}{40} a^{2} n^{2/3}$.

Note that the renormalization group estimate of the excluded volume parameter for the fully swollen chain is ν = 0.588 (instead of the 0.6 mean field value).

Note also that the radius of gyration for a thin rigid rod can be recovered from this excluded volume approach by setting ν = 1 and defining the rod length as L = na.

$$R_g{}^2 = \frac{a^2}{(2\nu+1)(2\nu+2)} n^{2\nu} = \frac{a^2 n^2}{12} = \frac{L^2}{12}. \qquad (26)$$

This is the same result derived earlier for a thin rod.

REFERENCES

http://en.wikipedia.org/wiki/List_of_moments_of_inertia

P.J. Flory, "Statistical Mechanics of Chain Molecules", Interscience Publishers (1969)

QUESTIONS

1. How is the radius of gyration measured by SANS?
2. How is the center-of-mass of an object defined?
3. Why is the radius of gyration squared for an object related to the moment of inertia for that object?
4. Calculate $R_g{}^2$ for a full sphere of radius R. Calculate $R_g{}^2$ for a thin spherical shell of radius R.
5. What is the value of $R_g{}^2$ for a Gaussian coil of segment length a and degree of polymerization n? How about the end-to-end distance?
6. What is the radius of gyration squared for a rod of length L and radius R?

ANSWERS

1. The radius of gyration is measured by performing a Guinier plot on SANS data. The slope of the linear variation of ln[I(Q)] *vs* Q^2 is $R_g{}^2/3$.
2. The center-of-mass of an object is defined as the spot where the first moment is zero.
3. The radius of gyration squared and the moment of inertia for that object are both expressed in terms of the second moment.
4. $R_g{}^2$ for a full sphere of radius R is given by:
$R_g{}^2 = \left(\int_0^\pi \sin(\theta) d\theta \int_0^R r^2 dr r^2 \right) / \left(\int_0^\pi \sin(\theta) d\theta \int_0^R r^2 dr \right) = \frac{3R^2}{5}$. $R_g{}^2$ for a thin spherical shell is simply given by: $R_g{}^2 = R^2$.
5. For a Gaussian coil of segment length a and degree of polymerization n, one can calculate the radius of gyration squared as $R_g{}^2 = a^2 n/6$ and the end-to-end distance squared as $R_{1n}{}^2 = a^2 n$.
6. The radius of gyration squared for a rod of length L and radius R is given by:
$R_g{}^2 = \frac{R^2}{2} + \frac{1}{3}\left(\frac{L}{2}\right)^2$.