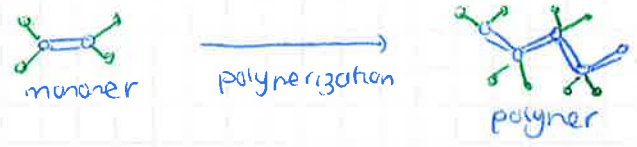


Lecture 10. Polymers

Polymers are long chain molecules made by repetition of a basic monomeric unit.



Polymerization: Process by which chain molecules are grown. Polymerization is a stochastic process. For large n the relative fluctuations in the degree of polymerization are small since $\Delta n \sim \sqrt{n}$ so the relative fluctuations vanish as $\frac{\Delta n}{n} \sim \frac{1}{\sqrt{n}}$ for large n .

Examples of polymers:

- Synthetic polymers:
 - polystyrene
 - polyethylene
- biopolymers:
 - DNA, RNA
 - proteins:
 - actin
 - microtubules

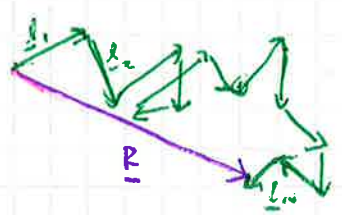
} great conformational freedom
 } flexibility is noticeable at the molecular scale
 } stiff enough its better to think of them as thin inextensible rods
 } flexibility becomes noticeable on a sufficiently long length scale (persistence length)

when their degree of polymerization is high, the properties of a polymer can be captured by simple statistical physics models.

The ideal chain model

The simplest possible description of a polymer consists of N identical segments, all taken to be stiff rods of length l , joined sequentially without constraints on their angles.

The total end-to-end vector after N segments is:



$$\underline{R} = \sum_{i=1}^N \underline{l}_i$$

\therefore We assume the rods are stiff and the vectors \underline{l}_i are uncorrelated:

$$\langle \underline{l}_i \rangle = 0$$

$$\langle \underline{l}_i \cdot \underline{l}_j \rangle = \langle |\underline{l}|^2 \rangle \delta_{ij} = l^2 \delta_{ij}$$

Here l is known as the Kuhn length. The Kuhn length is not the monomer size, but an effective length after which successive sections can be thought to be directionally uncorrelated. Similarly N , the number of statistically independent units is not the actual number of monomers.

For most synthetic polymers the Kuhn length is $\sim 1-2$ nm, for biopolymers the Kuhn length is comparable to the persistence length, i.e. much larger, for instance for DNA its 50 nm.

The expectation value of \underline{R} is:

$$\langle \underline{R} \rangle = \left\langle \sum_{i=1}^N \underline{l}_i \right\rangle = 0 \quad \text{since the relative orientations of the segments are random.}$$

$$\langle |\underline{R}|^2 \rangle = \langle \underline{R} \cdot \underline{R} \rangle = \left\langle \sum_{i=1}^N \underline{l}_i \cdot \sum_{j=1}^N \underline{l}_j \right\rangle = \sum_{i,j=1}^N \langle \underline{l}_i \cdot \underline{l}_j \rangle = \sum_{i=1}^N \langle \underline{l}_i \cdot \underline{l}_i \rangle = N l^2$$

In polymer physics we commonly focus on the root mean square end-to-end distance

$$R_0 = \langle |\underline{R}|^2 \rangle^{1/2} = \sqrt{N} l$$

This average end-to-end distance is much shorter than the contour length Nl . Polymer blobs will assume a configuration that is much more compact than a straight line.

Since we will often focus on how polymer properties scale with N , we can write:

$$R_0 = l N^\nu, \quad \text{with } \nu = \frac{1}{2} \text{ for ideal chains}$$

The probability distribution of end-to-end distances of the polymer can be calculated using the central limit theorem. As the end-to-end distance is the sum of many independent and identically distributed random variables (or uncorrelated random vectors), the probability distribution is a Gaussian and in d dimensions we have:

$$P(N, \underline{R}) \approx \left(\frac{1}{2\pi R_0^2/d} \right)^{d/2} e^{-dR^2/2R_0^2}$$

Notice that the distribution of the end-to-end distance of a polymer as well as its mean and variance are identical to the solution of the diffusion equation, which makes sense since both diffusing particles and our polymer chain are undergoing a random walk.

Instead of the average end-to-end distance, the shape of the polymer chain can be described by the radius of gyration R_g of the polymer, which is the radius with respect to its center of mass.
 $R_g = \sqrt{(N/6)l}$ so it follows the same scaling as the end-to-end distance.

The shape of a polymer is termed its conformation. If we denote by $\Omega(N, \underline{R})$ the number of conformations associated with a given end-to-end distance of a polymer of size N , we can see that:

$$P(N, \underline{R}) = \frac{\Omega(N, \underline{R})}{\int d^d R \Omega(N, \underline{R})} = \left(\frac{1}{2\pi R_0^2/d} \right)^{d/2} e^{-dR^2/2R_0^2}$$

Fraction of all conformations that have end-to-end distance between \underline{R} and $\underline{R} + d\underline{R}$

Recall from statistical physics that the entropy for this state is given by:

$$S(N, \underline{R}) = k_B \ln P(N, \underline{R}) \quad \text{in our case, the only } R \text{ dependence comes from the term in the exponent so!}$$

$$\Delta S(N, \underline{R}) \equiv S(N, \underline{R}) - S(N, 0) = -\frac{dk_B}{2} \left(\frac{R}{R_0} \right)^2 \quad \text{change in conformational entropy as } R \text{ increases.}$$

The chain's entropy decreases as R increases, and there are fewer states available the more it is stretched. Note that this expression is valid for "small stretching" since when the chain is stretched to its maximum length, there is only one available state.

And the conformational contribution to the free energy ($F = U - TS$) is:

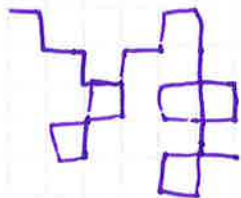
$$\Delta F(N, \underline{R}) = \frac{dk_B T}{2} \left(\frac{R}{R_0} \right)^2 = \frac{dk_B T R^2}{2l^2 N} \quad \text{we have a quadratic increase in the free energy as } R \text{ increases as the polymer is being stretched.}$$

At equilibrium the ideal chain responds like an elastic spring, whose energy grows quadratically with extension, which implies its force is linear in the extension.

The ideal polymer chain does not take into account excluded volume interactions. Many configurations can have parts of the chain very near each other or even on top of each other. To account for excluded volume interactions we draw again an analogy with random walks.

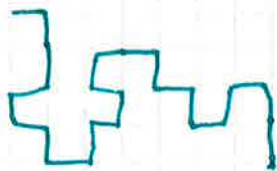
We will still think of ^{chain} configurations as random walks, but now we put the random walks into a lattice, in other words we have a self-avoiding walk.

Random walk



points can be revisited many times

self-avoiding random walk



points cannot be revisited

For 1D a self-avoiding random walk is trivial, walk cannot turn back, so the end-to-end distance grows linearly with N .

$$\text{For 1D } R_0 = lN^1, \nu = 1$$

For 2D self-avoiding random walks are much faster, than regular random walks (see example above)

$$\text{For 2D } R_0 = lN^{\nu}, \nu = \frac{3}{4} \quad (\text{exact analytical result})$$

For 3D self-avoidance intuitively the self-avoidance is less constraining than in 2D.

$$\text{For 3D } R_0 = lN^{\nu}, \nu = 0.588 \quad (\text{result from simulations})$$

1. The Flory argument for excluded volume interactions

The entropic elastic force favors end-to-end polymer distance to be minimal (as we stretch the polymer fewer configurations are available)

While entropic forces prevent the polymer from being too large, the repulsive forces prevent it from contracting into a small volume.



To estimate the repulsive energy we imagine each monomer has a repulsive interaction with other monomers in the neighborhood \bigcirc around it.

As the monomer density in d dimensions scales as $n_m = \frac{N}{R^d}$, the average number of monomers each \bigcirc interacts with is $n_m \times \text{Volume of } \bigcirc$

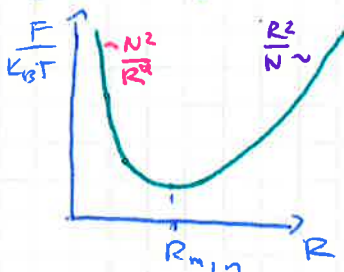
And as the number of monomers also scales with N , we estimate the total repulsive interaction as

$$\frac{U_{int}}{k_B T} = v N n_m = v \frac{N^2}{R^d} \quad \text{where } v \text{ measures the strength of the effective interaction.}$$

So the total free energy in this approximation is the energy for this interaction plus the entropic (conformational) contribution so we have:

$$\frac{F}{k_B T} = \frac{v N^2}{R^d} + \frac{d R^2}{2 l^2 N}$$

↑ short range repulsion ↑ entropic attraction



Free energy is large if monomers get too close \rightarrow repulsive interaction

Free energy is large if R is large because we need to do work against configurational entropy.

Minimizing the free energy with respect to R we get:

$$-\frac{dV N^2}{R^{d+1}} + \frac{dR}{N l^2} = 0 \Rightarrow R = (V l^2 N^3)^{1/(d+2)} \sim N^{3/(d+2)}$$

So for the Flory self-avoiding random walk we get:

$$R_0 = (V l^2 N^3)^{1/(d+2)} \sim N^{\nu}, \quad \nu = \frac{3}{d+2}$$

Excluded volume effects are especially important for synthetic polymers and less so for biopolymers, which tend to behave more like ideal chains.

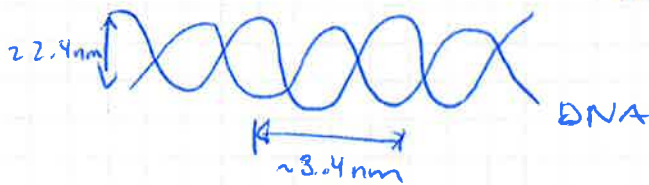
In practice the Flory ν exponent is remarkably accurate.

	ν_{Flory}	$\nu_{\text{self-avoiding random walk}}$
$d=1$	1	1
$d=2$	3/4	3/4
$d=3$	3/5	0.588
$d=4$	1/2	1/2

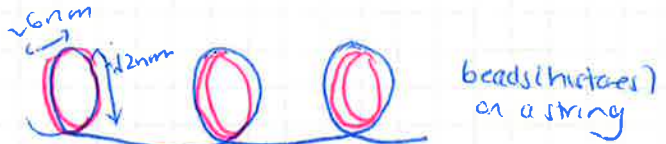
Flory's theory does reasonably well as two effects more or less compensate for each other. On one hand the conformational entropy in the ideal chain ~~overestimates~~ largely overestimates it on the other hand the repulsive interactions neglect any correlations so it ~~overestimates~~ the repulsive potential for local configurations in which chain segments get near each other w/o interacting significantly. *more nice example of how approximations cancel each other out.*

The worm-like chain model for biopolymers.

The models we discussed so far work for synthetic polymers since their Kuhn length is a few times their monomer size. Most biopolymers are ~~not~~ ^{not} flexible at the molecular scale.



DNA



DNA is bent in θ (50 nm)

Biopolymers are often referred as **semiflexible** and it's better to think of them as thin bendable rods. This motivates describing biopolymers by the **wormlike chain model (WLC)**. This model takes into account the bending energy and configurational entropy of a polymer.

The WLC model is characterized by the important length scale the **persistence length**, which is defined as the length scale at which the elastic and thermal energies become comparable:

$$l_p = \frac{\alpha}{k_B T} \quad \text{where } \alpha \text{ is the bending stiffness}$$

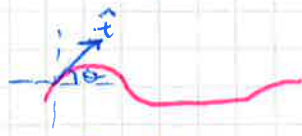
The WLC model has the elastic beam and the freely jointed chain as limiting cases, for polymers that are much shorter & much longer than their persistence length respectively.

The WLC model ~~describes~~ for a free chain of length L amounts to using the bending energy of a thin rod as the defining energy:

$$E_{\text{WLC}} = \int_0^L ds \frac{1}{2} \alpha \kappa^2 \quad ; \quad \text{where } s \text{ is the coordinate along the chain modelled as a smooth curve in 3D with local curvature } \kappa.$$

Note that E_{WLC} does not include an energy penalty for self-intersections of the curve, so the WLC is essentially a continuum version of the ideal non-interacting chain.

We will thus define a WLC by a curve in space



\hat{t} = unit vector tangent to the curve
 θ = angle \hat{t} makes with the x axis

$$\hat{t}_x(s) = \cos \theta \quad ; \quad \frac{d\theta}{ds} = \kappa$$

$$\hat{t}_y(s) = \sin \theta$$

To analyze the "shape" fluctuations we will follow again our analogy with diffusion. We will think of the coordinates along the curve as time and realize that $\kappa = \frac{d\theta}{ds}$, understanding

the fluctuations is equivalent to that of a random walker making steps in θ space.

Considering E_{WLC} as the energy of the WLC, the probability distribution of a whole chain configuration is simply given by:

$$P[\theta] \sim \exp \left[-\frac{1}{k_B T} \int_0^L ds \frac{1}{2} \alpha \left(\frac{d\theta}{ds} \right)^2 \right]$$

The connection with the random walk suggests that we should focus on the probability $P(\theta, s)$ that the chain has an angle θ at positions:

$$P(\theta, s+ds) = \int d\theta' W(\theta, \theta') P(\theta', s) \quad ; \quad \text{where } W(\theta, \theta') \equiv \text{transition probability for the } \theta \text{ changing from } \theta' \text{ to } \theta \text{ in } ds.$$

Or explicitly

$$W(\theta, \theta') = C \exp \left[-\frac{(\Delta\theta)^2}{2l_p^2 ds} \right], \quad \Delta\theta = \theta - \theta'$$

$C = \frac{1}{\sqrt{2\pi l_p^2 ds}}$ normalization constant needed for $\int d\theta W(\theta, \theta') = 1$

Since for small ds , $\Delta\theta \sim 0$, we can expand the integrand on $P(\theta, s+ds)$ about θ :

$$P(\theta, s+ds) = \int d(\Delta\theta) W(\Delta\theta) \left[1 + (\Delta\theta) \frac{\partial}{\partial \theta} + \frac{1}{2} (\Delta\theta)^2 \frac{\partial^2}{\partial \theta^2} + \dots \right] P(\theta, s)$$

These integrals (Gaussian moments) are straightforward to compute

$$\int W(\Delta\theta) d(\Delta\theta) = 1, \quad \int \Delta\theta W(\Delta\theta) d(\Delta\theta) = 0, \quad \int \Delta\theta^2 W(\Delta\theta) d(\Delta\theta) = \frac{ds}{l_p}$$

So we have:

$$P(\theta, s+ds) = P(\theta, s) + \frac{1}{2} \frac{ds}{l_p} \frac{\partial^2}{\partial \theta^2} P(\theta, s) + \dots$$

$$\Rightarrow \frac{P(\theta, s+ds) - P(\theta, s)}{ds} = \frac{1}{2l_p} \frac{\partial^2}{\partial \theta^2} P(\theta, s) + \dots \quad \text{taking the limit } ds \rightarrow 0$$

$$\Rightarrow \frac{\partial P(\theta, s)}{\partial s} = \frac{1}{2l_p} \frac{\partial^2 P(\theta, s)}{\partial \theta^2}$$

or $\frac{\partial P(\theta, s)}{\partial s} = D_\theta \frac{\partial^2 P(\theta, s)}{\partial \theta^2}$ with $D_\theta = \frac{1}{2l_p}$ the "diffusion" coefficient.

And as discussed, the solution to the F-P equation (for $\Theta(0) = 0$) is a Gaussian:

$$P(\theta, s) = \frac{1}{\sqrt{4\pi D_\theta s}} e^{-\theta^2 / (4D_\theta s)}$$

This expression implies a mean squared displacement:

$$\langle \theta^2(s) \rangle = 2 D_\theta s$$

We now have everything we need to calculate the correlation function of the tangent vectors,

$$\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \langle \cos \theta(0) \cdot \cos \theta(s) \rangle = \left\langle \frac{e^{i\theta(s)} + e^{-i\theta(s)}}{2} \right\rangle = \frac{\langle e^{i\theta(s)} \rangle + \langle e^{-i\theta(s)} \rangle}{2}$$

taking $\theta(s=0) = 0$

We can compute the average of $\langle e^{\pm i\theta(s)} \rangle$ as:

$$\langle e^{\pm i\theta} \rangle = \int_{-\infty}^{\infty} d\theta P(\theta, s) e^{\pm i\theta} = \frac{1}{\sqrt{4\pi D_\theta s}} \int_{-\infty}^{\infty} d\theta \exp\left(\frac{-1}{4 D_\theta s} [\theta^2 \mp 4i\theta D_\theta s]\right)$$

$$= \frac{1}{\sqrt{4\pi D_\theta s}} \int_{-\infty}^{\infty} d\theta \exp\left(-\frac{1}{4 D_\theta s} [\theta^2 \mp 2\theta (2i D_\theta s) + i^2 (2 D_\theta s)^2]\right)$$

completing the square

$$= \frac{1}{\sqrt{4\pi D_\theta s}} \int_{-\infty}^{\infty} d\theta \exp\left(-\frac{1}{4 D_\theta s} [\theta \mp 2i D_\theta s]^2 - i^2 (2 D_\theta s)^2\right)$$

$$= \frac{1}{\sqrt{4\pi D_\theta s}} \int_{-\infty}^{\infty} d\theta \exp\left(-\frac{(\theta \mp 2i D_\theta s)^2}{4 D_\theta s}\right) \cdot \exp\left(\frac{i^2 (2 D_\theta s)^2}{4 D_\theta s}\right)$$

$$= \frac{e^{-s D_\theta}}{\sqrt{4\pi D_\theta s}} \int_{-\infty}^{\infty} \exp\left(-\frac{(\theta \mp 2i D_\theta s)^2}{4 D_\theta s}\right) d\theta$$

$$= \frac{e^{-s D_\theta}}{\sqrt{4\pi D_\theta s}} \int_{z \in C_\pm} dz \exp\left(-\frac{z^2}{4 D_\theta s}\right) = \frac{e^{-s D_\theta}}{\sqrt{4\pi D_\theta s}} \sqrt{4\pi D_\theta s} = e^{-s D_\theta}$$

change variables by defining the curve C_\pm as the real line shifted up/down the complex plane by a constant value $\mp 2i D_\theta s$

Defining $f(z) = \exp(z^2 / 4 D_\theta s)$ and integrate it over the contour $\Gamma(a, b) = \gamma_1 + \gamma_2 + \gamma_3$ in the complex plane, γ_0 is the path along

the real line from $z = -a$ to $z = a$, C_+ is a vertical path from $z = a$ to $z = a + ib$, C_2 is a path parallel to the real line from $z = a + ib$ to $z = -a + ib$ and γ_3 closing the loop from $z = -a + ib$ to $z = -a$. Now $f(z)$ is analytic in the complex plane, so $\oint dz f(z) = 0$
 $z \in \Gamma(a, b)$

so the correlation of the tangent vectors becomes:

$$\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \frac{e^{-s D_\theta} + e^{-s D_\theta}}{2} = e^{-s D_\theta} = e^{-s/2\ell_p}$$

In two dimensions, so we can see that in 2D, $2\ell_p$ is the length over which the angular correlations decay, so the persistence length is $2\ell_p$.

In the limit $a \rightarrow \infty$, the γ_1 and γ_3 contributions are proportional to $e^{-a^2} \rightarrow 0$ thus setting $b = \mp 2 D_\theta s$ we can write

$$\lim_{a \rightarrow \infty} \oint dz f(z) = \int_{z \in C_+} dz f(z) - \int_{z \in C_-} dz f(z) = 0$$

$$\Rightarrow \int_{z \in C_+} dz f(z) = \int_{z \in C_-} dz f(z) = \sqrt{4\pi D_\theta s}$$

In 3D the bending in the other direction gives a similar contribution to the decay of angular correlations, so the persistence length equals:

$$\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = e^{-s/2\ell_p}$$

Typical values of the persistence length of biopolymers are:

	l_p
DNA	50 nm
dsRNA	64 nm
collagen	100 nm
actin	1 μ m
microtubules	1 mm

"semiflexible" covers a range of lengths (100 nm).

Now that we know the value of $\langle \hat{t}(0) \cdot \hat{t}(L) \rangle$ we can calculate the mean end-to-end distance:

$$\begin{aligned} \langle R^2 \rangle &= \int_0^L ds_1 \int_0^L ds_2 \langle \hat{t}(s_1) \cdot \hat{t}(s_2) \rangle \\ &= \int_0^L ds_1 \left[\int_0^{s_1} ds_2 e^{-(s_1-s_2)/l_p} + \int_{s_1}^L ds_2 e^{-(s_2-s_1)/l_p} \right] \\ &= l_p \int_0^L ds_1 \left[(1 - e^{-s_1/l_p}) + (1 - e^{-(L-s_1)/l_p}) \right] \\ &= 2l_p L \left[1 - \frac{l_p}{L} (1 - e^{-L/l_p}) \right] \end{aligned}$$

For $L \ll l_p$ this reduces to $\langle R^2 \rangle = L^2$ polymer behaves like a rigid rod since the chain is completely straight.

For $L \gg l_p$ this reduces to $\langle R^2 \rangle = 2l_p L = (2l_p)^2 \left(\frac{L}{2l_p} \right) = l_k^2 \left(\frac{L}{l_k} \right)$ where $l_k = 2l_p$ is the Kuhn length. polymer behaves like an ideal chain with Kuhn length $l_k = 2l_p$ and $N = \frac{L}{l_k}$ Kuhn segments.

The force extension curve of the WLC

Like with the freely-jointed chain model, the way to test the WLC model is to calculate its force extension curve and compare it to experimental data.

The energy of a WLC under an external force f applied to its end is:

$$\bar{E} = \int_0^L ds \left[\frac{1}{2} \alpha k^2 - f \cdot \hat{t}(s) \right] \quad \text{where } \alpha = \text{bending stiffness} \\ k = \text{curvature}$$

To get the force extension curve, the expectation value of the extension z , for a given force f can be calculated by:

$$\langle z \rangle = \frac{1}{Z(f)} \int \mathcal{D} \hat{t}(s) z \exp \left[-\frac{1}{2} l_p \int_0^L \left(\frac{d\hat{t}}{ds} \right)^2 + f \int_0^L \hat{t}_z(s) ds \right]$$

sum over all possible curves $\hat{t}(s)$ the polymer can adopt

where

$$Z(f) = \int \mathcal{D} \hat{t}(s) \exp \left[-\frac{1}{2} l_p \int_0^L \left(\frac{d\hat{t}}{ds} \right)^2 + f \int_0^L \hat{t}_z(s) ds \right]$$

partition function of WLC model with the external force added to the internal energy

For small forces $f = \frac{3k_B T R}{2l_p L}$; WLC behaves like an elastic spring with constant $\frac{3k_B T}{2l_p L}$

(For $\frac{L}{l_p} \gg 1$ we can get this more directly from the elastic free energy of the ideal chain)

For large forces $\frac{fl_p}{k_B T} = \frac{1}{4} \left(1 - \frac{\langle R_z \rangle}{L} \right)^2$

For intermediate forces $\frac{fl_p}{k_B T} = \frac{\langle R_z \rangle}{L} + \frac{1}{4(1 - \langle R_z \rangle / L)^2} - \frac{1}{4}$

Summary:

Ideal chain

- Polymer is modeled as N rigid segments of fixed length b
- No bending energy \rightarrow thermal fluctuations can bend the chain arbitrarily at any point
- No correlation between orientations of neighboring segments \rightarrow chain is "fully flexible"
- Chain behaves like a pre-random walk
- Model works well for synthetic polymers.

- end-to-end distance $\langle R^2 \rangle = Nb^2$
- tangent correlations $\langle \underline{t}(s) \cdot \underline{t}(s') \rangle = 0$ for $s \neq s'$
- no notion of stiffness or persistence

Worm-like chain

• Polymer is a continuous elastic rod with bending energy

$$E = \frac{\alpha}{2} \int_0^L \left(\frac{d\underline{t}}{ds} \right)^2 ds \quad \text{where } \alpha \text{ is a finite bending stiffness.}$$

• The chain has a persistence length

$$l_p = \frac{\alpha}{k_B T} \quad \text{setting the scale over which the tangent direction remains correlated.}$$

• Chain is smooth on short scales & not fully flexible since bending costs energy

• tangent correlations decay exponentially

$$\langle \underline{t}(s) \cdot \underline{t}(s') \rangle = e^{-|s-s'|/l_p}$$

• End-to-end distance

$$\langle R^2 \rangle = 2Ll_p \left[1 - \frac{l_p}{L} \left(1 - e^{-L/l_p} \right) \right]$$

Ideal chain

- "Random walk" with freely rotating steps
- No stiffness
- Completely uncorrelated bond directions

WLC

- Smooth elastic filament
- Finite stiffness, measured by l_p
- Neighboring segments maintain directional correlation over distances up to l_p .