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Course Notes of Chapter 2

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1. Introduction: What is the “Size” of a Polymer Chain?

The remarkable properties of polymer materials are due to the large size of their macromolecules. But how can we express this “size”?

Take a simple example: polyethylene (PE). All backbone bonds are carbon-carbon single bonds. The lowest-energy conformation is a “zig-zag” shape, in which all torsion angles are fixed at $\varphi = 180°$. The length of such a fully stretched chain is called the **contour length**:

$$l_{\text{contour}} = na \quad , \tag{1}$$

where n is the number of bonds and a is the bond length (Slide 88).

However, for large n, this perfectly extended conformation is extremely unlikely. Entropy favors a vast number of different conformations in which the torsional angles vary. Ideal polymer chains therefore fold into **random coils.** Instead of measuring the maximum possible length, it is more useful to describe the **average size of the coil** (either as a time average of one chain or as an ensemble average over many chains).

2. Polymer Chain Conformations

Because the energy barrier for rotations of C-C single bonds is very low, polymer chains can explore many different conformations. A long, stretched chain placed in a solvent will quickly relax into a random coil. Solvent molecules transfer kinetic energy by collisions, and within just a few picoseconds the original zig-zag conformation is lost. The chain forms a fluctuating "ball" that constantly changes shape.

2.1 The Mean-Square End-to-End Distance of a Freely Jointed Linear Chain

One natural way to describe the chain size is the **end-to-end distance, R_n.** To calculate it statistically, we use the **freely jointed chain model** (Slide 90), which assumes:

- the chain consists of n identical rigid bonds of length a,
- each bond vector $\vec{a}_i$ can point into any direction independently of its neighbors,
- bond and torsional angle restrictions are ignored.

It can be shown (for details, see the Reader on the Freely Jointed Chain Model) that the **root-mean-square end-to-end distance** is

$$\sqrt{\langle {R_n}^2 \rangle} = \sqrt{n}\, a \quad . \tag{2}$$

This scaling law is fundamental and will be **a key result throughout the course**: the chain size grows only with the square root of the number of bonds (or equivalently, the square root of molar mass). For example, if the molar mass of a polymer doubles, its end-to-end distance increases only by a factor of $\sqrt{2} \approx 1.4$.

Moreover, because the distribution of R_n is governed by a Gaussian distribution function in the large-n limit, an ideal polymer chain is often referred to as a **Gaussian chain** (Slide 91).

Another, more general way to describe the size of the polymer coil is the **radius of gyration, R_g** (Slide 101), which is related to the end-to-end distance for linear chains in case of large n (see the Reader for a derivation):

$$\sqrt{\langle {R_g}^2 \rangle} = \frac{1}{\sqrt{6}} \sqrt{\langle {R_n}^2 \rangle}\, . \tag{3}$$

This relation is universal: in the long-chain limit it holds regardless of the details of the ideal chain model. Thus, both R_n and R_g capture the same scaling of polymer size and enter physcial properties in the same way.

2.2 Chain Rigidity

So far, we have treated bonds as if they could freely rotate. Real polymer chains, however, have fixed bond angles. For example, in PE the bond angle is about $\alpha \approx 70°$ ($180° - 110°$). A more realistic model is the **freely rotating chain**, in which α is fixed but the torsional angle ϕ is still free (Slide 93). In this case, one can derive a modified expression for the root-mean-square end-to-end distance:

$$\sqrt{\langle {R_n}^2 \rangle} = \sqrt{n}\, a \sqrt{\frac{1+\cos\alpha}{1-\cos\alpha}} \quad . \tag{4}$$

Compared to the freely jointed chain, the end-to-end distance is always larger: fixing the bond angle makes the chain less flexible and increases its effective size. More generally, any restriction of rotational freedom leads to a stiffer chain and a larger end-to-end distance. This idea is often summarized by introducing **Flory's characteristic ratio**:

$$\sqrt{\langle {R_n}^2 \rangle} = \sqrt{C_\infty n}\, a \quad , \tag{5}$$

where **$C_\infty \geq 1$ quantifies the stiffness of the chain** (Slide 95). Typical values of C_∞ differ considerably, even among vinyl polymers: PE, PP PS all have the same bond angle $\alpha \approx 70°$, yet steric hindrance of the side groups increases stiffness in the order PE < PP < PS (Slide 97).

Steric effects can be understood with the "**hindered rotation model**" (also called the *rotational isomeric state model*). Different torsion angles are not equally probable: staggered conformations (*trans*, *gauche*$^+$, *gauche*$^-$) are favored and associated with lower energies than eclipsed conformations (Slide 87). Bulky side groups such as $-CH_3$ (in PP) or phenyl rings (in PS) strongly disfavor certain torsional states, thus making the chain effectively stiffer.

Special cases, however, highlight the limits of this model. For example, in *para*-linked polyphenylene, the bond angle is effectively $\alpha = \pi/2$. In this case, the chain is completely rigid and $R_n = na$. The problem in this case is that correlations between successive bond vectors never decay to zero, even for long chains. The freely rotating chain model, however, only works in the limit of long chains, where correlations between $\bar{a}_i$ and $\bar{a}_j$ vanish, when i and j are far apart. Since this condition is never fulfilled in this example, the model fails.

In practice, polymer backbones are chemically much more complex than a simple sequence of identical bonds. Rigorous predictions of R_n require detailed conformational analysis (see Mattice & Suter: *Conformational Theory of Large Molecules: The Rotational Isomeric State Model in Macromolecular Systems*). Nevertheless, one robust qualitative rule remains: **stiffer catenary bonds or steric hindrance increase chain size relative to the freely jointed model.**

3. Real Polymer Chain Behavior

For real polymer chains, two important effects can no longer be ignored: the finite volume of chain segments and interactions between them.

- **excluded volume**: each monomer occupies space and prevents other monomers from overlapping. Real polymer chains may therefore be better mapped onto a **self-avoiding random walk**. Compared to the random coil of an ideal chain, the real chain is therefore more expanded because some conformations are forbidden (Slide 103).

- **monomer-monomer and monomer-solvent interactions**: chain segments interact both with each other and with their environment (e.g. solvent molecules). These interactions can be attractive or repulsive. If monomer-monomer and monomer-solvent interactions are equally favorable, there is no net effect. This special case is often modeled by a hard-sphere potential. Usually, however, monomers attract each other more strongly than they attract solvent molecules (due to their identical chemical nature). The result is a net attractive interaction, well described by the Lennard-Jones potential (Slide 104).

To quantify this balance, we use the **Mayer f-function** (from statistical mechanics). Its negative integral defines the excluded volume, i.e. the effective space blocked by each monomer segment (Slide 105). Both steric repulsion (positive contribution) and attractive interactions (negative contribution) determine its value. This framework allows us to classify solvents by quality:

- in good solvents, excluded volume is positive → chains are swollen.
- in poor solvents, attractive interactions dominate → chains collapse.
- in **the $\boldsymbol{\theta}$-state**, the two contributions cancel exactly → the excluded volume is zero and the polymer behaves like an ideal random coil.

The $\boldsymbol{\theta}$-state is of fundamental importance in polymer physics, because ideal chain models become valid. It is realized, for example, in polymer melts at any temperature (Slide 108). Ideal chain models are therefore not just an abstraction. They become quantitatively accurate in melts and provide a fundamental baseline for understanding viscoelastic and mechanical behavior in this state.