Polymer models

Talk given for:

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Polymers

Overview

- Polymer basics and definitions

- The ideal chain

  - Freely jointed chain (FJC)

  - Freely rotating chain (FRC)

  - Kuhn length and persistence length

  - End-to-end vector distribution function

  - Gaussian chain

- Force extension relation

- Worm-like-chain

- Real chains

- Conclusion

Definition:

Polymers are usually long molecules (high molecular weight) consisting of repeated units (monomers) of relatively small and simple molecules covalently bonded.

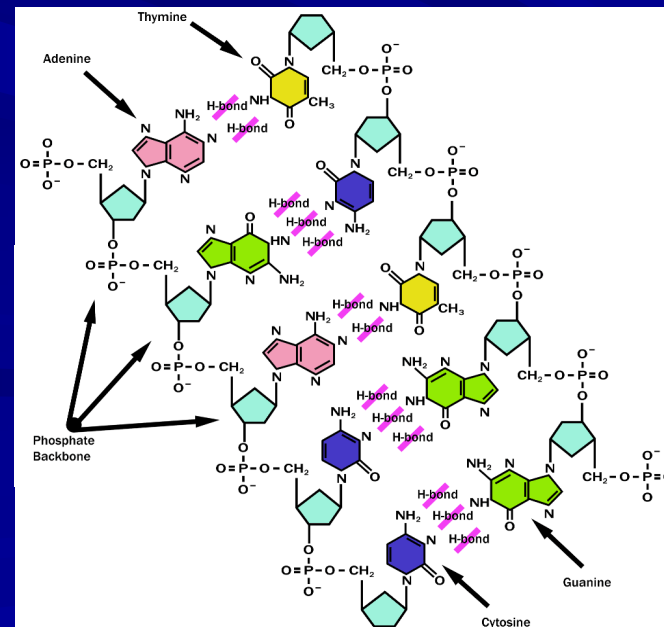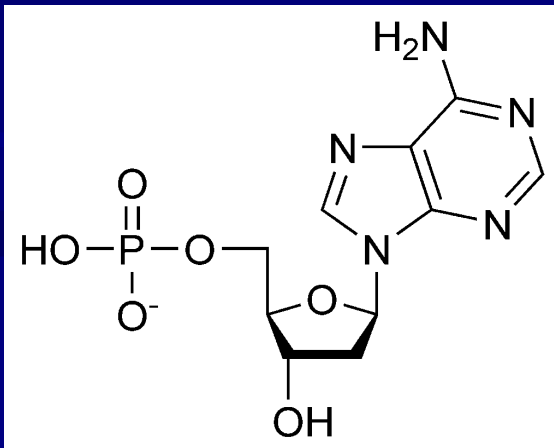The process of covalent joining of the monomers is known as polymerization

Synthetic polymers:
Plastics, fibers, glues…
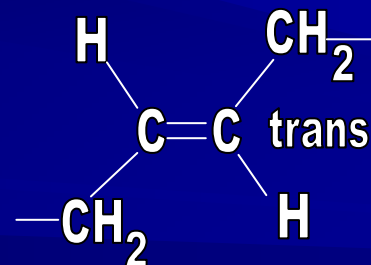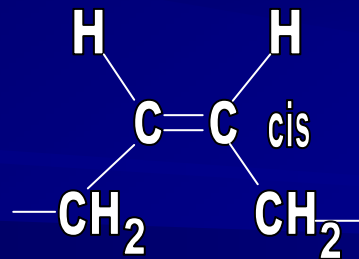
Biopolymers:
Proteins, polysaccharides, Actin, DNA…

Deoxyadenosine monophosphate

Other structural factors

- Polymers can have different kinds of branched architectures

- Structural isomerisms (double bonds) → hindered rotations

- Stereoisomerism: Orientation of –R and –H groups to carbon plane

- Different types of monomer repeats: homopolymers, alternating, random….

$$C=C \quad cis$$

$$C=C \quad trans$$

-A-A-A-A-A-A-A-

-A-B-A-B-A-B-A-

-A-A-C-A-B-C-B-A-

The ideal chain

No correlation between polymer monomers seperated by long distances along the polymer.

❑ Short range correlations between neighboring monomers are not excluded

❑ Ideal chain models do not take interactions caused by conformations in space into account

❑ Ideal chains allow the polymer to cross itself

Modelling a polymer

Imagining a blown up picture of a section of the polymer polyethylene in a certain conformation, could look like this:

Conformations:

❑ Torsion angle φ

❑ Bond angle θ

Bond vectors:

Starting from one end we use vectors r_i to represent the bonds

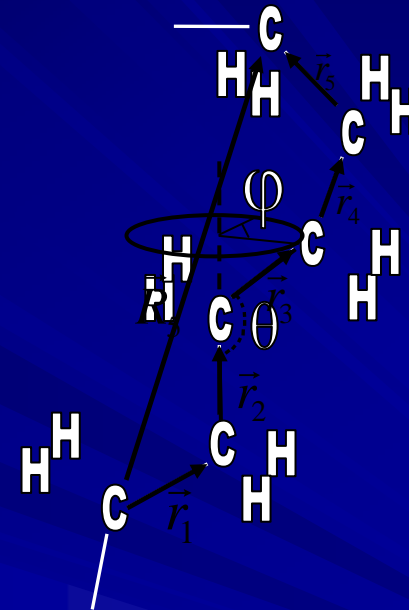## End-to-end vector:

The sum of all bond vectors

The ensamble average of $<\bar{\mathbf{R}}_\mathbf{n}>=0$ due to isotropy

$$\vec{R}_n = \sum_{i=1}^{n} \vec{r}_i$$

Mean square end-to-end distance:

Simplest non-zero average

$$\left\langle R^2 \right\rangle = \left\langle \vec{R}_n \cdot \vec{R}_n \right\rangle = \sum_{i=1}^{n}\sum_{j=1}^{n} \left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle$$

Freely jointed chain

No correlation between the directions of different bond vectors. Θ and φ are free to rotate. All bond vectors have length l

$$\left\langle \vec{R}^2 \right\rangle = \left\langle \vec{R}_n \cdot \vec{R}_n \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle$$

$$\left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = \left\langle ll\cos\theta_{ij} \right\rangle \Rightarrow \left\langle \vec{R}^2 \right\rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle \cos\theta_{ij} \right\rangle$$
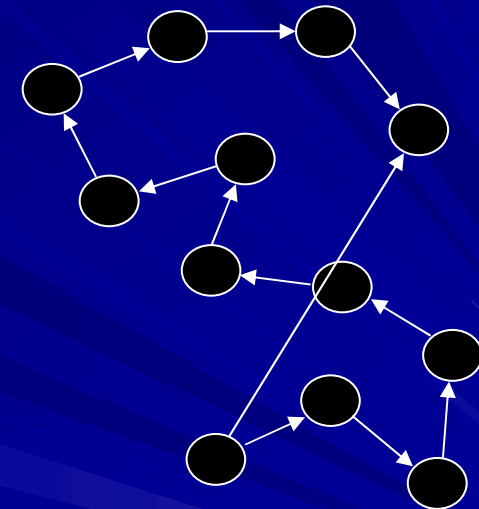
No correlation between different bond vectors, i≠j

$$\left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = \left\langle \vec{r}_i \right\rangle \cdot \left\langle \vec{r}_j \right\rangle = 0$$

$$\left\langle R^2 \right\rangle = nl^2$$

$$R \propto \sqrt{n}$$

Freely rotating chain

Bond angle θ is fixed. Torsion angle φ still free to rotate.

$$\left\langle \vec{R}^2 \right\rangle = \sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle \rightarrow \left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = ?$$
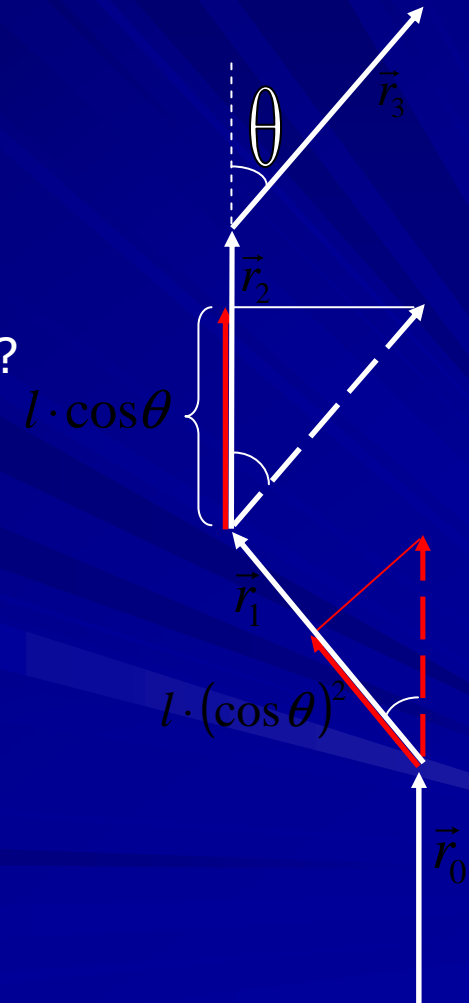
Ex: what is the correlation between vector r_3 and r_0?

Due to the free rotation around the torque angle, only the perpendicular component of r_3 is passed down.

$$\left\langle \vec{r}_3 \cdot \vec{r}_0 \right\rangle = l\left(\cos\theta\right)^2 \cdot l\cos\theta = l^2\left(\cos\theta\right)^3$$

The generel expression becomes:

$$\left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = l^2\left(\cos\theta\right)^{|i-j|}$$

θ

$\vec{r}_3$

$\vec{r}_2$

$l\cdot\cos\theta$

$\vec{r}_1$

$l\cdot\left(\cos\theta\right)^2$

$\vec{r}_0$

$$\left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = l^2 \left(\cos \theta \right)^{|i-j|}$$

Inserting this expression in our equation for $\langle R^2 \rangle$

$$\left\langle R^2 \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \left(\cos \theta \right)^{|i-j|}$$

This is solved by manipulating sums, and by writing the rapidly decaying cosine terms as an infinite series.

For calculation see Rubinstein p.56

The end result is:

$$\left\langle R^2 \right\rangle = nl^2 \frac{1+\cos \theta}{1-\cos \theta}$$

We see, that the introduction of correlation has not changed the $n^{1/2}$ proportionality. We have just added a constant >1

For range limited interactions this will always be the case

$$\lim_{|j-i|\to\infty} \left\langle \cos\theta_{ij} \right\rangle = 0 \Rightarrow \sum_{j=1}^{n} \left\langle \cos\theta_{ij} \right\rangle = C_i'$$

$$\left\langle R^2 \right\rangle = l^2 \sum_{i=1}^{n}\sum_{j=1}^{n} \left\langle \cos\theta_{ij} \right\rangle = l^2 \sum_{i=1}^{n} C_i' = nl^2 C_\infty$$

C_∞ is called Flory's characteristic ratio, and can be seen as a measure of the stiffness of the polymer in a given ideal chain model. For the rotating chain we have:

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta}$$

Kuhn length:

ideal chains can be rescaled into a freely jointed chain, as long as the chain is long compared to the scale of short range interactions

New segment length b is choosen so long, that neighbooring segments are non-correlated → New chain is a freely jointed chain

$$\langle R^2 \rangle = Nb^2$$

$$R \propto \sqrt{N}$$

b is called the Kuhn length, and obviously holds information on short scale interactions and stiffness.

$$R_{\max} = Nb$$
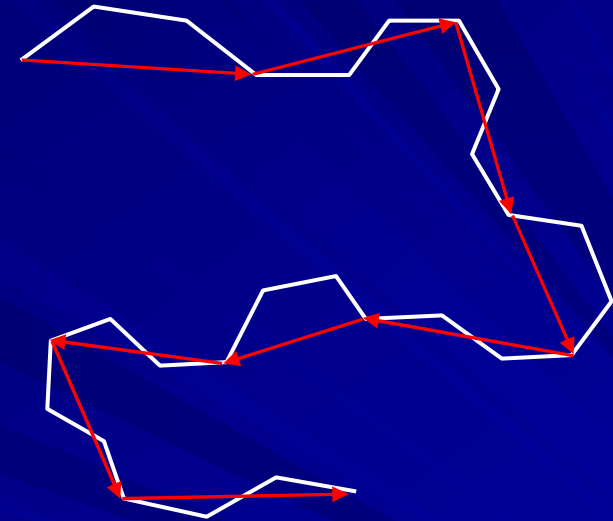
$$\langle R^2 \rangle = nl^2 C_\infty = Nb^2$$

$$\Longrightarrow \quad b = \frac{\langle R^2 \rangle}{R_{\max}} = \frac{nl^2 C_\infty}{R_{\max}}$$

Persistence length

The vector correlation term from the freely rotating chain, decays quickly and can be written in terms of an exponential function

$$\left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = l^2 \left(\cos\theta \right)^{|i-j|}$$

$$\left(\cos\theta \right)^{|i-j|} = \exp\left[|j-i| \ln(\cos\theta) \right] = \exp\left[-\frac{|j-i|}{s_p} \right]$$

$$s_p = \frac{1}{\ln(\cos\theta)} \qquad l_p = l \cdot s_p$$

This is a consequence of the range limited interactions, and will always be the case

S_p is the number of bonds in a persistence segment

The persistence length l_p is the length of the persistence segment

The persistence length l_p is the length scale with which the decay occurs

End-to-end vector distribution:

We use the Central Limit Theorem which states:

CLT: Given a series of random variables; X1,X2,…Xn sampled from the same pool of probability with a defined mean μ and variance σ^2, the distribution of the sum S=X1+X2+…Xn will converge to a gaussian distibution.

Mean and variance of the end-to-end vector is already known:

Mean μ=<R>=0

Variance σ^2=<R^2>-<R>^{2}=<R^2>=Nb^2

we get the probability distribution function in 3D:

$$P_{3D}(N,\vec{R}) = \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3\vec{R}}{2Nb^2} \right)$$

The Gaussian chain:

The gaussian chain is a chain made up of kuhn bonds that are assumed gaussianly distributed

$$P(\vec{r}) = \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3\vec{r}^2}{2b^2}\right)$$

We can now create the conformational distribution function of the entire chain, by multiplying each bond distribution

$$\Psi(\{r_n\}) = \prod_{n=1}^{N}\left[\frac{3}{2\pi b^2}\right]^{\frac{3}{2}} \exp\left(\frac{-3\vec{r}_n^2}{2b^2}\right)$$

$$= \left[\frac{3}{2\pi b^2}\right]^{\frac{3N}{2}} \exp\left[-\sum_{n=1}^{N}\frac{3\vec{r}_n^2}{2b^2}\right]$$

The bead-spring model is a mechanical representation of the Gaussian chain

Each spring represents a Gaussianly distributed Kuhn segment

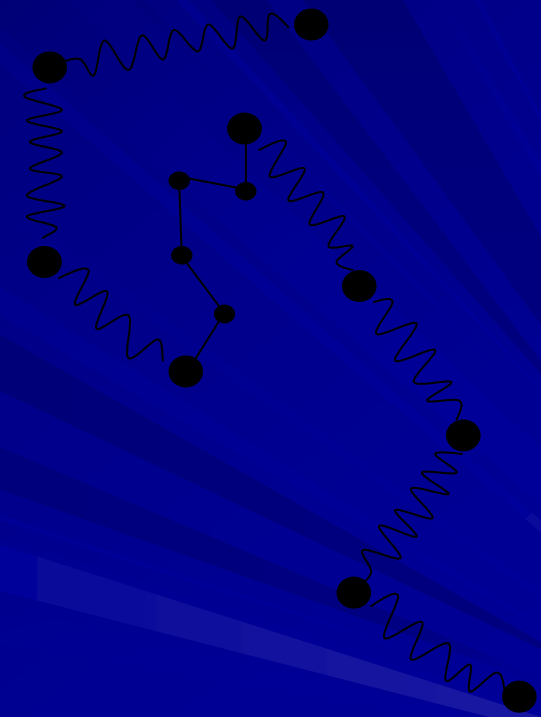If the spring potential between two beads is defined as:

$$U_0(\vec{r}_n) = \frac{3}{2b^2} k_B T \vec{r}_n^{\,2}$$

The bond distribution function for a single segment can be found.

$$P(\vec{r}_n) \propto \exp\left(-\frac{U_0}{k_B T}\right) = \exp\left(\frac{3\vec{r}_n^{\,2}}{2b^2}\right)$$

Normalizing we get the known Gaussian distribution.

One will also find the same mean quare end-to-end distance.

Force extension relations:

What happens when we apply a force F to stretch the polymer
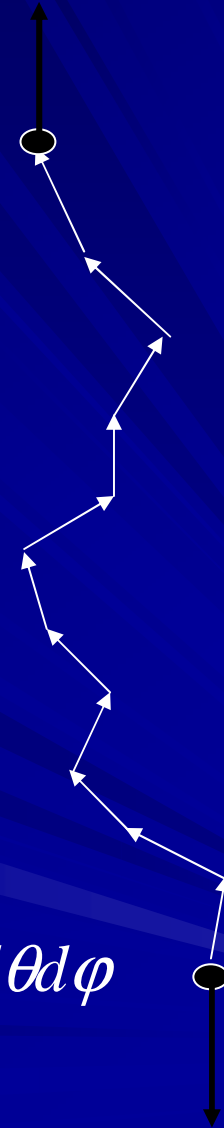
Looking at first at one segment

$$E_{segment} = -\vec{r}_i \cdot \vec{F}$$

⬇

Orientations are boltzmann weigted

⬇

$$Z_{segment} = \sum_{\substack{states= \\ orientations}} \exp\left(\frac{\vec{r} \cdot \vec{F}}{k_B T}\right) = \int \exp\left(\frac{\vec{r} \cdot \vec{F}}{k_B T}\right) \sin\theta d\theta d\varphi$$

Energy for the entire chain

$$E_{chain} = \sum_{i=1}^{n} \vec{r_i} \cdot \vec{F} = \vec{R} \cdot \vec{F}$$

Partition function for the entire chain

$$Z(N,F) = \int \exp\left(\frac{1}{k_B T} \vec{F} \cdot \sum_{i=1}^{N} \vec{r_i} \right) \prod_{i=1}^{N} \sin \theta_i d\theta_i d\varphi_i$$

This can be factorized and solved to give:

$$Z(N,F) = \left[\int 2\pi \sin \theta_i \exp\left(\frac{1}{k_B T} \vec{F} \cdot \vec{r_i} \right) d\theta_i \right]^{N}$$

$\Downarrow$

$\Downarrow$

$$Z(N,F) = \left[\frac{4\pi \sinh\left(\dfrac{fb}{kT} \right)}{\dfrac{fb}{kT}} \right]^{N}$$

The free energy is found in the standard way from the partition function, and the average end-to-end distance for a given force can finally be found by differentiating the free energy

$$G(F,N) = -k_B T \ln Z(N,F) = -k_B TN \left[\ln(4\pi \sinh\left(\frac{Fb}{k_B T}\right) - \ln\left(\frac{Fb}{k_B T}\right) \right]$$

$$\langle R \rangle = -\frac{\partial G}{\partial F} = bN \left[\coth\left(\frac{Fb}{k_B T}\right) - \frac{1}{\frac{Fb}{k_B T}} \right] = bNL\left(\frac{Fb}{k_B T}\right)$$

$$L(x) = \coth(x) - \frac{1}{x} = \frac{x}{3} - \frac{x^3}{45} + O(x)^5 \quad \text{Langevin function}$$

$$\frac{\langle R \rangle}{R_{\max}} = L\left(\frac{Fb}{k_B T}\right)$$

One important limit to the force extension expression is that of a small force. Taking only the first order of the Langevin functions gives us:

$$\langle R \rangle = N l \frac{Fl}{3 k_B T}$$

$$\Rightarrow F = \frac{3 k_B T}{N l^2} \langle R \rangle = \frac{3 k_B T}{\langle R^2 \rangle} \langle R \rangle$$

We obtain spring like behavior with the spring constant

$$k_{spring} = \frac{3 k_B T}{\langle R^2 \rangle}$$

Spring constant is proportional to temperature. Higher temperatures → greater forces necessary to stretch

Entropic effect → entropic spring

The worm like chain:

Continous development of the freely rotating chain for small bond angles θ, used for polymers with high stiffness

The meaningfull limits to take in this development are:

l → 0, θ → 0, but contour length nl and persistence length l_p remain the same

We calculate the mean square end-to-end distance:

We change the sum over segments into an integral over contour

$$\left\langle R^2 \right\rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle \vec{r}_i \cdot \vec{r}_j \right\rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \left(\cos\theta \right)^{|i-j|} = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \exp\left[-\frac{|j-i|}{l_p} l \right]$$

$$l \sum_{i=1}^{n} \rightarrow \int_0^{R_{\max}} ds \quad \text{and} \quad l \sum_{j=1}^{n} \rightarrow \int_0^{R_{\max}} ds'$$

$$\left\langle R^2 \right\rangle = \int_0^{R_{\max}} \left[\int_0^{R_{\max}} \exp\left(\frac{-|s-s'|}{l} \right) ds \right] ds'$$

The integral can be solved to give the result:

$$\left\langle R^2 \right\rangle = 2l_p R_{max} - 2l_p^2 \left(1 - \exp\left(-\frac{R_{max}}{l_p} \right) \right)$$

The two interesting limits are for the maximum end-to-end distance $R_{max} >> l_p$ and $R_{max} << l_p$

The ideel chain limit:

$$\left\langle R^2 \right\rangle \cong 2l_p R_{max} \text{ for } R_{max} >> l_p$$

For $b = 2l_p$ the freely jointed chain is recovered

The rod like limit:

$$\text{For } R_{max} << l_p \rightarrow \exp\left(-\frac{R_{max}}{l_p} \right) \cong 1 - \frac{R_{max}}{l_p} + \frac{1}{2}\left(\frac{R_{max}}{l_p} \right)^2$$

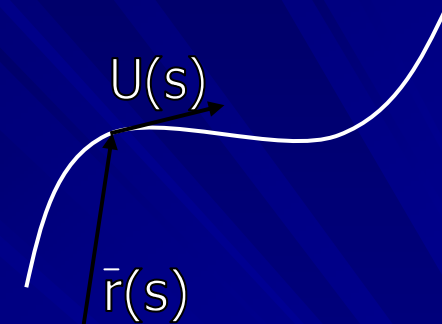$$\Rightarrow \left\langle R^2 \right\rangle \cong R_{max}^2$$

That is, it is fully extended

The worm like chain as a space curve:

r(s) is the radius vector of an arbitrary point on the space curve s. The tangentvector u(s) and the curvature are then:

U(s)

$$\vec{u}(s) = \frac{\partial \vec{r}}{\partial s} \quad \text{and} \quad \vec{c}(s) = \frac{\partial \vec{u}}{\partial s} = \left(\frac{\partial^2 \vec{r}}{\partial s^2} \right)$$

r̄(s)

The energy per unit length of a bended beam is proportional to the inverse of the radius of curvature squared which is the curvature squared

$$U_{bending\ /unitlength} = \frac{1}{2} \varepsilon (\text{radius of curvature})^{-2} = \frac{1}{2} \varepsilon \left(\frac{\partial \vec{u}}{\partial s} \right)^2$$

$$\Rightarrow U_{contour} = \frac{1}{2} \varepsilon \int_0^s \left(\frac{\partial \vec{u}}{\partial s} \right)^2 ds$$

Polymers

Real chains:

❑ Long range interactions between monomers are taken into account

❑ Interactions between solute and polymer and between different polymers

❑ Excluded volume and self avoiding random walks

❑ Dynamics

❑

❑

❑

Conclusion:

❑ For ideal chains correlations are finite. → for long chains we generally have the expression: $<R^2>=C_\infty nl^2$

❑ For chains much longer than range of correlation → rescaling into freely jointed chain with chain length b (Kuhn length): $<R^2>=Nb^2$

❑ Probability distribution function for end-to-end vector is Gaussian

❑ The force-extension relation for the freely jointed chain is well discribed by the Langevin function

❑ For low forces, a Hook's relationship with an entropic spring constant descibes the extension

Polymers

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www.its.caltech.edu/~bois/pdfs/poly.pdf

[5] Thomas Franosch.

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[6] Fredrik Wagner. Diploma thesis

   Polymers in confined geometry