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The Freely Jointed Chain Model

1. The End-to-End Distance

A polymer chain can adopt many different conformations because rotation around the covalent single bonds in the backbone is associated with very low energetic barriers. On a timescale of just a few picoseconds, the chain can change its shape, and over longer times it explores an astronomically large number of possible conformations. Because of this random motion, the **size of a polymer chain** cannot simply be taken as the straight sum of all bond lengths, which would correspond to the fully stretched chain. Instead, **entropy drives the chain to coil up**. To describe the typical size of such a coil, we need a statistical description of the end-to-end distance, R_n.

A simple but powerful starting point is the **freely jointed chain model**, where we imagine a polymer chain consisting of n perfectly rigid segments of fixed length a. Each segment is represented by a vector $\vec{a}_i$, and we assume that:

- all vectors have the same length: $|\vec{a}_i| = a$,
- the segments can rotate freely and independently in any direction,
- the angle between two segments a_i and a_j is denoted as $\theta_{i,j}$,
- torsional angles and bond angles are ignored.

The **end-to-end distance** is then just the sum of all bond vectors:

$$\vec{R}_n = \vec{a}_1 + \vec{a}_2 + \cdots \vec{a}_i + \cdots + \vec{a}_n \quad . \tag{1}$$

Because each bond vector points in a random direction, the average chain has no preferred orientation and the average of $\vec{R}_n$ is zero:

$$\langle \vec{R}_n \rangle = \langle \vec{a}_1 + \vec{a}_2 + \cdots \vec{a}_i + \cdots + \vec{a}_n \rangle = \langle \sum_1^n \vec{a}_n \rangle = 0 \quad . \tag{2}$$

This does not mean the polymer has no size. It only tells us that if we average over many chains (or over a long time), the end-to-end vector cancels because the chain equally likely points in every direction.

To quantify the size of the chain, we therefore look at the **mean-square end-to-end distance, $\langle \boldsymbol{R_n^2} \rangle$**, which measures the squared magnitude (always positive), independent of direction. Expansion gives two contributions for $i = j$ and $i \neq j$:

$$\langle \vec{\mathrm{R}}_\mathrm{n}{}^2 \rangle = \langle (\vec{a}_1 + \vec{a}_2 + \cdots + \vec{a}_n) \cdot (\vec{a}_1 + \vec{a}_2 + \cdots + \vec{a}_n) \rangle = \langle \sum_{i=1}^n \vec{a}_i \cdot \vec{a}_i + \sum_{i \neq j}^n \vec{a}_i \cdot \vec{a}_j \rangle \quad . \tag{3}$$

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The first sum ($i = j$) contains just the squared lengths of each bond vector, giving na^2. The second sum ($i \neq j$) contains the scalar products of two different bond vectors, which can be rewritten in terms of the angle between them:

$$\langle \vec{R}_n{}^2 \rangle = na^2 + a^2 \left\langle \sum_{i \neq j}^{n} cos\, \theta_{i,j} \right\rangle \quad . \tag{4}$$

For a freely jointed chain, each bond is completely independent on the others and can point in any direction with equal probability. This means that $\theta_{i,j}$ can take any value between 0 and 2π and the average $\cos \theta_{i,j}$ is zero:

$$\langle \vec{R}_n{}^2 \rangle = na^2 \quad . \tag{5}$$

It is common to also use the **root-mean-square (rms) end-to-end distance**, which has the unit of a length:

$$\sqrt{\langle \vec{R}_n{}^2 \rangle} = \sqrt{n}a \quad . \tag{6}$$

This is the fundamental size scaling of an ideal chain: the size of the polymer coil increases linearly with the square root of the number of bonds, *n*. Equivalently, it scales with the square root of molar mass (since molar mass is proportional to n). If the molar mass doubles, the chain size increases only by a factor of $\sqrt{2} \approx 1.4$.

This square-root law is one of the most important results in polymer physics: it shows that polymers are **much more compact** than a fully stretched chain of the same number of bonds.

2. The Radius of Gyration

While the end-to-end distance is a natural size measure for linear chains, it is not useful for branched or ring polymers that either have too many ends or no ends at all. A more general measure of polymer size that applies to any architecture is the **radius of gyration**, R_g, which quantifies how the entire chain is spread around its center of mass. For a chain with n bonds (and hence $n + 1$ beads of equal mass), the positions of the beads are given by the vectors $\vec{r}_0$, $\vec{r}_1$, …, $\vec{r}_n$. The center of mass of the chain is then

$$\vec{r}_{\mathrm{cm}} = \frac{1}{n+1} \sum_{i=0}^{n} \vec{r}_i \quad . \tag{7}$$

The **squared radius of gyration** is defined as the mean-squared distance of all beads from the center of mass (and is usually averaged over the ensemble of polymer conformations):

$$\langle R_g{}^2 \rangle = \frac{1}{n+1} \sum_{i=0}^{n} \langle (\vec{r}_i - \vec{r}_{\mathrm{cm}})^2 \rangle \quad . \tag{8}$$

R_g thus represent the radius of the cloud of monomers around the center of the coil and also connects to its moment of inertia about the center of mass ($MR_g{}^2$). To evaluate Equation 8 directly, which contains

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the random center of mass, it is more convenient to rewrite the same quantity in terms of mean-square distances between all bead pairs (see Equations A1 to A6 in the Appendix for a derivation):

$$\langle {R_g}^2 \rangle = \frac{1}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{n} \langle (\vec{r}_i - \vec{r}_j)^2 \rangle \quad . \tag{9}$$

This identity is useful because, for an ideal freely jointed chain (see Equation 5), the mean-square distance between two beads depends only on the number of bonds separating them, not on their absolute positions along the chain:

$$\langle (\vec{r}_i - \vec{r}_j)^2 \rangle = |i-j|\, a^2 \quad . \tag{10}$$

Inserting Equation 10 into Equation 9 gives

$$\langle {R_g}^2 \rangle = \frac{1}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{i} |i-j|\, a^2 \quad . \tag{11}$$

Since the terms are symmetric in i and j, the inner sum can be restricted to $j < i$ and multiplied by 2 (see Equations A7 to A14 in the Appendix for a detailed derivation). The double sum can then be evaluated explicitly:

$$\langle {R_g}^2 \rangle = \frac{a^2}{(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{i-1} (i-j) = \frac{a^2}{(n+1)^2} \cdot \frac{n(n+1)(n+2)}{6} = \frac{a^2 n(n+2)}{6(n+1)} \quad . \tag{12}$$

For long chains ($n \gg 1$), the factor $(n+2)/(n+1)$ tends to 1. Thus, **the radius of gyration relates to the end-to-end distance as**

$$\langle {R_g}^2 \rangle = \frac{na^2}{6} = \frac{1}{6} \langle {R_n}^2 \rangle \quad . \tag{13}$$

The factor $1/6$ is universal for the freely jointed chain in the long-chain limit. This relation is particularly useful: experiments (light scattering, SAXS) typically measure R_g, while theory or simulations often provide R_n.

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Appendix

To derive the expression for the squared radius of gyration in terms of pairwise distances (Equation 9), let us denote the total number of beads by $N = n + 1$. Expanding the square in Equation 8 gives:

$$\langle {R_\mathrm{g}}^2 \rangle = \frac{1}{n+1} \sum_{i=0}^{n} \langle (\vec{r}_i - \vec{r}_\mathrm{cm})^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \left({\vec{r}_i}^2 - 2\vec{r}_i \vec{r}_\mathrm{cm} + {\vec{r}_\mathrm{cm}}^2 \right) \quad . \tag{A1}$$

Inserting the definition of the center-of-mass (Equation 7) into the terms containing $\vec{r}_\mathrm{cm}$ gives:

$$\langle {R_\mathrm{g}}^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \left[{\vec{r}_i}^2 \frac{1}{N} \sum_{j=1}^{N} 1 - 2\vec{r}_i \frac{1}{N} \sum_{j=1}^{N} \vec{r}_j + \left(\frac{1}{N} \sum_{j=1}^{N} \vec{r}_j \right)^2 \right] . \tag{A2}$$

Here, we introduced a redundant sum in the first term so that later all terms will share the denominator. The last term requires some care: since its inner sum does not depend on i, every contribution in the outer sum is identical. Summing N identical terms and dividing by N just gives back the same expression:

$$\frac{1}{N} \sum_{i=1}^{N} \left(\frac{1}{N} \sum_{j=1}^{N} \vec{r}_j \right)^2 = \left(\frac{1}{N} \sum_{j=1}^{N} \vec{r}_j \right)^2 \quad . \tag{A3}$$

This square can be expanded as the scalar product of two identical sums, which can be combined into a double sum:

$$\left(\frac{1}{N} \sum_{j=1}^{N} \vec{r}_j \right)^2 = \left(\frac{1}{N} \sum_{i=1}^{N} \vec{r}_i \right) \left(\frac{1}{N} \sum_{j=1}^{N} \vec{r}_j \right) = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{r}_i \vec{r}_j \quad . \tag{A4}$$

Substituting this back into Equation A2 gives

$$\langle {R_\mathrm{g}}^2 \rangle = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left({\vec{r}_i}^2 - 2\vec{r}_i \vec{r}_j + \vec{r}_i \vec{r}_j \right) = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left({\vec{r}_i}^2 - \vec{r}_i \vec{r}_j \right) . \tag{A5}$$

At this point, the expression looks asymmetric, since only ${\vec{r}_i}^2$ appears explicitly squared. However, the definition of ${R_\mathrm{g}}^2$ is symmetric in all beads. To restore this symmetry, we add the same expression with i and j swapped (the double sum does not depend on which index is called i or j) and divide by 2. In this way, both indices contribute equally:

$$\begin{aligned} \langle {R_\mathrm{g}}^2 \rangle &= \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left({\vec{r}_i}^2 - \vec{r}_i \vec{r}_j \right) = \frac{1}{2} \left[\frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left({\vec{r}_i}^2 - \vec{r}_i \vec{r}_j \right) + \frac{1}{N^2} \sum_{j=1}^{N} \sum_{i=1}^{N} \left({\vec{r}_j}^2 - \vec{r}_j \vec{r}_i \right) \right] \\ &= \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left({\vec{r}_i}^2 - 2\vec{r}_i \vec{r}_j + {\vec{r}_j}^2 \right) = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\vec{r}_i - \vec{r}_j \right)^2 . \end{aligned} \tag{A6}$$

Finally, reinserting $n = N - 1$ recovers Equation 9 in the main text.

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For evaluating the double sum in Equation 11, note that the inner term is symmetric: $|i-j| = |j-i|$. This means that every off-diagonal pair (i,j) with $i \neq j$ is counted twice in the full sum, while the diagonal terms $|i-i| = 0$ contribute nothing. We can therefore restrict the inner sum to the case $j < i$ and multiply by 2 to account for the symmetric contributions with $j > i$:

$$\sum_{i=0}^{n}\sum_{j=0}^{i}|i-j| = 2\sum_{i=0}^{n}\sum_{j=0}^{i-1}(i-j) = 2\sum_{i=0}^{n}\sum_{k=1}^{i}k \quad . \tag{A7}$$

For each fixed i, the inner sum runs over all $j < i$. Let us define $k = i - j$, with an increasing order, $k = 1$, …, i (although k runs from i down to 1, when j goes from 0 to $i-1$). Note that when $i = 0$, the inner sum is empty and contributes zero, so including $i = 0$ does not cause problems. The inner sum is a standard arithmetic series:

$$\sum_{k=1}^{i}k = 1 + 2 + \cdots + (i-1) + i = \frac{i(i+1)}{2} \quad . \tag{A8}$$

This formula can be rationalized by pairing the first and last term of the expansion, the second and second-to-last term, etc. There are $i/2$ such pairs, each giving $(i+1)$. Substituting Equation A2 into Equation A1 gives

$$\sum_{i=0}^{n}\sum_{j=0}^{i}|i-j| = 2\sum_{i=0}^{n}\frac{i(i+1)}{2} = \sum_{i=0}^{n}(i^2+i) = \sum_{i=0}^{n}i^2 + \sum_{i=0}^{n}i \quad , \tag{A9}$$

which reduces the original double sum to two well-known sums, one over the integers (see Equation A2), and one over their squares. A standard way to derive the latter is by using the identity obtained from expanding the differences of two consecutive cubes:

$$i^3 - (i-1)^3 = 3i^2 - 3i + 1 \quad . \tag{A10}$$

Summing both sides of Equation A4 from $i = 1$ to n gives:

$$\sum_{i=1}^{n}i^3 - \sum_{i=1}^{n}(i-1)^3 = 3\sum_{i=1}^{n}i^2 - 3\sum_{i=1}^{n}i + \sum_{i=1}^{n}1 \quad . \tag{A11}$$

On the left-hand side, each term in the first sum is canceled by a term in the second sum, except for the very last term n^3. Thus, only n^3 remains, and we obtain using the result from A2:

$$n^3 = 3\sum_{i=1}^{n}i^2 - 3\frac{n(n+1)}{2} + n \quad . \tag{A12}$$

Rearranging gives the closed form for the sum of squares:

$$\sum_{i=1}^{n}i^2 = \frac{1}{3}\left(n^3 + \frac{3n(n+1)}{2} - n\right) = \frac{2n^3+3n^2+n}{6} = \frac{n(2n^2+3n+1)}{6} = \frac{n(n+1)(2n+1)}{6} \quad . \tag{A13}$$

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Finally, substituting the results from Equations A2 and A7 into Equation A1 gives the explicit result for the double sum:

$$\sum_{i=0}^{n}\sum_{j=0}^{i}|i-j| = \sum_{i=0}^{n} i^2 + \sum_{i=0}^{n} i = \frac{n(n+1)(2n+1)}{6} + \frac{n(n+1)}{2} = \frac{n(n+1)(n+2)}{3}\,. \qquad \text{(A14)}$$

Here, the outer sum is written from $i = 0$, as in Equations A1 and A3. This is equivalent to starting at $i = 1$ (as used in Equations A5–A7) because the $i = 0$ term is zero and does not change the result.

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