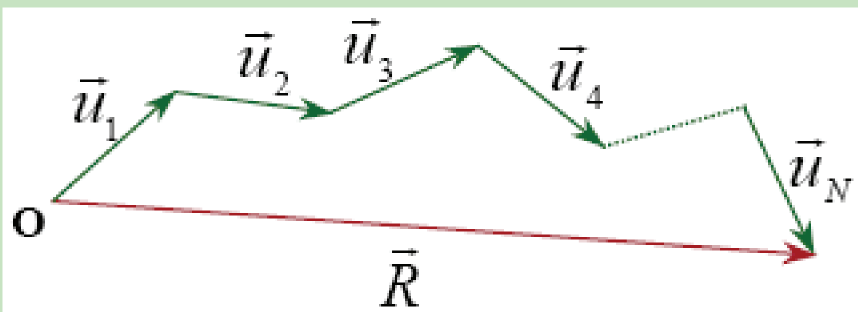
Ideal Polymer Chain.

Ideal Polymer Chain.

Ideal chain is a chain in which the links do not interact if they are not close long the chain. In other words, the so-called volume interactions, i.e. interactions between distant links which come close to each other due to the chain flexibility, are neglected.
Polymer chains behave as ideal ones at the so-called Θ-conditions, (we will discuss this issue in more detail in one of the next lectures).

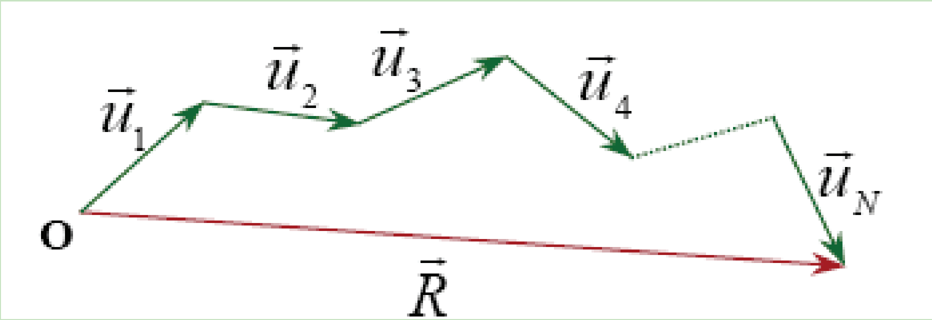
Consider first a freely-jointed chain of N segments of length l:



From the symmetry considerations, it is obvious that the mean end-to-end distance of the chain $\vec{\mathbf{R}}$ equals 0. The size of the coil is therefore characterized by

$$R \propto \sqrt{\langle R^2 \rangle}$$

Freely-Jointed Chain.



$$R^2 = \left(\sum_{i=1}^{n} \vec{u}_i\right)\left(\sum_{j=1}^{n} \vec{u}_j\right) = \sum_{i=1}^{n}\sum_{j=1}^{n} \vec{u}_i \vec{u}_j$$

$$\left\langle R^2 \right\rangle = \sum_{i=1}^{n}\sum_{j=1}^{n} \left\langle \vec{u}_i \vec{u}_j \right\rangle = \sum_{i=1}^{n} \left\langle \vec{u}_i^{\,2} \right\rangle + \sum_{\substack{i,j=1,\\ i\neq j}}^{n} \left\langle \vec{u}_i \vec{u}_j \right\rangle$$

but for the freely-jointed chain $\left\langle \vec{u}_i \vec{u}_j \right\rangle = 0$ for $i \neq j$, and therefore

$\left\langle R^2 \right\rangle = \sum_{i=1}^{n} \left\langle \vec{u}_i^{\,2} \right\rangle = Nl^2 = Ll, \; L = Nl,$ where L is the contour length of the chain

$$\boxed{R \sim \sqrt{\left\langle R^2 \right\rangle} = N^{1/2} l, \quad R \ll L}$$

Freely-Jointed Chain.

$$\boxed{R \sim \sqrt{\langle R^2 \rangle} = N^{1/2} l, \quad R \ll L}$$

We see that:

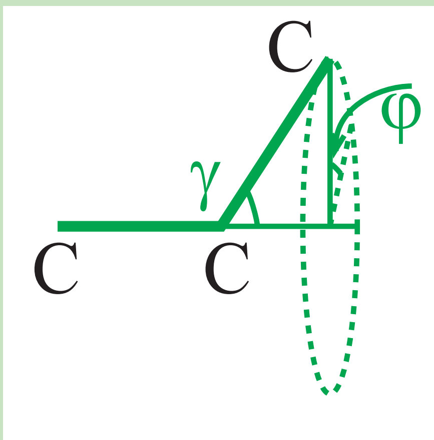
- the conformation of the ideal chain is far from rectilinear;

- the ideal chain forms an entangled coil;

- the trajectory of the chain is equivalent to the trajectory of a Brownian particle.

Chain with a Fixed Valency Angle.

The aforementioned result for the typical coil size $R \sim N^{1/2}$, is valid for an ideal chain with any flexibility mechanism. Indeed, consider for example the model with fixed valency angle γ between the segments of length b (assume for simplicity that $u(\varphi) = 0$):



As before

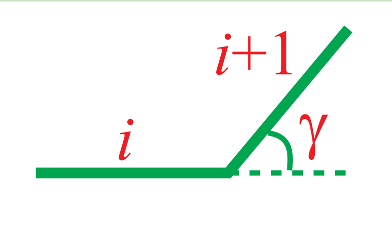
$$\left\langle R^2 \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle \vec{u}_i \vec{u}_j \right\rangle = \sum_{i=1}^{n} \left\langle \vec{u}_i^{\,2} \right\rangle + \sum_{\substack{i,j=1,\\ i \neq j}}^{n} \left\langle \vec{u}_i \vec{u}_j \right\rangle,$$

$\left\langle \vec{u}_i^{\,2} \right\rangle = b^2$, but now $\left\langle \vec{u}_i \vec{u}_j \right\rangle \neq 0$

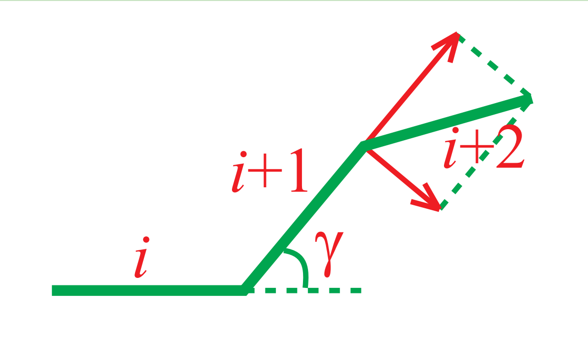
Instead of that we have:

$\left\langle R^2 \right\rangle = Nb^2 + b^2 \sum_{\substack{i,j=1\\ i \neq j}}^{n} \left\langle \cos\theta_{ij} \right\rangle$, where θ_{ij} is an angle between ith and jth segments.

Chain with a Fixed Valency Angle.



$$\langle \cos\theta_{i,i+1} \rangle = \cos\gamma$$



$$\langle \cos\theta_{i,i+2} \rangle = \cos^2\gamma$$

Continuing in the same way, we get $\langle \cos\theta_{i,i+k} \rangle = \cos^k\gamma$, and thus

$$\langle R^2 \rangle = Nb^2 + 2b^2 \sum_{i=1}^{N} \sum_{k=1}^{N-i} \langle \cos\theta_{i,i+k} \rangle = Nb^2 + 2b^2 \sum_{i=1}^{N} \sum_{k=1}^{N-i} \cos^k\gamma \approx$$

$$\approx Nb^2 + 2Nb^2 \frac{\cos\gamma}{1-\cos\gamma} = \boxed{Nb^2 \frac{1+\cos\gamma}{1-\cos\gamma}}$$

(where $k = j - i$)

Chain with a Fixed Valency Angle.

The final result is, therefore:

$$\boxed{R \sim \sqrt{\left\langle R^2 \right\rangle} = N^{1/2} b \sqrt{\frac{1+\cos\gamma}{1-\cos\gamma}}}$$

Thus, within the model with a fixed valency angle we once again get an entangled coil: the typical size of the coil is once again proportional to the square root of the contour length of the chain. This result is a universal feature of the ideal chains regardless of the particular flexibility model.

For $\gamma < 90^{\circ}$ the value of R is larger than for the freely-jointed chain, while for $\gamma > 90^{\circ}$ it is smaller.

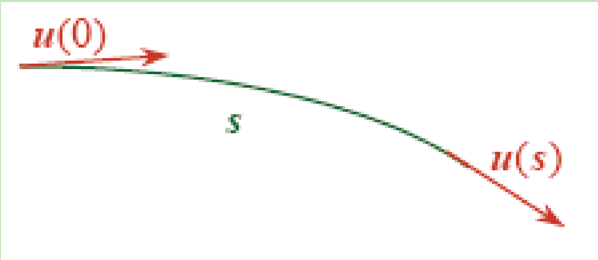
Persistent Length of a Polymer Chain.

Consider once again the results we obtained for the model with a fixed valency angle. Let us rewrite the formula for the orientational correlations as follows:

$$\left\langle \cos\theta_{i,i+k} \right\rangle = \left(\cos\gamma\right)^{k} = \exp\left(-k\left|\ln\cos\gamma\right|\right) = \exp\left(-\frac{kb}{b/\left|\ln\cos\gamma\right|}\right) =$$

$$= \exp\left(-s/\tilde{l}\right), \text{ где } \tilde{l} = b/\left|\ln\cos\gamma\right|$$

We introduced here the contour distance between two monomer units of the chain $s = kb$.



In terms of the unit tangent vectors $\vec{u}$ this result can be rewritten as follows

$$\left\langle \vec{u}(0)\vec{u}(s)\right\rangle = \exp\left(-s/\tilde{l}\right)$$

Persistent Length of a Polymer Chain.

We derived the formula $\left\langle \vec{u}(0)\vec{u}(s) \right\rangle = \exp\left(-s/\tilde{l}\right)$ within a model with a fixed valency angle. It is, however universal, i.e. valid for any model of polymer flexibility:
orientational correlations decay exponentially along the chain.

The characteristic length of this decay $\tilde{l}$ is called a persistent length of the chain.

For $s \ll \tilde{l}$ the chain stays almost rectilinear, while at $s \gg \tilde{l}$ the memory about the chain orientation is completely lost. Therefore, one can divide an ideal chain into segments of length $\tilde{l}$ and assume them to be rectilinear and independent from each other. Thus,

$$R \sim \sqrt{\left\langle R^2 \right\rangle} \sim \sqrt{\frac{L}{\tilde{l}}\tilde{l}^2} = \sqrt{L\tilde{l}}$$

We get once again the same result: the size of the coil R is proportional to the square root of the chain length L.

Kuhn Segment of a Polymer Chain.

We know now that for idea chain $\left\langle R^2 \right\rangle \sim L$

The Kuhn segment length l of a chain is defined as

$l = \left\langle R^2 \right\rangle / L$ (for large L)

(i.e., the equality $\left\langle R^2 \right\rangle = Ll$ is valid by definition)

Both l and $\tilde{l}$ are used in actual practice.
The Kuhn segment length l has an intrisic advantage of being easily measurable in the experiment, while
an intrinsic advantage of the persistent length $\tilde{l}$ is that it has a simple and transparent microscopic meaning.

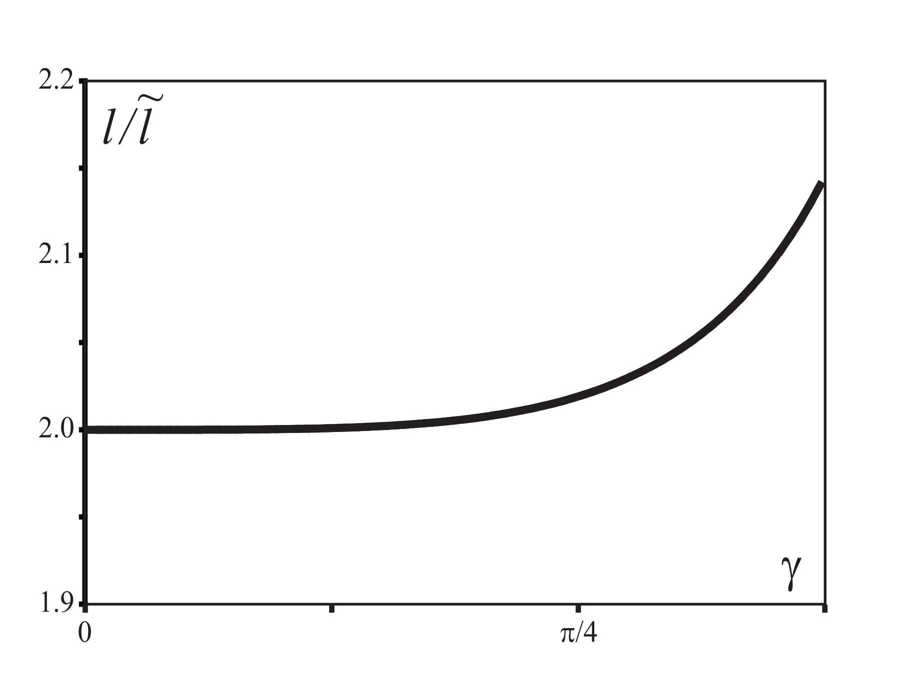
One always has $l \sim \tilde{l}$. For example, for the model with a fixed valency angle

$$l = b\frac{1+\cos\gamma}{1-\cos\gamma}, \quad \tilde{l} = b/\left|\ln\cos\gamma\right| \quad \Rightarrow \quad \boxed{l/\tilde{l} = \left|\ln\cos\gamma\right|\frac{1+\cos\gamma}{1-\cos\gamma}}$$

Kuhn Segment of a Polymer Chain.

$$\boxed{l/\tilde{l} = \left|\ln\cos\gamma\right| \frac{1+\cos\gamma}{1-\cos\gamma}}$$

The ratio $l/\tilde{l}$ is always close to 2. In the limit of $\gamma \to 0$ it exactly equals two.
This limit corresponds to the persistent flexibility mechanism.



Indeed, let simultaneously $\gamma \to 0, N \to \infty, b \to 0$ in such a way that

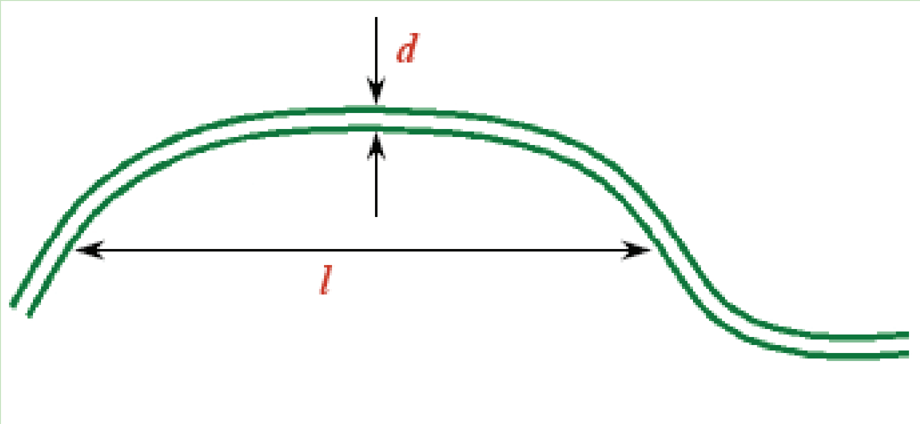
$$Nb = L = const \quad \text{и} \quad l = b\frac{1+\cos\gamma}{1-\cos\gamma} = \frac{2b}{1-1+\gamma^2/2} = \frac{4b}{\gamma^2} = const$$

We get in this way a filament whose flexibility is evenly distributed, i.e. a persistent chain.
Thus, for a persistent chain $l/\tilde{l} = 2$. The meaning of the factor 2 is quite simple: the correlations along the chain spread in two directions.

Stiff Chains vs. Flexible Chains.

Thus, we have now a quantitative parameter that characterizes the chain stiffness: the length of the Kuhn segment l (or the persistent length $\tilde{l}$, which is proportional to l).

From the macroscopic point of view a polymer chain can be considered as a filament characterized by two lengths: the typical chain diameter d and the Kuhn segment length l:



Normally, the Kuhn segment length is larger than the typical size of a monomer unit characterized either by d or by the contour length per one unit l_0.

Stiff Chains vs. Flexible Chains.

The chains are called flexible if $l \sim d\left(l_0\right)$, and stiff if $l \gg d\left(l_0\right)$.

Most of the polymers with carbone backbone belong to the flexible class, e.g.:

	l/l_0		l/l_0
Poly(ethylene oxide)	2.5	Poly(vinyl chloride)	4
Poly(ethylene)	3.5	Poly(styrene)	5
Poly(methyl metacrylate)	4	Poly(acrylamide)	6.5

To the stiff class belong double-stranded DNA, helical polypeptides, aromatic polyamides, etc. Here are several examples:

	l/l_0		l/l_0
Cellulose diacetate	26	DNA (in double helix)	300
Poly(para-benzamide)	200	Poly(benzyl-L-glutamate)	500

Polymer Volume Fraction inside an Ideal Coil.

The typical size of an ideal coil is

$$R \sim (Ll)^{1/2},$$

therefore, its volume V is of order

$$V \sim (Ll)^{3/2}$$

Thus., the volume fraction of the polymer in a coil

$$\phi \sim \frac{Ld^2}{(Ll)^{3/2}} = \left(\frac{d}{L}\right)^{1/2} \left(\frac{d}{l}\right)^{3/2} \ll 1$$

is extremely small for large L.

Gyration Radius of an Ideal Coil.

Center of mass of a mechanical system (and polymer coil, in particular) is defined as

$$\vec{r}_0 = \frac{1}{NM}\sum_{i=1}^{N} m_i \vec{r}_i = \frac{1}{N}\sum_{i=1}^{N} \vec{r}_i$$

where the second equation is vaid for a homopolymer whose monomer units all have a same mass.

Moreover, gyration radius of a coil is defined by

$$S^2 = \frac{1}{NM}\sum_{i=1}^{N} m_i \left(\vec{r}_i - \vec{r}_0\right)^2 = \frac{1}{N}\sum_{i=1}^{N} \left(\vec{r}_i - \vec{r}_0\right)^2$$

The value of gyration radius can be measured directly in the light scattering experiments, which will be discussed in one of the subsequent lections.

For an ideal coil one can show that

$$\left\langle S^2 \right\rangle = \frac{1}{6}\left\langle R^2 \right\rangle = \frac{1}{6} Ll$$

Probability Distribution for the End-to-End Distance in the Ideal Coil.

The trajectory of a freely-jointed chain is analogous to that of a Brownian particle, the contribution of each segment is independent of others. Therefore, according to the central limit theorem, if $N >> 1$ the probability distribution $P_N\left(\vec{R}\right)$ for the end-to-end distance in the ideal chain takes the Gaussian form

$$P_N\left(\vec{R}\right) = \left(2\pi N l^2/3\right)^{-3/2} \exp\left(-\frac{3R^2}{2Nl^2}\right)$$

This is the reason why the ideal polymer coil is also often called "Gaussian coil".

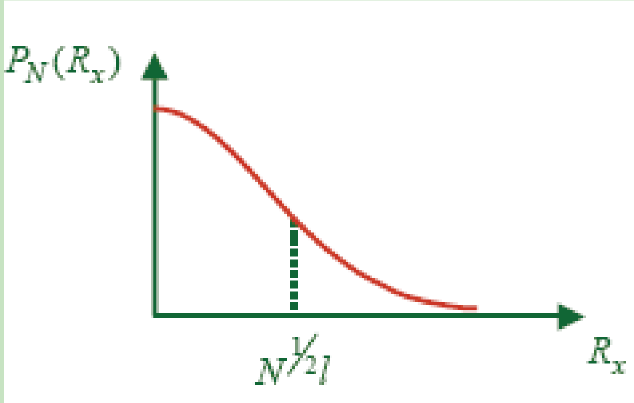
Note, the normaliztion condition, and the fact that the dependences of different coordinates are factorisable:

$$\int P_N\left(\vec{R}\right) d^3\vec{R} = 1$$

$$P_N\left(\vec{R}\right) = P_N\left(R_x\right) P_N\left(R_y\right) P_N\left(R_z\right)$$

Probability Distribution for the End-to-End Distance in the Ideal Coil.

$$P_N\left(\vec{R}\right) = \left(2\pi N l^2/3\right)^{-3/2} \exp\left(-\frac{3R^2}{2Nl^2}\right)$$



$\vec{R}$ undergoes extremely large fluctuations.

For other models with exponentially decaying orientational correlations the Gaussian distribution remains valid, if one rewrites it in the universal form:

$$P_N\left(\vec{R}\right) = \left(2\pi N l^2/3\right)^{-3/2} \exp\left(-\frac{3R^2}{2Nl^2}\right) \Rightarrow \left(2\pi \left\langle R^2\right\rangle/3\right)^{-3/2} \exp\left(-\frac{3R^2}{2\left\langle R^2\right\rangle}\right)$$

This form does not depend of any microscopic details of a model in question.