3. Chain conformation

3.1 Constitution, configuration, conformation

Macromolecule ⇔ build-up from large number of small, connected subunits (monomers)

a) **Constitution:** The constitution of a macromolecule describes the type and the order of the subunits (monomers) and the resulting molecular structure.

Example:

... —A—A—A—A—A—A—A—A—A—A—A—A— ...

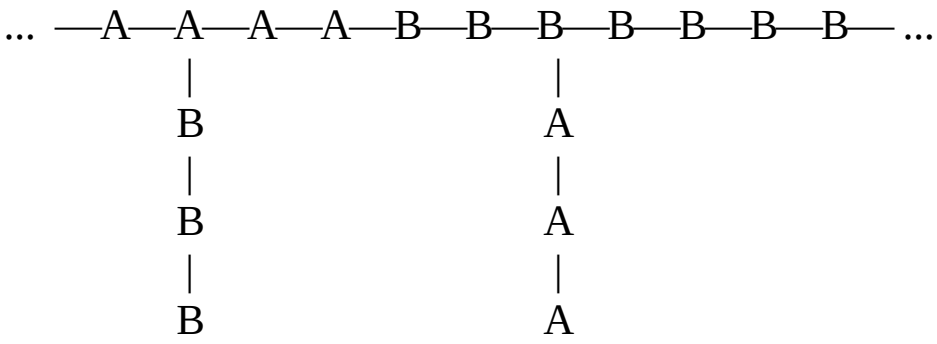
homopolymer

... —A—B—A—B—A—B—A—B—A—B—A— ...

alternating copolymer

... —A—A—A—A—B—B—B—B—B—B—B— ...

diblock copolymer



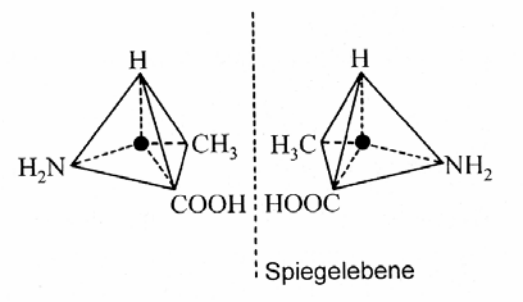
graft-copolymer

Other examples: statistical copolymer, star-polymer, ...

b) **Configuration:** describes the spatial position of atoms within the molecule: The geometrical arrangement in polymers arising from the order of atoms determined by chemical bonds.

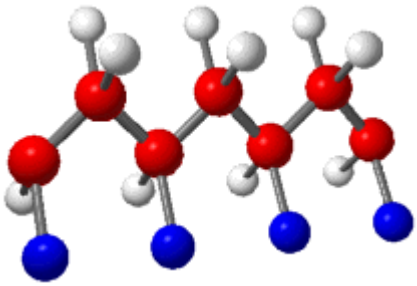
- The regularity and symmetry of the side-groups can affect strongly the properties of polymers. Side groups are atoms or molecules with free bonds, called free-radicals, like H, O, methyl, etc.
- The configuration of a polymer cannot be altered unless chemical bonds are broken and reformed.
- asymmetric C-atom ⇔ all substituents are different

Example: Alanin

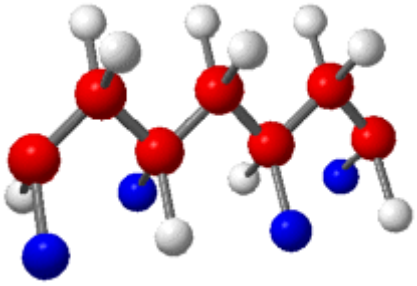


Tacticity: The orderliness of the succession of configurationally repeating units in the main chain of a polymer molecule (important for crystallization).

- if the radicals are linked in the same order, the configuration is called isotatic
- in a stereoisomer in a syndiotactic configuration, the radical groups are at alternative sides in the chain
- in the atactic configuration, the radical groups are positioned at random



isotatic



syndiotactic

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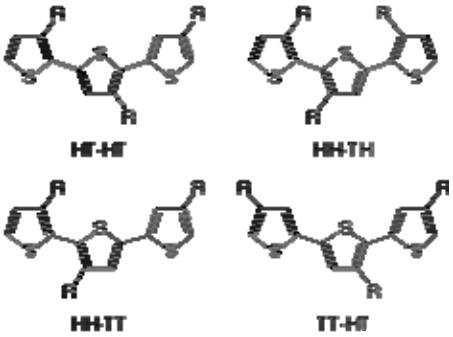
Regioregularity: describing a polymer in which each repeat unit is derived from the same isomer of the monomer

Example: asymmetry of 3-substituted thiophenes results in three possible couplings when two monomers are linked between the 2- and the 5-positions

- 2,5', or head–tail (HT), coupling
- 2,2', or head–head (HH), coupling
- 5,5', or tail–tail (TT), coupling

→ these three diads can be combined into four distinct triads



wikepedia

poly(3-hexylthiophene) P3HT having regioregularities of 86, 90, and 96%

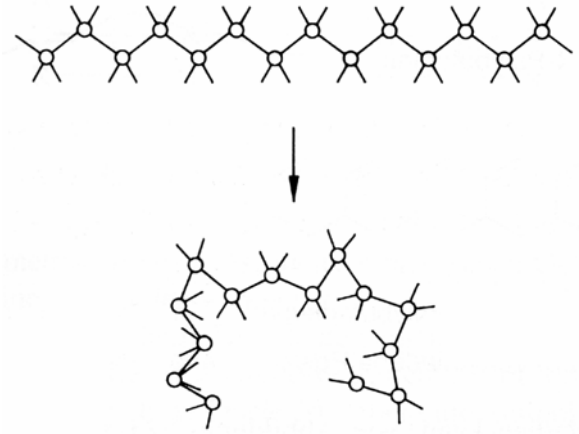
Regiorandom: describing a polymer in which each repeat unit is derived from a random isomer of the monomer

c) Conformation:

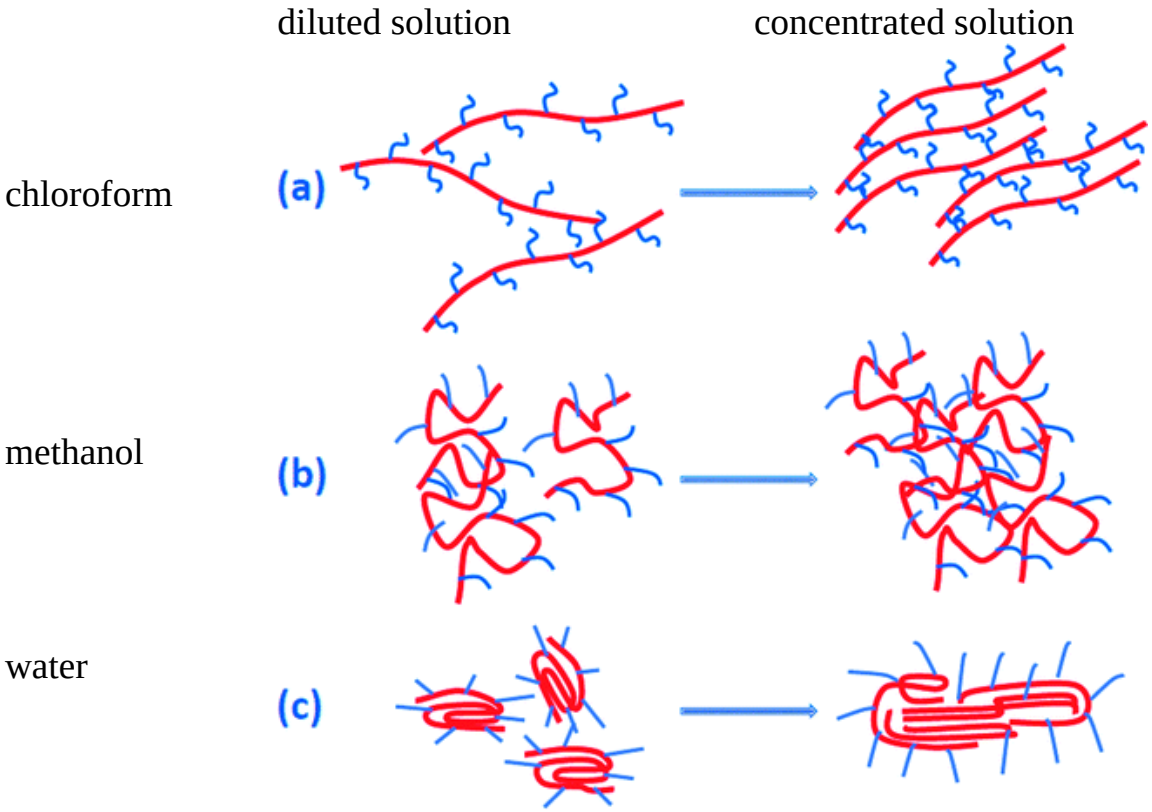
Conformation refers to order that arises from the rotation of molecules about the single bonds:

- thermal fluctuation of the bond length (3%) and bond angle (3-5°) are small at room temperature
- rotations around the bonds are well possible

Example: Well flexible macromolecule ⇔ back-folded chain



Example: solvent polarity effect on chain conformation of DEATG-PPV



Xu et al. J. Phys. Chem. B 114, 11746–11752 (2010)

3.2 Characteristic length scales and sizes

Contour length of a polymer chain is its length at maximum physically possible extension, but polymer chain is coiled and not fully stretched!

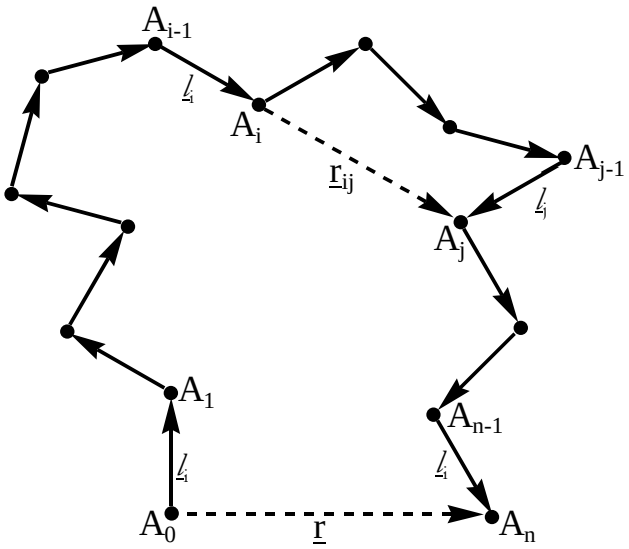
⇒ need for a measure of the mean chain size

- conformation is fully described with bond vectors $\underline{l}_i$
- whole bond vectors is difficult to handle

⇒ statistical quantity

a) Mean-square end-to-end distance R_e

Description via bond vectors $\underline{l}_i$ which connect the skeleton atoms A_i



Not end-to-end vector **r** but its absolute value is of interest: Time average $\langle \underline{r} \rangle = 0$

n degree of polymerization

$$r^2 = \underline{r}^2 = \underline{r} \cdot \underline{r} = \sum_{i,j=1}^{n} \underline{l}_i \cdot \underline{l}_j = \sum_{i=1}^{n} l_i^2 + 2 \sum_{0<i<j}^{n} \underline{l}_i \cdot \underline{l}_j$$

Analog for the distance of the atoms i and j

$$r_{ij}^{\ 2} = \sum_{i'=i+1}^{j} l_{i'}^2 + 2 \sum_{i<i'<j'}^{j} \underline{l}_{i'} \cdot \underline{l}_{j'}$$

Statistical mean value

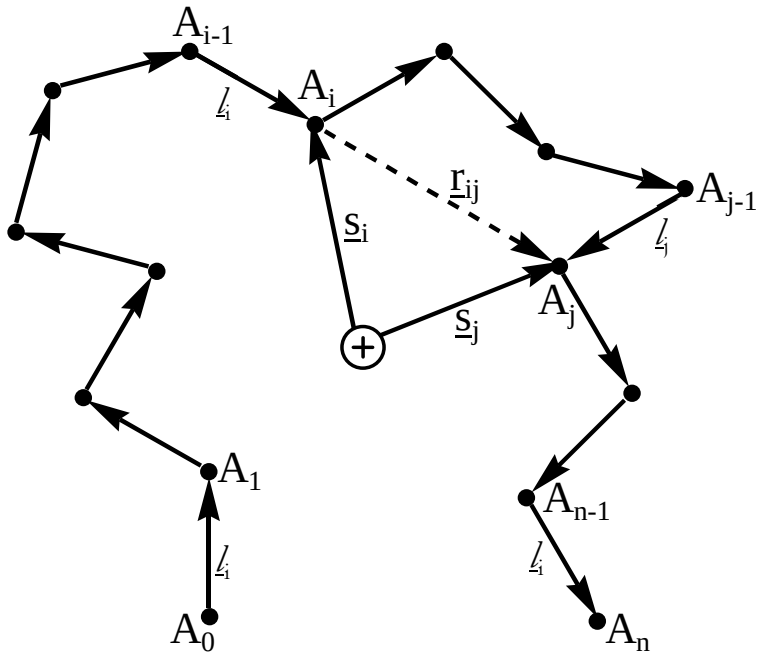
$$\left\langle r^2 \right\rangle = \sum_{i=1}^{n} \left\langle l_i^2 \right\rangle + 2 \sum_{0<i<j}^{n} \left\langle \underline{l}_i \cdot \underline{l}_j \right\rangle$$

Special case of equal bond length $l_i = l$ (homopolymer)

$$\boxed{R_e^2 = \left\langle r^2 \right\rangle = nl^2 + 2 \sum_{0<i<j}^{n} \left\langle \underline{l}_i \cdot \underline{l}_j \right\rangle}$$

b) Radius of gyration R_g

describes chain by the distance vectors $\underline{s}_i$ of the skeleton atoms A_i to the center of mass of the chain (position or radius vector $\underline{s}_i$ of the atoms A_i in the center of mass system of the chain)



Absolute value of the radius of gyration

$$s^2 = \sum_{i=0}^{n} m_i \underline{s}_i^2 \Big/ \sum_{j=0}^{n} m_j = (1/M) \sum_{i=0}^{n} m_i \underline{s}_i^2$$

In case of homopolymers with $m_i = m$ it is

$$s^2 = \left(\frac{1}{n+1} \right) \sum_{i=0}^{n} \underline{s}_i^2$$

Relation of position vectors in the center of mass system with the distance vectors between atoms and chain

$$\underline{r}_{ij} = \underline{s}_j - \underline{s}_i$$

Insert into equation: (Lagrange Theorem)

$$s^2 = \frac{1}{(n+1)^2} \sum_{0 \le i < j}^{n} r_{ij}^2$$

Statistical mean value

$$\boxed{R_g^2 = \langle s^2 \rangle = \frac{1}{(n+1)^2} \sum_{0 \le i < j}^{n} \langle r_{ij}^2 \rangle}$$

3.3 Special chain models

a) Freely-jointed chain

- fixed length polymer segments are linearly connected
  → all bond vectors $\underline{l}_i = \underline{l}$
- all bond angles Θ and torsion angles are equiprobable

$$\Rightarrow \left\langle \underline{l}_i \cdot \underline{l}_j \right\rangle = 0 \text{ for } i \neq j$$

assumes a polymer as a random walk and neglects any kind of interactions among monomers → end-to-end distance:

$$\left\langle r^2 \right\rangle = nl^2 + 2\sum_{0<i<j}^{n} \left\langle \underline{l}_i \cdot \underline{l}_j \right\rangle = nl^2 \rightarrow R_e = l\sqrt{n}$$

Analog to end-to-end distance: $\left\langle r_{ij}^{\,2} \right\rangle = |j-i| \cdot l^2$

Radius of gyration:

$$\left\langle s^2 \right\rangle = \frac{l^2}{(n+1)^2} \sum_{0\le i<j}^{n} (j-i) = \frac{1}{6} \cdot \frac{n+2}{n+1} \cdot nl^2 = \frac{1}{6} \cdot \frac{n+2}{n+1} \cdot \left\langle r^2 \right\rangle$$

Limit of infinite chain (n→∞):

$$\left\langle s^2 \right\rangle = \frac{1}{6}\left\langle r^2 \right\rangle \quad \Leftrightarrow \quad R_g = \frac{R_e}{\sqrt{6}}$$

with $R_e = 6.7\sqrt{n} \quad [Å]$

Example: PS (C_8H_8) with M=104.088

M_w=	1.75 k	n=	17	R_g=	11.2 Å
	9 k		86		25.4 Å
	28 k		269		44.9 Å
	70 k		673		70.9 Å
	102 k		980		85.6 Å
	630 k		6053		212.8 Å

Characteristic ratio of chain with degree of polymerization n (definition):

$$\boxed{C_n = \frac{\left\langle r^2 \right\rangle}{nl^2}}$$

with $n \rightarrow \infty$: $C_n \rightarrow C_\infty$

freely-jointed chain: $\boxed{C_n = 1}$

C_∞ measured in dilute solutions at the Θ-temperature, example:

polyethylene	140°C	C_∞=6.8
polyoxyethylen	40°C	C_∞=4.0
polystyrene, atactic	34°C	C_∞=10.0
polymethylmethacrylate, atactic	4-70°C	C_∞=6.9
PMMA, isotactic	27°C	C_∞=9.4
PMMA syndiotactic	35°C	C_∞=7.2

the more bulky the side groups, the higher C_∞ and freely-jointed chain model too simple

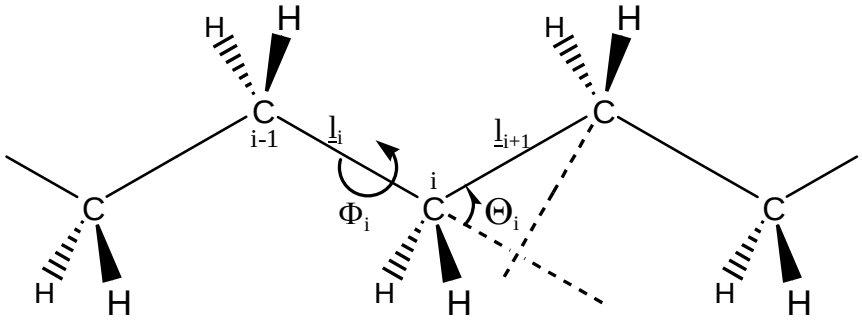
b) Freely-rotating chain

polymer segments make a fixed angle to neighboring units because of specific chemical bonding: assumption of free bond angles contradicts to the tetrahedra configuration of the C-atoms

→ Improvement:

- fixed Bond angles $\Theta_i = \Theta$ and fixed bond lengths $\underline{l}_i = \underline{l}$
- all bond rotation angles Φ (torsion angles) are equally likely

Mean angle between neighboring segments $\langle \underline{l}_i \cdot \underline{l}_{i+1} \rangle = l^2 \cos\Theta$ for $i \neq j$



In general with k segments distance: $\langle \underline{l}_i \cdot \underline{l}_{i+k} \rangle = l^2 (\cos\Theta)^k \equiv l^2 \alpha^k$

End-to-end distance with degree of polymerization n:

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{0<i<j}^{n} \alpha^{j-i} = nl^2 + 2l^2 \sum_{k=1}^{n-1} (n-k)\alpha^k$$

$$\langle r^2 \rangle = nl^2 \left[\frac{1+\alpha}{1-\alpha} - \frac{2\alpha}{n} \frac{(1-\alpha^n)}{(1-\alpha)^2} \right]$$

Characteristic ratio: $C_n = \frac{\langle r^2 \rangle}{nl^2} = \left[\frac{1+\alpha}{1-\alpha} - \frac{2\alpha}{n} \frac{(1-\alpha^n)}{(1-\alpha)^2} \right] \rightarrow \boxed{C_\infty = \frac{1+\cos\Theta}{1-\cos\Theta}}$

Radius of gyration:

$$\left\langle s^2 \right\rangle = \frac{1}{6} n l^2 \frac{(n+2)(1+\alpha)}{(n+1)(1-\alpha)} - \frac{\alpha}{(n+1)(1-\alpha)^2} + \frac{2\alpha^2}{(n+1)^2(1-\alpha)^2} - \frac{2\alpha^3}{n(n+1)^2(1-\alpha)^4}$$

In case of $n \to \infty$ follows:

$$\left\langle s^2 \right\rangle = \frac{1}{6}\left\langle r^2 \right\rangle \qquad \Leftrightarrow \qquad R_g = \frac{R_e}{\sqrt{6}}$$

c) Chain with separable energy

Assumption of free bond rotation angles Φ is too simple, because steric hindering of the rotation due to side-groups is neglected, and yields wrong values of C_∞

→ Improvement:

- bond rotation angles Φ get fixed from the bond rotation potential
- total energy of chain for all configurations can be separated into individual contributions from the single bonds

$$E\{\underline{l}\} = \sum_{i=1}^{n-1} E_i(\Theta_i, \Phi_i) = E\{\Phi\} = E(\Phi_1 ... \Phi_{i-1}, \Phi_i, \Phi_{i+1} ... \Phi_n)$$

Bond rotation angles Φ which are sterically more likely get more probable in the description with statistical mechanics. In thermal equilibrium, to find a conformation {Φ} has the probability

$$P\{\Phi\} d\{\Phi\} = \frac{1}{Z} \exp(-E\{\Phi\}/(RT)) d\{\Phi\}$$

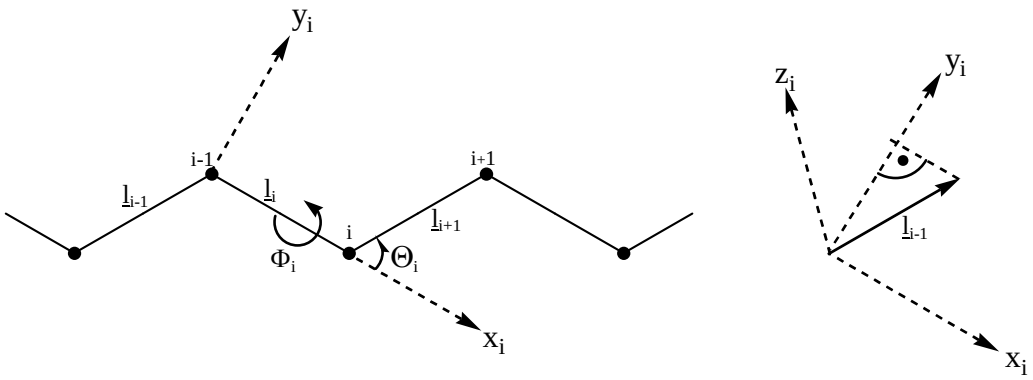
with $d\{\Phi\} = d\Phi_1 \ldots d\Phi_n$

partition function of all conformations

$$Z = \int ... \int d\{\Phi\} \exp(-E\{\Phi\}/(RT))$$

Selection of cartesian coordinate system for each individual bond with

- x_i parallel to $\underline{l}_i$
- y_i in the plane, given by $\underline{l}_i$ and $\underline{l}_{i-1}$
- z_i perpendicular to this plane



Transfer matrix T_i:

Transform vector in *i+1* coordinate system into the *i*-te coordinate system

$$\begin{pmatrix} v_x' \\ v_y' \\ v_z' \end{pmatrix}^i = \underline{\underline{T}}_i \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix}^{i+1} = \begin{pmatrix} \cos\Theta_i & \sin\Theta_i & 0 \\ \sin\Theta_i \cos\Phi_i & -\cos\Theta_i \cos\Phi_i & \sin\Phi_i \\ \sin\Theta_i \sin\Phi_i & -\cos\Theta_i \sin\Phi_i & -\cos\Phi_i \end{pmatrix} \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix}^{i+1}$$

iterative: bond vector $\underline{l}_j$ in the i-ten coordinate system: $\left(\underline{l}_j\right)^i = \underline{\underline{T}}_i \cdot \underline{\underline{T}}_{i+1} \cdots \underline{\underline{T}}_{j-1} \cdot \underline{l}_j$

Scalar product between bond vectors:

$$\underline{l}_i \cdot \underline{l}_j = l_i l_j \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \underline{\underline{T}}_i \cdots \underline{\underline{T}}_{j-1} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = l_i l_j \left(\underline{\underline{T}}_i \cdots \underline{\underline{T}}_{j-1} \right)_{11}$$

statistical mean value (needed to calculate $\left\langle r^2 \right\rangle = \sum_{i=1}^{n} l_i^2 + 2 \sum_{0<i<j}^{n} \left\langle \underline{l}_i \cdot \underline{l}_j \right\rangle$):

$$\left\langle \underline{l}_i \cdot \underline{l}_j \right\rangle = l_i l_j \left\langle \underline{\underline{T}}_i \cdots \underline{\underline{T}}_{j-1} \right\rangle_{11} \text{ mit: } \left\langle \underline{\underline{T}}_i \cdots \underline{\underline{T}}_{j-1} \right\rangle = \frac{\int \ldots \int \left(\underline{\underline{T}}_i \ldots \underline{\underline{T}}_{j-1} \right) \exp\left(-\frac{E\{\underline{l}\}}{RT} \right) d\{\underline{l}\}}{\int \ldots \int \exp\left(-\frac{E\{\underline{l}\}}{RT} \right) d\{\underline{l}\}}$$

Very difficult to calculate exactly, need for simplifications (approximations)

$\rightarrow$ statistical mean value (for fixed $\Theta_i = \Theta$):

$$\left\langle \underline{\underline{T}}_i \cdots \underline{\underline{T}}_{j-1} \right\rangle = \prod_{m=i}^{j-1} \left\langle \underline{\underline{T}}_m \right\rangle = \prod_{m=i}^{j-1} \frac{\int_0^{2\pi} \underline{\underline{T}}_m \exp\left(-\frac{E(\Phi_m)}{RT} \right) d\Phi_m}{\int_0^{2\pi} \exp\left(-\frac{E(\Phi_m)}{RT} \right) d\Phi_m}$$

only one type of bonds $\Rightarrow \left\langle \underline{\underline{T}}_m \right\rangle = \left\langle \underline{\underline{T}} \right\rangle$ and $l_i = l$

End-to-end distance: $\left\langle r^2 \right\rangle = \sum_{i=1}^{n} l_i^2 + 2 \sum_{0<i<j}^{n} \left\langle \underline{l}_i \cdot \underline{l}_j \right\rangle = nl^2 + 2l^2 \sum_{0<i<j}^{n} \left(\left\langle \underline{\underline{T}} \right\rangle^{j-i} \right)_{11}$

$$\left\langle r^2 \right\rangle = nl^2 \left(1 + \frac{2}{n} \sum_{k=1}^{n-1} \left((n-k) \left\langle \underline{\underline{T}} \right\rangle^k \right)_{11} \right)$$

with identity matrix $\underline{\underline{E}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Characteristic ratio:

$$C_n = \frac{\langle r^2 \rangle}{nl^2} = \left[\left(\underline{\underline{E}} + \langle \underline{\underline{T}} \rangle\right)\left(\underline{\underline{E}} - \langle \underline{\underline{T}} \rangle\right)^{-1} - \frac{2\langle \underline{\underline{T}} \rangle}{n}\left(\underline{\underline{E}} - \langle \underline{\underline{T}} \rangle^n\right)\left(\underline{\underline{E}} - \langle \underline{\underline{T}} \rangle\right)^{-2} \right]_{11}$$

Special case of E(Φ)=E(-Φ) (*Symmetry*): $\Rightarrow \langle \sin\Phi \rangle = 0$

$$\langle \underline{\underline{T}} \rangle = \begin{pmatrix} \cos\Theta & \sin\Theta & 0 \\ \sin\Theta\langle\cos\Phi\rangle & -\cos\Theta\langle\cos\Phi\rangle & 0 \\ 0 & 0 & -\langle\cos\Phi\rangle \end{pmatrix}$$

In case of n→∞ follows:

$$C_\infty = \frac{1+\cos\Theta}{1-\cos\Theta} \cdot \frac{1+\langle\cos\Phi\rangle}{1-\langle\cos\Phi\rangle}$$

Main contribution of C_∞ results from $\Phi \approx 0 \rightarrow C_\infty$ can reach large values
only bad agreement of measured and calculated values (e.g. calculated polyethylene with $\langle\cos(\Phi)\rangle = 0.22$ yields C_∞=3.4 instead of 6.8 (measured)

d) Chain with discrete isomeric rotational states
RIS (Rotational Isometrie State)

Assumption of independent bond rotation potentials not valid

$$\sum_{i=1}^{n-1} E_i(\Theta_i, \Phi_i) \neq E\{\Phi\}$$

Interdependence of the bond rotation potentials in the polymer chain not taken into account, but bond rotation angle at position Φ_i depends on the bond rotation angle at the positions Φ_{i-1} and Φ_{i+1}

bond rotation potentials have (relative) minima, which are separated from each other by energy barriers

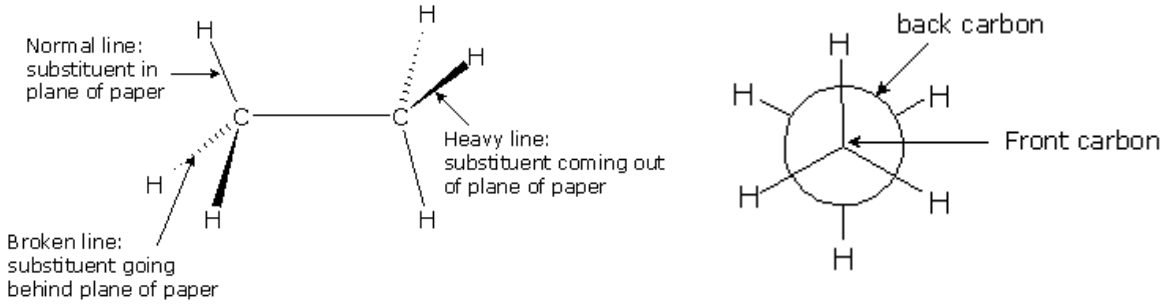
Example: conformation of n-pentane, resulting from rotation around the two inner C-C bonds:

a) trans, trans — with $\Phi_2 = \Phi_3 = 0$ — energetically favorable
b) gauche+, gauche+ — with $\Phi_2 = \Phi_3 = 120°$ — head-tail distance 3.6Å
c) gauche+, gauche- — with $\Phi_2 = -\Phi_3 = 120°$ — head-tail distance 2.5Å

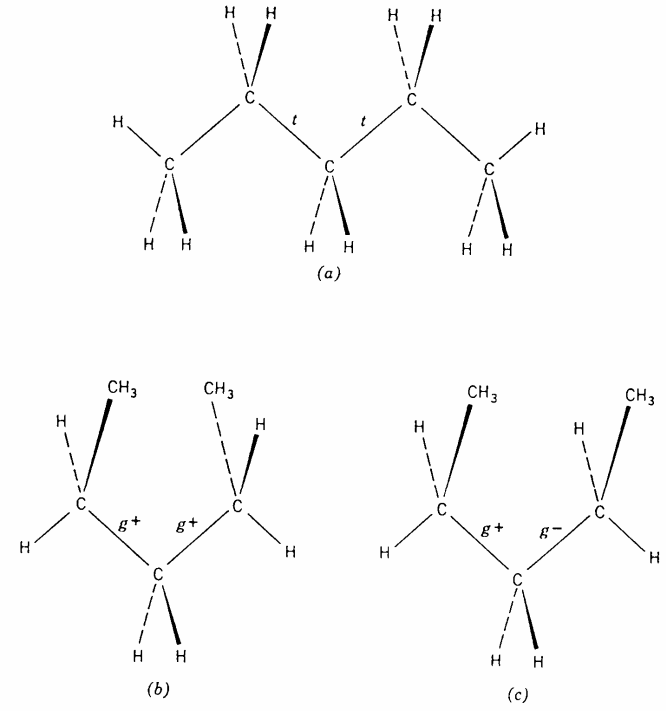
→ suppression of the configuration gauche+, gauche
⇒ pentane effect

Sawhorse representation: The spatial orientation are indicated by employing heavy tapered lines for substituents coming out of the page, normal lines for substituents in the plane of the page, and dashed lines for substituents going back behind the plane of the page.
Newman projection: in this representation one views the carbon-carbon bond directly end-on and represents the two carbon atoms by a circle. Lines going to the center of the circle represent substituents on the front carbon, and lines going to the edge of the circle represent substituents on the rear carbon.

Sawhorse representation **Newman projection**



Example: conformation of n-pentane



Assumption: 3 rotational isomeric states per bond
→ energy of the conformation of such chain

$$E\{\Phi\} = \sum_{i=2}^{n-1} E_i(\Phi_{i-1}\Phi_i) = \sum_{i=2}^{n-1} E_{\xi\eta;i}$$

with ξ denoting rotational state of bond i-1
η denoting rotational state of bond i

Put into Boltzmann factor gives a statistical weight $u_{\xi\eta}$ for the energy $E_{\xi\eta}$

$$u_{\xi\eta;i} = \exp(-\beta E_{\xi\eta;i})$$

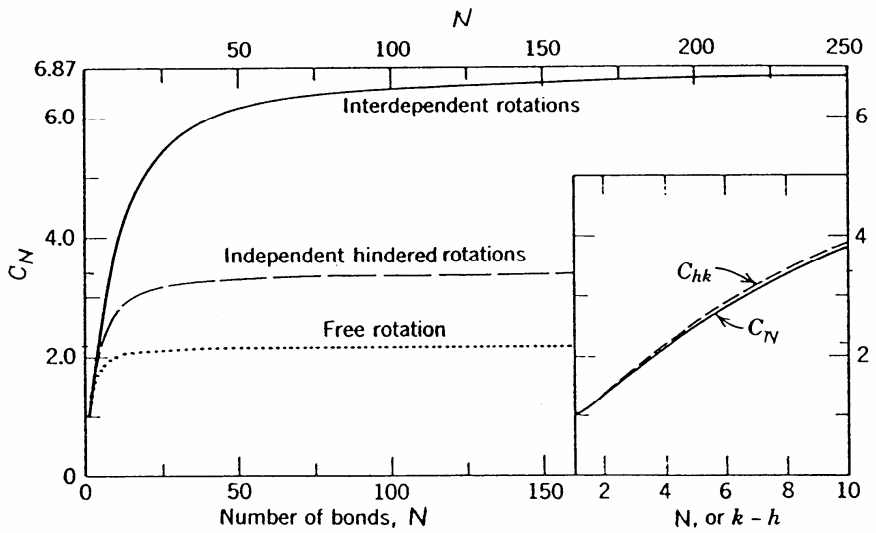
In case of homogeneous chain 3x3 combinations, which can be combined into a formalism using a 3x3 matrix of statistical weights

$$\underline{\underline{U}} = \begin{array}{c} \\ t \\ g+ \\ g- \end{array} \begin{array}{c} \begin{array}{ccc} t & g+ & g- \end{array} \\ \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{pmatrix} \end{array} \quad \text{with } \sigma = \exp\left(-\frac{E}{RT}\right)$$

After some lengthily calculation the characteristic ratio is obtained

$$C_n = \frac{\langle r^2 \rangle}{nl^2} = \left[\left\| B_1^* \right\| \left\| E + S \right\| \left\| E - S \right\|^{-1} \left\| A_1 \right\| \right]_{11}$$

Example: polyethylene at T=140°C



RIS model only good for $n \to \infty$

e) Kuhn Segment

Adapt concept of freely-jointed chain to real chain by introduction of Kuhn segment and Kuhn length l'. Each Kuhn segment can be thought of as if they are freely jointed with each other.

Maximum chain length $r_{max} = n' l'$

end-to-end distance $\langle r^2 \rangle = n' l'^2 = C_n n l^2$

→ knowing r_{max} and $\langle r^2 \rangle$ allows to calculate n' and l'

Example: polyethylene n'≈0.1n and l'≈8l yields c_n=6.8

3.4 Real chain models

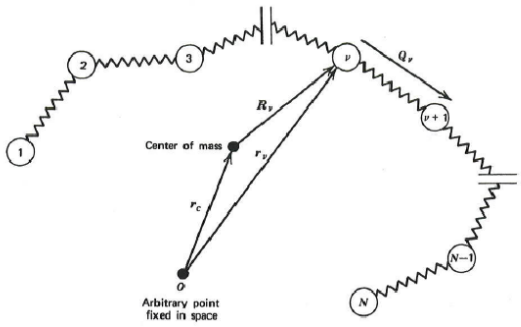
a) Gaussian Chain Model

generalization of the freely-jointed chain with polymer segments that are connected with bond vectors following a Gaussian distribution

$$\Psi(\underline{l}) = \left(\frac{3}{2\pi N d^2}\right)^{3/2} \exp\left[-\frac{3l^2}{2Nd^2}\right]$$

$$\text{with } d^2 = \langle l^2 \rangle = \int d^3 l \Psi(\underline{l}) l^2$$

e.g. Gaussian bead-spring chain with N springs of mean-squared length d*d



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because all directions of bond vectors are equally probable (random walk), the distribution function of the distanced vectors follows a Gaussian-type as well

with $\int_0^\infty 4\pi l^2 \Psi(l) dl = 1$

average end-to-end distance

$$\langle r^2 \rangle = \int_0^\infty l^2 4\pi l^2 \Psi(l) dl = Nd^2$$

→ similar to freely-jointed chain, but d^2 replaces l^2

However, note that, $\langle r \rangle = \int_0^\infty l 4\pi l^2 \Psi(l) dl = \sqrt{\frac{8}{3\pi}} N^{1/2} d = 0.9212\sqrt{N}\, d$

which means that average spring length ($N=1$) is smaller d. Therefore the average contour length is not Nd.

excluded volume refers to the idea that one part of a long chain molecule can not occupy space that is already occupied by another part of the same molecule

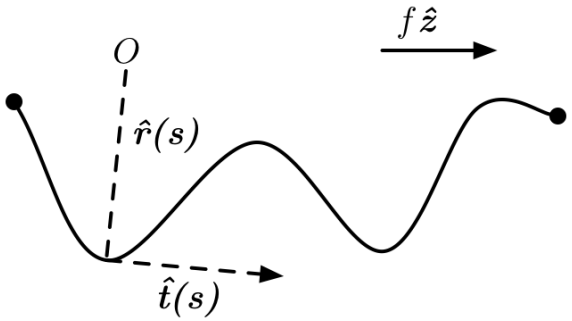
→ excluded volume causes the ends of a polymer chain in a solution to be further apart (on average) than they would be were there no excluded volume

b) Worm-like Chain Model

A short-coming of the above models (besides they being phantom chains, i.e. no self-avoidance) is that there is no intrinsic stiffness. Intuitively, we expect a bending of the chain to cost energy.

The WLC model envisions an isotropic rod that is continuously flexible; this is in contrast to the freely-jointed chain model that is flexible only between discrete segments.

→ behavior of semi-flexible polymers



Define ***r(s)*** as the position as a function of the relaxed-state contour length, *s*.

Also shown is the tangent vector ***t(s)***, which is the first derivative of ***r(s)*** with respect to a line segment ds.

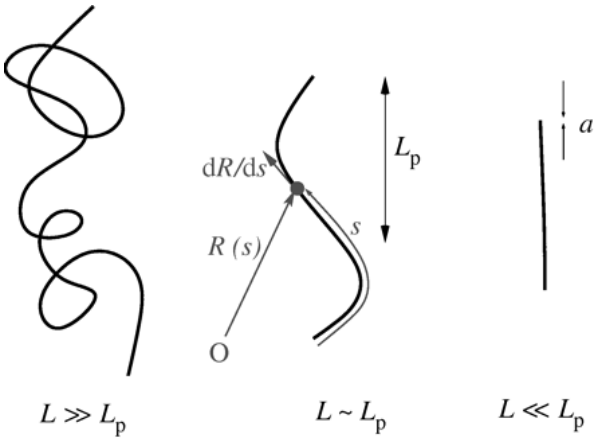
Similar to the one-dimensional Heisenberg model for ferromagnets

$$H = -\varepsilon \sum_{i=1}^{n-1} \underline{l}_i \cdot \underline{l}_{i+1} \quad \text{with bending modulus } \kappa = \varepsilon b$$

After some calculations with the persistence length $L_p=\kappa/(kT)$, the length over which correlations in the direction of the tangent are lost (mechanical property quantifying the stiffness of a polymer)

For pieces of the polymer that are shorter than the persistence length, the molecule behaves rather like a flexible elastic rod, while for pieces of the polymer that are much longer than the persistence length, the properties can only be described statistically, like a three-dimensional random walk.

Examples: PS (M_n=98000 g/mol) L_p =15 nm
PVC (M_n=70500 g/mol) L_p =13 nm
Double-helical DNA L_p =50 nm



The ratio of filament length, *L*, to persistence length, L_p, showing flexible $L>>L_p>>a$, semiflexible $L\sim L_p>>>a$ and rigid $L_p>>L>>a$ regimes.

T.Liverpool *Phil. Trans. R. Soc. A 15*, 364, 3335-3355 (2006)

→ end-to-end-distance $\left\langle r^2 \right\rangle = 2L_p l\left[1-\frac{L_p}{l}\left(1-\exp\left(-\frac{l}{L_p}\right)\right)\right]$

$$R_e^2 = \left\langle r^2 \right\rangle = 2L_p^2\left[\frac{l}{L_p}-1+\exp\left(-\frac{l}{L_p}\right)\right]$$

with $f_D=2(x-1+\exp(-x))/x^2$ being the Debye-function: $R_e^2 = \left\langle r^2 \right\rangle = l^2 f_D\left(\frac{l}{L_p}\right)$

in the limit $l>>L_p$: $R_e^2 = \left\langle r^2 \right\rangle = 2L_p l^2$

→ a Kuhn segment is equal to twice the persistence length of a worm-like chain

c) Self-Avoiding Chains

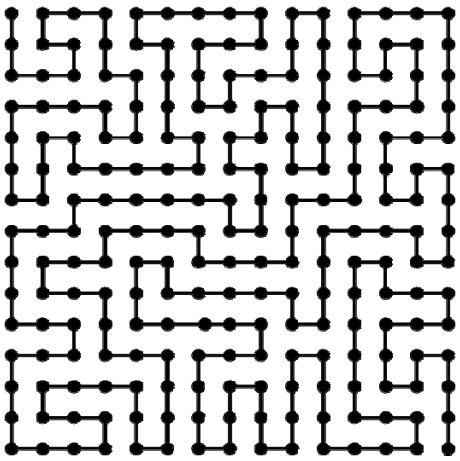
The above models all lack the excluded volume interaction between the monomers.

→ polymer model with a self-avoiding random walk

→ monomer-monomer interaction potential assumed to handle the excluded volume

The self-avoiding random walk (SAW) on a periodic lattice as a model of a polymer chain.

first introduced by Flory



average end-to-end distance

$$R_e^2 = \left\langle r^2 \right\rangle = n^{2\nu} l^2$$

with $\nu = \frac{3}{d+2}$

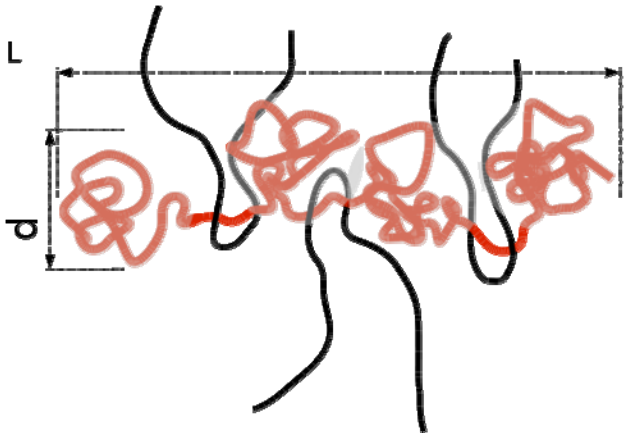
with ν= 0.59 (numerically in 3d)

excluded volume (within mean field theory on d=3 lattice) ν = 3/5

ideal chain (freely-jointed chain, without self avoidance) ν = 1/2

d) Blob model

In the 'blob' model, the polymer chain is made up of n Kuhn lengths of individual length l. The chain is assumed to form tangled 'blobs' between each effective cross-links, containing n_e Kuhn length segments in each.



polymer chain made up of n_e Kuhn lengths

A blobs on a particular chain: $A = \frac{n}{n_e}$

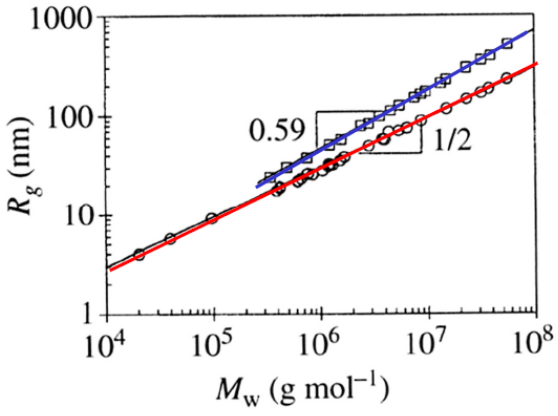
average end-to-end distance

$$R_e^2 = \langle r^2 \rangle = \frac{n^2 l^2}{n_e}$$

e) compare with measurements

x-ray and neutron scattering give access to radius of gyration R_g

Example: PS in different solvents



polystyrene in benzene

(good solvent) $R_g = \langle s^2 \rangle^{1/2} \propto n^{0.59}$

polystyrene in cyclohexane

(theta solvent) $R_g = \langle s^2 \rangle^{1/2} \propto n^{0.50}$

from Rubinstein, Colby.
Data compiled by L.J. Fetters, J. Phys. Chem. 1994

→ chain conformation depends on solvent, thus on interaction polymer-solvent