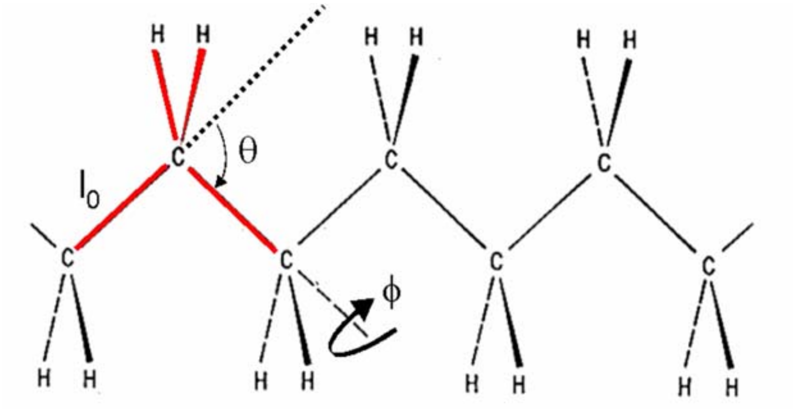
Chapter 3: CHAIN MODELS

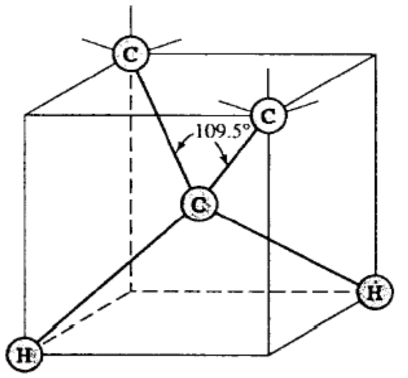
3.1 Definitions

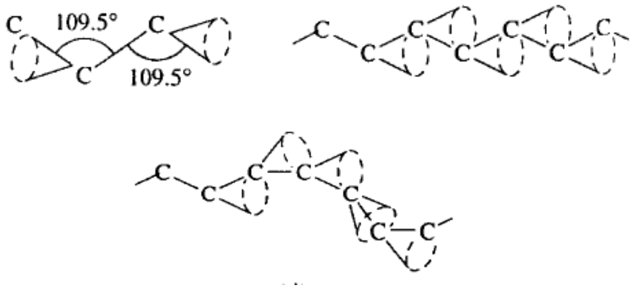
Configuration is the arrangement of a polymer in space.



bond angle θ
bond-rotation angle ϕ
bond length l_0

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 $\boldsymbol{R}_i$ (i=1,…, N) or (N+1) position vectors $\boldsymbol{r}_i$ (i=0,..., N). **N is the degree of polymerization.**

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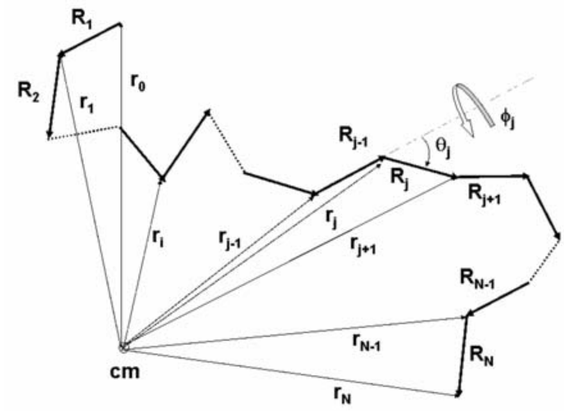


polar coordinates (θ_i,ϕ_i,$|R_i|$)

Degree of freedom (θ_1, ϕ_1, ϕ_2) and the start vector r_0 are undefined

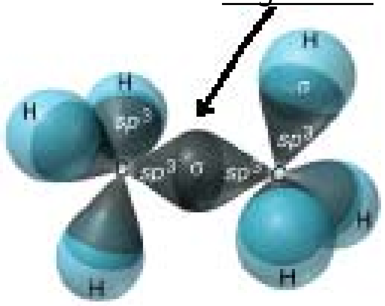
⇒ global degree of freedom of rotation and translation
⇒ all others internal degree of freedom

Restrictions in the degree of freedom:

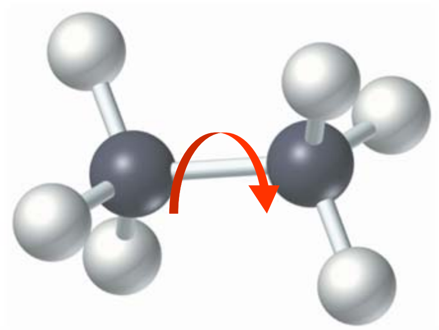
1. fixed bond length: covalent bond energy >> thermal energy
2. fixed bond angle: determined by electronic configuration of atoms building the backbone
3. bond-rotation angle: relatively unrestricted

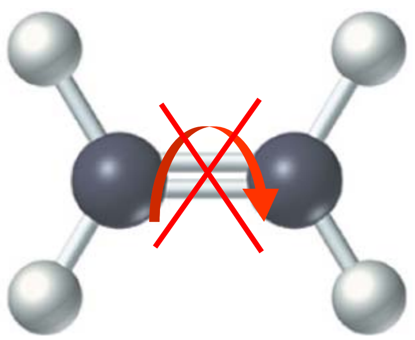
Comparison of single-bond in ethane and double-bond in ethene:

single-bond



double-bond





3.2 Characteristic quantities

End-to-End distance: $R_E = r_N - r_0 = \sum_{j=i}^{N} R_j$

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

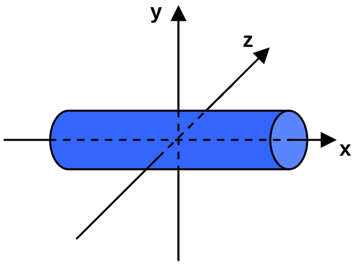
look at the mean-square average (norm):

$$\overline{R}_E^2 = \langle R_E^2 \rangle = \langle R_E R_E \rangle = \sum_{j=1}^{N}\sum_{k=1}^{N} \langle R_j R_k \rangle = \sum_{j=1}^{N} \langle R_j^2 \rangle + 2\sum_{j=1}^{N}\sum_{k=j+1}^{N} \langle R_j R_k \rangle$$

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.

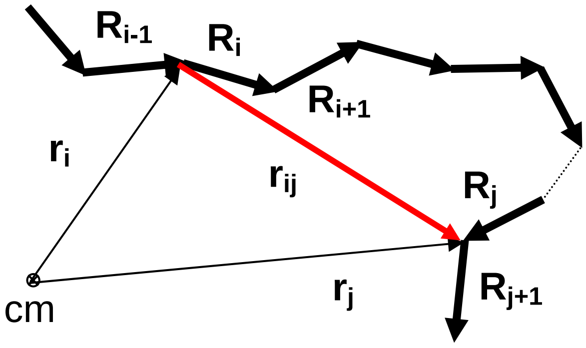
$$R_g^2 = R_{g,x}^2 + R_{g,y}^2 + R_{g,z}^2$$



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

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

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

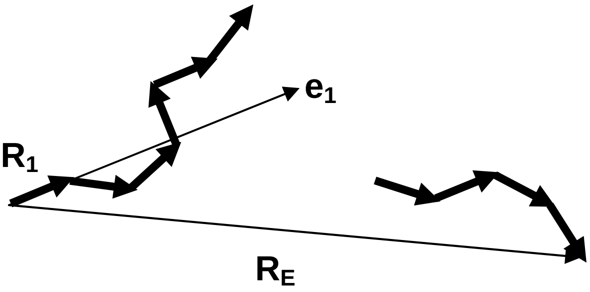


In case all masses are identical $m_j = m$: $\overline{R}_g^2 = \frac{1}{N+1}\sum_{j=0}^{N} \left\langle \left(r_j - r_{cm}\right)^2 \right\rangle$ with $r_{cm} = \frac{1}{N+1}\sum_{j=0}^{N} r_j$

With the help of the Lagrange Theorem: $\overline{R}_g^2 = \frac{1}{(N+1)^2}\sum_{i=1}^{N}\sum_{j=i+1}^{N} \langle r_{ij}^2 \rangle$ with $\langle r_{ij}^2 \rangle = \left\langle \left(r_i - r_j\right)^2 \right\rangle$

Characterization of the stiffness of a polymer:

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



Projection H_N of R_E on the unit vector e_1
(pointing in the direction of R_1)

H_N is the sum of the projections of all bond vectors R_j on the direction of the first bond vector R_1.

$$H_N = e_1 R_E = \frac{R_1 R_E}{|R_1|} = \frac{R_1}{|R_1|}\sum_{j=1}^{N} R_j = \sum_{j=1}^{N} \frac{R_1 R_j}{|R_1|}$$

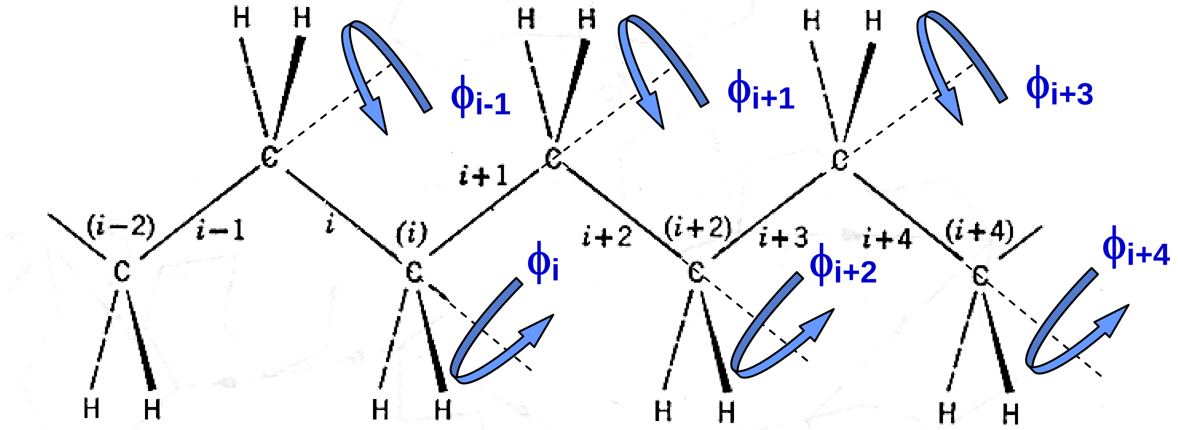
The **persistence length l_P** is defined as the thermal average in the limit of infinate long chain:

$$l_P \equiv \lim_{N\to\infty} \langle H_N \rangle = \lim_{N\to\infty} \sum_{j=1}^{\infty} \left\langle \frac{R_1 R_j}{|R_1|} \right\rangle$$

3.3 Chain models

For the calculation of the correlations between bond vectors $\langle R_j R_k \rangle$ and position vectors $\langle r_{ij}^2 \rangle$ detailed assumptions about the chain statistics are necessary.

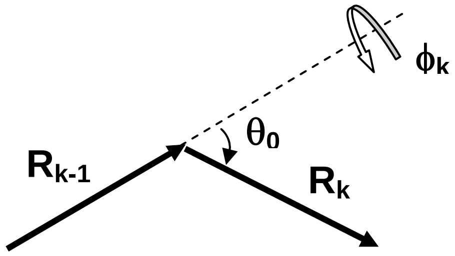
3.3.1 Freely rotating chain



bond angles	are fixed = θ_0
bond lengths	are fixed = l_0
bond-rotation angles	are evenly distributed over $0 \le \phi \le 2\pi$

average over all orientations φ_k of vector $R_k \Rightarrow$

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



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

continue until k-1=j:

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

($\langle \cos\theta_0 \rangle$ since θ_0 fixed average not necessary but useful for freely jointed chain model)

End-to-End distance:

$$\overline{R}_E^2 = \sum_{j=1}^{N} \langle R_j^2 \rangle + 2\sum_{j=1}^{N}\sum_{k=j+1}^{N} \langle R_j R_k \rangle = \frac{Nl_0^2}{1-\langle \cos\theta_0 \rangle}\left[1+\langle \cos\theta_0 \rangle - \frac{2\langle \cos\theta_0 \rangle [1-\langle \cos\theta_0 \rangle^N]}{N(1-\langle \cos\theta_0 \rangle)}\right]$$

For N>>1 $\left(\langle \cos\theta_0 \rangle < 1\right)$: $\overline{R}_E^2 = Nl_0^2 \dfrac{1+\langle \cos\theta_0 \rangle}{1-\langle \cos\theta_0 \rangle} \Rightarrow \overline{R}_E \propto \sqrt{N}$

Fully stretched chain $\left(\langle \cos\theta_0 \rangle = 1\right)$: $\overline{R}_E^2 = N^2 l_0^2 \quad \Rightarrow \quad \overline{R}_E = Nl_0$

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

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

Persistence length:

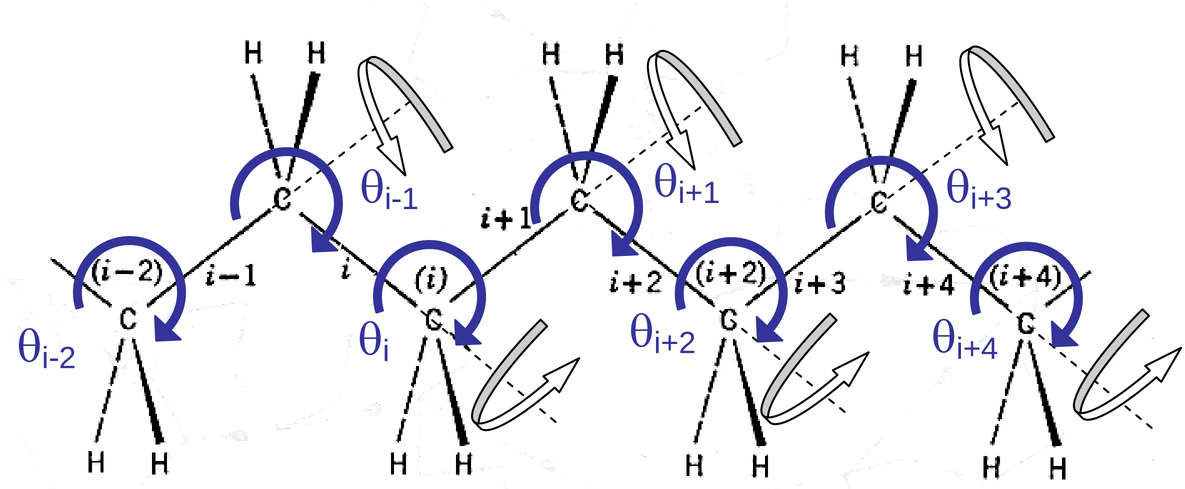
$$l_P = \lim_{N\to\infty} \sum_{j=1}^{\infty} \left\langle \frac{R_1 R_j}{|R_1|} \right\rangle = \frac{l_0}{1-\langle \cos\theta_0 \rangle}$$

Radius of gyration:

$$\overline{R}_g^2 = \frac{1}{(N+1)^2}\sum_{j=1}^{N}\sum_{i=j+1}^{N} \langle r_{ij}^2 \rangle \approx \frac{1}{6} Nl_0^2 \left(\frac{N+2}{N+1}\right)\left(\frac{1+\langle \cos\theta_0 \rangle}{1-\langle \cos\theta_0 \rangle}\right)$$

For N>>1: $\overline{R}_g^2 \approx \dfrac{1}{6} Nl_0^2 \left(\dfrac{1+\langle \cos\theta_0 \rangle}{1-\langle \cos\theta_0 \rangle}\right) = \dfrac{1}{6} R_E^2$

3.3.2 Freely jointed chain



bond angles	are evenly distributed over $0 \le \theta \le 2\pi$
bond lengths	are fixed $= l_0$
bond-rotation angles	are evenly distributed over $0 \le \phi \le 2\pi$

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

End-to-End distance:

$$\overline{R}_E^2 = \frac{Nl_0^2}{1-\langle\cos\theta_0\rangle}\left[1+\langle\cos\theta_0\rangle - \frac{2\langle\cos\theta_0\rangle[1-\langle\cos\theta_0\rangle^N]}{N(1-\langle\cos\theta_0\rangle)}\right] = Nl_0^2$$

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

$\langle r_{ij}^2 \rangle = |i-j| l_0^2$

Persistence length:

$$l_P = \frac{l_0}{1-\langle\cos\theta_0\rangle} = l_0$$

Radius of gyration:

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

For N>>1: $\overline{R}_g^2 \approx \frac{1}{6} Nl_0^2 = \frac{1}{6}\overline{R}_E^2$

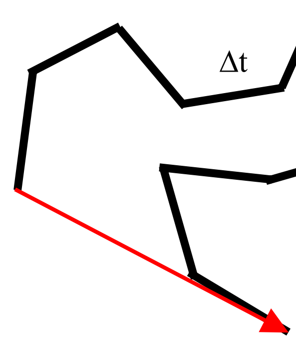
The end-to-end distance $\overline{R}_E^2 = Nl_0^2$ is in analogy to a 3-dimensional random walk!

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:

$\left\langle \Delta r^2 \right\rangle = \left\langle \left[r(t) - r(t=0) \right]^2 \right\rangle \propto t$ compare to $\overline{R}_E^2 = \left\langle \left[r_N - r_0 \right]^2 \right\rangle = N l_0^2$



$l_0 \equiv$ distance covered in Δt

$N \equiv t$

snap shots of the random flight in time intervals Δt

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 $\delta(r) = \frac{1}{(2\pi)^3} \int e^{ikr} dk$

$$\Phi(R)=\frac{1}{(2\pi)^3}\int dk\int dR_1\int dR_2...\int dR_N\,\exp[ik(R-\sum_{j=1}^{N}R_j)]\Psi(\{R_j\})$$

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

$$=\frac{1}{(2\pi)^3}\int dk\exp(ikR)\underbrace{\left[\int dR\exp(-ikR\ )\Psi(R)\right]^N}_{=\frac{\sin(kl_0)}{kl_0}}$$

up to here: same for the gaussian chain
with polar coordinates $(\theta_i\ \phi_i\ r)$

$$\Phi(R)=\frac{1}{(2\pi)^3}\int dk\exp(ikR)\ \underbrace{\left[\frac{\sin(kl_0)}{kl_0}\right]}_{\text{small apart for small kl}_0}{}^N$$

approximation for large N:

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

vanishs 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 $kR=k_xR_x+k_yR_y+k_zR_z$ and $\mathrm{k}^2=k_x^2+k_y^2+k_z^2$

$$\Phi(R)=\left(\frac{3}{2\pi N{l_0}^2}\right)^{\frac{3}{2}}\exp\left(-\frac{3}{2}\frac{R^2}{2N{l_0}^2}\right)$$

Result:

$$\boxed{\Phi(R)=\left(\frac{3}{2\pi Nl_0^2}\right)^{3/2}\exp\left(-\frac{3}{2}\frac{R^2}{2Nl_0^2}\right)}$$

Gaussian distribution

Effective bond length

In case only local correlations are effective, so that

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

the real chain can always be described by a freely jointed chain with larger effective bond length, so that the relations $\overline{R}_E^2=Nl^2$ and $\overline{R}_g^2=\frac{1}{6}\overline{R}_E^2$ for large N still hold.

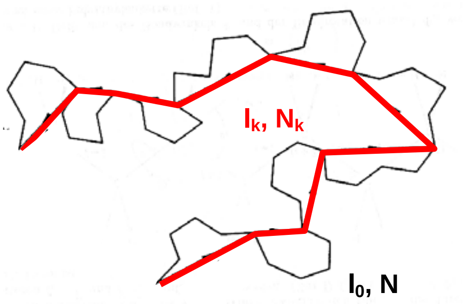
Characteristic ratio

$$C_\infty = \lim_{N\to\infty} \frac{\overline{R}_E^2}{N l_0^2} = \frac{l^2}{l_0^2} \Rightarrow \quad l = \sqrt{C_\infty}\, l_0$$

e.g. freely rotating chain $C_\infty = \dfrac{1+\langle\cos\theta_0\rangle}{1-\langle\cos\theta_0\rangle}$

Kuhn segment

is defined by a transformation of the real chain onto a freely jointed chain under preservation of the end-to-end distance $\overline{R}_E^2$ and the maximal possible end-to-end distance of the fully stretched chain $R_{E,\max}$



$$\overline{R}_E^2 = N_k l_k^2 \quad \text{and} \quad R_{E,\max} = N_k l_k$$

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

$$l_k = \frac{\overline{R}_E^2}{R_{E,\max}} \quad \text{and} \quad N_k = \frac{R_{E,\max}^2}{\overline{R}_E^2}$$

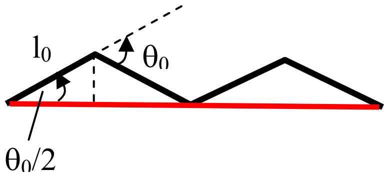
Segments of length l_k are the smallest units being statistically uncorrelated. The Kuhn segment is like the persistence length a measure of the chain stiffness.

e.g. freely rotating chain

$\theta_0 = 70.53°$ (tetrahedron angle)

$$\overline{R}_E^2 = N l_0^2 \frac{1+\langle\cos\theta_0\rangle}{1-\langle\cos\theta_0\rangle}$$

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



$$\Rightarrow \quad l_k = \frac{\overline{R}_E^2}{R_{E,\max}} = \sqrt{2(1+\langle\cos\theta_0\rangle)}\,\frac{l_0}{1-\langle\cos\theta_0\rangle} \approx 2.45 \times l_0$$

$$N_k = \frac{R_{E,\max}^2}{\overline{R}_E^2} = N\,\frac{1-\langle\cos\theta_0\rangle}{2} \approx 0.33 \times N$$

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:

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

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

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

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

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

⇒ 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 $H(\{R_j\})$

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

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?

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

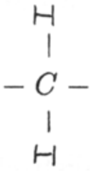
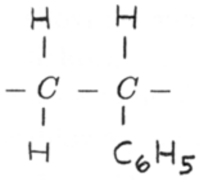
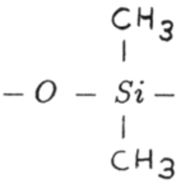
$$\Rightarrow H(\{R_j\}) = \frac{1}{2} \underbrace{\frac{3k_B T}{l^2}}_{\text{spring constant}} \sum_{j=1}^{N} R_j^2 \quad \text{(harmonic potential)}$$

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

polymer	**solvent**	T(°C)	C_∞
polyethylen  $-\overset{H}{\underset{H}{C}}-$	Dodecanol 1	138	6.7
	Diphenylmethan	142	6.8
	α–Cl–Naphtalin	140	6.6
polystyrene, atactic  $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{C_6H_5}{C}}-$	Cyclohexan	34.8	10.2
	Diäthylmalonat	35.9	9.9
polydimethylsiloxan  $-O-\overset{CH_3}{\underset{CH_3}{Si}}-$	**various**	2 **to** 90	5.7 **to** 6.2

freely rotating chain:

$$C_\infty = \frac{1+\langle\cos\theta_0\rangle}{1-\langle\cos\theta_0\rangle}$$

with:

$$\theta = 70.53^\circ$$
$$\Rightarrow \quad C_\infty \approx 2$$

However, real chains are much stiffer!

RIS

Bond rotational potentials

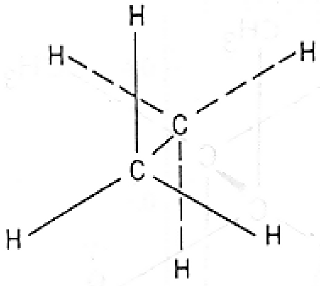
The picture of unrestricted freedom of bond-rotation angles is oversimplified. Finite extension of atoms and side groups lead to "long-ranged" (excluded volume interactions, prohibition of chain intersections) as well as "short-ranged interactions".
Due to sterical hindrance not all bond rotation angles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

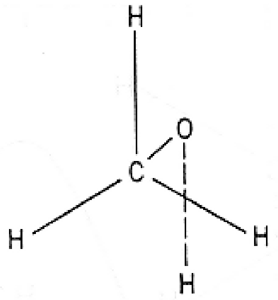
Bond rotational potentials $H = H(\{\Phi_i\}) = H(\Phi_1, \ldots, \Phi_{i-1}, \Phi_i, \Phi_{i+1}, \ldots, \Phi_N)$

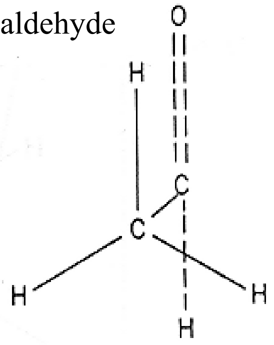
$$\Psi(\{\Phi_i\}) = \frac{1}{Z} e\mathrm{xp}\left(-\frac{H(\{\Phi_i\})}{k_B T}\right) \quad \text{with normalization} \quad Z = \int e\mathrm{xp}\left(-\frac{H(\{\Phi_i\})}{k_B T}\right) d^N\{\Phi_i\}$$

RIS (rotational isomeric state)-model (l and θ fixed) replaces the continuous variable Φ_i by a discret set of angles $\Phi_{i,\nu}$

e.g. ethane, methane, azethaldehyde





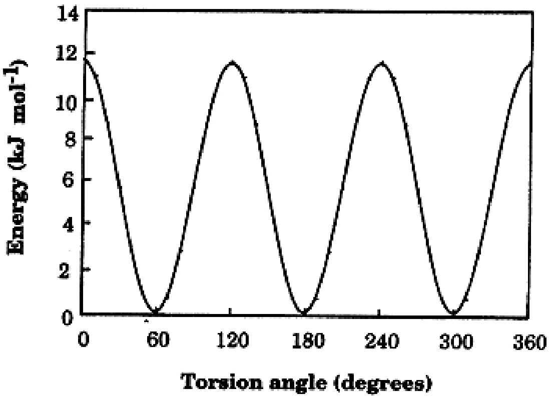


staggered conformation

$H(\Phi) = \frac{H_0}{2}[1 - \cos(3\Phi)]$ rotation barrier H_0 as a measure of the sterical interaction

$H_0 >> k_B T$ localized rotational states

equal minima

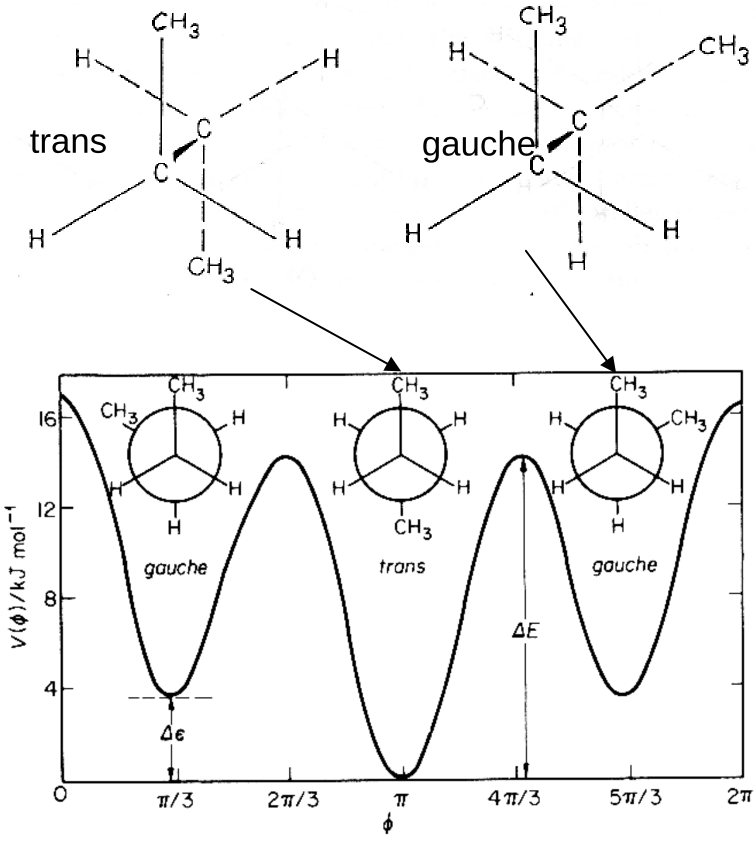


Barrier height

thermal energy at 300K $\approx$ 0.6 kcal/mole (1 Joule = 2.390×10^{-4} kcal)

	Compound and bond	Barrier height, kcal mole^{-1}
ethane	$CH_3—CH_3$	2.9
propylene	$CH_3—CH=CH_2$	1.98
azethaldehyde	$CH_3—CH=O$	1.17
butane	$CH_3CH_2—CH_2CH_3$	3.5^a
methane	$CH_3—OH$	1.07
dimethylether	$CH_3—OCH_3$	2.72
methanethiol	$CH_3—SH$	1.27
methylphosphine	$CH_3—PH_2$	1.96

e.g. n-butane



minima are not equal *trans* $\Phi_t = 180^o$: $H_t = 0$

gauche$^+$ $\Phi_g^+ = 60^o$: $H_g^+ > 0$

gauche$^-$ $\Phi_g^- = 300^o$: $H_g^- = H_g^+ > 0$

with the probability $\Psi(\Phi_\nu) = \frac{1}{Z}\exp\left(-\frac{H_\nu}{k_B T}\right)$ mit $Z = \sum_\nu \exp\left(-\frac{H_\nu}{k_B T}\right)$

Independent bond rotation potentials

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

e.g. polyethylene @ $T = 140\ ^\circ\mathrm{C} : H_g^{\pm} = 0.5$ kcal/mole; $\Phi_g^{\pm} \approx \pm 120^\circ$; $\theta = 70.53^\circ$

$$H_t = 0; \quad \Phi_t \approx 0^\circ$$

$$\langle\cos\theta\rangle = \frac{1}{3}; \quad \sigma = \exp\left(-\frac{H_\nu}{k_B T}\right) = 0.54$$

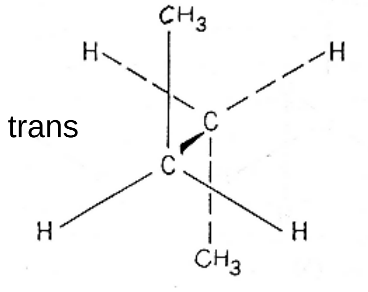
$$\langle\cos\Phi\rangle = \frac{1}{Z}\sum_\nu \exp\left(-\frac{H_\nu}{k_B T}\right)\cos\Phi_\nu = 1 - \frac{\sigma}{2} - \frac{\sigma}{2} = 1 - \sigma \quad \text{with} \quad Z = \sum_\nu \exp\left(-\frac{H_\nu}{k_B T}\right) = 1 + \sigma + \sigma = 1 + 2\sigma$$

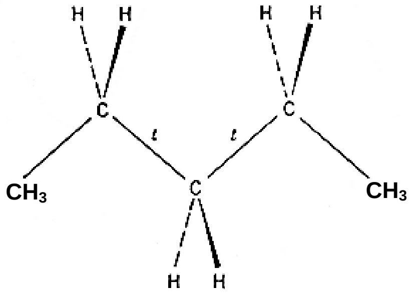
$$\Rightarrow \quad \langle\cos\Phi\rangle = \frac{1-\sigma}{1+2\sigma} \approx 0.22 \quad \Rightarrow \quad C_\infty \approx 3.14$$

still much smaller than experimental value: $C_\infty^{\exp} \approx 6.7$ => **real chains are much stiffer!**

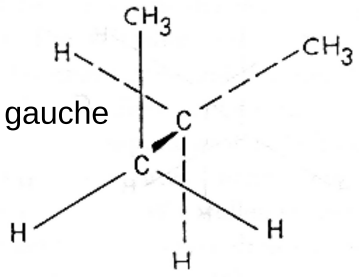
Bond rotation potentials are not independent!

rotation around single bond: rotation around two bonds:

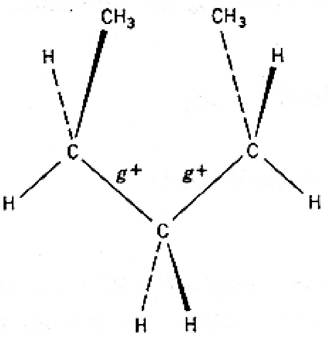


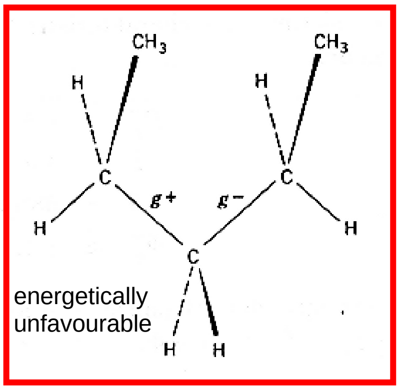


n-pentane



n-butane

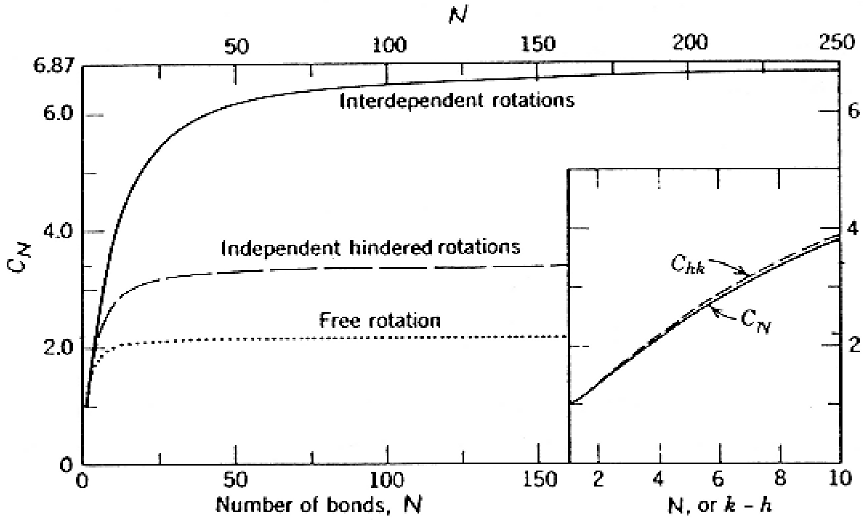




Interdependent rotation potentials of adjascent bonds $H\left(\{\Phi_i\}\right) = \sum_{i=2}^{N} H\left(\Phi_{i-1}, \Phi_i\right)$

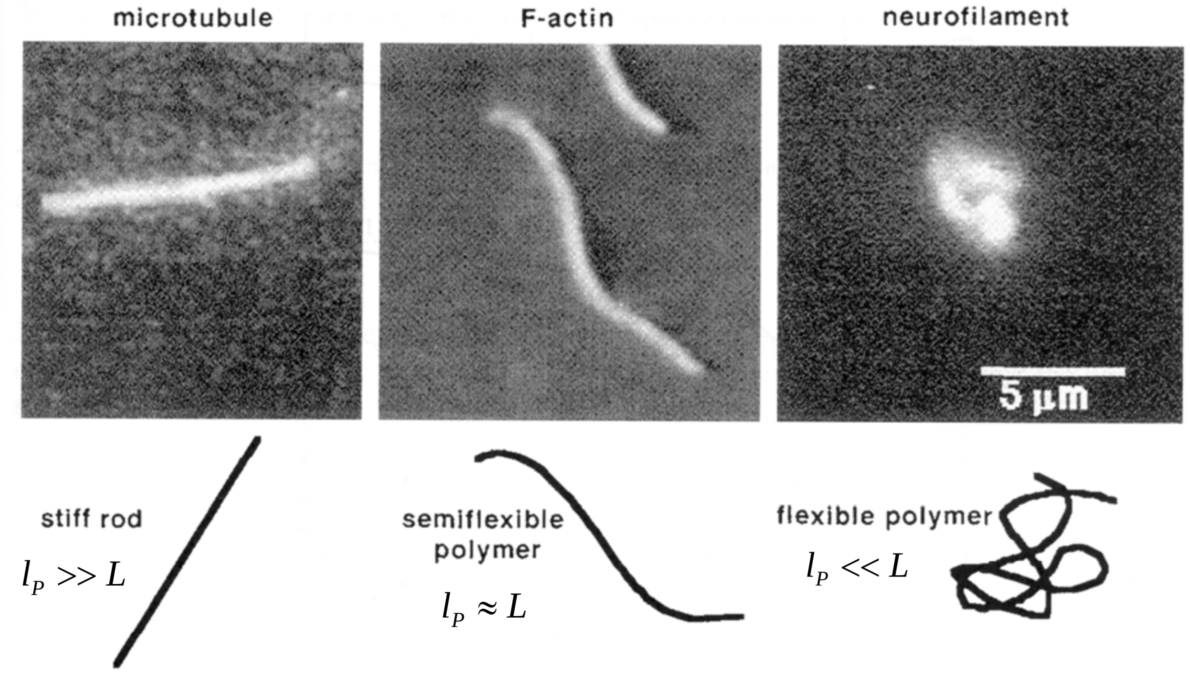
Ab-initio calculations: microscopic, quantum mechanic problem.
Semi-empirical methods: "molecular force field" calculations based on Newton's mechanics and electrostatics. Atoms are replaced by beads and bonds by springs.
Goal: find 3-dim structure with minimal energy.

e.g. polyethylene:



3.3.4 Worm-like chain (Kratky-Porod model)

Examples



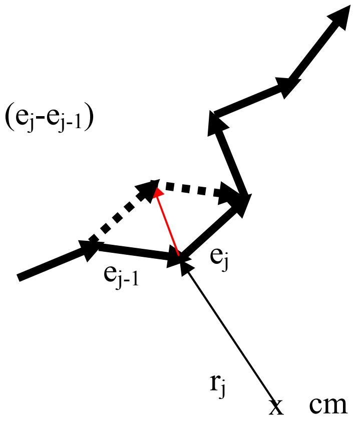
contour length L = maximum end-to-end distance of a polymer

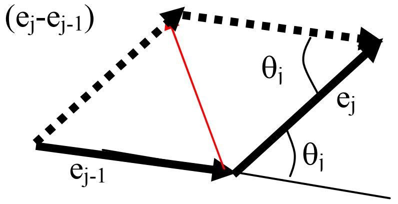
bond lengths	are fixed = l_0
bond-rotation angles	are evenly distributed over $0 \leq \phi \leq 2\pi$
bond angles $\{\theta_i\}$	subsequent segments should posses a certain stiffness against bending

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})





Pythagoras $\left(e_j - e_{j-1}\right)^2 = 2\left(1-\cos\theta_j\right)$

Ansatz:

Bending energy is given by harmonic potential: $H_B = \frac{\kappa}{2}\sum_{j=2}^{N}\left(e_j - e_{j-1}\right)^2 = \kappa\sum_{j=2}^{N}\left(1-\cos\theta_j\right)$

If bending energy κ is large $\kappa >> k_BT$, the bond angles θ_j will be small:

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

⇒ for the distributions of the conformations

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

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

$$\overline{R}_E^2 = \frac{Nl_0^2}{1-\langle\cos\theta\rangle}\left[1+\langle\cos\theta\rangle - \frac{2\langle\cos\theta\rangle[1-\langle\cos\theta\rangle^N]}{N(1-\langle\cos\theta\rangle)}\right] \text{ and } l_P = \frac{l_0}{1-\langle\cos\theta\rangle}$$

the problem reduces to the calculation of $\langle\cos\theta\rangle$

$$\langle \cos\theta \rangle = \int \Psi\left(\{\theta_i\}\right) \cos\theta_i \, d^{N-1}\{\theta_i\} = \exp\left(-\frac{k_B T}{2\kappa}\right)$$

$$l_P = \frac{l_0}{1-\exp\left(-\frac{k_B T}{2\kappa}\right)} \approx \frac{2\kappa}{k_B T} l_0 \qquad \text{for } \kappa >> k_B T$$

$$\overline{R}_E^2 = \frac{N l_0^2}{1-\exp\left(-\frac{k_B T}{2\kappa}\right)} \left[1+\exp\left(-\frac{k_B T}{2\kappa}\right) - \frac{2\exp\left(-\frac{k_B T}{2\kappa}\right)[1-\exp^N\left(-\frac{k_B T}{2\kappa}\right)]}{N(1-\exp\left(-\frac{k_B T}{2\kappa}\right))} \right]$$

$\overline{R}_E^2$ expressed as a function of l_P, l_0 and $L = N l_0$

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

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

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

e.g. DNA

length 10-100μm
extension to full length

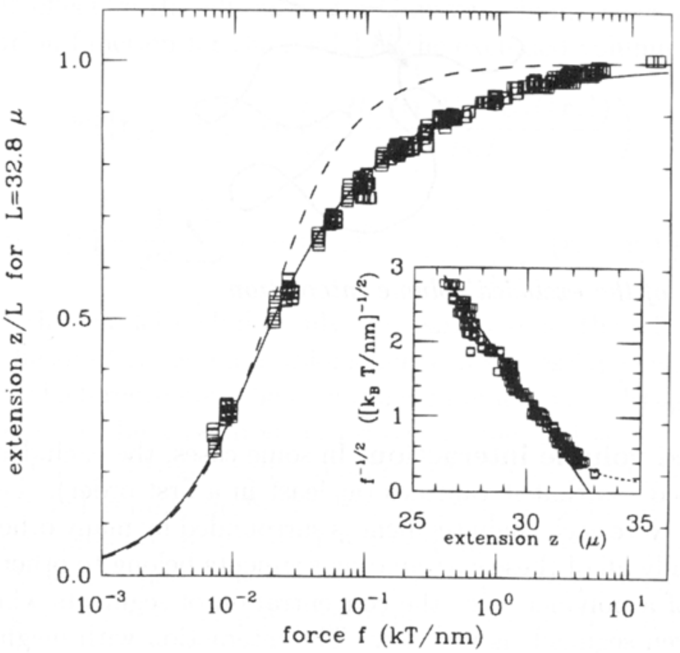
persistence length of 50nm
Kuhn segments: 100nm

dashed line:
freely-jointed chain model

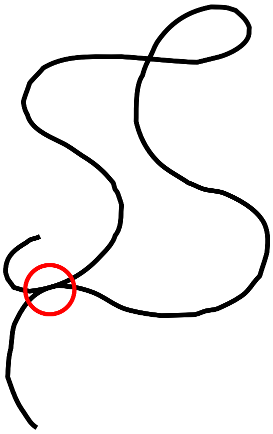
solid line:
worm like chain model

free energy: $F = \frac{3k_B T}{2} \frac{z^2}{\langle R_{E,0}^2 \rangle}$

required force: $f = \frac{\partial F}{\partial z} = 3k_B T \frac{z}{\langle R_{E,0}^2 \rangle}$



3.4 Polymer solutions



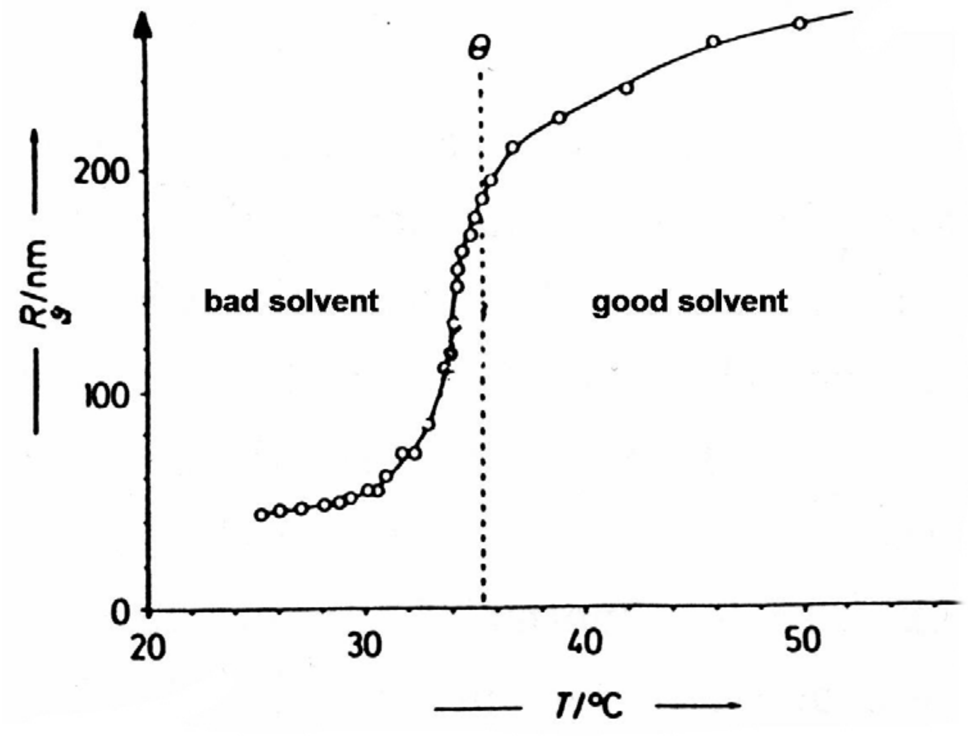
Up to now we neglected any "long-ranged" interactions involving chain segments well separated along the chain. Backfolding of the chain due to the high chain flexibility has the consequence that distant chain segments can become very close to each other. However, chain segments have finite extension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

$$H_{ij,excl} = \upsilon k_B T \delta(r_i - r_j) \quad \Rightarrow \quad \text{in total } H_{excl} = \frac{1}{2}\upsilon k_B T \sum_{j=0}\sum_{i=0} \delta(r_i - r_j)$$

Here υ represents the excluded volume and δ the delta function.

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

$$\Psi\left(\left\{r_j\right\}\right) \propto \exp\left[-\frac{H_G\left(\left\{r_j\right\}\right) + H_{excl}\left(\left\{r_j\right\}\right)}{k_B T}\right] \propto \exp\left(\underbrace{-\frac{3}{2l^2}\sum_j \left(r_j - r_{j-1}\right)^2}_{\substack{\text{interaction between}\\ \text{neighbouring segments}}} \underbrace{-\frac{\upsilon}{2}\sum_i\sum_j \delta\left(r_j - r_i\right)}_{\substack{\text{interaction between}\\ \text{distant segments}}}\right)$$

Rigorous solution of the problem not possible!

Flory theory

Question:
What is the end-to-end distance $\left\langle R_E^2 \right\rangle$ 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: $c_{\text{int}} = \dfrac{N}{R^d}$

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

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

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

$$F_{excl} \approx k_B T \upsilon(T) R^d c_{\text{int}}^2 l^d = k_B T \upsilon(T)\, N^2 l^d \big/ R^d$$

Entropy contributes as elastic term relative to ideal chain:

$$F_{el} \approx k_B T \, R^2 \big/ \left\langle R_E^2 \right\rangle = k_B T \, R^2 \big/ \left(N l^2 \right)$$

Total free energy: $$\frac{F_{el}}{\left(k_B T\right)} \approx \frac{\upsilon(T) N^2 l^d}{R^d} + \frac{k_B T R^2}{N l^2}$$

Minimum for: $R^{d+2} \propto l^{d+2} N^3 \Leftrightarrow R \propto l N^{3/(d+2)} \propto N^{\nu} l$

=> **Flory exponent** $\nu = 3/(d+2)$

$\nu =$ 3/5 for d=3

3/4 d=2

1 d=1

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.

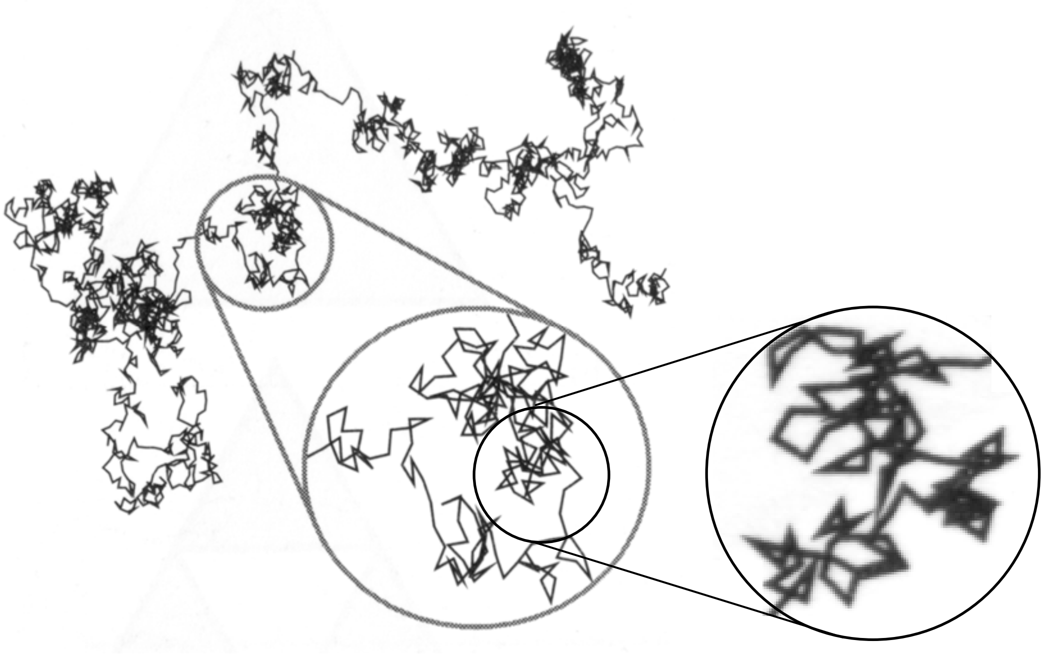
The goal of mean field theory (MFT, also known as self-consistent field theory) is to resolve these combinatorial problems. The main idea of MFT is to replace all interactions to any one body with an average or effective interaction. This reduces any multi-body problem into an effective one-body problem. 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:	ideal chain	$R^2 = Nl^2 \Rightarrow D_f = 2$	
	with excluded volume interaction	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 probabilty in isotropic system ⇒ $\langle R_g \rangle, \langle R_E \rangle = 0$

- ⇒ look at the norms (mean square values) $\langle R_g^2 \rangle$, $\langle R_E^2 \rangle$
- ⇒ geometrical considerations lead to $\langle R_g^2 \rangle$, $\langle R_E^2 \rangle$ and l_P in terms of $\langle R_i R_j \rangle$ and $\langle (r_i - r_j)^2 \rangle$
- ⇒ for the calculation of <RiRj> and $\langle (ri-rj)^2 \rangle$ assumptions about the chain statistics are necessary / probability to find a certain l,ϕ, θ

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

⇒ **chain models**

1. **freely rotating chain** l, θ = fixed & ϕ totaly free
2. **freely jointed chain** l = fixed & θ, ϕ = totaly free

⇒ $\langle R_E^2 \rangle = Nl^2$ and $\langle R_g^2 \rangle = Nl^2$
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 $\Psi(\{R_j\}) = \prod_{j=1}^{N-j_c} \Psi(R_j, R_{j+1}, R_{j+2}, \ldots, R_{j+j_c}) \quad mit \quad j_c << N$

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

⇒ this led us to definition of **characteristic ratio** & **Kuhn length** (measure of chain stiffness).

one effective segment is made up by several real bonds ⇒

3. **Gaussian chain** θ, ϕ = totaly free

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

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

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

global properties are preserved!

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

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

which Hamiltonian describes the Gaussian chain?

⇒ harmonic potential $H(\{R_j\}) = \frac{1}{2} \underbrace{\frac{3k_B T}{l^2}}_{\text{spring constant}} \sum_{j=1}^{N} R_j^2$

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

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

5. **worm-like chain model** l = fixed & ϕ = totally free
   restrictions to θ: 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.

⇒ **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	ν =	3/5	for	d=3
		3/4		d=2
		1		d=1

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.

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