Polymers as Long Molecular Chains

 $-CH_2-CH_2-CH_2-CH_2-Poly(ethylene)$



 $-CH_2 - CH_2 -$

Number of monomer units in the chain N >> 1. For synthetic macromolecules usually

 $N \sim 10^2 \div 10^4.$

For DNA macromolecules

 $N \sim 10^9 \div 10^{10}$

Polymers as Long Molecular Chains



Electron microscope picture of bacterial DNA partially released from its native shell. (*Source: Dictionary of Science and Technology*, Christopher Morris, ed., San Diego, CA: AcademicPress, 1992.) Physical properties of polymers are governed by three main factors:

- Number of monomer units in the chain, N, is large: N >> 1.
- Monomer units are connected in the chain.
 ⇒ They do not have the freedom of independent motion (unlike systems of disconnected particles, e.g. low molecular gases and liquids). ⇒ Polymer systems are *poor in entropy*.
- Polymer chains are generally *flexible*.



History of Polymer Physics

• Discovery of chain structure of polymer molecule

H.Staudinger, 1920-1930

• First papers in polymer physics:

molecular explanation of rubber high elasticity

W.Kuhn, E.Guth, H.Mark, 1930-1935 ***Physico-Chemical" Period* (1935-1965) P.Flory, V.A.Kargin *Discovery of DNA double helix* Watson and Crick, 1953 *Penetration of physical methods to polymer science* (from 1965) I.M.Lifshitz (Russia), P.de Gennes (France), S.Edwards (England)

Now polymer physics is an important subfield of condensed matter physics, basis for "Soft Condensed Matter Physics"

Flexibility of a Polymer Chain



Rectilinear conformation of a poly(ethylene) chain corresponding to the *minimum of the energy*. All the monomer units are in *transposition*. This would be an equilibrium conformation at T = 0.

At $T \neq 0$ due to thermal motion the deviation from the minimum-energy conformation are possible. According to the *Boltzmann law* the probability of realization of the conformation with the excess energy U over the minimumenergy conformation is

 $p(U) \sim \exp(-\frac{U}{kT})$.

Rotational-Isomeric Flexibility Mechanism

For carbon backbone the *valency angle* γ is fixed (for different chains 50° < γ <80°),



however the rotation with fixed φ (changing the angle of internal rotation γ) is possible. Any value $\gamma \neq 0$ gives rise to the deviations from rectilinear conformation, i.e. to chain flexibility.



Positions corresponding to $\varphi = 120^{\circ}$ and 240° gauche rotational isomers, $\varphi = 0^{\circ}$ - trans rotational isomers. Gauche isomers induce sharp bends of the chain and give dominant contribution to chain flexibility.

Persistent Flexibility Mechanism



In the case when rotational isomers are not allowed (e.g. for α -helical polypeptides or DNA double helix) *small thermal vibrations* around the equilibrium position of atoms are still possible; accumulation of these vibrations over large distances along the chain gives rise to the deviations from the straight conformation \Rightarrow to the chain flexibility. This is a *persistent flexibility mechanism*, it is analogous to the flexibility of a *homogeneous elastic filament*.

Freely-Jointed Flexibility Mechanism



The flexibility is located in the freelyrotating junction points. This mechanism is normally not characteristic for real chains, but it is used for model theoretical calculations.

Portrait of a Polymeric Coil

(freely-jointed chain of **N** segments; interactions between the segments are not taken into account).



A typical conformation of a polymer coil. The freely jointed chain of 10^4 segments has been simulated on a computer in threedimensional space.

• Chain trajectory is analogous to the trajectory of a *Brownian particle*.

• The *volume fraction* occupied by the *monomer units* inside coil *is very small*. Inside the coil there are many "*holes*".



Polymer coil conformations can be realized in *dilute polymer solutions* when macromolecules do not overlap.

Types of Polymer Molecules

 <u>Homopolymers</u>: all monomer units are the same.
 <u>Copolymers</u>: monomer units of different types.
 (*for example, proteins - 20 types of units* DNA - 4 types of units).

Sequence of monomer units along the chain is called primary structure.

2 Branched macromolecules









a) Comb-like*b*) Star-like

c) Randomly branched*d*) Polymer network

3 <u>Ring macromolecules</u>



- a) unknotted ring macromolecule
- b) knotted ring macromolecule
- c) tangling of two ring macromolecule
- d) olympic gel
- e) tangling of two complementary strands into a double helix

Topological restrictions



Possible Physical States for Polymer Materials

Traditional classification of physical states (*gases, liquids, crystals*) is not informative for polymer materials.



Classification for polymer materials:

- 1 Partially crystalline state
- 2 Viscoelastic state (polymer melt)
- 3 Highly elastic state (*e.g. rubbers*)
- 4 Glassy state (*e.g. organic glasses from poly(styrene), poly(methylmethacrylate), poly(vinyl chloride)).*

Polymer Solutions



- a) Dilute polymer solution;
- b) Crossover from dilute to semidilute solution;
- c) Semidilute solution;
- d) Concentrated solution;
- e) Liquid-crystalline solution;

Ideal polymer chain: interactions of monomer units which are far from each other along the chain are neglected.

Polymer chains behave as ideal ones in the socalled Θ - *conditions* (see below).

Let us consider ideal *N*-segment *freely-jointed chain* (each segment of length *l*).



$$\boldsymbol{R} \propto \sqrt{\left\langle \boldsymbol{R}^2 \right\rangle}$$

$$\vec{u}_{1} \qquad \vec{u}_{2} \qquad \vec{u}_{3} \qquad \vec{u}_{4} \qquad \vec{u}_{N}$$

$$R^{2} = \left(\sum_{i=1}^{N} \vec{u}_{i}\right) \left(\sum_{j=1}^{N} \vec{u}_{j}\right) = \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{u}_{i} \vec{u}_{j}$$

$$\left\langle R^{2} \right\rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{u}_{i} \vec{u}_{j} \rangle = \sum_{i=1}^{N} \langle \vec{u}_{i}^{2} \rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{u}_{i} \vec{u}_{j} \rangle$$

$$\sum_{\substack{i=1,j=1\\j\neq i}}^{N} \langle \vec{u}_{i} \vec{u}_{j} \rangle = 0 \quad (different segments are uncorrelated) \implies$$

$$\left\langle R^{2} \right\rangle = \sum_{i=1}^{N} \langle \vec{u}_{i}^{2} \rangle = Nl^{2} = Ll, \quad L = Nl$$

$$L - contour length of the chain$$

$$\overline{R} \propto \sqrt{\langle R^{2} \rangle} = N^{\frac{1}{2}}l, \quad R << L$$

Thus, the conformation of an ideal chain is far from the rectilinear one. Ideal chain forms an *entangled coil*. The chain trajectory is equivalent to the trajectory of a *Brownian particle*. Model with fixed valency angle

The conclusion $R \sim N^{1/2}$ is valid for *ideal chain* with *any flexibility mechanism*. E.g., let us consider *the model with fixed valency angle*

 γ between the segments of length *b* and free internal rotation ($u(\varphi) = 0$).

$$\frac{b}{\gamma}$$
As before $\langle \mathbf{R}^2 \rangle = \sum_{i=1}^N \langle \mathbf{u}_i^2 \rangle + \sum_{\substack{i=1 \ j=1 \ j\neq i}}^N \langle \mathbf{u}_i \mathbf{u}_j \rangle, \ \langle \mathbf{u}_i^2 \rangle = b^2$
but now $\langle \mathbf{u}_i \mathbf{u}_j \rangle \neq 0$
 $\langle \mathbf{u}_i \mathbf{u}_j \rangle = b^2 \langle \cos \theta_{ij} \rangle, \ \theta_{ij}$ - angle between segments
 $i \text{ and } j$
 \downarrow
 $\langle \mathbf{R}^2 \rangle = \mathbf{N}b^2 + b^2 \sum_{i=1}^N \sum_{j=1}^N \langle \cos \theta_{ij} \rangle$



By continuing these arguments, we have

$$\left\langle \cos \theta_{i,i+k} \right\rangle = (\cos \gamma)^{k}$$

$$\left\langle \mathbf{R}^{2} \right\rangle = \mathbf{N}\mathbf{b}^{2} + 2\mathbf{b}^{2} \sum_{i=1}^{N} \sum_{k=1}^{N-i} \left\langle \cos \theta_{i,i+k} \right\rangle =$$

$$= \mathbf{N}\mathbf{b}^{2} + 2\mathbf{b}^{2} \sum_{i=1}^{N} \sum_{k=1}^{N-i} \left(\cos \gamma \right)^{k} =$$

$$= \mathbf{N}\mathbf{b}^{2} + 2\mathbf{b}^{2} \sum_{i=1}^{N} \frac{\cos \gamma}{1 - \cos \gamma} =$$

$$= \mathbf{N}\mathbf{b}^{2} + 2\mathbf{N}\mathbf{b}^{2} \frac{\cos \gamma}{1 - \cos \gamma} \Longrightarrow$$

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

Conclusions

•
$$\boldsymbol{R} \propto \sqrt{\langle \boldsymbol{R}^2 \rangle} = \boldsymbol{N}^{1/2} \boldsymbol{b}_{\sqrt{\frac{1+\cos \gamma}{1-\cos \gamma}}}$$

Average size of the macromolecule is proportional to $N^{1/2} \Rightarrow$ for this model we have *entangled coil* as well. This is a *general property* of *ideal polymer chains independently* of the model.

• At $\gamma < 90^{\circ}$ the value of *R* is larger than for the freely-jointed chain. At $\gamma > 90^{\circ}$ the relationship is reverse.

Persistent Length of a Polymer Chain

Let us return to the formula derived for the *model with fixed valency angle*

$$\langle \cos \theta_{i,i+k} \rangle = (\cos \gamma)^k = \exp(k \ln \cos \gamma) =$$

= $\exp(-k |\ln \cos \gamma|) = \exp\left(-\frac{kb}{b/|\ln \cos \gamma|}\right) =$
= $\exp(-s/\tilde{l}), \qquad \tilde{l} = b/|\ln \cos \gamma|$

Here *s=kb* is *the contour distance* between two monomer units along the chain.



 $\langle \cos \theta_{\vec{u}(o),\vec{u}(s)} \rangle \propto \exp(-s/\tilde{l})$

This formula was derived for the model with *fixed valency angle* γ , but it is valid for *any* model: orientational correlations decay exponentially along the chain. The characteristic length of this decay, \tilde{I} , is called a *persistent length* of the chain.

At $s \ll \tilde{l}$ the chain is approximately rectilinear, at $s \gg \tilde{l}$ the memory of chain orientation is lost. Thus, different chain segments of length \tilde{l} can be considered as independent, and

$$\boldsymbol{R} \propto \sqrt{\langle \boldsymbol{R}^2 \rangle} \propto \sqrt{\frac{\boldsymbol{L}}{\boldsymbol{\tilde{l}}}} \, \boldsymbol{\tilde{l}}^2 \propto \sqrt{\boldsymbol{L}\boldsymbol{\tilde{l}}}$$

Therefore, *R* is always proportional to $L^{1/2}$.

Kuhn Segment Length of a Polymer Chain

We know that for ideal chain $\langle \mathbf{R}^2 \rangle \sim \mathbf{L}$ *Kuhn segment length* l is defined as $l = \langle \mathbf{R}^2 \rangle / L$ (at large L)

Thus the equality $\langle \mathbf{R}^2 \rangle = \mathbf{L}\mathbf{l}$ is exact by definition.

<u>Advantage of</u> *l* : it can be directly experimentally measured.

<u>Advantage of</u> \tilde{l} : it has a direct microscopic meaning.

We always have $l \propto \tilde{l}$. Let us examine this relationship for the model with *fixed valency angle*.

Since
$$\langle \mathbf{R}^2 \rangle = N b^2 \frac{1 + \cos \gamma}{1 - \cos \gamma} = L b \frac{1 + \cos \gamma}{1 - \cos \gamma} \implies$$

 $\mathbf{l} = b \frac{1 + \cos \gamma}{1 - \cos \gamma}$
On the other hand, $\widetilde{\mathbf{l}} = \frac{b}{|\ln \cos \gamma|} \implies$
 $\mathbf{l}/\widetilde{\mathbf{l}} = |\ln \cos \gamma| \frac{1 + \cos \gamma}{1 - \cos \gamma}$

Stiff and Flexible Chains

Now we have a quantitative parameter that characterizes the chain stiffness: *Kuhn segment length l* (or *persistent length* $\tilde{l} \propto l$). The value of *l* is normally larger than the contour length per monomer unit l_0 . The ratios l/l_0 for most common polymers are

shown below.

2.5
3
3.5
4
4
5
6.5
26
200
300
500



From macroscopic viewpoint a polymer chain can be represented as a filament characterized by two lengths:

- Kuhn segment l
- characteristic chain diameter d

Stiff chains: 1 >> d

(DNA, helical polypeptides, aromatic polyamides etc.)

<u>Flexible chains: $l \propto d$ </u>

(most carbon backbone polymers)

Polymer Volume Fraction Inside Ideal Coil

End-to-end vector is $R \propto \sqrt{\langle R^2 \rangle} \propto (Ll)^{1/2} \Rightarrow$

the volume of the coil
$$V \propto \frac{4}{3}\pi R^3 \propto (Ll)^{3/2}$$
.

Polymer volume fraction within the coil is very small for long chains.

$$\Phi \propto \frac{\pi d^2 L/4}{(Ll)^{3/2}} \propto \frac{d^2}{L^{1/2} l^{3/2}} \propto \left(\frac{l}{L}\right)^{1/2} \left(\frac{d}{l}\right)^2 <<1$$

Radius of Gyration of Ideal Coil

Center of mass of the coil $\vec{r}_0 = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i$, where \vec{r}_i is the coordinate of the *i*-th monomer unit.

Radius of gyration, by definition, is

$$S^{2} = \frac{1}{N} \sum_{i=1}^{N} (\vec{r}_{i} - \vec{r}_{0})^{2}.$$

It can be shown that for ideal coils

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

The value of $\langle S^2 \rangle$ can be directly measured in the light scattering experiments (see below).

<u>Gaussian Distribution for the End-to-End</u> <u>Vector for Ideal Chain</u>

 $P_{N}(\vec{R})$ -probability distribution for the end-toend vector of N- segment freely-jointed chain. Since each step gives *independent* contribution to \vec{R} , by analogy with the trajectory of a Brownian particle

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

-Gaussian distribution. Therefore, the ideal coil is sometimes called a Gaussian coil. Since $P_{N}(\vec{R})$ is a probability distribution,

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

Also, $P_N(\vec{R}) = P_N(R_x)P_N(R_y)P_N(R_z)$.



For other models, since orientational correlations decay exponentially, *Gaussian distribution* is still valid:

$$P_{N}(\vec{R}) = \left(\frac{3}{2\pi N l^{2}}\right)^{\frac{3}{2}} \exp\left(-\frac{3R^{2}}{2N l^{2}}\right) = \left(\frac{3}{2\pi \langle R^{2} \rangle}\right)^{\frac{3}{2}} \exp\left(-\frac{3R^{2}}{2\langle R^{2} \rangle}\right).$$

This form of $P_{N}(\vec{R})$ is independent of *any* specific model.

Elasticity of a Single Ideal Chain



For crystalline solids the elastic response appears, because external stress changes the equilibrium inter-atomic distances and increases the *internal energy* of the crystal *(energetic elasticity).*



Since the energy of ideal polymer chain is equal to zero, the elastic response appears by purely entropic reasons *(entropic elasticity)*. Due to the stretching the chain adopts the less probable conformation \Rightarrow *its entropy decreases.*

According to Boltzmann, the entopy $S(\vec{R}) = k \ln W_N(\vec{R})$

Where *k* is the Boltzmann constant and $W_N(\vec{R})$ is the number of chain conformations compatible with the end-to-end distance \vec{R} .

 $W_N(\vec{R}) = const \cdot P_N(\vec{R}) \implies$ $S(\vec{R}) = k \ln P_N(\vec{R}) + const$

But,
$$\boldsymbol{P}_{N}(\boldsymbol{\vec{R}}) = \left(\frac{3}{2\pi Ll}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{R}^{2}}{2Ll}\right)$$

Thus, $S(\vec{R}) = -\frac{3kR^2}{2Ll} + const$

The free energy F: $F = E - TS = -TS = \frac{3kTR^2}{2Ll} + const$ $\vec{f}d\vec{R} = dF \implies \vec{f} = \frac{\partial F}{\partial \vec{R}} = \frac{3kT}{Ll}\vec{R}$