

Complex Disordered Systems

Polymers: definitions

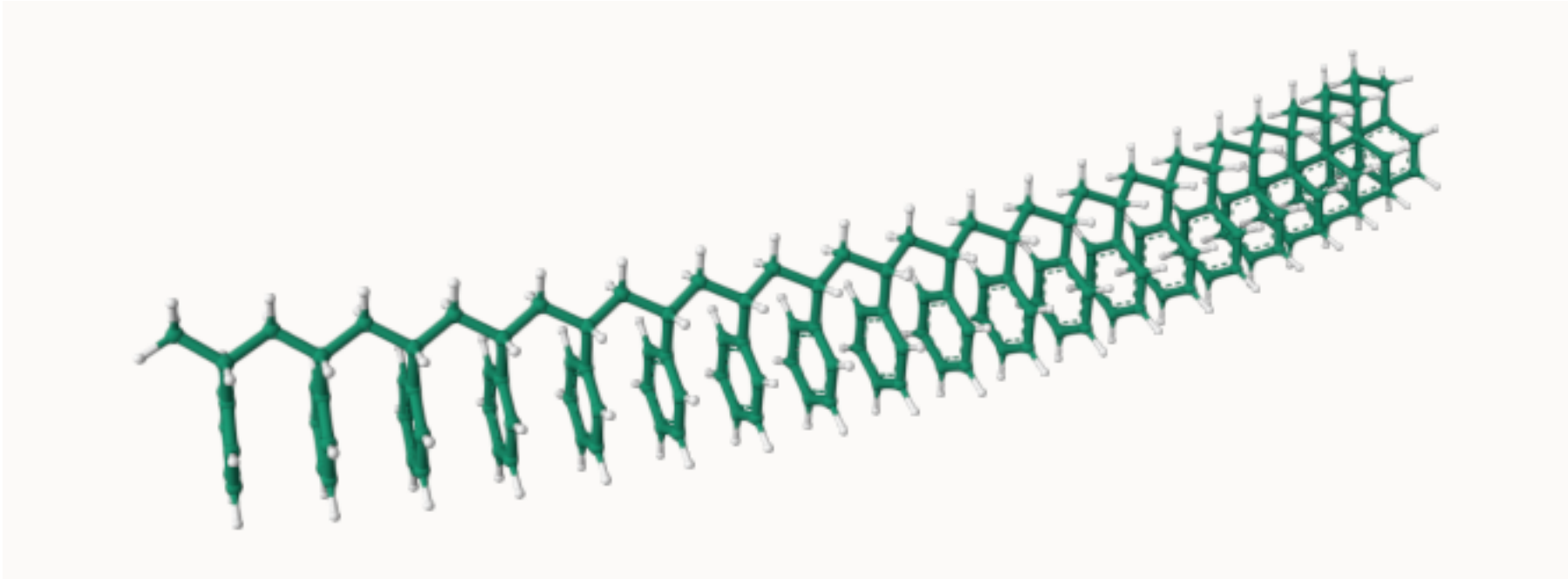
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What are Polymers?

- **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**

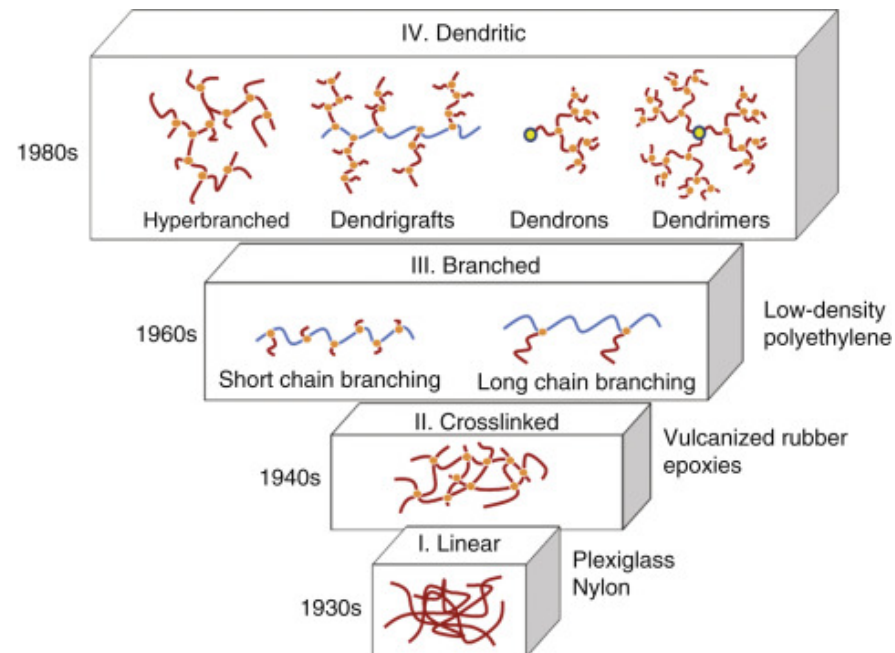


Polymer Architectures

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) Downloading package: plotly

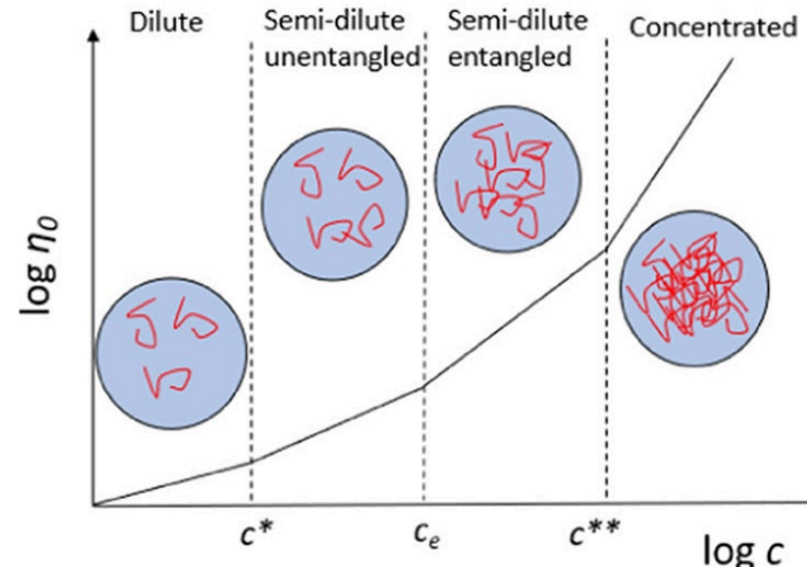


Statistical Nature of Polymer Conformations

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}_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 the **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 Code

[↺ Start Over](#)

[▶ Run Code](#)

```
1 import plotting
2 N, b = 100, 1
3 # Plot the end-to-end vector as a red arrow
4 x, y, z = generate_free_polymer(N, b)
5 fig = plotting.plotly_3d(x, y, z, name=f"{N}-step polymer")
6 fig = plotting.plot_vector([x[0], x[-1]], [y[0], y[-1]], [z[0], z[-1]], fig, name="end-to-end vector")
7 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

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

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

$$\langle \mathbf{R}^2 \rangle = Nb_0^2 + \langle \mathbf{r}_i \mathbf{r}_j \rangle$$

We assume that successive segments are independent, so

$$\langle \mathbf{R}^2 \rangle = Nb_0^2$$

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 monomers) with t (the number of steps).

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

where σ 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 :

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

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**

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

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

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

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

Gyration tensor and radius of gyration

The elements of \mathbf{S} are given by

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

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

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

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

The tensor is symmetric and real \rightarrow diagonalisable.

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 .

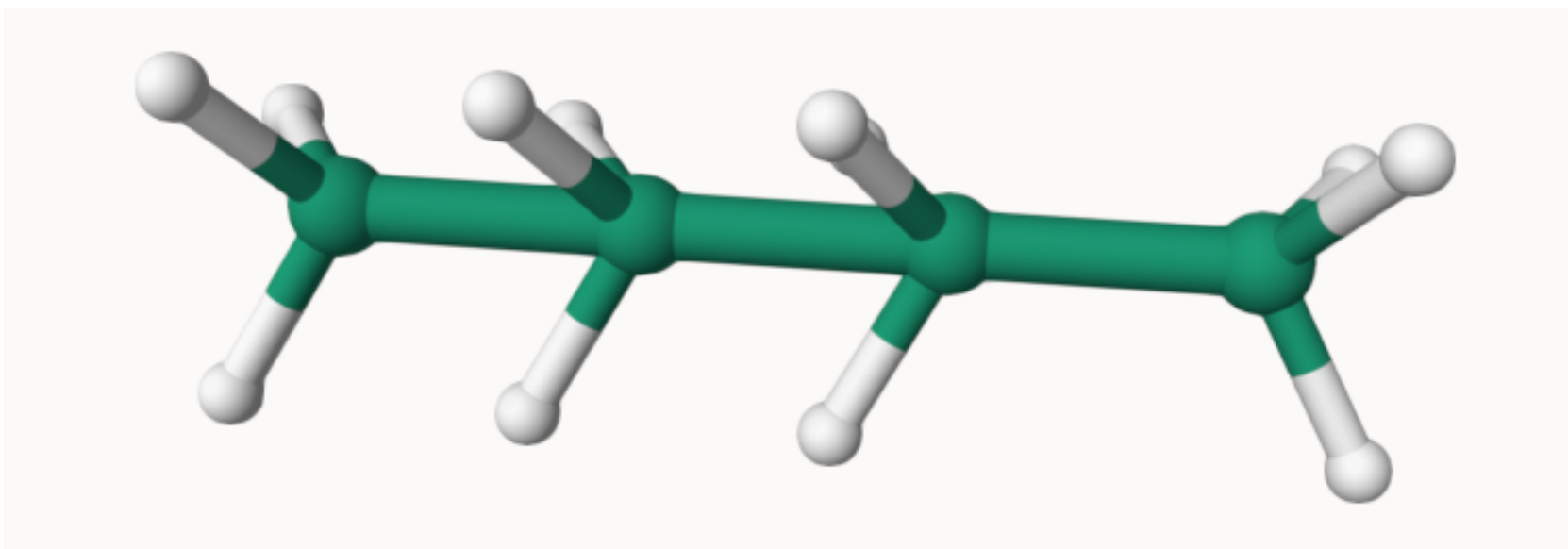
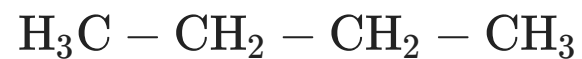
For the ideal freely-jointed chain, the end-to-end vector and the radius of gyration are linked

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

Freely-Rotating Chain

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

Take *n*-butane:

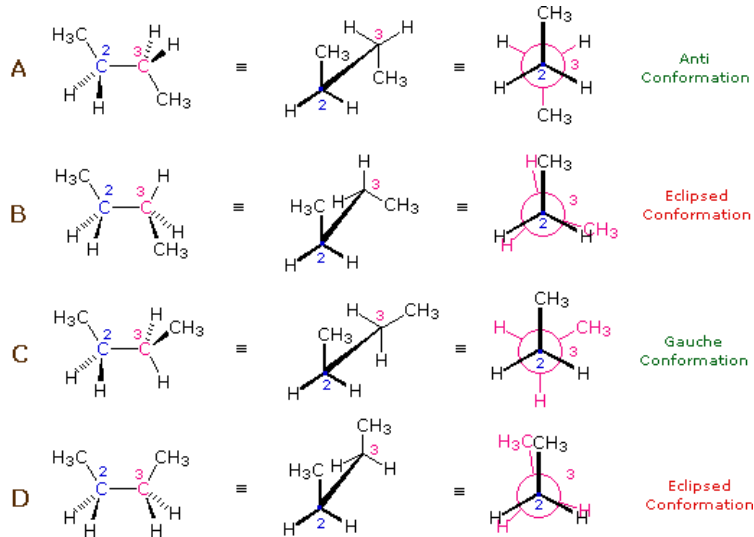


n-butane

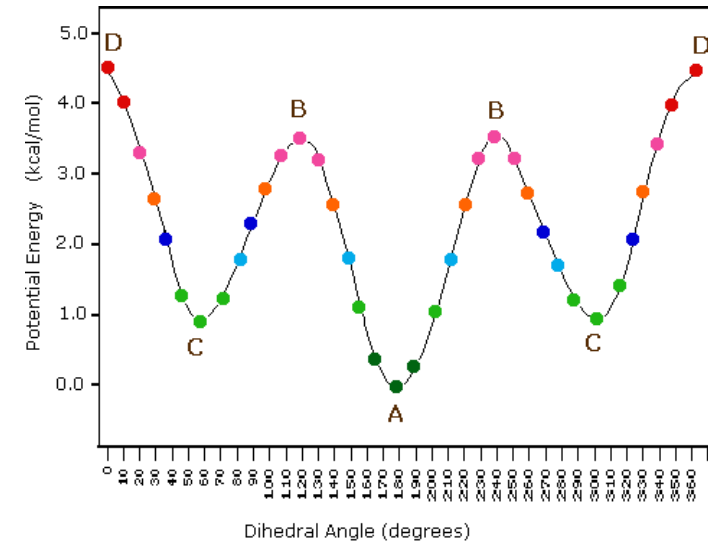
The valence (or bond) angle is the angle between two adjacent chemical bonds. The $\text{C} - \text{C} - \text{C}$ is around 112° .

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 ($k_B T \gg \text{config. energy}$), any angle will be possible.

Freely-Rotating Chain Model

Simple but richer model than the freeley jointed model:

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

Imagine we have a configuration $\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{j-1}\}$ and want to add the **next segment**.

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

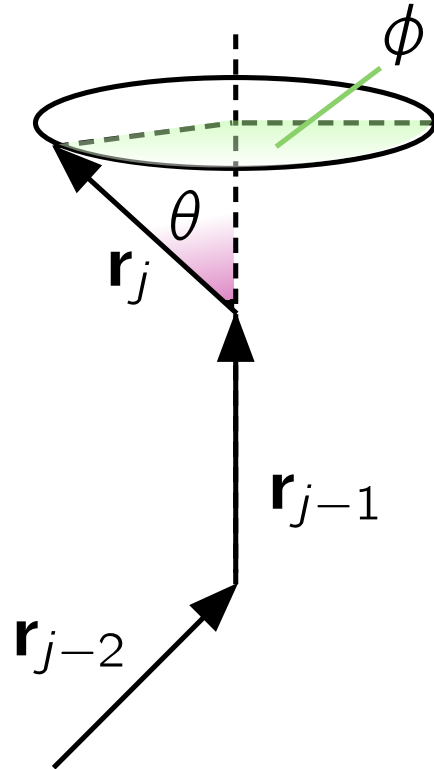
$$\langle \mathbf{r}_j \rangle_{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{j-1} \text{ fixed}} = \cos \theta \mathbf{r}_{j-1}$$

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

$$\langle R^2 \rangle \approx Nb_0^2 + \frac{2b_0^2}{1 - \cos \theta} N \cos \theta = Nb_0^2 \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) = CNb_0^2$$

with

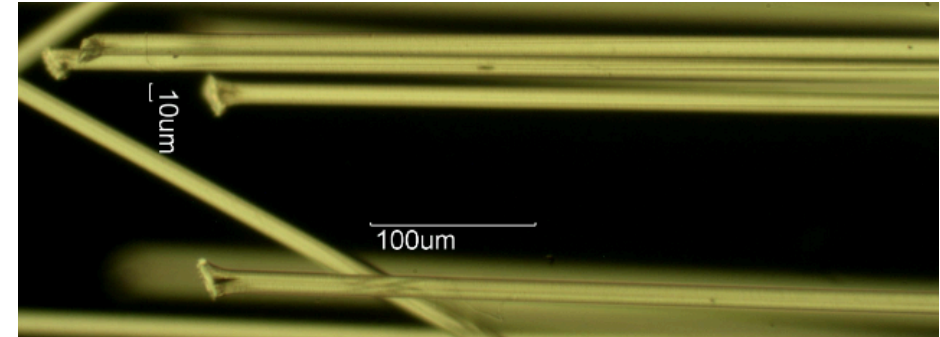
$$C = (1 + \cos \theta) / (1 - \cos \theta).$$

Freely-Rotating Chain Model: Effect of Bond Angle

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

$$\langle R^2 \rangle \gg Nb_0^2$$

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



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

$$\langle R^2 \rangle \ll Nb_0^2$$

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

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

$$\langle R^2 \rangle = Nb_0^2$$

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

 [Play with models](#)

