# Complex Disordered Systems

Polymers: definitions

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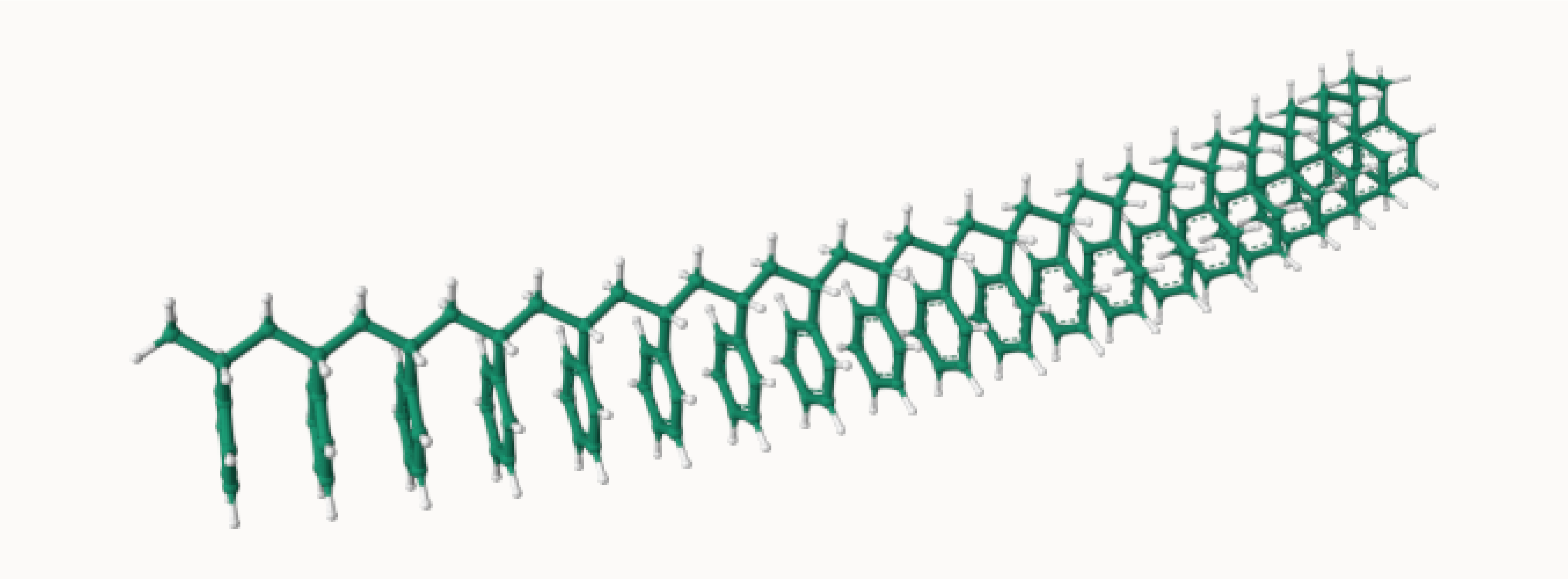
# What are Polymers?

- **Large molecules** made of many individual units: **monomers**
- Degree of polymerization: $N > 10^5$ units possible
- **Macroscopic behavior** dominated by large-scale properties
- **Statistical mechanics** needed even for single chains as they have many components subject to thermal fluctuations

Typical modelling progressing from fine structure details → **coarse-grained models**



Play with Polystyrene.

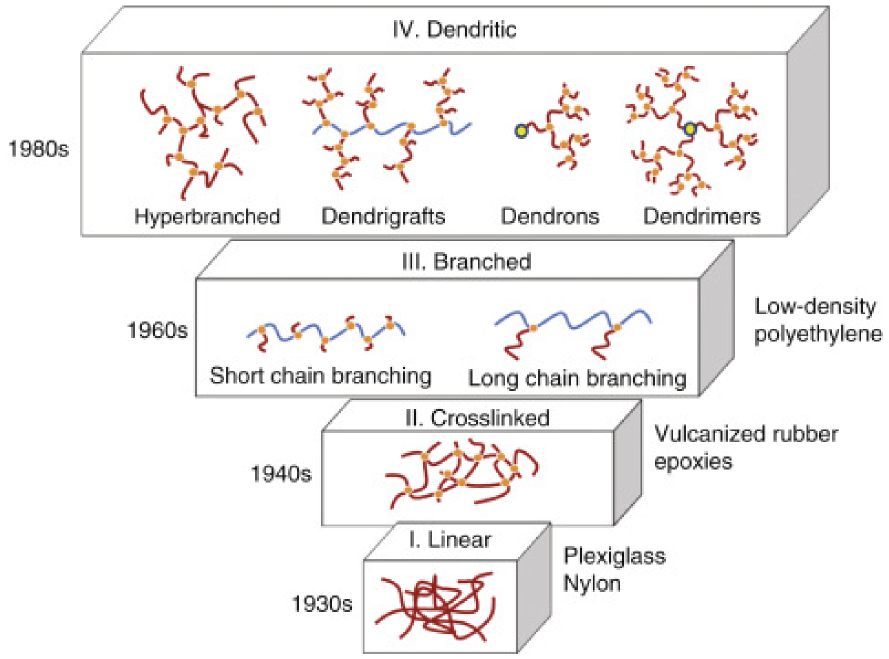
Downloading package: plotly

# Polymer Architectures

Polymers have many possible architectures:

- **Linear**: Straight chains (e.g., polyethylene)
- **Branched**: Main chain + side branches
- **Star**: Multiple arms from central core
- **Cross-linked**: Network structures (rubbers, thermosets)

**Focus**: We will only discuss linear homopolymers for theoretical simplicity.



the many possible polymer architectures, from Matyjaszewski and Möller, *Polymer Science: A Comprehensive Reference*, Elsevier (2012)

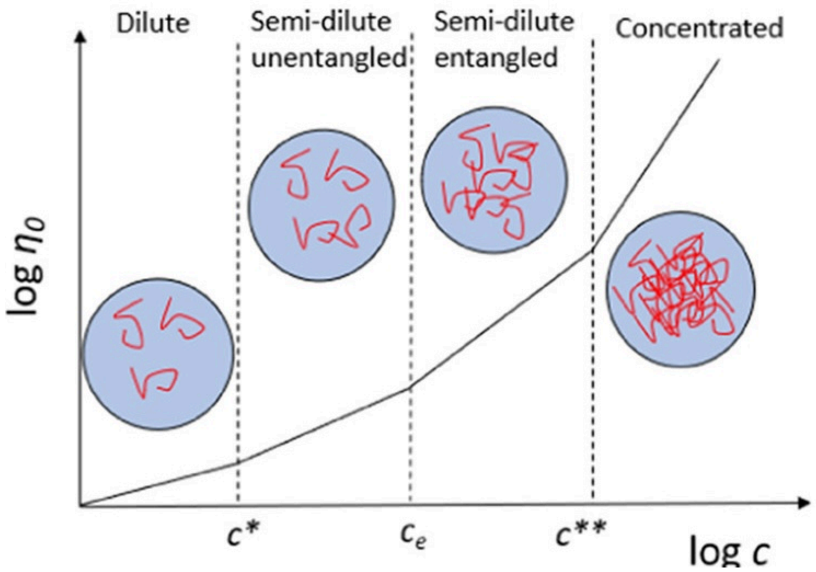
# Statistical Nature of Polymer Conformations

**Why statistical?**

- Enormous number of configurations
- Thermal fluctuations drive conformational changes
- Only **average properties** are measurable

**Separate regimes**

- *Dilute solutions*: Polymer-solvent interactions dominate
- *Concentrated*: Polymer-polymer **entanglements**



Viscosity as a function of polymer concentration

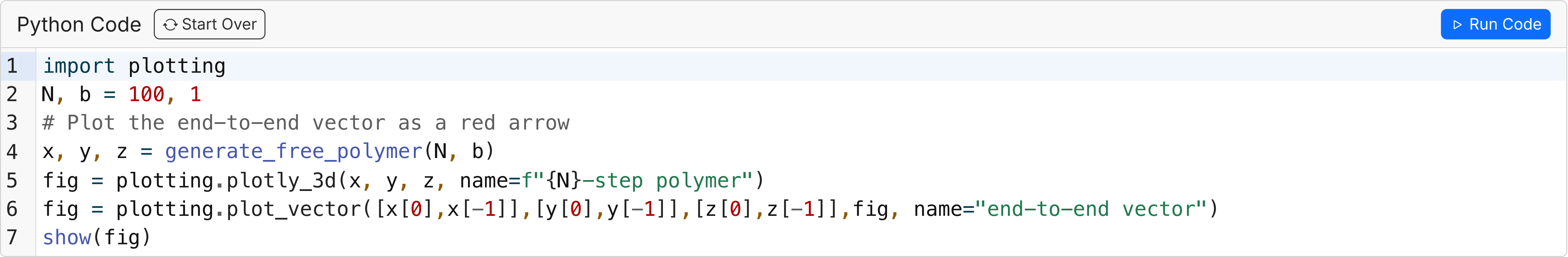
# Freely-Jointed Chain Model

**Assumptions:**

- Monomers at positions $\mathbf{R}_\mathrm{j}$ and connected by bonds $\mathbf{r}_j = \mathbf{R}_j - \mathbf{R}_{j-1}$ of length $|\mathbf{r}_j| = b_0$.
- $N$ segments of fixed length $b_0$
- All bond angles equally likely
- effectively, it produces a **random walk** in 3D
- The key quantity is th **end-to-end vector:**

$$\mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_N = \sum_{j=1}^{N} \mathbf{r}_j .$$

# Freely-Jointed Chain Model



```python
import plotting
N, b = 100, 1
# Plot the end-to-end vector as a red arrow
x, y, z = generate_free_polymer(N, b)
fig = plotting.plotly_3d(x, y, z, name=f"{N}-step polymer")
fig = plotting.plot_vector([x[0],x[-1]],[y[0],y[-1]],[z[0],z[-1]],fig, name="end-to-end vector")
show(fig)
```

# End-to-end vector statistics

The polymer fluctuates between all possible random-walk-like configurations at **fixed** inter-monomer distance.

The mean squared end-to-end distance is then simply

$$\begin{aligned}\langle \mathbf{R}^2 \rangle &= \left\langle \left( \sum_{i=1}^{N} \mathbf{r}_i \right) \cdot \left( \sum_{j=1}^{N} \mathbf{r}_j \right) \right\rangle \\ &= \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \mathbf{r}_i \mathbf{r}_j \right\rangle\end{aligned}$$

We can split the sum into the terms where $i = j$ and the rest. This yields in general

$$\langle \mathbf{R}^2 \rangle = N b_0^2 + \langle \mathbf{r}_i \mathbf{r}_j \rangle$$

We assume that successive segments are independent, so

$$\langle \mathbf{R}^2 \rangle = N b_0^2$$

> ⓘ **Note**
>
> Any similarities with previous results? Think about the MSD.

# End-to-end vector statistics

We can then use the results of by identifying $N$ (the number of moonomers) with $t$ (the number of steps).

$$\left\langle \mathbf{R}^2 \right\rangle = \left\langle R_x^2 \right\rangle + \left\langle R_y^2 \right\rangle + \left\langle R_z^2 \right\rangle = 3\sigma^2 = Nb_0^2 \Rightarrow \sigma^2 = \frac{Nb_0^2}{3}$$

where $\sigma$ is the variance per component.

For long chains the end-to-end distance is distributed as a **3D Gaussian**, centered at zero, with variance proportional to $N$:

$$P(\mathbf{R}) = \left( \frac{3}{2\pi N b_0^2} \right)^{3/2} \exp\left( -\frac{3\mathbf{R}^2}{2Nb_0^2} \right)$$

# Gyration tensor and radius of gyration

- The end-to-end vector is most meaningful for linear structures.
- Other conformation (compact, branched or star-shaped polymers) are better characterised by a measure of the (average) extent of the polymer chain: the**radius of gyration**,

The radius of gyration is a generic quantity that can be measured from any point cloud. It is closely linked to the (co)-variance of the set of points.

We start with the standard **centre of mass**

$$\mathbf{R}_{\mathrm{CM}} = \frac{1}{N}\sum_{j=1}^{N}\mathbf{R}_j$$

In general terms, we cna define a matrix called the **gyration tensor** (also called the configuration tensor):

$$\mathbf{S} = \frac{1}{N}\sum_{j=1}^{N}(\mathbf{R}_j - \mathbf{R}_{\mathrm{CM}}) \otimes (\mathbf{R}_j - \mathbf{R}_{\mathrm{CM}})$$

where $\otimes$ denotes the outer product, and $\mathbf{S}$ is a $3 \times 3$ symmetric matrix.

# Gyration tensor and radius of gyration

The elements of $\mathbf{S}$ are given by

$$S_{\alpha\beta} = \frac{1}{N}\sum_{j=1}^{N}(R_{j,\alpha} - R_{\mathrm{CM},\alpha})(R_{j,\beta} - R_{\mathrm{CM},\beta})$$

where $\alpha, \beta \in \{x, y, z\}$.

The **radius of gyration squared** is then simply the trace of this tensor (hence, invariant):

$$R_g^2 = \mathrm{Tr}(\mathbf{S}) = S_{xx} + S_{yy} + S_{zz}$$

The tensor is symmetric and real $\rightarrow$ diagonasable.

Eigenvalues and eigenvectors of $\mathbf{S}$ provide information about the principal axes and shape anisotropy of the polymer coil (do you remember 3D mechanics and Euler angles?).

The **tensor of gyration** corresponds to the **covariance matrix** of the positions $\mathbf{R}_j$.

For the ideal freely-jointed chain, the end-to-end vector and the radius of gyration are linked

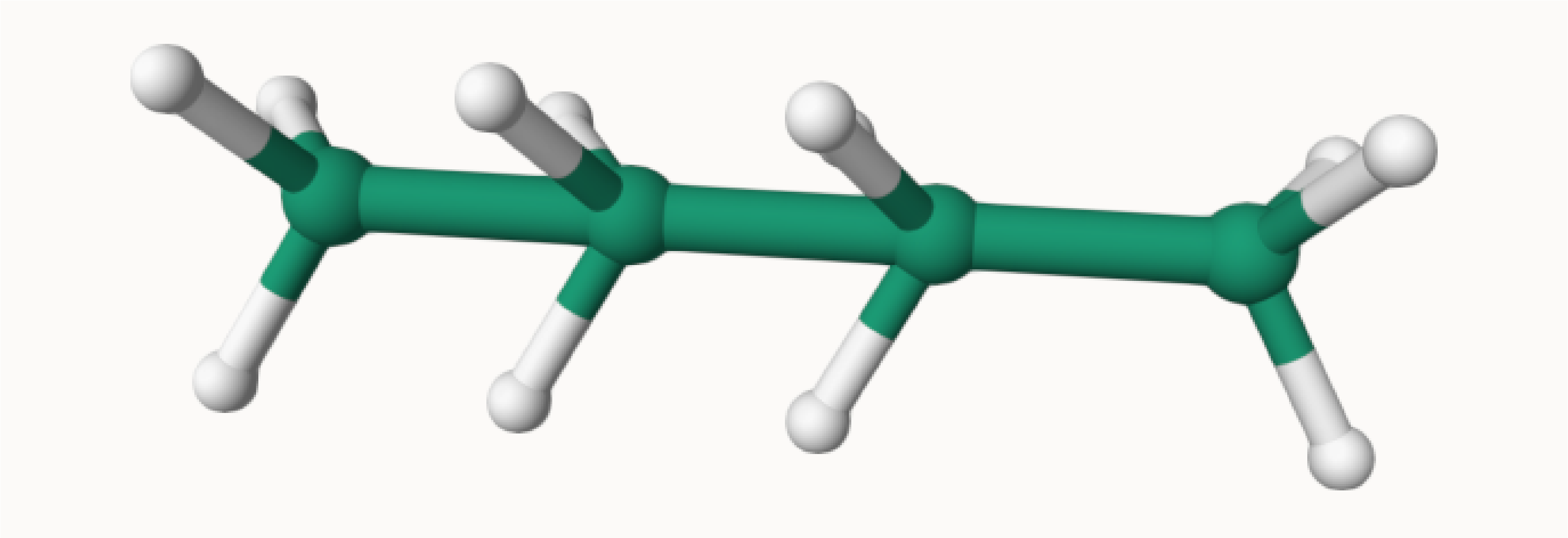
$$\boxed{\langle R_g^2\rangle = \frac{1}{6}\langle R^2\rangle}$$

# Freely-Rotating Chain

A more realistic model takes into account that bond angle are usually restricted.

Take $n$-butane:

$$\mathrm{H_3C - CH_2 - CH_2 - CH_3}$$

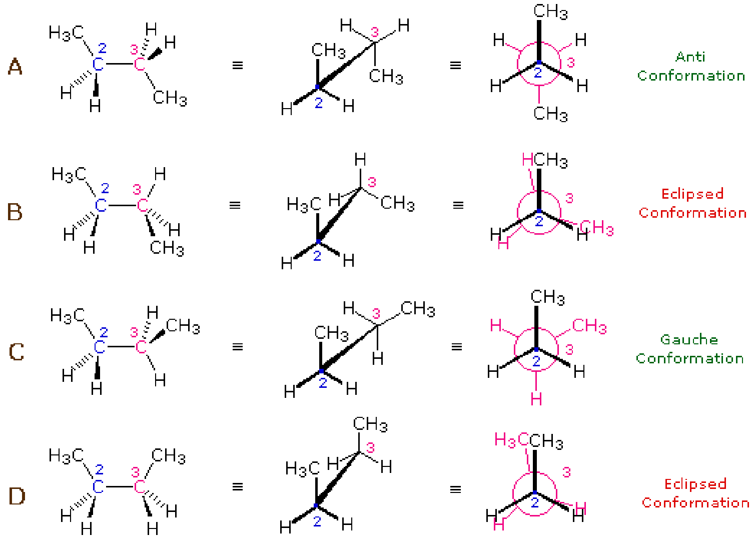


n-butane

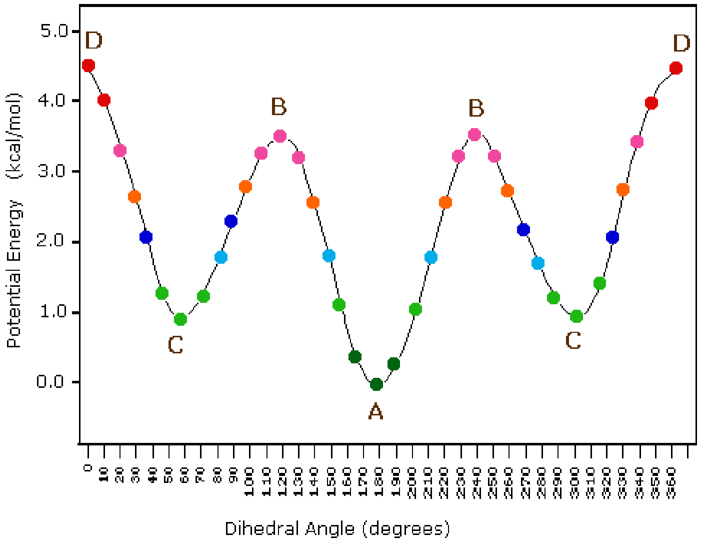
The valence (or bond) angle is the angle between two adjacent chemical bonds. The $C - C - C$ is around $112^\circ$.

# Freely-Rotating Chain: dihedral angle

**Rotations** about the C-C bond are possible and are qualified by the **dihedral (or torsional) angle**



Four conformers of butane, from LibreText Chemistry



Potential energy of the conformers

- At low temperatures ( $k_B T < \text{configurational energy}$) **A** (an *anti* conformation) .
- Rising $k_B T \sim$ there will also be **C** (gauche) configurations.
- At high temperatures ( $k_B T \gg$ config. energy), any angle will be possible.

# Freely-Rotating Chain Model

Simple but richer model than the freely jointed model:

- Fixed bond angle $\theta$
- Torsional angle $\varphi$ can take any value $0 \leq \varphi \leq 2\pi$.

Imagine we have a configuration $\{\mathbf{r}_l, \mathbf{r}_2, \ldots, \mathbf{r}_{j-1}\}$ and want to add the **next segment**.

- Average $\mathbf{r}_j$ over $\varphi$, while keeping $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{j-1}$ fixed, only the component in $\mathbf{r}_j$ direction remains:

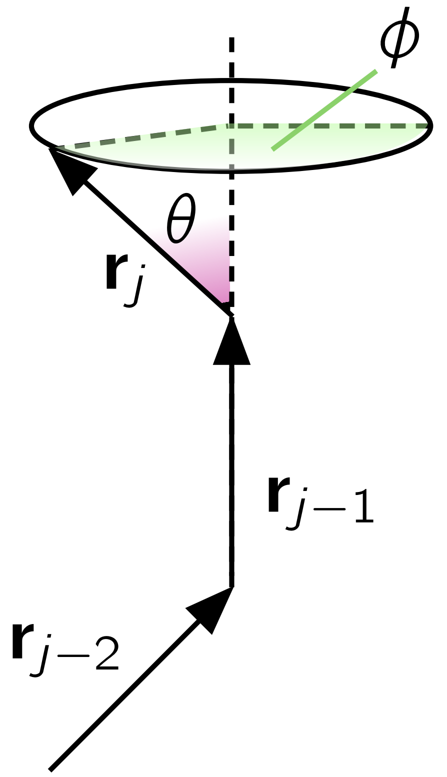
$$\langle \mathbf{r}_j \rangle_{\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_{j-1} \quad \text{fixed}} = \cos\theta \mathbf{r}_{j-1}$$

Multiplying both sides by $\mathbf{r}_k$ and averaging over all configurations gives

$$\langle \mathbf{r}_j \cdot \mathbf{r}_k \rangle = \cos\theta \, \langle \mathbf{r}_{j-1} \cdot \mathbf{r}_k \rangle \, .$$

Applying this relation recursively leads to

$$\langle \mathbf{r}_j \cdot \mathbf{r}_k \rangle = b_0^2 (\cos\theta)^{|j-k|}$$



Freely rotating chain model

# Freely-Rotating Chain Model

Given

$$\langle \mathbf{r}_j \cdot \mathbf{r}_k \rangle = b_0^2 (\cos\theta)^{|j-k|}$$

for $\cos\theta < 1$, correlations between $\mathbf{r}_j$ and $\mathbf{r}_k$ decrease with increasing distance $|j-k|$ .

We can link this to the **end-to-end distance** (proof in the lecture notes) and get the large $N$ limit

$$\left\langle R^2 \right\rangle \approx N b_0^2 + \frac{2b_0^2}{1-\cos\theta} N \cos\theta = N b_0^2 \left( \frac{1+\cos\theta}{1-\cos\theta} \right) = C N b_0^2$$

with

$$C = (1+\cos\theta)/(1-\cos\theta).$$

# Freely-Rotating Chain Model: Effect of Bond Angle

1. $\theta \to 0$: $C \gg 1$ → **Rigid rod**

   $$\langle R^2 \rangle \gg N b_0^2$$

   Nearly straight chain. The end-to-end distance is much larger than that of a flexible chain with the same number of segments.

2. $\theta \to \pi$: $C \ll 1$ → **Collapsed globule**

   $$\langle R^2 \rangle \ll N b_0^2$$

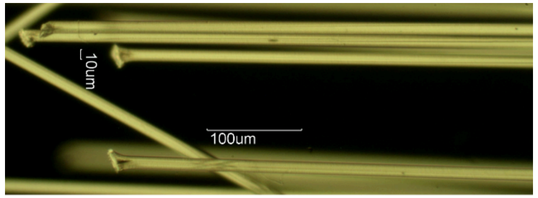
   Compact, globular, collapsed assembly. Examples: polypeptides, polystyrene in water, chromatin

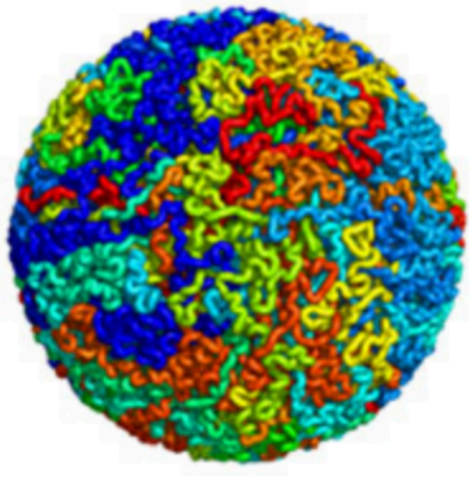
3. $\theta = 90^\circ$: $C = 1$ → **Ideal random walk**

   $$\langle R^2 \rangle = N b_0^2$$

   Corresponds to our original **freely jointed chain** (random walk).

   🪁 Play with models





Kevlar fiber (top) and chromatin globule model (bottom)

# Persistence and Kuhn Length

So in general $\langle R^2 \rangle \propto N$

- Replace real chain with equivalent **freely-jointed** chain
- Same contour length: $Nb_0 = N'b$
- Same end-to-end distance: $CNb_0^2 = N'b^2$

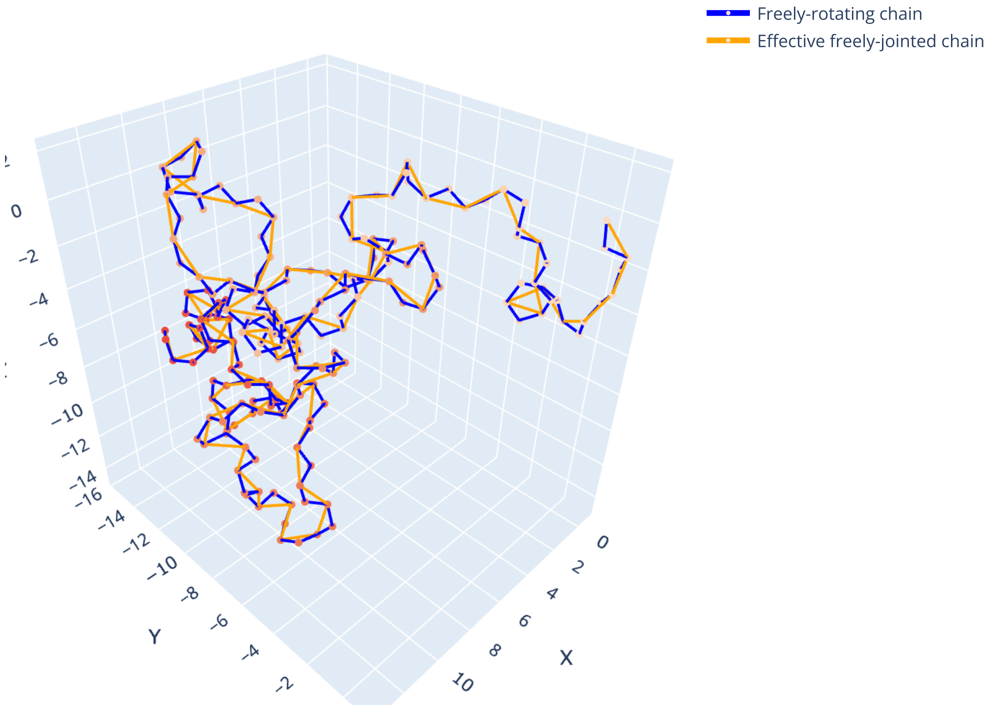
**Results:**

- **Kuhn length**: $b = Cb_0$
- **Persistence length**: correlations along the chain decay like

$$\langle \mathbf{r}_i \cdot \mathbf{r}_{i+n} \rangle = b_0^2 \langle \cos\theta \rangle^n = b_0^2 e^{-nb_0/l_p}$$

  with $\ell_p = b/2$
- **Kuhn segments**: $N' = N/C$

```
Original contour length: 200.0000
Coarse-grained contour length: 163.8304
```



# Excluded Volume Effects

True monomers **cannot occupy** same space

- local scale: restrictions on the bond angles stopping them from overlapping
- large distance excluded volume interactions between monomers, also deforming the chain

Consider that for a coiled polymer

$$V_{\text{coil}} = \frac{4\pi}{3}\left(\langle R_g^2 \rangle^{1/2}\right)^3 \sim \frac{4\pi}{3} N^{3/2} b^3$$

So

$$\frac{V_{\text{monomers}}}{V_{\text{coil}}} = \frac{N b^3}{N^{3/2} b^3} \sim N^{-1/2}$$

For $N = 10^4$: only ~1% of coil volume occupied!

So **excluded-volume** interactions are meant to present a **small contribution**.

Yet they affect the **scaling properties**.

=

# Self-Avoiding Walk

**Balance of competing effects:**

1. **Entropy**: Favors compact configurations
2. **Excluded volume**: Favors chain expansion

Entropy :

$$S = k_B \ln(\text{ number of configurations })$$

For a given end-to-end vector the number of configurations scales as

$$P(\mathbf{R}) = \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{3/2} e^{-\frac{3R^2}{2\langle R^2\rangle}}$$

and so

$$S \sim \frac{-3k_B R^2}{2Nb^2} + \text{ terms indep. of R}$$

# Self-Avoiding Walk

The configurational part of the internal energy can be estimated by focusing on monomer-monomer contacts for monomers of volume $V_1$.

We approximate this with a *segment gas* confined in a volume $R^3$. The density (or probability) of contacts is

$$\rho_c = N^2 V_1 / R^3 \sim N^{1/2}$$

by using $R^2 \sim N$.

We have $\sim N^2 \rho_c$ pairs at some energy scale per bond $\varepsilon$ so

$$U \sim \varepsilon N^2 V_1 / R^3$$

and the total free energy is approximately

$$F = \frac{\varepsilon N^2 V_1}{R^3} + \frac{3 k_B T R^2}{2 N b^2}$$

(we are interested in scaling behaviour)

# Self-avoiding walk

From

$$F = \frac{\varepsilon N^2 V_1}{R^3} + \frac{3k_B T R^2}{2Nb^2}$$

we can find the minimum that satisfies $dF/dR = 0$

and get

$$R^5 = \frac{\varepsilon V_1 b^2}{k_B T} N^3 \sim \frac{\varepsilon}{k_B T} N^3 b^5$$

which ultimately is

$$\boxed{R \sim N^{3/5} b}$$

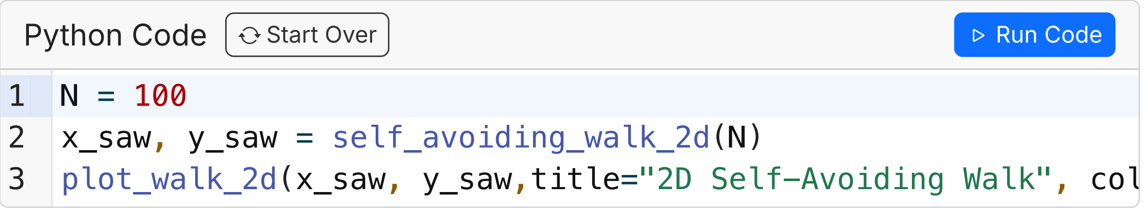
So ultimately we get a scaling exponent **different** from freely jointed chain:

- **freely jointed chain**: $R \sim N^{1/2}$
- **self-avoidign walks**: $R \sim N^{3/5}$

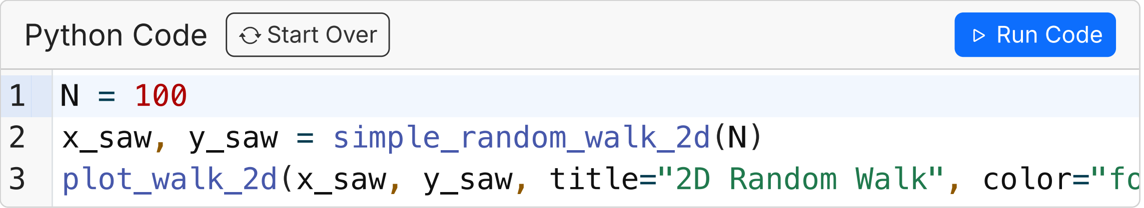
$$0.6 \neq 0.5$$

(if you are precise!)

# Self avoiding walk



```python
N = 100
x_saw, y_saw = self_avoiding_walk_2d(N)
plot_walk_2d(x_saw, y_saw,title="2D Self-Avoiding Walk", col
```



```python
N = 100
x_saw, y_saw = simple_random_walk_2d(N)
plot_walk_2d(x_saw, y_saw, title="2D Random Walk", color="fc
```