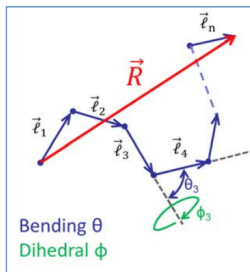


7.1: Segment Models

Segment Models¹



- $(n + 1)$ beads link by n segments or bonds of length ℓ .
- Each bead has a position \vec{r}_i .
- Each bond is assigned a vector, $\vec{\ell}_i = \vec{r}_i - \vec{r}_{i-1}$.
- The bending angle between adjacent segments i and $(i + 1)$ is θ_i : $\cos \theta = \frac{\vec{\ell}_i \cdot \vec{\ell}_{i+1}}{\ell_i \ell_{i+1}}$
- For each bending angle there is an associated dihedral angle ϕ_i defined as the rotation of segment $(i + 1)$ out of the plane defined by segments i and $(i - 1)$.
- There are $n - 1$ separate bending and dihedral angles.

Statistical Variables for Macromolecules

End-to-end distance

The contour length is the full length of the polymer along the contour of the chain:

$$L_C = n\ell$$

Each chain has the same contour length, but varying dimensions in space that result from conformational flexibility. The primary structural variable for measuring this conformational variation is the end-to-end vector between the first and last bead, $\vec{R} = \vec{r}_n - \vec{r}_0$, or equivalently

$$\vec{R} = \sum_{i=1}^n \vec{\ell}_i$$

Statistically, the dimensions of a polymer can be characterized by the statistics of the end-to-end distance. Consider its mean-square value:

$$\langle \vec{R}^2 \rangle = \langle \vec{R} \cdot \vec{R} \rangle = \left\langle \left(\sum_{i=1}^n \vec{\ell}_i \right) \cdot \left(\sum_{j=1}^n \vec{\ell}_j \right) \right\rangle \quad (7.1.1)$$

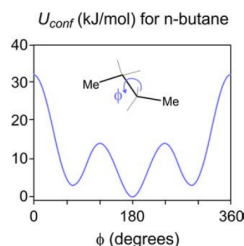
After expanding these sums, we can collect two sets of terms: (1) the self-terms with $i = j$ and (2) the interbond correlations ($i \neq j$):

$$\begin{aligned} \langle \vec{R}^2 \rangle &= n\ell^2 + \sum_{j \neq i} \langle \vec{\ell}_i \cdot \vec{\ell}_j \rangle \\ &= n\ell^2 + \ell^2 \sum_{j \neq i} \langle \cos \theta_{ij} \rangle \end{aligned} \quad (7.1.2)$$

Here θ_{ij} is the angle between segments i and j . This second term describes any possible conformational preferences between segments along the chain. We will call the factor $\langle \cos \theta_{ij} \rangle$ the segment orientation correlation function, which is also written

$$\begin{aligned} g(k) &= \langle \cos \theta_k \rangle \\ \theta_k &= \angle(\vec{\ell}_i, \vec{\ell}_{i+k}) \quad k = |j - i| \end{aligned} \quad (7.1.3)$$

Here k refers to the separation between two segments. This correlation function can vary in value from 1 to -1, where +1 represents a highly aligned or extended chain and negative values would be very condensed or compact. No interband correlations ($g = 0$) is expected for placement of segments by a random walk.



Interbond correlation can be inserted into segment models, both through ad hoc rules, or by applying an energy function that constrains the intersegment interactions. For instance, the torsional energy function below, U_{conf} , would be used to weight the probability that adjacent segments adopt a particular torsional angle. A general torsional energy function $U_{\text{conf}}(\Theta)$ involves all $2(n-1)$ possible angles $\Theta = \{\theta_1, \phi_1, \theta_2, \phi_2, \dots, \theta_{n-1}, \phi_{n-1}\}$, the joint probability density for adopting a particular conformation is

$$P(\Theta) = \frac{e^{-U_{\text{conf}}(\Theta)/k_B T}}{\int d\Theta e^{-U_{\text{conf}}(\Theta)/k_B T}}$$

The integral over Θ reflects $2(n-1)$ integrals over polar coordinates for all adjacent segments,

$$\int d\Theta = \int_0^\pi \int_0^{2\pi} \sin \theta_1 d\theta_1 d\phi_1 \cdots \int_0^\pi \int_0^{2\pi} \sin \theta_{n-1} d\theta_{n-1} d\phi_{n-1}$$

Then the alignment correlation function is

$$\langle \vec{\ell}_i \cdot \vec{\ell}_j \rangle = \ell^2 \int d\Theta \cos \theta_{ij} P(\Theta)$$

This is not a practical form, so we will make simplifying assumptions about the form of this probability distribution. For instance, if any segments configuration depends only on its nearest neighbors then $P(\Theta) = P(\theta, \phi)^{(n-1)}$.

Persistence Length

For any polymer, alignment of any pair of vectors in the chain becomes uncorrelated over a long enough sequence of segments. To quantify this distance we define a "persistence length" ℓ_p .

$$\ell_p = \langle \hat{\ell}_i \cdot \sum_{j=1}^n \hat{\ell}_j \rangle \quad \hat{\ell}_i = \frac{\vec{\ell}_i}{|\ell|}$$

This is the characteristic distance along the chain for the decay for the orientational correlation function between bond vectors,

$$g(k) = \ell^2 \langle \cos^k \theta \rangle$$

How will this behave? If you consider that $|\cos \theta| < 1$, then $\langle \cos^k \theta \rangle$ will drop with increasing k , approaching zero as $k \rightarrow \infty$. That is the memory of the alignment between two bond vectors drops with their separation, where the distance scale for the loss of correlation is ℓ_p . We thus expect a monotonically decaying form to this function:

$$g(k) = \ell^2 e^{-k\ell/\ell_p} \quad (7.1.4)$$

For continuous thin rod models of the polymer, this expression is written in terms of the contour distance s , the displacement along the contour of the chain (i.e., $s = \ell k$),

$$g(s) = \ell^2 e^{-|s|/\ell_p}$$

How do we relate θ and ℓ_p ?² Writing $\langle \cos^k \theta \rangle \approx \exp(k \ln \langle \cos \theta \rangle)$ and equating this with eq. (7.1.4) indicates that

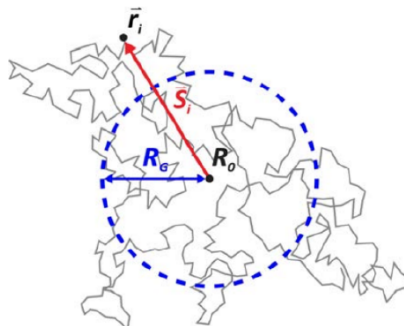
$$\ell_p = -\ell \ln \langle \cos \theta \rangle$$

For stiff chains, we can approximate $\ln(x) \approx (1 - x)$, so

$$\ell_p \approx \frac{\ell}{1 - \langle \cos \theta \rangle}$$

Radius of Gyration

The **radius of gyration** is another important structural variable that is closely related to experimental observables. Here the polymer dimensions are expressed as extension relative to the center of mass for the chain.



This proves useful for branched polymers and heteropolymers (such as proteins). Denoting the position and mass of the i^{th} bead as \vec{r}_i and m_i , we define the center of mass for the polymer as a mass-weighted mean position of the beads in space:

$$\vec{R}_0 = \frac{\sum_{i=0}^n m_i \vec{r}_i}{\sum_{i=0}^n m_i}$$

The sum index starting at 0 is meant to reflect the sum over $n + 1$ beads. The denominator of this expression is the total mass of the polymer $M = \sum_{i=0}^n m_i$. If all beads have the same mass, then $m_i/M = 1/(n + 1)$ and R_0 is the geometrical mean of their positions.

$$\vec{R}_0 = \frac{1}{n + 1} \sum_{i=0}^n \vec{r}_i$$

The radius of gyration R_G for a configuration of the polymer describes the mass-weighted distribution of beads R_0 , and is defined through

$$\langle R_G^2 \rangle = \frac{1}{n + 1} \sum_{i=0}^n \langle \vec{S}_i^2 \rangle$$

where \vec{S}_i is gyration radius, i.e., the radial distance of the i^{th} bead from the center of mass

$$\begin{aligned} \vec{S}_i^2 &= \frac{m_i}{M} (\vec{r}_i - \vec{R}_0)^2 && \text{(mass-weighted)} \\ \vec{S}_i^2 &= \frac{1}{n + 1} (\vec{r}_i - \vec{R}_0)^2 && \text{(equal mass beads)} \end{aligned}$$

Additionally, we can show that the mean-squared radius of gyration is related to the average separation of all beads of the chain.

$$\langle R_G^2 \rangle = \frac{1}{(n + 1)^2} \sum_{i=0}^n \sum_{j=0}^n \langle (\vec{r}_i - \vec{r}_j)^2 \rangle$$

Freely Jointed Chain

The freely jointed chain describes a macromolecule as a backbone for which all possible θ and ϕ are equally probable, and there are no correlations between segments. It is known as an "ideal chain" because there are no interactions between beads or excluded volume, and configuration of the polymer backbone follows a random walk. If we place the first bead at $r = 0$, we find that $\langle R \rangle = 0$, as expected for a random walk, and eq. (7.1.2) reduces to

$$\langle R^2 \rangle = n\ell^2$$

$$\text{or } R_{rms} = \langle R^2 \rangle^{1/2} = \sqrt{n}\ell$$

While the average end-to-end distance may be zero, the variance in the end-to-end distribution is

$$\sigma_r = \sqrt{\langle R^2 \rangle - \langle R \rangle^2} = \sqrt{n}\ell$$

The radius of gyration for an ideal chain is:

$$R_G = \sqrt{\frac{\langle R^2 \rangle}{6}} = \sqrt{\frac{n\ell^2}{6}}$$

Gaussian Random Coil

The freely jointed chain is also known as a Gaussian random coil, because the statistics of its configuration are fully described by $\langle R \rangle$ and $\langle R^2 \rangle$, the first two moments of a Gaussian end-to-end probability distribution $P(R)$. The end-to-end probability density in one dimension can be obtained from a random walk with n equally sized steps of length ℓ in one dimension, where forward and reverse steps are equally probable. If the first bead is set at $x_0 = 0$, then the last bead is placed by the last step at position x . In the continuous limit:

$$P(x, n) = \sqrt{\frac{1}{2\pi n\ell^2}} e^{-x^2/2n\ell^2} \quad (7.1.5)$$

$P(x, n)dx$ is the probability of finding the end of the chain with n beads at a distance between x and $x + dx$ from its first bead. Note this equates the rms end-to-end distance with the standard deviation for this distribution: $\langle R^2 \rangle = \sigma^2 = n\ell^2$.

To generalize eq. (7.1.5) to a three-dimensional chain, we recognize that propagation in the x, y , and z dimensions is equally probable, so that the 3D probability density can be obtained from a product of 1D probability densities $P(r) = P(x)P(y)P(z)$. Additionally, we need to consider the constraint that the distribution of end-to-end distances are equal in each dimension:

$$\langle \vec{R}^2 \rangle = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = n\ell^2$$

and since $\sigma_x^2 = \sigma_y^2 = \sigma_z^2$,

$$\langle \vec{R}^2 \rangle = 3\sigma_x^2 = n\ell^2$$

Therefore,

$$\begin{aligned} P(r, n) &= \sqrt{12\pi\sigma_x^2} e^{-x^2/2\sigma_x^2} \sqrt{12\pi\sigma_y^2} e^{-y^2/2\sigma_y^2} \sqrt{12\pi\sigma_z^2} e^{-z^2/2\sigma_z^2} \\ &= \left(\frac{3}{2\pi\sigma^2} \right)^{3/2} e^{-3r^2/2\sigma^2} \end{aligned}$$

To simplify, we define a scaling parameter with dimensions of inverse length

$$\beta = \sqrt{\frac{3}{2n\ell^2}} = \sqrt{\frac{3}{2}} \langle R^2 \rangle^{-1/2}$$

Then, the probability density in Cartesian coordinates,

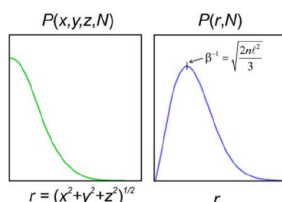
$$P(x, y, z, n) = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2 r^2} \quad \text{where } r^2 = x^2 + y^2 + z^2$$

Note the units of $P(x, y, z, n)$ are inverse volume or concentration. The probability of finding the end of a chain of n beads in a box of volume $dx dy dz$ at the position x, y, z is $P(x, y, z, n) dx dy dz$. This function illustrates that the most probable end-to-end distance for a random walk polymer is at the origin. On the other hand, we can also express this as a radial probability density that gives the probability of finding the end of a chain at a radius between r and $r + dr$ from the origin. Since the volume of a spherical shell grows in proportion to its surface area:

$$P(r, n)dr = 4\pi r^2 P(x, y, z, n)dr$$

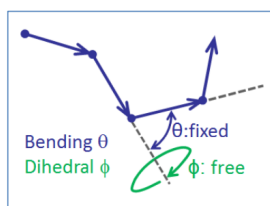
$$P(r, n) = 4\pi r^2 \left(\frac{3}{2\pi n \ell^2} \right)^{3/2} \exp \left[-\frac{3}{2} \frac{r^2}{n \ell^2} \right] \quad (7.1.6)$$

The units of $P(r, n)$ are inverse length. For the freely jointed chain, we see that $\beta^{-1} = \sqrt{2\langle R^2 \rangle / 3}$ is the most probable end-to-end distance.



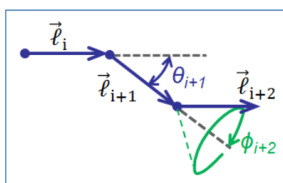
Freely Rotating Chain

An extension to the freely jointed chain that adds a single configurational constraint that better resembles real bonding in polymers is the freely rotating chain. In this case, the backbone angle θ has a fixed value, and the dihedral angle ϕ can rotate freely.



To describe the chain dimensions, we need to evaluate the angular bond correlations between segments. Focusing first on adjacent segments, we know that after averaging over all ϕ , the fixed θ assures that $\langle \vec{\ell}_i \cdot \vec{\ell}_{i+1} \rangle = \ell^2 \cos \theta$. For the next segment in the series, only the component parallel to $\vec{\ell}_{i+1}$ will contribute to sequential bond correlations as we average over ϕ_{i+2} :

$$\begin{aligned} \langle \vec{\ell}_i \cdot \vec{\ell}_{i+2} \rangle &= \langle \cos(\theta_i) \cos(\theta_{i+1}) - \sin(\theta_i) \sin(\theta_{i+1}) \cos(\phi_{i+1}) \rangle \\ &= \ell^2 \cos^2 \theta \end{aligned}$$



Extending this reasoning leads to the observation

$$\langle \vec{\ell}_i \cdot \vec{\ell}_j \rangle = \ell^2 (\cos \theta)^{j-i}$$

To evaluate the bond correlations in this expression, it is helpful to define an index for the separation between two bond vectors:

$$k = j - i$$

and

$$\alpha = \cos \theta$$

Then the segment orientation correlation function is

$$g(k) = \langle \vec{\ell}_i \cdot \vec{\ell}_j \rangle = \ell^2 \alpha^k$$

For a separation k on a chain of length n , there are $n - k$ possible combinations of bond angles,

$$\sum_{j \neq i} \langle (\cos \theta)^{j-i} \rangle = \sum_{k=1}^{n-1} (n-k) \alpha^k$$

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

From this you can obtain

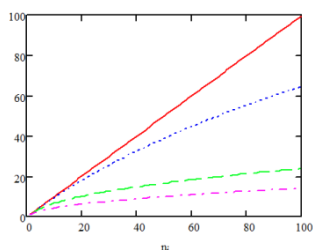
$$\langle R^2 \rangle = n\ell^2 \left(\frac{1+\alpha}{1-\alpha} - \frac{2\alpha(1-\alpha^n)}{n(1-\alpha)^2} \right)$$

In the limit of long chains ($n \rightarrow \infty$), we find

$$\langle R^2 \rangle \rightarrow n\ell^2 \left(\frac{1+\alpha}{1-\alpha} \right)$$

and

$$R_G = \sqrt{\frac{n\ell^2}{6} \left(\frac{1+\alpha}{1-\alpha} \right)}$$



$$\theta = \begin{pmatrix} 1 \\ 15 \\ 45 \\ 70.5 \end{pmatrix}$$

RMS end-to-end distance $\langle R^2 \rangle^{1/2}$ in units of ℓ as a function of n and θ

Restricted dihedrals

When the freely rotating chain is also amended to restrict the dihedral angle ϕ , we can solve the mean square end-to-end distance in the limit $n \rightarrow \infty$. Given an average dihedral angle,

$$\beta = \langle \cos \phi \rangle$$

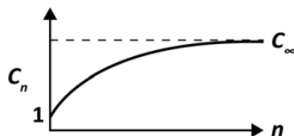
$$\langle R^2 \rangle = n\ell^2 \left(\frac{1+\alpha}{1-\alpha} \right) \left(\frac{1+\beta}{1-\beta} \right)$$

Nonideal Behavior

Flory characteristic ratio

Real polymers are stiff and have excluded volume, but the $R \sim \sqrt{n}$ scaling behavior usually holds at large n ($R \gg \ell_p$). To characterize non-ideality, we use the [Flory characteristic ratio](#):

$$C_n = \frac{\langle R^2 \rangle}{n\ell^2}$$



For freely jointed chains $C_n = 1$. For nonideal chains with angular correlations, $C_n > 1$. C_n depends on the chain length n , but should have an asymptotic value for large n : C_∞ . For example, if we examine long freely rotating chains

$$C_{\infty} = \lim_{n \rightarrow \infty} \frac{\langle R^2 \rangle}{n\ell^2} = \frac{1 + \alpha}{1 - \alpha} \quad \alpha = \cos \theta$$

(In practice, this limit typically holds for $n > 30$). Consider a tetrahedrally bonded polymer with full angle 109° ($\theta = 54^\circ$). then $\cos \theta = 1/3$, and $C_n = 2$. In practice, we reach the long chain limit C_{∞} at $n \approx 10$. This relation works well for polyglycine and polyethylene glycol (PEG).

Statistical segment or Kuhn length

How stiff or flexible a polymer is depends on the length scale of observation. What is stiff on one scale is flexible for another. For an infinitely long polymer, one can always find a length scale for which its statistics are that of a Gaussian random coil. As a result for a segment polymer, one can imagine rescale continuous segments into one longer "effective segment" that may not represent atomic dimensions, but rather is defined in order to correspond to a random walk polymer, with $C_n = 1$. Then, the effective length of the segment is ℓ_e (also known as the Kuhn length) and the number of effective segments is n_e . Then the freely jointed chain equations apply:

$$L_C = n_e \ell_e$$

$$\langle R^2 \rangle = n_e \ell_e^2$$

From these equations, $\ell_e = \langle R^2 \rangle / L_C$. We see that $\ell_e \gg \ell$ applies to stiff chains, whereas $\ell_e \approx \ell$ are flexible.

We can also write the contour length as $L_C = \gamma n \ell$, where γ is a geometric factor < 1 that describes constraint on bond angles. For a freely rotating chain: $\gamma = \cos(\theta/2)$. Using the long chain chain expressions ($n \rightarrow \infty$): $\langle R^2 \rangle = C_{\infty} n \ell^2$, we find

$$\ell_e = \left(\frac{C_{\infty}}{\gamma} \right) \ell$$

$$n_e = \left(\frac{\gamma^2}{C_{\infty}} \right) n$$

$$\ell_p = \left(\frac{C_{\infty} + 1}{2} \right) \ell$$

Representative values for polymer segment models

	C_{∞}	(n_e/n)	ℓ (nm)	ℓ_e (nm)	γ	ℓ_p (nm)
Polyethylene	6.7	($n > 10$)	0.154	1.24	0.83	
PEG	3.8			0.34		
Polyalanine	9	($n > 70$)	0.38	3.6	0.95	0.5
Polyproline	90	($n > 700$)				5-10
dsDNA	86		0.35	30-100	1	50
ssDNA						1.5
Cellulose						6.2
Actin				16700		10000-20000

1. C. R. Cantor and P. R. Schimmel, *Biophysical Chemistry Part III: The Behavior of Biological Macromolecules*. (W. H. Freeman, San Francisco, 1980), Ch. 18.; K. Dill and S. Bromberg, *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*. (Taylor & Francis Group, New York, 2010); P. J. Flory, *Principles of Polymer Chemistry*. (Cornell University Press, Ithaca, 1953).
2. C. R. Cantor and P. R. Schimmel, *Biophysical Chemistry Part III: The Behavior of Biological Macromolecules*. (W. H. Freeman, San Francisco, 1980), Ch. 19 p. 1033.

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