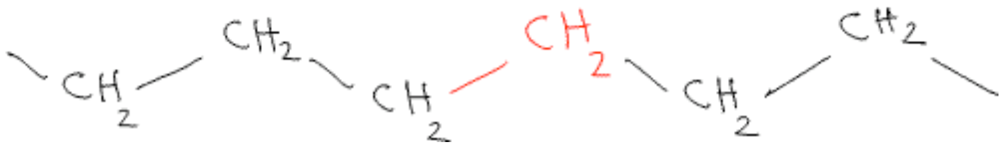
1. CONFORMATIONAL PROPERTIES OF POLYMERS

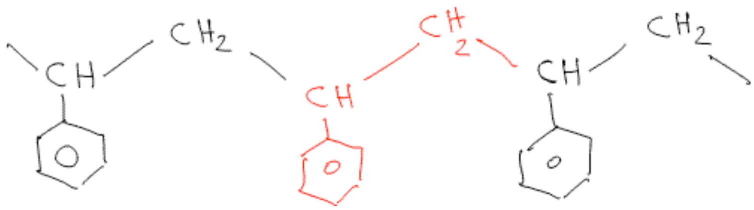
1.1. Local and global properties:

Consider the following examples of polymers.

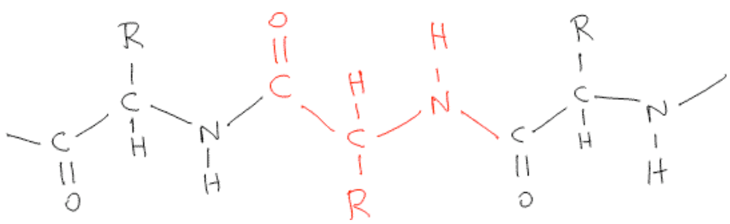
Polyethylene:



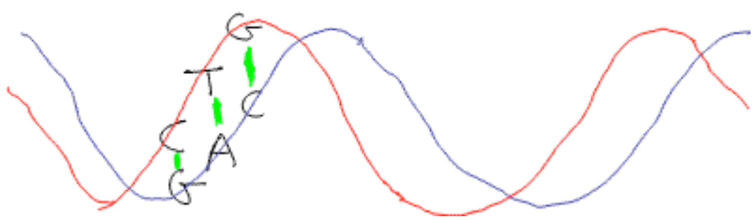
Polystyrene:



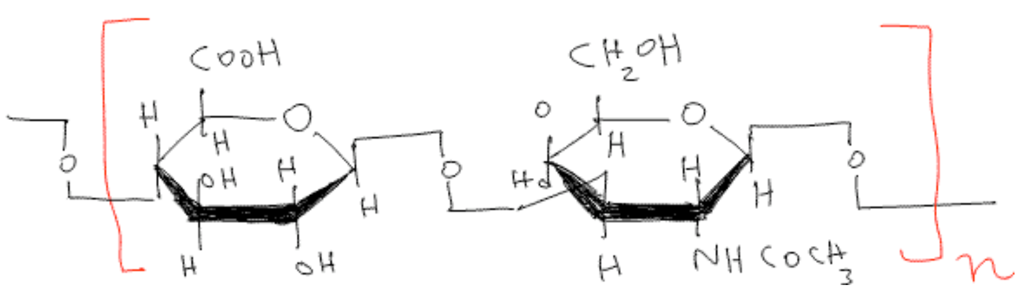
Protein:



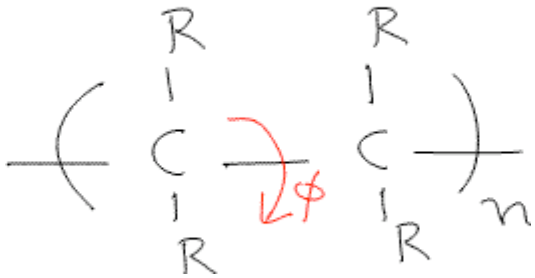
ds-DNA:

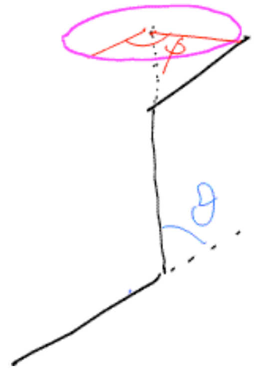


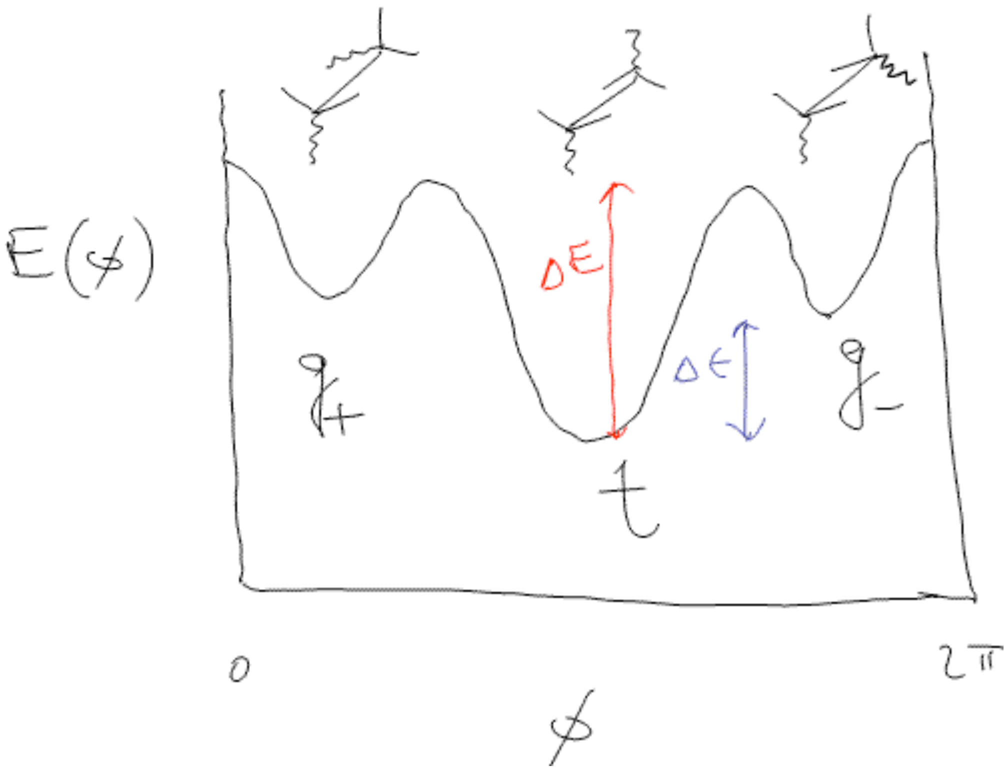
Polysaccharide:



Typically,







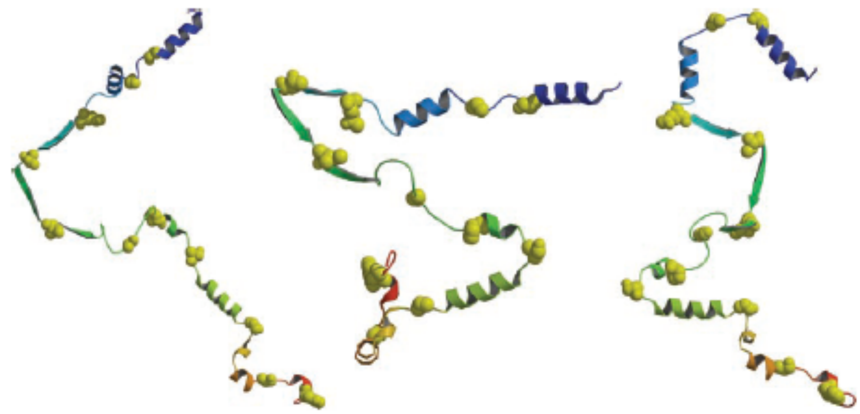
Chain flexibility for $\Delta\varepsilon/k_BT \ll 1$. $\Delta\varepsilon/k_BT$ defines persistence length l_p

Dynamical flexibility $\Delta E/k_BT \ll 1$. $\Delta E/k_BT$ defines a characteristic correlation time τ

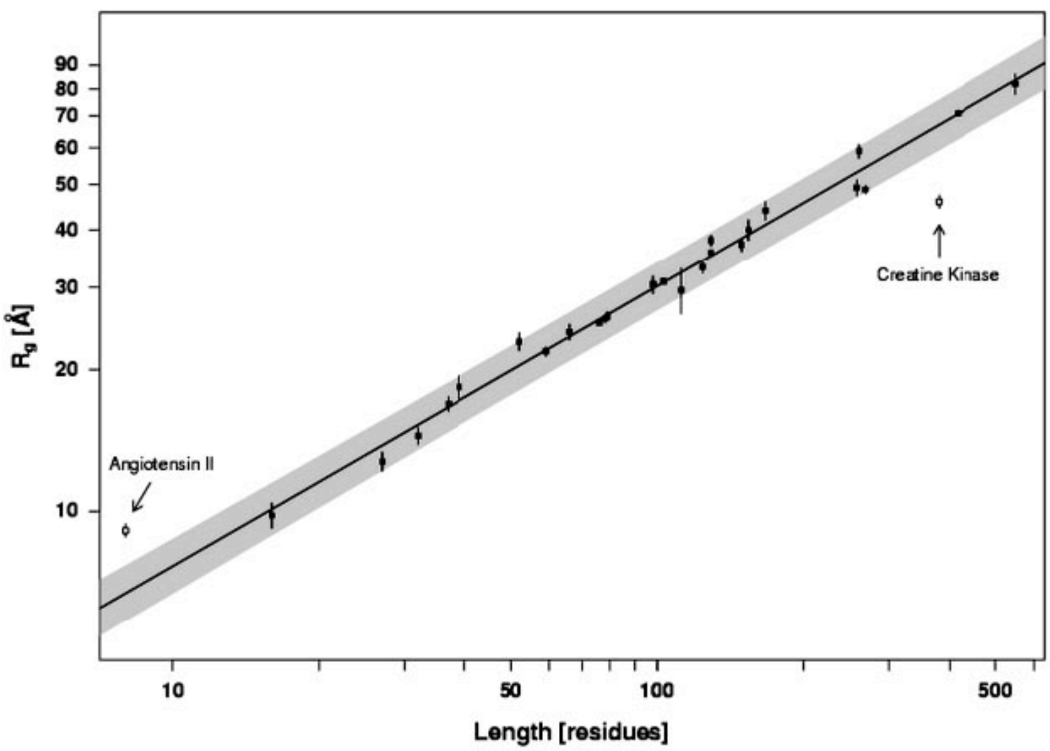
For length scales larger than l_p and time scales longer than τ, we deal with GLOBAL properties; otherwise, we deal with LOCAL properties.

1.2. An example:

"locally, helical"



"globally, 30 different proteins follow a universal law"

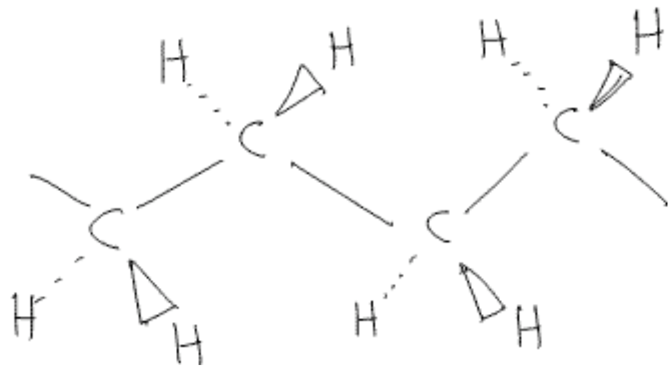


$$R_g = R_0\, N^{\nu}$$

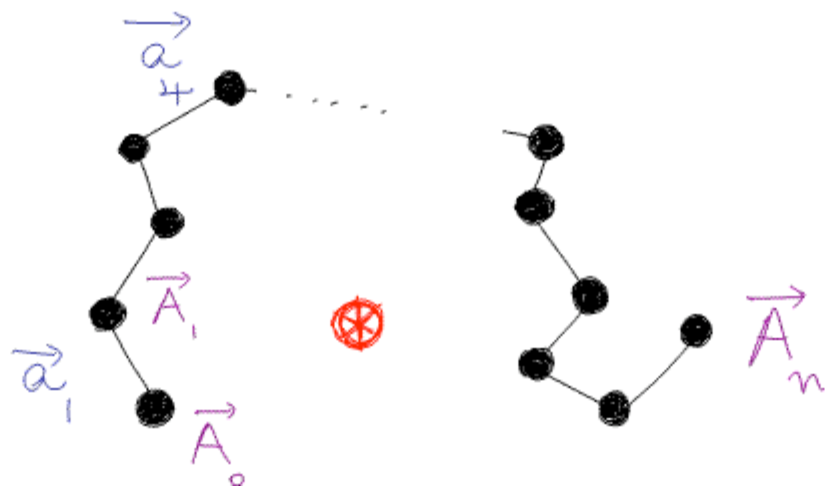
$$R_0 = 0.133 \text{ nm};\ \nu = 0.6$$

1.3. Skeletal chain and simple models:

Consider a particular configuration of a polymethylene chain:



The skeletal structure can be written as



$\mathbf{A}_i$ is the position of the ith skeletal atom (or united atom); $\mathbf{a}_i$ is the bond vector of the ith skeletal bond. Red star is the center of mass of the configuration.

Mean square end-to-end distance:

$$\langle R^2 \rangle = \left\langle \left(\sum_{i=1}^{n} \vec{a}_i \right)^2 \right\rangle$$

$$= \sum_{i=1} \langle a_i^2 \rangle + 2 \sum_{i<j=1} \langle \vec{a}_i \cdot \vec{a}_j \rangle$$

Mean square radius of gyration:

$$R_g^2 = \frac{1}{(n+1)} \sum_{i=0}^{n} \langle A_i^2 \rangle$$

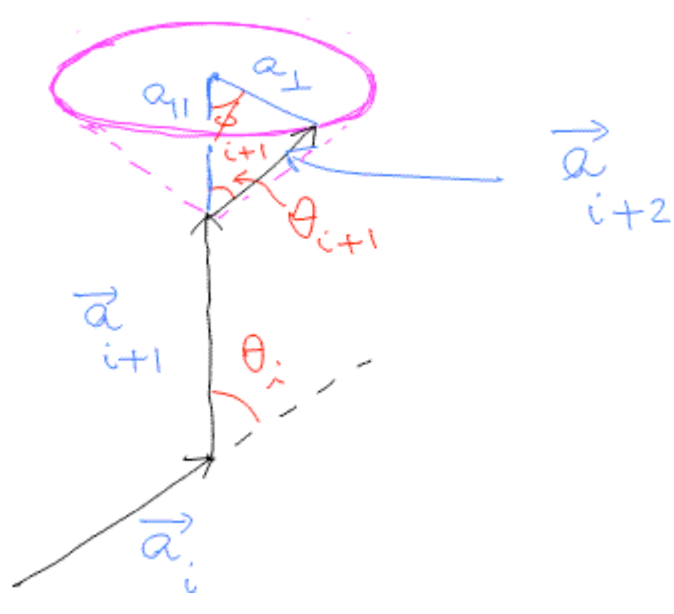
$$= \frac{1}{(n+1)^2} \sum_{i<j=1}^{n} \langle R_{ij}^2 \rangle$$

$\mathbf{R}_{ij}$ is the distance between the ith and jth groups. The angular brackets indicate the averaging over all possible configurations of the chain. For example, the average of a quantity X is:

$$\langle X \rangle = \frac{\sum_\alpha X_\alpha p_\alpha}{\sum_\alpha p_\alpha}$$

where X_α is the value of X in the αth configuration and p_α is the probability of realizing the αth configuration:

$$p_\alpha = p_\alpha(\{\theta_i\}, \{\phi_i\})$$



1.3.1. Freely-jointed chain:

$$\langle \vec{a}_i \cdot \vec{a}_j \rangle_0 = 0 , \qquad i \neq j$$

$$\langle R^2 \rangle_0 = n a^2$$

$$R_{go}^2 = \frac{n a^2}{6} \frac{(n+2)}{(n+1)} = \frac{\langle R^2 \rangle_0}{6} , \quad n \to \infty$$

(All bonds have equal length a.) The subscript zero on the angular brackets indicates that we consider the "unperturbed state" without any excluded volume interaction.

1.3.2. Freely-rotating chain:

$$\langle \vec{a}_i \cdot \vec{a}_{i+1} \rangle_0 = a^2 \cos\theta$$

$$\langle \vec{a}_i \cdot \vec{a}_{i+2} \rangle_0 = a \, a_{\parallel} \cos\theta$$
$$= a^2 \cos^2\theta$$

By induction,

$$\langle \vec{a}_i \cdot \vec{a}_j \rangle_0 = a^2 \cos^{|i-j|}\theta$$

It can be shown that

$$\langle R^2 \rangle_0 = n a^2 + 2 a^2 \sum_{i<j} \cos^{j-i} \theta$$

$$\langle R^2 \rangle_0 = n a^2 \left[\frac{1+\alpha}{1-\alpha} - \frac{2\alpha (1-\alpha^n)}{n (1-\alpha)^2} \right]$$

where

$$\alpha = \cos \theta$$

1.3.3. Chain with preferred rotation angles:

$$\langle R^2 \rangle_0 = n a^2 \frac{(1+\alpha)(1+\eta)}{(1-\alpha)(1-\eta)}$$

where

$$\eta = \langle \cos \phi \rangle_0$$

1.3.4. Rotational Isomeric States:

Probability of the dihedral angle (about the ith bond) lying between ϕ_i and $\phi_i+d\phi_i$ is:

$$p(\phi_i)\,d\phi_i = \frac{e^{-\frac{E(\phi_i)}{k_B T}}\,d\phi_i}{\int_0^{2\pi} d\phi_i\, e^{-\frac{E(\phi_i)}{k_B T}}}$$

Approximate the infinite number of states by only the three states (trans, gauche+, and gauche-) corresponding to the local energy minima. These are called the rotational isomeric states of the chain.

$$p(\phi_{i\mu}) = \frac{e^{-E_i(\phi_{i\mu})/k_B T}}{\sum_{\mu=1}^{3} e^{-E_i(\phi_{i\mu})/k_B T}}$$

Therefore, and average can be easily computed:

$$\langle X\rangle_0 = \frac{\sum_{\mu_2=1}^{3}\cdots\sum_{\mu_{n-1}=1}^{3} X \exp\left[-E(\phi_{\mu_2},\phi_{\mu_3},\cdots\phi_{\mu_{n-1}})/k_B T\right]}{\sum_{\mu_2=1}^{3}\cdots\sum_{\mu_{n-1}=1}^{3} \exp\left[-E(\phi_{\mu_2},\phi_{\mu_3},\cdots\phi_{\mu_{n-1}})/k_B T\right]}$$

1.3.5. Characteristic Ratio:

The characteristic ratio of a polymer is defined as

$$C_n = \frac{\langle R^2 \rangle_0}{n a^2}$$

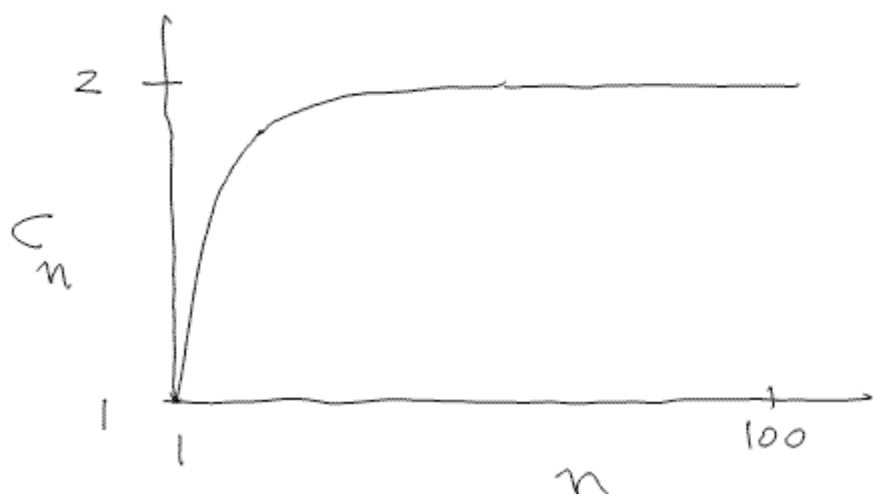
For very large values of the degree of polymerization,

$$\lim_{n \to \infty} C_n \equiv C_\infty$$

For example, for freely-rotating chains,

$$C_\infty = \frac{1+\alpha}{1-\alpha}$$

In the case of tetrahedral coordination, ($\theta = 70.53^{o}$) for the skeletal atom, $\alpha = 1/3$, and C_n is as follows:



1.4. Key message:

For an unperturbed chain, **the mean square end-to-end distance and the mean square radius of gyration are proportional to the degree of polymerization, in the long chain limit**!

1.5. Home work problems:

1.5.1. Show that the square of the radius of gyration of a configuration of a chain of n+1 identical united atoms is

$$R_g^2 = \frac{1}{(n+1)^2} \sum_{i<j=1}^{n} \langle R_{ij}^2 \rangle$$

where $\mathbf{R}_{ij}$ is the distance vector between the ith and jth united atoms.

1.5.2. Assuming that there are three rotational isomeric states at $\phi = 0^\circ$, 120°, and -120° and that the energy difference between the gauche and trans states for polymethylene is 550 cal/mole, (a) find the probabilities with which the trans and gauche states are populated at 140°C and (b) calculate the characteristic ratio in the infinite chain limit.