Chapter 3: CHAIN MODELS

3.1 Definitions

Configuration is the arrangement of a polymer in space.

Conformations are all accessible configurations a polymer can attain as a consequence of its flexibility.

We can reduce the polymer to the chain backbone. It is well defined by \( N \) bond vectors \( R_i \) (\( i=1,..., N \)) or \( (N+1) \) position vectors \( r_i \) (\( i=0,..., N \)). \( N \) is the degree of polymerization.
Degree of freedom \((\theta_1, \phi_1, \phi_2)\) and the start vector \(r_0\) are undefined

\[ \Rightarrow \quad \text{global degree of freedom of rotation and translation} \]

\[ \Rightarrow \quad \text{all others internal degree of freedom} \]

Restrictions in the degree of freedom:

1. fixed bond length: covalent bond energy >> thermal energy
2. fixed bond angle: determined by electronic configuration of atoms building the backbone
3. bond-rotation angle: relatively unrestricted

Comparison of single-bond in ethane and double-bond in ethene:
3.2 Characteristic quantities

**End-to-End distance:** \( R_E = r_N - r_0 = \sum_{j=1}^{N} R_j \)

Thermal movements: polymers adopt with time a large number of conformations, thus, thermal averages are considered. For an isotrope system: \( \overline{R_E} = \langle R_E \rangle = 0 \)

look at the mean-square average (norm):

\[
\overline{R_E^2} = \langle R_E^2 \rangle = \sum_{j=1}^{N} \sum_{k=1}^{N} \langle R_j R_k \rangle = \sum_{j=1}^{N} \langle R_j^2 \rangle + 2 \sum_{j=1}^{N} \sum_{k=j+1}^{N} \langle R_j R_k \rangle
\]

**General definition of the radius of gyration** \( R_g \):

The radius of gyration of a mass about a given axis is a distance \( R_g \) from the axis at which an equivalent mass is thought of as a point mass. The moment of inertia of this point mass and original mass about the axis are the same.

\[
R_g^2 = R_{g,x}^2 + R_{g,y}^2 + R_{g,z}^2
\]

**Radius of gyration** \( R_g \) is defined as the (average) of second moment (relative to the center of mass (rcm)) of the mass distribution:

\[
\overline{R_g^2} = \langle R_g^2 \rangle = \frac{\sum_{j=0}^{N} m_j \left( \langle r_j - r_{cm} \rangle \right)^2}{\sum_{j=0}^{N} m_j}
\]

with \( r_{cm} = \frac{\sum_{j=0}^{N} m_j r_j}{\sum_{j=0}^{N} m_j} \)

In case all masses are identical \( m_j = m \):

\[
\overline{R_g^2} = \frac{1}{N+1} \sum_{j=0}^{N} \left( \langle r_j - r_{cm} \rangle \right)^2 \quad \text{with} \quad r_{cm} = \frac{1}{N+1} \sum_{j=0}^{N} r_j
\]

With the help of the Lagrange Theorem:

\[
\overline{R_g^2} = \frac{1}{(N+1)^2} \sum_{j=1}^{N} \sum_{j=1}^{N} \langle r_j^2 \rangle \quad \text{with} \quad \langle r_j^2 \rangle = \langle (r_j - r_{j-1})^2 \rangle
\]
Characterization of the stiffness of a polymer:

How is the orientation of the end-to-end vector relative to the first bond vector?

**Projection Hₙ of Rₑ on the unit vector e₁**
(pointing in the direction of R₁)

Hₙ is the sum of the projections of all bond vectors Rᵢ on the direction of the first bond vector R₁.

\[ Hₙ = e₁Rₑ = \frac{RₑRₑ}{|R₁|} = \frac{R₁}{|R₁|} \sum_{j=1}^{N} R_j = \sum_{j=1}^{N} \frac{R_jR_j}{|R_j|} \]

The **persistence length lₚ** is defined as the thermal average in the limit of infinite long chain:

\[ lₚ = \lim_{N \to \infty} \langle Hₙ \rangle = \lim_{N \to \infty} \sum_{j=1}^{N} \frac{R_jR_j}{|R_j|} \]

### 3.3 Chain models

For the calculation of the correlations between bond vectors \( \langle R_jR_k \rangle \) and position vectors \( \langle \rhoᵢ² \rangle \) detailed assumptions about the chain statistics are necessary.

#### 3.3.1 Freely rotating chain

- bond angles are fixed = \( \theta₀ \)
- bond lengths are fixed = \( l₀ \)
- bond-rotation angles are evenly distributed over \( 0 \leq \phi \leq 2\pi \)
average over all orientations $\varphi_k$ of vector $R_k \Rightarrow$

projection on vector $R_{k-1}$: $\langle R_k \rangle_{\varphi_k} = R_{k-1} \langle \cos \theta_0 \rangle \times R_j$

average over remaining $\varphi_j$: $\langle R_k R_j \rangle = \langle R_{k-1} R_j \rangle \langle \cos \theta_0 \rangle$

continue until $k-1=j$:

$$\langle R_k R_j \rangle = \langle R_{k-1} R_j \rangle \langle \cos \theta_0 \rangle = l_0^2 \langle \cos \theta_0 \rangle^{k-j} \text{ with } \langle R_j^2 \rangle = l_0^2$$

$\langle \cos \theta_0 \rangle$ since $\theta_0$ fixed average not necessary but useful for freely jointed chain model

**End-to-End distance:**

$$\overline{R}_x = \sum_{j=1}^{N} \langle R_j^2 \rangle + 2 \sum_{j=1}^{N} \sum_{k=j+1}^{N} \langle R_j R_k \rangle = \frac{N l_0^2}{1 - \langle \cos \theta_0 \rangle} \left[ 1 + \langle \cos \theta_0 \rangle - \frac{2 \langle \cos \theta_0 \rangle [1 - \langle \cos \theta_0 \rangle^{N-1}]}{N (1 - \langle \cos \theta_0 \rangle)} \right]$$

For $N \gg 1$ ($\langle \cos \theta_0 \rangle \ll 1$):

$$\overline{R}_x = \frac{N l_0^2}{1 - \langle \cos \theta_0 \rangle} \Rightarrow \overline{R}_x \propto \sqrt{N}$$

Fully stretched chain ($\langle \cos \theta_0 \rangle = 1$):

$$\overline{R}_x = N l_0^2 \Rightarrow \overline{R}_x = N l_0$$

and the end-to-end distance of a chain with $|i-j|$ elements replace $N$ by $|i-j|$:

$$\langle r_{ij}^2 \rangle = \frac{|i-j| l_0^2}{1 - \langle \cos \theta_0 \rangle} \left[ 1 + \langle \cos \theta_0 \rangle - \frac{2 \langle \cos \theta_0 \rangle [1 - \langle \cos \theta_0 \rangle^{N-1}]}{|i-j| (1 - \langle \cos \theta_0 \rangle)} \right]$$

**Persistence length:**

$$l_p = \lim_{N \to \infty} \frac{\sum_{j=1}^{N} \langle R_j R_{j+1} \rangle}{\sum_{j=1}^{N} \langle R_j \rangle} \approx \frac{l_0}{1 - \langle \cos \theta_0 \rangle}$$

**Radius of gyration:**

$$\overline{R}_g^2 = \frac{1}{(N+1)^2} \sum_{j=1}^{N} \sum_{i=j+1}^{N} \langle r_{ij}^2 \rangle \approx \frac{1}{6} N l_0^2 \left( \frac{N+2}{N+1} \right) \left( 1 + \langle \cos \theta_0 \rangle \right)$$

For $N \gg 1$:

$$\overline{R}_g^2 \approx \frac{1}{6} N l_0^2 \frac{1 + \langle \cos \theta_0 \rangle}{1 - \langle \cos \theta_0 \rangle} \approx \frac{1}{6} \overline{R}_x^2$$
3.3.2 Freely jointed chain

Bond angles are evenly distributed over $0 \leq \theta \leq 2\pi$

Bond lengths are fixed $l_0$

Bond-rotation angles are evenly distributed over $0 \leq \phi \leq 2\pi$

$\Rightarrow$ Special case of a freely rotating chain with $\langle \cos \theta \rangle = 0$

End-to-End distance:

$$\overline{R}_E^2 = \frac{Nl_0^2}{1 - \langle \cos \theta \rangle} \left[ 1 + \langle \cos \theta \rangle - \frac{2\langle \cos \theta \rangle [1 - \langle \cos \theta \rangle^N]}{N(1 - \langle \cos \theta \rangle)} \right] = Nl_0^2$$

and for the end-to-end distance of a chain with $|i-j|$ elements replace $N$ by $|i-j|

$$\langle R_i^2 \rangle = |i-j|l_0^2$$

Persistence length:

$$l_p = \frac{l_0}{1 - \langle \cos \theta \rangle} = l_0$$

Radius of gyration:

$$\overline{R}_g^2 = \frac{1}{(N+1)^2} \sum_{i<j} (i-j)^2 = \frac{1}{6} \frac{(N-1)(N+1)}{N} l_0^2$$

For $N \gg 1$:

$$\overline{R}_g^2 \approx \frac{1}{6} N l_0^2 = \frac{1}{6} \overline{R}_E^2$$

The end-to-end distance $\overline{R}_E^2 = Nl_0^2$ is in analogy to a 3-dimensional random walk!
Brownian motion:

Any minute particle suspended in a liquid (or gas) moves chaotically under the action of collisions with surrounding molecules. The intensity of this chaotic motion is increased with an increase in temperature. (R. Brown in 1827)

With a random velocity, a Brownian particle of size $R$ will move in a tangled zigzag path, and will progress with time away from its initial location. The mean-square displacement of a Brownian particle is described by:

$$\langle \Delta r^2 \rangle = \langle [r(t) - r(t = 0)]^2 \rangle \propto t$$

compare to

$$\overline{R}_x^2 = \langle [r_N - r_0]^2 \rangle = N l_0^2$$

$l_0 = \text{distance covered in } \Delta t$

$N \equiv t$

snap shots of the random flight in time intervals $\Delta t$

Probability distribution

To determine the probability distribution of any global property of a polymer we need to know the single probabilities for the occurrence of a certain conformation.

The bond vectors in the freely jointed chain are not correlated, thus, the total probability is given by the product of the single probabilities.

$$\Psi(\{R_j\}) = \prod_{j=1}^{N} \Psi(R_j),$$

where the single probabilities are given by:

$$\Psi(R_j) = \frac{1}{4\pi l_0^2} \delta(|R_j| - l_0)$$

**Question:** What is the probability that a given vector $R$ is equal to the end-to-end vector?

**Ansatz:**

$$\Phi(R) = \int \Psi(\{R_j\}) \delta(R - R_E) d^3N \{R_j\}$$

**Calculation:**

$$\Phi(R) = \int \Psi(\{R_j\}) \delta(R - R_E) d^3N \{R_j\}$$

$$= \int dR_1 \int dR_2 \ldots \int dR_N \delta(R - \sum_{j=1}^{N} R_j) \Psi(\{R_j\})$$

with the definition of the delta-function

$$\delta(r) = \frac{1}{(2\pi)^3} \int e^{i\kappa r} dk$$
\[ \Phi(R) = \frac{1}{(2\pi)^3} \int dk \int dR_1 \int dR_2 \ldots \int dR_N \exp[ik(R - \sum_{j=1}^{N} R_j)] \Psi(\{R_j\}) \]

\[ = \frac{1}{(2\pi)^3} \int dk \exp(ikR) \int dR_1 \ldots \int dR_N \prod_{j=1}^{N} \exp(-ikR_j) \Psi(R_j) \]

\[ = \frac{1}{(2\pi)^3} \int dk \exp(ikR) \left[ \int dR \exp(-ikR) \Psi(R) \right]^N \]

up to here: same for the gaussian chain with polar coordinates \((\theta, \phi, r)\)

\[ \Phi(R) = \frac{1}{(2\pi)^3} \int dk \exp(ikR) \left[ \frac{\sin(kl_0)}{kl_0} \right]^N \]

approximation for large \(N\):

replace \( \left[ \frac{\sin(kl_0)}{kl_0} \right]^N \approx \left( 1 - \frac{(kl_0)^2}{6} \right)^N \approx \exp\left( -\frac{N(kl_0)^2}{6} \right) \)

vanishes also for large \( N \)!

\[ \Phi(R) = \frac{1}{(2\pi)^3} \int dk \exp(ikR) \exp\left( -\frac{N(kl_0)^2}{6} \right) \]

with \( kR = k_x R_x + k_y R_y + k_z R_z \) and \( k^2 = k_x^2 + k_y^2 + k_z^2 \)

\[ \Phi(R) = \exp\left( -\frac{3}{2} \frac{R^2}{2Nl_0^2} \right) \]

Result:

\[ \Phi(R) = \exp\left( -\frac{3}{2} \frac{R^2}{2Nl_0^2} \right) \]

Gaussian distribution

Effective bond length

In case only local correlations are effective, so that

\[ \Psi(\{R_j\}) = \prod_{j=1}^{N-j} \Psi(R_j, R_{j+1}, R_{j+2}, \ldots, R_{j+j_c}) \quad \text{with} \quad j_c << N \]

the real chain can always be described by a freely jointed chain with larger effective bond length, so that the relations \( \bar{R}_x^2 = Nl^2 \) and \( \bar{R}_y^2 = \frac{1}{6} \bar{R}_x^2 \) for large \( N \) still hold.
Characteristic ratio

\[ C_\infty = \lim_{N \to \infty} \frac{R_E^2}{N l_0^2} = \frac{l^2}{l_0^2} \Rightarrow l = \sqrt{C_\infty l_0} \]

e.g. freely rotating chain \[ C_\infty = \frac{1 + \langle \cos \theta_0 \rangle}{1 - \langle \cos \theta_0 \rangle} \]

Kuhn segment

is defined by a transformation of the real chain onto a freely jointed chain under preservation of the end-to-end distance \( R_E \) and the maximal possible end-to-end distance of the fully stretched chain \( R_{E,\text{max}} \)

\[ R_E^2 = N_k l_k^2 \quad \text{and} \quad R_{E,\text{max}} = N_k l_k \]

\( \Rightarrow \) the number and the length of the (effective) segments are rescaled.

\[ l_k = \frac{R_E^2}{R_{E,\text{max}}} \quad \text{and} \quad N_k = \frac{R_{E,\text{max}}^2}{R_E^2} \]

Segments of length \( l_k \) are the smallest units being statistically uncorrelated. The Kuhn segment is like the persistence length a measure of the chain stiffness.

e.g. freely rotating chain

\[ \theta_0 = 70.53^\circ \quad \text{(tetrahedron angle)} \]

\[ R_E^2 = N l_0^2 \frac{1 + \langle \cos \theta_0 \rangle}{1 - \langle \cos \theta_0 \rangle} \]

\[ R_{E,\text{max}} = N l_0 \langle \cos (\theta_0/2) \rangle = N l_0 \sqrt{\frac{1 + \langle \cos \theta_0 \rangle}{2}} \]

\[ l_k = \frac{R_E^2}{R_{E,\text{max}}} = \sqrt{2(1 + \langle \cos \theta_0 \rangle)} \frac{l_0}{1 - \langle \cos \theta_0 \rangle} \approx 2.45 \times l_0 \]

\[ N_k = \frac{R_{E,\text{max}}^2}{R_E^2} = N \frac{1 - \langle \cos \theta_0 \rangle}{2} \approx 0.33 \times N \]
3.3.3 Gaussian chain

On length scales much larger than the Kuhn length, the local nature of the chain segments plays no role. Many segments contribute to a Kuhn segment.

Assume that the effective segments are variable in length and follow a Gaussian-distribution with a standard deviation corresponding to the effective segment length:

$$\Psi(R_j) = \left(\frac{3}{2\pi l^2}\right)^{3/2} \exp\left(\frac{3R_j^2}{2l^2}\right) \quad \text{with} \quad l^2 = \langle R_j^2 \rangle = \int \Psi(R_j) R_j^2 d^3 R_j$$

Apart from this, the orientations of the bond vectors are completely free as for the freely jointed chain

$$\Phi(r_{ij}) = \left(\frac{3}{2\pi |i-j| l^2}\right)^{3/2} \exp\left(-\frac{3r_{ij}^2}{2|i-j|l^2}\right) \quad \text{Gaussian distribution}$$

$$\Rightarrow \quad \bar{R}_E^2 = Nl^2 \quad \text{and} \quad \bar{R}_g^2 \approx \frac{1}{6} Nl^2$$

in $\Phi(r_{ij})$ and $\bar{R}_E^2, \bar{R}_g^2$ the global properties are preserved!

$$\Rightarrow \quad \text{easy calculation of characteristic quantities when using independent variable following Gaussian distributions}$$

General description of chain configuration

Global properties can be calculated once the probability distribution of the chain configurations is known. Statistical mechanics: in thermal equilibrium $\Psi(\{R_j\})$ can be obtained from the Hamiltonian $H(\{R_j\})$

$$\Psi(\{R_j\}) = \frac{1}{Z} \exp\left(-\frac{H(\{R_j\})}{k_B T}\right) \quad \text{with normalization (state sum)} \quad Z = \int \exp\left(-\frac{H(\{R_j\})}{k_B T}\right) d^{3N} \{R_j\}$$

Enables the introduction of binding potential (see RIS model) and the calculation of the chain conformations in the presence of external fields, such as walls, electric, and stress fields.

Question: Which Hamiltonian describes the Gaussian chain?

$$\Psi(\{R_j\}) = \prod_{j=1}^{N} \Psi(R_j) = \left(\frac{3}{2\pi l^2}\right)^{3N} e^{-\frac{3}{2} \sum_{j=1}^{N} R_j^2}$$

$$\Rightarrow H(\{R_j\}) = \frac{1}{2} \sum_{\text{spring constant}} \sum_{j=1}^{N} R_j^2 \quad \text{(harmonic potential)}$$
The beads of the chain appear to be connected by harmonic springs with spring constant 
\[ k = 3k_B T / l^2 \]

see dynamics:
Rouse model (overdamped coupled harmonic oscillator)

Stretching of the chain results in a reduction of accessible conformations and consequently in a reduction of the entropy of the polymer chain. The elastic forces between the segments are purely of entropic nature and are not due to changes in the internal energy. Thus, the Hamiltonian of a Gaussian chain is considered to describe a pseudo-potential rather than a real interaction potential.

**Characteristic ratio for different polymers**

<table>
<thead>
<tr>
<th>polymer</th>
<th>solvent</th>
<th>T(°C)</th>
<th>( C_\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyethylene</td>
<td>Dodecanol 1</td>
<td>138</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>Diphenylmethan</td>
<td>142</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>α-Cl-Naphtalin</td>
<td>140</td>
<td>6.6</td>
</tr>
<tr>
<td>polystyrene, atactic</td>
<td>Cyclohexan</td>
<td>34.8</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>Diäthylmalonat</td>
<td>35.9</td>
<td>9.9</td>
</tr>
<tr>
<td>polydimethysiloxan</td>
<td>various</td>
<td>2 to 90</td>
<td>5.7 to 6.2</td>
</tr>
</tbody>
</table>

freely rotating chain:

\[ C_\infty = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \]

with:

\[ \theta = 70.53° \]

\[ \Rightarrow \quad C_\infty \approx 2 \]

However, real chains are much stiffer!
RIS

Bond rotational potentials

The picture of unrestricted freedom of bond-rotation angles is oversimplified. Finite extension of atoms and side groups lead to "long-ranged" (excluded volume interactions, prohibition of chain intersections) as well as "short-ranged interactions". Due to sterical hindrance not all bond rotation angles have the same probability. Some bond-rotation angles are compared to other energetically favorable.

Bond rotational potentials

\[ H = H(\{\Phi_i\}) = H(\Phi_1, \ldots, \Phi_{i-1}, \Phi_i, \Phi_{i+1}, \ldots, \Phi_N) \]

\[ \Psi(\{\Phi_i\}) = \frac{1}{Z} e^{\frac{-H(\{\Phi_i\})}{k_B T}} \]

with normalization

\[ Z = \int e^{\frac{-H(\{\Phi_i\})}{k_B T}} dN(\{\Phi_i\}) \]

RIS (rotational isomeric state)-model (l and \( \theta \) fixed) replaces the continuous variable \( \Phi_i \) by a discret set of angles \( \Phi_{i,v} \)

e.g. ethane, methane, azethaldehyde

staggered conformation

\[ H(\Phi) = \frac{H_0}{2} [1 - \cos(3\Phi)] \]

rotation barrier \( H_0 \) as a measure of the sterical interaction

\( H_0 \gg k_B T \) localized rotational states

equal minima
Barrier height

thermal energy at 300K ≈ 0.6 kcal/mole (1 Joule = 2.390 ×10⁻⁴ kcal)

<table>
<thead>
<tr>
<th>Compound and bond</th>
<th>Barrier height, kcal mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane C-H3—C-H3</td>
<td>2.9</td>
</tr>
<tr>
<td>propylene CH3—CH=CH2</td>
<td>1.98</td>
</tr>
<tr>
<td>azethaldehyde CH3—CH=O</td>
<td>1.17</td>
</tr>
<tr>
<td>butane CH3—CH=CH2</td>
<td>3.5e</td>
</tr>
<tr>
<td>methane CH3—OH</td>
<td>1.07</td>
</tr>
<tr>
<td>dimethylether CH3—OCH3</td>
<td>2.72</td>
</tr>
<tr>
<td>methanethiol CH3—SH</td>
<td>1.27</td>
</tr>
<tr>
<td>methylphosphine CH3—PH3</td>
<td>1.96</td>
</tr>
</tbody>
</table>

e.g. n-butane

\[
\begin{align*}
\text{trans} & : \Phi_t = 180^\circ : H_t = 0 \\
\text{gauche}^+ & : \Phi_g^+ = 60^\circ : H_g^+ > 0 \\
\text{gauche}^- & : \Phi_g^- = 300^\circ : H_g^- = H_g^+ > 0
\end{align*}
\]

with the probability \( \Psi(\Phi_v) = \frac{1}{Z} \exp \left(-\frac{H_v}{k_B T}\right) \) mit \( Z = \sum_v \exp \left(-\frac{H_v}{k_B T}\right) \)
Independent bond rotation potentials

\[ H(\{\Phi_i\}) = \sum_{i=1}^{N} H_i(\Phi_i) \Rightarrow C_{\infty} = \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \times \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \approx 2 \text{ for freely rotating chain} \]

\[ \langle \cos \theta \rangle = \frac{1}{3}; \quad \sigma = \exp \left( -\frac{H_v}{k_B T} \right) = 0.54 \]

\[ \langle \cos \Phi \rangle = \frac{1}{Z} \sum_{\nu} \exp \left( -\frac{H_v}{k_B T} \right) \cos \Phi_{\nu} = 1 - \frac{\sigma}{2} = 1 - \sigma \text{ with } Z = \sum_{\nu} \exp \left( -\frac{H_v}{k_B T} \right) = 1 + \sigma + \sigma = 1 + 2\sigma \]

\[ \Rightarrow \langle \cos \Phi \rangle = \frac{1 - \sigma}{1 + 2\sigma} \approx 0.22 \Rightarrow C_{\infty} \approx 3.14 \]

still much smaller than experimental value: \( C_{\infty}^{\exp} \approx 6.7 \Rightarrow \text{real chains are much stiffer!} \)

Bond rotation potentials are not independent!

rotation around single bond: rotation around two bonds:

\( \text{n-butane} \)

\( \text{trans} \) \( \text{gauche} \)

\( \text{n-pentane} \)

energetically unfavourable
Interdependent rotation potentials of adjacent bonds \( H(\{\Phi_i\}) = \sum_{i=2}^{N} H(\Phi_{i-1}, \Phi_i) \)

Ab-initio calculations: microscopic, quantum mechanic problem.
Semi-empirical methods: "molecular force field" calculations based on Newton's mechanics and electrostatics. Atoms are replaced by beads and bonds by springs.
Goal: find 3-dim structure with minimal energy.

e.g. polyethylene:

\[ C_N = \begin{cases} \text{Interdependent rotations} \\ \text{Independent hindered rotations} \\ \text{Free rotation} \end{cases} \]

\[ C_{44} \quad C_{40} \]

3.3.4 Worm-like chain (Kratky-Porod model)

Examples

\[ l_p \gg L \quad l_p \approx L \quad l_p \ll L \]

contour length \( L = \) maximum end-to-end distance of a polymer
bond lengths are fixed = \( l_0 \)

bond-rotation angles are evenly distributed over \( 0 \leq \phi \leq 2\pi \)

bond angles \( \{\theta_i\} \) subsequent segments should possess a certain stiffness against bending

**Question:** What is the persistence length and end-to-end distance of a worm-like chain?

**Discrete case:** tangential unit vector of the chain at position \( r_j \) is given by unit vector \( e_j \) parallel to the bond \( R_j \)

Curvature at the position \( r_j \): change in tangential unit vectors \( (e_j-e_{j-1}) \)

\[
\text{Pythagoras: } (e_j - e_{j-1})^2 = 2 \left( 1 - \cos \theta_j \right)
\]

**Ansatz:**

Bending energy is given by harmonic potential:

\[
H_B = \frac{\kappa}{2} \sum_{j=2}^{N} (e_j - e_{j-1})^2 = \kappa \sum_{j=2}^{N} \left( 1 - \cos \theta_j \right)
\]

If bending energy \( \kappa \) is large \( \kappa \gg k_B T \), the bond angles \( \theta_j \) will be small:

series expansion: \( \cos(\theta_j) \approx 1 - \frac{1}{2} \theta_j^2 + \ldots \Rightarrow H_B = \kappa \sum_{j=2}^{N} \left( 1 - \cos \theta_j \right) = \frac{\kappa}{2} \sum_{j=2}^{N} \theta_j^2 \)

\( \Rightarrow \) for the distributions of the conformations

\[
\Psi(\{\theta_i\}) = \left( \frac{\kappa}{2\pi k_B T} \right)^{N-1} \exp \left( -\frac{\kappa}{2k_BT} \sum_{j=2}^{N} \theta_j^2 \right) \text{ Gaussian distribution}
\]

since the \( \Phi_i = \Phi \) are free, the results of the freely-rotating chain can be taken:

\[
\overline{R_e^2} = \frac{Nl_0^2}{1-\langle \cos \theta \rangle} \left[ 1 + \langle \cos \theta \rangle - \frac{2\langle \cos \theta \rangle^2}{N(1-\langle \cos \theta \rangle)} \right]
\]

and \( l_p = \frac{l_0}{1-\langle \cos \theta \rangle} \)

the problem reduces to the calculation of \( \langle \cos \theta \rangle \)
\[ \langle \cos \theta \rangle = \int \Psi(\{\theta_i\}) \cos \theta_i \, d^{N-1} \{\theta_i\} = \exp\left( -\frac{k_B T}{2\kappa} \right) \]

\[ l_p = \frac{l_0}{1 - \exp\left( -\frac{k_B T}{2\kappa} \right)} \approx \frac{2\kappa}{k_B T} l_0 \quad \text{for} \quad \kappa >> k_B T \]

\[ \overline{R}^2_e = \frac{Nl_0^2}{1 - \exp\left( -\frac{k_B T}{2\kappa} \right)} \left[ 1 + \exp\left( -\frac{k_B T}{2\kappa} \right) - \frac{2\exp\left( -\frac{k_B T}{2\kappa} \right)[1 - \exp^{N}\left( -\frac{k_B T}{2\kappa} \right)]}{N(1 - \exp\left( -\frac{k_B T}{2\kappa} \right))} \right] \]

\[ \overline{R}^2_e \] expressed as a function of \( l_p, l_0 \) and \( L = Nl_0 \)

\[ \overline{R}^2_e = L(2l_p - l_0) - 2l_p(l_p - l_0) \left[ 1 - \left( 1 - \frac{l_0}{l_p} \right)^N \right] \]

for large \( N \) replace \( \left( 1 - \frac{l_0}{l_p} \right)^N \approx \exp\left( -\frac{Nl_0}{l_p} \right) \)

\[ \Rightarrow \overline{R}^2_e = L(2l_p - l_0) - 2l_p(l_p - l_0) \left[ 1 - \exp\left( -\frac{L}{l_p} \right) \right] \]

e.g. DNA

length 10-100\( \mu \)m
extension to full length

persistence length of 50nm
Kuhn segments: 100nm

dashed line:
freely-jointed chain model

solid line:
worm like chain model

free energy: \( F = \frac{3k_B T}{2} \frac{z^2}{\langle R^2_{E,0} \rangle} \)

required force: \( f = \frac{\partial F}{\partial z} = 3k_B T \frac{z}{\langle R^2_{E,0} \rangle} \)
3.4 Polymer solutions

Up to now we neglected any "long-ranged" interactions involving chain segments well separated along the chain. Backfolding of the chain due to the high chain flexibility has the consequence that distant chain segments can become very close to each other. However, chain segments have finite extension and interpenetration of volume occupied by other segments is forbidden.

This effect is called excluded volume interaction with the consequence that the extension of the coil will be larger than that of an "ideal chain" without excluded volume interactions. Excluded volume interactions lead to swelling! In the melt the interaction between segments in one chain is equal to the interaction with neighboring chains. The segment concentration is high and a segment of one chain is in the average surrounded by many segments belonging to other chains.

⇒ excluded volume interaction is screened!

In the melt the chains behave like "ideal chains" and the simple chain model introduced so far hold. In solution the interaction between solvent molecules and monomers is in the general case different to the monomer-monomer interactions. Solvent-monomer interaction is temperature dependent and only at the so called θ temperature, both solvent-monomer as well as monomer-monomer interaction are equal.

Radius of PS in cyclohexane as a function of the solvent quality
Gaussian chain with excluded volume interaction

Also excluded volume interaction is short-ranged (of local nature), it effects distant segments on the chain. The concrete nature might be complicated but unimportant on larger scales.

\[ H_{ij, \text{excl}} = \nu k_B T \delta(r_i - r_j) \Rightarrow \text{in total } H_{\text{excl}} = \frac{1}{2} \nu k_B T \sum_{i=0}^{n} \sum_{j=0}^{n} \delta(r_i - r_j) \]

Here \( \nu \) represents the excluded volume and \( \delta \) the delta function.

For a Gaussian chain with excluded volume interactions we obtain for the probability distribution:

\[ \Psi\left(\{r_i\}\right) \propto \exp\left[-\frac{H_G\left(\{r_i\}\right) + H_{\text{excl}}\left(\{r_i\}\right)}{k_B T}\right] \propto \exp\left[-\frac{3}{2} \sum_j (r_j - r_{j-1})^2 - \frac{\nu}{2} \sum_{i,j} \delta(r_i - r_j)\right] \]

Rigorous solution of the problem not possible!

**Flory theory**

*Question:*
What is the end-to-end distance \( \langle R^2_e \rangle \) of a chain with excluded volume interaction?

We start with a chain with radius \( R \) and \( N \) segments for a particle with arbitrary dimension \( d \).

Excluded volume interaction is proportional to the number of pair contacts \( \propto c^2 \) where \( c \) is the concentration.

We obtain for the internal chain concentration: \( c_{\text{int}} = \frac{N}{R^d} \)

Energy for one pair contact \( f_{\text{excl}} \approx k_B T \nu(T)c^2l^d \) \( (\nu \text{ excluded volume has dimension of a } d\text{-dimensional volume}) \)

In mean field theory the specific correlation between monomers (local heterogenities) are neglected \( \Rightarrow \) assumption: \( \left\langle c^2 \right\rangle \rightarrow \left\langle c \right\rangle^2 \propto c_{\text{int}}^2 \)

Total free energy by integration over total volume \( R^d \):

\[ F_{\text{excl}} \approx k_B T \nu(T)R^d c_{\text{int}}^2 l^d = k_B T \nu(T) \frac{N^2 l^d}{R^d} \]

Entropy contributes as elastic term relative to ideal chain:
Mean field approach (MFT)

The main idea of MFT is to replace all interactions to any one body with an average or effective interaction. This reduces any multi-body problem into an effective one-body problem. A many-body system with interactions is generally very difficult to solve exactly, except for extremely simple cases (Gaussian field theory, 1D Ising model.) The great difficulty (e.g. when computing the partition function of the system) is the treatment of combinatorics generated by the interaction terms in the Hamiltonian when summing over all states.

The goal of mean field theory (MFT, also known as self-consistent field theory) is to resolve these combinatorial problems. The main idea of MFT is to replace all interactions to any one body with an average or effective interaction. This reduces any multi-body problem into an effective one-body problem. The ease of solving MFT problems means that some insight into the behavior of the system can be obtained at a relatively low cost.

In field theory, the Hamiltonian may be expanded in terms of the magnitude of fluctuations around the mean of the field. In this context, MFT can be viewed as the "zeroth-order" expansion of the Hamiltonian in fluctuations. Physically, this means a MFT system has no fluctuations, but this coincides with the idea that one is replacing all interactions with a "mean field". Quite often, in the formalism of fluctuations, MFT provides a convenient launch-point to studying first or second order fluctuations.

In general, dimensionality plays a strong role in determining whether a mean-field approach will work for any particular problem. In MFT, many interactions are replaced by one effective interaction. Then it naturally follows that if the field or particle exhibits many interactions in the original system, MFT will be more accurate for such a system. This is true in cases of high dimensionality, or when the Hamiltonian includes long-range forces. The Ginzburg criterion is the formal expression of how fluctuations render MFT a poor approximation, depending upon the number of spatial dimensions in the system of interest.

While MFT arose primarily in the field of Statistical Mechanics, it has more recently been applied elsewhere, for example for doing Inference in Graphical Models theory in artificial intelligence.
3.6 Self-similarity and fractal dimension of polymers

Looking at ensemble averages the relation between $n$ and $\sqrt{\langle R^2 \rangle}$ stays the same for any subsection of the chain with $n$ segments as long as $N >> n >> 1$.

The relation between mass and volume defines the fractal dimension $D_f$

$$\text{mass } \propto \text{ volume } \propto R^{D_f}$$

$$n \propto \left(\sqrt{\langle R^2 \rangle}\right)^{D_f}$$

solid body 3-dim body $D_f = 3$
2-dim $D_f = 2$
1-dim $D_f = 1$

Polymers:

with excluded volume interaction

ideal chain $R^2 = Nl^2 \Rightarrow D_f = 2$
3-dim $R \propto N^{3/5} l \Rightarrow D_f = 5/3$
2-dim $R \propto N^{3/4} l \Rightarrow D_f = 4/3$
1-dim $R \propto Nl \Rightarrow D_f = 1$
3.7 Summary

characteristic quantities:  $R_g$, $R_E$, $l_P$ describe dimension & stiffness in an ensemble of polymers. All orientations have same probability in isotropic system $\Rightarrow <R_g>, <R_E>=0$

$\Rightarrow$ look at the norms (mean square values) $<R_g^2>$, $<R_E^2>$
$\Rightarrow$ geometrical considerations lead to $<R_g^2>$, $<R_E^2>$ and $l_P$ in terms of $<R_iR_j>$ and $(r_i-r_j)^2$
$\Rightarrow$ for the calculation of $<R_iR_j>$ and $(r_i-r_j)^2$ assumptions about the chain statistics are necessary / probability to find a certain $l, \phi, \theta$

Determination of the probability distribution of any global property requires the knowledge of the single probabilities for the occurrence of a certain conformation.

$\Rightarrow$ chain models

1. freely rotating chain  $l, \theta$ fixed & $\phi$ totally free
2. freely jointed chain  $l$ fixed & $\theta, \phi$ totally free

$\Rightarrow <R_E^2>=Nl^2$ and $<R_g^2>=Nl_P^2$
and its analogy to random walk (chaotic motion) of Brownian particles.

total probability $\Psi\{R_j\} = \prod_{j=1}^{N}\Psi(R_j)$

only local correlations $\Psi\{R_j\} = \prod_{j=1}^{N-1}\Psi(R_j, R_{j+1}, R_{j+2}, ..., R_{j+j_c})$ mit $j_c << N$

$\Rightarrow$ real chain can be transformed onto freely jointed chain with different segment length (and) segment number under preservation of global properties.

$\Rightarrow$ this led us to definition of characteristic ratio & Kuhn length (measure of chain stiffness).

one effective segment is made up by several real bonds $\Rightarrow$

3. Gaussian chain  $\theta, \phi$ totally free

effective segments are variable in length and follow a Gauss-distribution with a standard deviation corresponding to the effective segment length

$$\Psi(R_j) = \left(\frac{3}{2\pi l^2}\right)^{3/2} \exp\left(\frac{3R_j^2}{2l^2}\right) \text{ mit } l^2 = \langle R_j^2 \rangle = \int \Psi(R_j) R_j^2 d^3R_j$$

$$\Psi\{R_j\} = \prod_{j=1}^{N}\Psi(R_j) = \left(\frac{3}{2\pi l^2}\right)^{3N/2} \exp\left(-\frac{3}{2l^2}\sum_{j=1}^{N} R_j^2\right)$$
global properties are preserved!

**Statistical mechanics:** \( \Psi(\{R_j\}) \) can be obtained from the Hamiltonian \( H(\{R_j\}) \)

\[
\Psi(\{R_j\}) = \frac{1}{Z} e^{\frac{-H(\{R_j\})}{k_BT}} \quad \text{normalization} \quad Z = \int e^{\frac{-H(\{R_j\})}{k_BT}} d^{3N}\{R_j\}
\]

which Hamiltonian describes the Gaussian chain?

\( \Rightarrow \) harmonic potential

\[
H(\{R_j\}) = \frac{1}{2} \sum_{j=1}^{N} 3k_BT \frac{R_j^2}{l^2} \quad \text{spring constant}
\]

chain appears to be made up by beads connected by harmonic springs \( \Rightarrow \) **Rouse model** (overdamped coupled harmonic oscillator)

4. **RIS (Rotational Isomeric State model)** \( l, \theta = \text{fixed} \)
   replaces the continuous variable \( \Phi_i \) by a discreet set of angles \( \Phi_{i,\nu} \) where adjacent bonds are interdependent.

5. **worm-like chain model** \( l = \text{fixed} \& \phi = \text{totally free} \)
   restrictions to \( \theta \): subsequent segments posses a certain stiffness against bending.

so far only local interactions involving close-by bonds

**excluded volume interactions**

- interpenetration of volume occupied by other segments is forbidden.
- short-ranged but can involve distant chain segments on one chain.
- rigorous calculation of global properties is not possible.

\( \Rightarrow \) **Mean-Field Theory of Flory** for the free energy

one obtains for the extension of a polymer chain under excluded volume interactions \( R \propto N^\nu l \)

with the Flory-Huggins exponent \( \nu = \begin{cases} 3/5 & \text{for } d=3 \\ 3/4 & \text{for } d=2 \\ 1 & \text{for } d=1 \end{cases} \)

compare to ideal chain \( R \propto N^{1/2} l \)

Looking at ensemble averages polymers are self-similar structures i.e. **fractal objects** as long as subsections of the chains are considered which comprise much more than only one and much less than N segments.
Literature