

Figure 1: Polymer

Introduction to Soft Matter Physics- Lecture 6 Submitted by: Ilya Osherov

Polymers

Polymer is a term used to describe a very large molecule consisting of structural units and repeating units connected by covalent chemical bonds. In this lecture we are going to study the physical properties of polymers. We will define polymer as a very long chain (coil) and with this we will construct formulas for general parameters that will describe its' behavior. Polymers depend on the one hand on the properties of each individual unit (its chemical arrangement) and on the other hand on the generic properties that are connected to the fact that were dealing with a very long structures. We are not going to find exact formulas but only characterize scaling for polymers. Usually the properties will depend on some exponent of the polymer length and the pre-factor will be defined by the chemical properties of monomers.

Polymer properties: Characteristic length

We imagine a linear polymer in a solvent. The polymer is nether completely straight because of entropy nor collapsed in a small globule mostly because of entropy but also because of hardcore interactions. It occupies some more or less defined portion of space whose size we want to characterize. Our polymer is a cloud of monomers and does not have a perfect structure. The distribution of the monomers is not constant in time and space. Nevertheless we will define *some characteristic size* of the coil and study its dependence on polymer length.

There are many possible **definitions** but only two of them are commonly

used:

1. **Mean square end to end distance:** $\langle R_{ee}^2 \rangle = R_0^2$. We discuss linear polymers with two ends. R_0 roughly defines the diameter of the polymer coil.

2. **Gyration radius:** R_G . In mechanics when we want to define the inertia of a body we measure its momentum of inertia around its center of mass. We will use this definition for polymers. We take the complex body and replace it with a sphere same mass and same center of mass in the following way

$$I_0 = \sum_i m_i (\vec{r}_i - \vec{r}_{cm})^2 = MR_g^2$$

$$R_G^2 = \frac{1}{N} \sum_{i=1}^N (\vec{r}_i - \vec{r}_{cm})^2$$

This definition describes the radius of the coil R_G . We will see that R_G is approximately $R_0/2$ (more precisely $R_G = R_0/\sqrt{6}$ for long linear polymers). Because the structure polymer coil is not well defined the definitions of coil radius and diameter arent very precise. However, their dependence on on polymer parameters, such length can be studied precisely.

Ideal Polymers

This is the most basic model in polymer physics (similar to ideal gas model in the gas theory). The most important property of ideal polymers is that we can neglect interactions between distant monomers.

Indeed under certain conditions we can neglect interactions between the monomers.

What are these conditions?

We define the interactions in the first approximation by the second virial coefficient.

$$a = \int d\vec{r} \left(1 - e^{-\beta u(r)} \right)$$

Attractive forces make a smaller and repulsive forces make it larger. Depending on the solvent a can be very close to zero ($a \approx 0$) and in this case we can neglect the collisions between the monomers. Statistically speaking attractive forces balance the repulsive forces in a perfect manner. We can always choose conditions and neglect the interactions between monomers. These conditions are called θ solvent.

We will see that for ideal polymers the length dependence of the mean square end to end distance is

$$R_0 \propto \sqrt{N} \text{ for } N \gg 1$$

We will discuss three models which behave like ideal polymers. In other words on a large scale (for large enough N) the size of the polymer coil is proportional to \sqrt{N} .

1. **Freely joint chain:** It is a chain of segments, where the chain can freely fold in every segment joint without restrains.

2. **Freely rotating chain:** This model tries in the simplest way to take into account the chemical bounding constrains. The angle θ between consecutive monomers is fixed. However, the consecutive monomers are free to rotate around each others axis (keeping θ constant of course).

Polymer in this model can rearrange in many strange configurations. The net result is that except the θ dependence the scaling is pretty similar to the FJC model.

3. **Semi Flexible Polymer:** Good for biological polymers like DNA. The idea is that folding occurs on a scale much larger than monomer size. The whole polymer behaves as an elastic body. *Thermal fluctuations* can fold the polymer on a large scale.

And now we are going to discuss each model providing further details:

3. **The simplest model is the FJC.** We want to explain: *why the size of the coil depends on the square root of N ?* Our only microscopic parameter is the length of the monomer b . There is a random angle between each pair of monomers. In fact we have a random walk in 3D space, N steps with length b . Knowing this we mark one end with index 0 and the other with N (we have N monomers).

Thus we expect

$$R_0^2 = Nb^2$$

Proof:

$$\vec{r}_{0N} = \sum_i^N \vec{b}_i$$

Where \vec{r}_{0N} is the distance between two ends.

And now we get mean square end to end distance.

$$\langle r_{0N}^2 \rangle = \left\langle \sum_{i=1}^N \sum_{j=1}^N \vec{b}_i \vec{b}_j \right\rangle$$

We divide this into two sums, for $i = j$ and $i \neq j$

$$R_0^2 = Nb^2 + \sum_{i \neq j} \langle \vec{b}_i \vec{b}_j \rangle = Nb^2$$

The second term equals zero because there is no correlation between the direction of \vec{b}_i and \vec{b}_j . For this model we can prove that $R_G^2 = \frac{R_0^2}{6}$ for $N \rightarrow \infty$

2. Next we talk about FRC model.

In order to calculate R_0 we make similar calculation as in previous model but this time because of correlation the second average will not be zero.

$$\vec{b}_i \vec{b}_{i+1} = b^2 \cos \theta$$

when θ is defined by the monomer.

$$\langle R_0^2 \rangle = \langle Nb^2 \rangle + \left\langle \sum_{i \neq j} \vec{b}_i \vec{b}_j \right\rangle$$

There is a constant angle between each two attached monomers but there are also many monomers that are not connected directly. Now we change index j to $k=i+1$ and write the sum in the following way

$$= Nb^2 + 2 \sum_{i=1}^N \sum_{k=1}^{N-i} \langle \vec{b}_i \vec{b}_{i+k} \rangle$$

Why is the new average simpler?

Because it is a function of only the separation between monomers along the chain..

Now we calculate the average.

For k=1:

$$\vec{b}_i \vec{b}_{i+1} = b^2 \cos \theta$$

For k=2 we use a trick:

$$\vec{b}_{i+2} = \vec{b}_{i+2,\parallel} + \vec{b}_{i+2,\perp}$$

Where $\vec{b}_{i+2,\parallel}$ and $\vec{b}_{i+2,\perp}$ are respectively the projections of vector \vec{b}_{i+2} on the directions parallel and perpendicular to \vec{b}_{i+1} . Obviously $\vec{b}_{i+2,\parallel} = \vec{b}_{i+1} \cos \theta$ and $\vec{b}_{i+2,\perp}$ is uncorrelated to \vec{b}_i (picture it).

Now we can write

$$\langle \vec{b}_i \vec{b}_{i+2} \rangle = \langle \vec{b}_i \vec{b}_{i+2,\parallel} \rangle + \langle \vec{b}_i \vec{b}_{i+2,\perp} \rangle = \langle \vec{b}_i \vec{b}_{i+1} \rangle \cos \theta = b^2 \cos^2 \theta$$

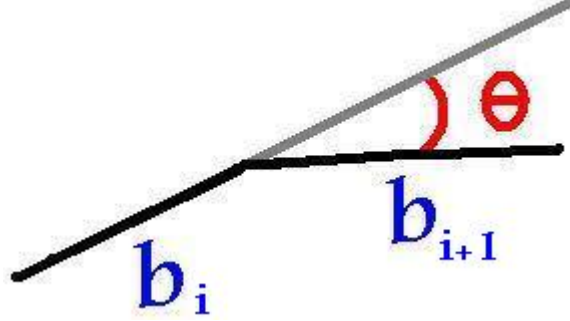


Figure 2: Angle between monomers

Similarly we can prove that in general:

$$\langle \vec{b}_i \vec{b}_{i+k} \rangle = b^2 \cos^k \theta$$

Then

$$\langle R_0^2 \rangle = Nb^2 + 2b^2 \sum_{i=1}^N \sum_{k=1}^{N-i} \cos^k \theta \approx Nb^2 + 2b^2 \sum_{i=1}^N \frac{\cos \theta}{1 - \cos \theta} \langle R_0^2 \rangle = Nb^2 + 2Nb^2 \frac{\cos \theta}{1 - \cos \theta}$$

And finally

$$\langle R_0^2 \rangle = Nb^2 \frac{1 + \cos \theta}{1 - \cos \theta}$$

We define two useful parameters which characterize microscopic properties of the polymer:

a. **Persistence length:** l_p . l_p Defines the ability of the polymer to maintain its direction. It is the characteristic segment length over which the direction of the chain does not change much.

We can write

$$\langle \vec{b}_i \vec{b}_{i+k} \rangle = \langle b^2 \cos^k \theta \rangle = b^2 e^{-s/l_p}$$

Proof:

$$\cos^k \theta = e^{-k |\ln \cos \theta|} = e^{-kb \frac{|\ln \cos \theta|}{b}} = e^{-s/l_p}$$

We can see that $s = kb$ is actually segment length along the chain. Now we write the **definition of persistence length**- as we go along the

length of the polymer and look at the average change in direction of the monomer we expect the correlation to fade exponentially. Persistence length is the parameter that defines the rate of fading. This definition is correct for many different models. In the FRC model the persistence length is related to b and θ in the following way

$$l_p = \frac{b}{|\ln \cos \theta|}$$

Persistence length is one of the macroscopic characteristics of elasticity of polymer. It depends on microscopic parameters of a specific model.

b. Kuhn length (Statistical Length): l_K

Kuhn length l_K is defined as an attempt to force FJC description onto the chain with finite flexibility: we demand that the polymer contour $L = Nb$ is divided into N' segments of length l_k (called Kuhn or statistical segments), i.e. $L = N'l_K$.

We look at the FJC and see that it is the simplest model. Each monomer can freely rotate with respect to its neighbors. This is not right for real polymers but if we take a number of monomers and instead of focusing on two neighbors we connect a few of them with a vector and call each group an effective "monomer", then the correlation between the new monomers is smaller they have more freedom, effectively they can move freely.

In FJC we saw that

$$\begin{aligned} L &= Nb \\ R_0^2 &= Nb^2 \end{aligned}$$

For this model we define $l_K = b$.

For a general case we define Kuhn length from polymer contour length and end-to-end distance, as:

$$\begin{aligned} L &= N'l_K \\ R_0^2 &= N'l_K^2 \end{aligned} \tag{1}$$

From this $R_0^2 = Ll_K$.

And we get *Kuhn length* as function of experimental parameters

$$l_K = \frac{R_0^2}{L}$$

For FRC model after substitution of L and R_0

$$l_K = \frac{R_0^2}{Nb} = b \frac{1 + \cos \theta}{1 - \cos \theta}$$

We see that l_K depends only on microscopic parameters of the polymer. l_K is an elasticity parameter, the more l_K is close to b the polymer is more flexible. Both l_k and l_p define polymer flexibility. l_k is easier to measure experimentally than l_p . However, l_p has more of theoretical meaning. Within any specific polymer model the relations between these two parameters can be found.

For FRC model the relations are given above. Interestingly, in the limit of $\theta \ll 1$:

$$l_K \approx 2l_p$$

3. Worm like chain (semi-flexible) - this model works mostly for biological polymers (biopolymers) like DNA, actin filaments, micro-tubules etc... behaving as elastic rods with a finite bending rigidity.

DNA for example is a double helix polymer and generally on a rough scale we can think of it as a cylinder. Inside the cylinder there are bases with constant separation between them. At zero temperature the cylinder is straight. Thermal fluctuations cause distortions; they can make it fold in a way that a distance between bases on one side is larger than on the other. These distortions aren't very strong; they don't accrue on a monomer scale but on a much bigger scale. For scales much larger than distance between atoms we can make continuum approximation and look at the cylinder as on a uniform body with certain elasticity, just like any elastic cylindrical body, like a pencil or a metal bar. The description of these polymers is based on ideas from theory of elasticity of rigid bodies combined with statistical physics.

We can already guess that the scale of the folding due to thermal fluctuations is in the order of magnitude of l_p or l_K of the polymer. At this scale elastic forces define the energy of the folding. At a larger scale all these folds sum up and the polymer looks pretty flexible.

Now we will try to see how elastic properties of the polymer are expressed in its statistics. We will use elasticity theory and write the Hamiltonian:

$$H = \frac{\kappa}{2} \int_0^L \left(\frac{\partial \vec{t}}{\partial s} \right)^2 ds$$

Where

s - monomer position along the contour $\vec{r}(s)$

κ - describes the bending stiffness of a polymer of a unit length.

We define tangent to the chain as

$$\vec{t} = \frac{\partial \vec{r}}{\partial s}; |\vec{t}| = 1$$

We will prove that $\left| \frac{\partial \vec{t}}{\partial s} \right| = \frac{1}{R}$ is the radius of the curvature.

We can write

$$\frac{\partial \vec{t}}{\partial s} = \frac{\vec{t}(s + \delta s) - \vec{t}(s)}{\Delta s}$$

And we also know that

$$|\vec{t}(s + \delta s)| = |\vec{t}(s)| = 1$$

$$\vec{t}(s + \delta s) - \vec{t}(s) = \sin \delta\theta \approx \delta\theta$$

From this we have $\delta s = R\delta\theta$ And this is what we wanted to prove

$$\frac{\partial \vec{t}}{\partial s} = \frac{1}{R}$$

Now we want to connect what we already know to the theory of elasticity. We imagine a thin elastic bar with length L_0 and diameter d folded to a certain curvature radius R . Inside the bar there is always a plane which is more or less in the center where the length is constant $= L_0$. Relative to this plain some planes are shrinking and some are extending. Let's say the most compressed plane facing the center of curvature got a length of L

What is the energy of elastic distortion per unit volume?

The answer is

$$E \left(\frac{\delta l}{l} \right)^2$$

Where $\delta l/l$ is the *relative deformation* and E is **Modulus Young**- prefactor which defines elasticity of a material.

The angle of the bar fold is

$$\frac{L_0}{R} = \frac{L}{R - d/2}$$

And the distortion up to a prefactor is

$$\Delta L = L_0 - L \approx \frac{d}{R} L_0$$

The energy of the distortion

$$H \approx E \left(\frac{\Delta L}{L_0} \right)^2 d^2 L_0 H \approx E d^4 \frac{L_0}{R^2}$$

Where $\approx E d^4$

We can also write elastic energy per unit length

$$\frac{H}{L_0} \approx \frac{\kappa}{2R^2} = \frac{\kappa}{2} \left(\frac{\partial \vec{t}}{\partial s} \right)^2$$

And finally we get

$$H = \frac{\kappa}{2} \int_0^L \left(\frac{\partial \vec{t}}{\partial s} \right)^2 ds = \frac{\kappa}{2} \int_0^L \left(\frac{\partial^2 \vec{r}}{\partial s^2} \right)^2 ds$$

After we know all this we can try to build statistical physics of the system. We say that thermal fluctuations are responsible for the energy of the folds. They can change the direction of the bar only on a large scale. They can only cause small folding on a small scale and when the folds sum up the direction changes on a larger scale.

What is the extent of the change in direction of the bar?

In order to answer this question we use the following definition for chain persistence length

$$\langle \vec{t}(s_1) \vec{t}(s_1 + \Delta s) \rangle = e^{-\frac{|\Delta s|}{l_p}}$$

We will prove this relation for semiflexible chain in one of the home problems. Overall this dependence is similar to $\langle \vec{b}_i \vec{b}_{i+k} \rangle$ in the FJC model.

Now we are going to prove that l_p is related to elasticity of the polymer. We will see that l_p is growing with increasing stiffness of the polymer. l_p also depends on the temperature. For large temperatures the persistence length is shrinking. We will find that $l_p = \frac{\kappa}{k_b T}$. In order to calculate the dependence we will use a trick. Lets think of a very small piece of the polymer $\Delta s \ll l_p$. On this piece the tangent vector does not change much. Then we can write

$$\langle \vec{t}(s_1) \vec{t}(s_1 + \Delta s) \rangle = 1 - \frac{|\Delta s|}{l_p}$$

We assume that the radius of the curvature does not change much on the small polymer piece. And we say that the energy of the piece is

$$H = \frac{\kappa \Delta s}{2R^2} = \frac{\kappa}{2} \Delta s \left[\left(\left(\frac{\Delta \theta_1}{\Delta s} \right)^2 + \left(\frac{\Delta \theta_2}{\Delta s} \right)^2 \right) \right]$$

The bending is divided into two angles in perpendicular planes instead of one total angle as before.

Why to divide into two angles and not to just use one total?

Because we want to work with independent parameters.

After some more algebra

$$H = \frac{\kappa}{2\Delta s} (\Delta\theta_1)^2 + \frac{\kappa}{2\Delta s} (\Delta\theta_2)^2$$

If we use equipartition theorem

$$\frac{\kappa}{2\Delta s} \langle \Delta\theta_1 \rangle^2 = \frac{k_B T}{2}$$

And now we write

$$\begin{aligned} \langle \Delta\theta^2 \rangle &= 2 \langle \Delta\theta_1^2 \rangle = \frac{2k_B T}{2} \Delta s \\ &\langle \vec{t}(s_1) \vec{t}(s_1 + \Delta s) \rangle = \\ &= \langle \cos \Delta\theta \rangle \approx 1 - \frac{\Delta\theta^2}{2} = 1 - \frac{\Delta s}{l_p} \end{aligned}$$

And we get

$$\begin{aligned} \frac{\langle \Delta\theta^2 \rangle}{2} &= \frac{\Delta s}{l_p} \\ \frac{k_B T}{\kappa} \Delta s &= \frac{\Delta s}{l_p} \end{aligned}$$

Finally,

$$l_p = \frac{\kappa}{k_B T}$$

Soft Matter Physics, Lectures Notes. 30.4

Submitted by: Eitan Rothstein

Reminder:

We spoke about ideal polymers and we have shown that for ideal polymers the distance from one end to the other is

$$R_0 = \sqrt{\langle R_{ee}^2 \rangle} \propto \sqrt{N}$$

We discussed three models:

1. freely jointed chain (FJC)

definition: there is a fixed distance between the monomers and each one can rotate at any angle.

$$R_0^2 = Nb^2$$

2. freely rotating chain (FRC)

definition: there is a fixed distance between the monomers and a fixed angle, the other angle can rotate freely.

we defined two parameters that will describe the flexibility of the polymer.

the persistence length l_p tells us how the polymer can bend and the definition is

$$\langle \vec{b}_i, \vec{b}_k \rangle = b^2 \exp \left[-\frac{s}{l_p} \right]$$

If one is interested in studying statistical properties of a polymer at large scale, it is possible to combine its monomers into groups (called statistical segments or Kuhn segments). The directions of these segments are relatively independent of each other, so that one can describe FRC chain or any other chain in terms of FJC model, just instead of monomers one has to use Kuhn segments of length l_k . The number of monomers in such a segment depends on the polymer flexibility and is defined by:

$$L = Nb = N_k l_k$$

$$R_0^2 = N_k l_k^2$$

and for the case of FRC we have

$$l_k = b \frac{1 + \cos \theta}{1 - \cos \theta}$$

3. worm like chain (WLC)

in this model we describe the polymer as an elastic rod.

the probability of finding the polymer in any state is $\propto e^{-\frac{\mathcal{H}}{k_B T}}$, and the hamiltonian is

$$\mathcal{H} = \frac{\kappa}{2} \int_0^L \left(\frac{\partial \vec{t}}{\partial s} \right)^2 ds$$

where $\vec{t} = \frac{\partial \vec{r}}{\partial s}$ is the tangent vector.

and $\vec{r}(s)$ is the monomer spatial position as a function of the monomer position s along the polymer contour. we also assumed that the correlations in directions of different polymer segments decay exponentially along the contour, similarly to FRC chain, i.e.:

$$\langle \vec{t}(\rho) \vec{t}(s) \rangle = e^{-\frac{|\rho-s|}{l_p}}$$

and from the limit $|\rho - s| \ll l_p$ we got the relation

$$l_p = \frac{\kappa}{k_B T}$$

The lesson: In this lesson we will explore two subjects:

1) in the first section we will continue with a WLC chain and define the end-to-end vector using the persistence length. in the end in order to understand better we will check the result for different limits of persistence length and we will see that in the limit of long chains ($L \gg l_p$) WLC statistics is similar to that of ideal chain.

2) in the second section we will determine the response of an ideal chain to external force. We will use random walk probability to find the entropy of an ideal chain, from that we will build the free energy function and we will see that it acts like a Hookean spring.

Section One

The equation that defines the end-to-end vector through the position vector is

$$\vec{R}_{ee} = \int_0^L d\vec{r}$$

from that we get the equation that connects end-to-end vector to the tangent vector

$$\vec{R}_{ee} = \int_0^L \frac{\partial \vec{r}}{\partial s} ds = \int_0^L \vec{t}_{(s)} ds$$

$$R_{ee}^2 = \int_0^L ds \int_0^L ds' \vec{t}_{(s)} \vec{t}_{(s')}$$

$$\langle R_{ee}^2 \rangle = \int_0^L ds \int_0^L ds' \langle \vec{t}_{(s)} \vec{t}_{(s')} \rangle$$

from the definition of the persistence length we get

$$\langle R_{ee}^2 \rangle = \int_0^L ds \int_0^L ds' e^{-\frac{|s-s'|}{l_p}}$$

let us assume that $s < s'$ and use the symmetry of the integral to get

$$\langle R_{ee}^2 \rangle = 2 \int_0^L ds \int_s^L ds' e^{-\frac{s-s'}{l_p}}$$

and after some algebra we get

$$\langle R_{ee}^2 \rangle = 2l_p^2 \left(\frac{L}{l_p} - 1 + e^{-\frac{L}{l_p}} \right)$$

in order to understand better this equation we will look at two limits, those of long and of short chains

- $L \gg l_p$

$$\langle R_{ee}^2 \rangle = 2l_p L$$

in this case we can define Kuhn length as

$$l_k = \frac{R_0^2}{L} = 2l_p$$

- For the second limit $L \ll l_p$ after some algebra we get

$$\langle R_{ee}^2 \rangle = L^2 \left(1 - \frac{1}{3} \frac{L}{l_p} \right)$$

WLC are called semi-flexible chains since they can behave as flexible at large scale and as stiff at the small scale. We saw that a long enough chain behaves as an ideal polymer: $R_0 \propto \sqrt{L}$. In the second case the polymer is very stiff and almost doesn't bend, therefore we get $R_0 \approx L$.

In all three models when we look at the limits $L \gg l_p, l_k$ we can consider a polymer to be flexible and we can use FJC model with the parameters N_k, l_k to describe the statistical properties of such polymer.

Section Two

Now that we have three models for ideal polymers, let us consider two situations (experimentally used) of a response of an ideal polymer to external constrains. In the first case is we will connect the ends of the polymers to some handles and use external force to stretch it. In the second case we will insert the polymer into a thin tube. We know that without external force, because of the entropy, the polymer tends to bring the end-to-end vector to zero (on average). when we apply some external force to polymer ends, the ends will separate (again on average), the polymer entropy will decrease. The decrease in entropy (and the respective increase in free energy) means that the polymer will exert the force on the handles trying to bring them back together. This force behaves very much like the force of an elastic spring, and is known as entropic elasticity. in this section we will develop the equation for the entropic elasticity and we will see how the polymer reacts to external force.

In FJC model we know that $R_0^2 = Nb^2$, but using the properties of random walks we can also calculate the probability of the end-to-end vector.

In one dimension:

$$P(x) = \frac{1}{\sqrt{2\pi \langle x^2 \rangle}} e^{-\frac{x^2}{2\langle x^2 \rangle}}$$

$$x \rightarrow R_{ee}$$

$$\langle x^2 \rangle \rightarrow \langle R_{ee}^2 \rangle = Nb^2$$

In three dimension:

$$P(\vec{R}_{ee}) = P(x, y, z) = P(x)P(y)P(z) \propto \text{Exp} \left[-\frac{1}{2} \left(\frac{x^2}{\langle x^2 \rangle} + \frac{y^2}{\langle y^2 \rangle} + \frac{z^2}{\langle z^2 \rangle} \right) \right]$$

Using the symmetry of the problem we know that

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{\langle R_{ee}^2 \rangle}{3}$$

$$P(\vec{R}_{ee}) = \dots \text{Exp} \left[-\frac{3}{2} \frac{x^2 + y^2 + z^2}{\langle R_{ee}^2 \rangle} \right] = \dots \text{Exp} \left[-\frac{3}{2} \frac{R_{ee}^2}{\langle R_{ee}^2 \rangle} \right]$$

We can understand the probability equation from above in a different way. the probability of finding the end-to-end vector in a certain length equals to the number of possibilities of arranging it in a specific length divided by the sum of all the possibilities of all the length.

$$P(\vec{R}_{ee}) = \frac{\text{number of possibilities of arranging the polymer in a specific length}}{\text{sum of all the possibilities of all the lengths}} = \frac{\mathcal{N}(\vec{R}_{ee})}{\sum_{\vec{R}_{ee}} \mathcal{N}(\vec{R}_{ee})}$$

using the fact that the sum is just a number (normalization factor) and the definition of entropy S we get

$$S = \ln \mathcal{N} = -\frac{3}{2} \frac{\langle R_{ee}^2 \rangle}{\langle R_{ee}^2 \rangle}$$

and the free energy function is

$$F(\vec{R}_{ee}) = U - k_B T S = -k_B T \ln \mathcal{N}(\vec{R}_{ee})$$

$$F(\vec{R}_{ee}) = \frac{3}{2} \frac{k_B T}{\langle R_{ee}^2 \rangle} R_{ee}^2 = \frac{3}{2} \frac{k_B T}{\langle R_{ee}^2 \rangle} (x^2 + y^2 + z^2),$$

where as before we substituted the coordinates of the end-to-end vector $R_{ee} = (x, y, z)$. This way the formula should remind us the free energy of a hookean spring

$$F(x) = \frac{K}{2} x^2$$

from that analogy it is easy to see that ideal polymer behaves like a 3D hookean spring with relaxed length of zero since the polymer ends want to get closer.

Now we will apply some force on polymer ends, say in x -direction and study the response of the polymer.

In fact we have two possibilities of doing this calculation:

1) We can consider the extension x to be a free parameter in free energy, then we find the force from the differential of the free energy. It is a bit like for systems we considered in Thermo class: volume and temperature are free parameters in canonical ensemble, $dF = -pdV - \sigma d\tau$ and pressure can be found from $p = -(\partial F / \partial V)_\tau$. In the linear case, such as extension of a polymer along an axis $-pdV$ is replaced by $-f dx$. Then

$$f = -\frac{\partial F}{\partial x} = -\frac{3k_B T}{\langle R_{ee}^2 \rangle} x$$

i.e. polymer reacts like a spring with spring constant of

$$K = \frac{3k_B T}{\langle R_{ee}^2 \rangle}$$

To stress, in this case we imagined that we fixed the extension x and measure the average force which the polymer exerts onto the handles.

2) The second possibility is to set the force and to measure the average extension $\langle x \rangle$

$$f \rightarrow \langle x \rangle = -\frac{f}{K}$$

The energy of polymer under extension is $\epsilon = -fx$. We find $\langle x \rangle$ from Boltzmann distribution. When counting states we should remember that for every extension x there are $\mathcal{N}(x) \propto e^{-\frac{3}{2} \frac{x^2}{\langle R_{ee}^2 \rangle}}$ microstates of the polymer. This way a calculation is a bit longer

$$\langle x \rangle = \frac{\int x e^{\beta x f} e^{-\frac{3}{2} \frac{x^2}{\langle R_{ee}^2 \rangle}} dx}{\int e^{\beta x f} e^{-\frac{3}{2} \frac{x^2}{\langle R_{ee}^2 \rangle}} dx} = \frac{1}{f} \frac{\partial}{\partial \beta} \ln \int e^{\beta x f} e^{-\frac{3}{2} \frac{x^2}{\langle R_{ee}^2 \rangle}} dx$$

but in the end we get the same result. Try it.

2. NOTES AND PROBLEM SET 2

2.1. Polymers: Ideal chains

We consider a linear polymer chain connecting $N \gg 1$ monomers. Monomer positions at any given time t are described by $\{\vec{r}_i\}_{i=1..N}$

Polymer coil size is usually characterized by the mean-square end-to-end distance $R_0 = \sqrt{\langle R_{ee}^2 \rangle} = \sqrt{\langle (\vec{r}_N - \vec{r}_1)^2 \rangle}$ or/and by a gyration radius $R_g^2 = \frac{1}{N} \sum_{i=1}^N \langle (\vec{r}_i - \vec{r}_{cm})^2 \rangle$, where $\vec{r}_{cm} = \frac{1}{N} \sum_{i=1}^N \vec{r}_i$ is coil's center-of-mass position.

Ideal chains are polymers with no long-range interactions between the monomers: the interactions enter only through the connectivity along the chain. Although ideal chain seems to be just a convenient theoretical idealization, there are many cases when real polymers behave as ideal, e.g. in the so-called θ -solvents, where the second virial coefficient of monomer-monomer interactions turns into zero.

For sufficiently long ideal chains $R_0^2 \propto N$ and

$$R_g^2 = \frac{R_{ee}^2}{6} \quad (2.1)$$

Probability density of finding the ends of an ideal polymer separated by $\vec{r} = \vec{r}_N - \vec{r}_1$ is:

$$P(\vec{r}) = \left(\frac{3}{2\pi} \right)^{3/2} \frac{1}{R_0^3} \exp\left(-\frac{3r^2}{2R_0^2} \right) \quad (2.2)$$

Similarly, the probability densities of finding any two monomers m and n ($|n-m| \gg 1$) separated by $\vec{r}_{nm} = \vec{r}_n - \vec{r}_m$ is:

$$P(\vec{r}) = \left(\frac{3}{2\pi \langle r_{nm}^2 \rangle} \right)^{3/2} \exp\left(-\frac{3r^2}{2 \langle r_{nm}^2 \rangle} \right) \quad (2.3)$$

Probability distribution Eq. 2.3 leads to entropy S and entropic elasticity of the polymer chain:

$$\begin{aligned} S &= \frac{3r^2}{2R_0^2} \\ F &= \frac{3T}{2R_0^2} r^2 = \frac{1}{2} K r^2 \\ K &= \frac{3T}{R_0^2}, \end{aligned} \quad (2.4)$$

where F is free energy and K is the entropic stiffness of the polymer chain.

Freely jointed chain model(FJC): N links of equal length b completely free to rotate at any joint: $R_0^2 = Nb^2$

Freely rotating chain: free to rotate around every joint keeping the angle between the consecutive links fixed: $\vec{b}_i \vec{b}_{i+1} = \cos \theta$. We derived in the class that:

$$\langle \vec{b}_i \vec{b}_{i+j} \rangle = \cos^j \theta = b^2 \exp(-s/l_p), \quad (2.5)$$

where s is the distance between the monomer along the polymer contour and $l_p = b/|\ln \cos \theta|$ is persistence length, which characterizes polymer flexibility.

Furthermore:

$$R_0^2 = Nb^2 \frac{1 + \cos \theta}{1 - \cos \theta} \quad (2.6)$$

Kuhn length l_K is defined in an attempt to force freely-jointed-chain description onto the chain with finite flexibility: we demand that the polymer contour $L = Nb$ is divided into N' segments of length l_K (called Kuhn or statistical segments), i.e. $L = N'l_K$, in such a way that $R_0^2 = N'l_K^2$. Then by definition:

$$l_K = \frac{R_0^2}{L} = b \frac{1 + \cos \theta}{1 - \cos \theta} \quad (2.7)$$

Kuhn length is another measure of polymer flexibility.

Semi-flexible or worm-like chain: typically, biopolymers (DNA, actin filaments, microtubules etc.) behaving as elastic rods with a finite bending rigidity.

The polymer configuration is parameterized vs. monomer position s along the contour $\vec{r}(s)$. Then the tangent vector to the contour and the contour curvature are respectively: $\vec{t} = \partial \vec{r} / \partial s$ and $c = 1/R_c = \partial \vec{t} / \partial s$. The elastic energy is proportional to the square of the curvature:

$$H = \frac{1}{2} \kappa \int_0^L ds \left(\frac{\partial \vec{t}}{\partial s} \right)^2 = \frac{1}{2} \kappa \int_0^L ds \left(\frac{\partial^2 \vec{r}}{\partial s^2} \right)^2, \quad (2.8)$$

where κ describes the bending stiffness of a polymer of unit length.

For worm-like chain polymer

$$\langle \vec{t}(s) \vec{t}(s') \rangle = \exp(-|s - s'|/l_p)$$

$$l_p = \kappa/T$$

$$R_0^2 = 2l_p^2(L/l_p - 1 + \exp(-L/l_p)) \quad (2.9)$$

$$l_K = R_0^2/L = 2l_p, \quad (\text{for } L \gg l_p) \quad (2.10)$$

2.1.1. Ideal chain under force

In response to the force $\vec{f} = f_x \vec{i}$ applied at the ends the ideal polymer extends as a Hookean spring:

$$\langle x \rangle = \frac{R_0^2}{3k_B T} f, \quad (2.11)$$

where $\langle x \rangle$ is an *ensemble average* of the vector connecting the two ends in the *extended* state and R_0 is the root mean square end-to-end distance between the ends in the *relaxed* state. For the ideal polymer, the range of the application of 2.11 is huge: $x \ll L$, where L is the polymer contour length.

2.1.2. Confinement of an Ideal Chain in a Tube

We would like to estimate a free energy change required to insert an ideal polymer into a thin pipe. We assume the pipe diameter D to be much smaller than R_0 that is $R_0 \gg D$, yet much larger than the polymer Kuhn length $D \gg b$.

As the polymer is placed into the pipe, the number of its possible conformations decreases (as compared to the coil freely floating in solution), and so its entropy decreases as well leading to the increase in the free energy. We can estimate the latter increase in the framework of the second virial coefficient, i.e. by counting the number of the collisions of the chain with the tube and multiplying that by the temperature T (in Joules). Another interpretation of this approach is realising that each collision reduces the number of possible configurations roughly by 2 (by preventing mirror symmetric conformations), that is reducing the entropy by $\ln 2$ and increasing the free energy by $T \ln 2 \approx T$.

From the statistics of the ideal chain, the number n of Kuhn segments between two consecutive collisions with the pipe is:

$$D \approx b\sqrt{n} \Rightarrow n \approx \frac{D^2}{b^2}. \quad (2.12)$$

Thus, the rise to the free energy due to the chain confinement is:

$$\Delta F \approx \frac{N}{n} T = \frac{Nb^2}{D^2} T = \frac{R_0^2}{D^2} T. \quad (2.13)$$

Notice that the final result does not depend on the microscopic details of the model (N , b , the nature of the Kuhn length), but only on the relevant length scales, R_0 and D . This is a common feature of scaling systems.

Notice also, that the ideal chain placed into the pipe is compressed by the pipe walls but does not change its conformation in the direction of the pipe axis, since the statistics for the ideal chain is along different axes is independent (e.g. a product of independent Gaussians). The situation is different for the real chain, that expands along the tube axis, as we will see.

2.2. Real Chains

So far we have talked about ideal chain models: these approximate the properties of polymers in θ -solvents, i.e. solvents in which the second virial coefficient of monomer interactions is $a = 0$. We saw that for long enough polymers, the statistics of the chain is similar to that of a random walk. In particular, the coil size given by its end-to-end distance or its gyration radius scales with the polymer length as $\propto N^{1/2}$.

We now switch to the properties of the real chains, i.e. polymers in good solvents, where $a > 0$, i.e. the repulsive interactions prevail over the attractive, which means that polymers like to dissolve in such media. In this context, the second virial coefficient a notation is often replaced by v , as it has a meaning of the excluded volume.

In simulations, real chains can be modelled by the so called, self-avoiding random walk (SAW), in which the random walker trajectory is not allowed to intersect itself. Such simulations demonstrate that the probability density of the polymer ends being located near each other is close to 0, reaching maximum at some distance that is called Flory radius R_F that plays a role of the coil size. The coil expands (swallows) as compared to the ideal chain due to the repulsive interactions between its monomers, and the coil size changes its scaling with the polymer length.

The simulation results show that in the general scaling

$$R_F \approx N^\nu$$

law, the exponent ν depends of the problem dimensionality as follows: $\nu = 1$ in $1D$ (well, this is trivial), $\nu = \frac{3}{4}$ in $2D$, $\nu = \frac{3}{5}$ in $3D$, $\nu = \frac{1}{2}$ for $d > 3$.

The rigorous mathematical derivation of these simulation results is rather cumbersome. Nevertheless, there is a simple model by Flory (historically the first model describing the real coils). The model has its flaws which mysteriously cancel out each other, and the model

produces surprisingly good predictions for the R_F scaling in any dimension. This is the model that we will discuss here.

The Flory model estimates the changes in the coil free energy that are introduced by the repulsive interactions between the monomers. The excluded volume interactions are calculated within the second virial coefficient approximation:

$$F_{rep} = \frac{vn^2}{2}TR_F^d,$$

where n is the segment density and R_F^d is an estimation of the coil volume (the model treats different dimensions d).

The segment density can be then estimated as $n \approx N/R_F^d$, so that:

$$F_{rep} = \frac{vT}{2} \frac{N^2}{R_F^2}$$

This addition to the coil free energy could be reduced if the coil expands (i.e. R_F increases). However, this would also lead to the decrease in the coil entropy. The change in the entropy is estimated based on the ideal chain model (compare to chain extension free energy):

$$F_{entropy} = \frac{3T}{2Nb^2}R_F^2$$

Then the total change in the free energy is

$$F = \frac{vk_B T}{2} \frac{N^2}{R_F^2} + \frac{3T}{2Nb^2}R_F^2.$$

R_F is then found from the minimization of F :

$$R_F \approx \left(\frac{dab^2}{6} \right)^{\frac{1}{d+2}} N^{\frac{3}{d+2}},$$

i.e. R_F scales with the power of N as $R_F \propto N^\nu$. Substituting different dimensionalities d into this equation, we get: $\nu = 1$ for $d = 1$, $\nu = 3/4$ for $d = 2$, $\nu = 3/5$ for $d = 3$ and $\nu = 1/2$ for $d = 4$, exactly as predicted by simulations and the more rigorous calculations. This is an amazing achievement for such a simple model, especially as it suffers from some obvious deficiencies.

As pointed by deGennes in his textbook, there are two major flaws with Flory's estimations:

1. As is usual in the mean-field type of theories, $\langle n^2 \rangle$ is estimated as $\langle n \rangle^2$. This is good for systems where the molecular density has only small fluctuations, but not in a polymer coil. Think of, say, collisions in the atmosphere. It is clear that the collision rate is proportional to local n^2 and that the most of the collisions happen in the bottom layer of ~ 10 km height where the molecule density is high. However, if we assume the whole height of the atmosphere of 100 km, and average the molecular density over the whole of it and base our estimations on the obtained $\langle n \rangle^2$, it is clear that we would underestimate the collision rates by a large margin. Yet if we use $\langle n^2 \rangle$ the estimation would give a right number.
2. The use of the expression for the entropy of the ideal chain to describe the properties of the real chain is questionable as well.

Nevertheless, as mentioned above, these two flaws somehow cancel out each other and the overall model produces a correct result in any dimension.

2.2.1. Real Chain under Force

We consider now the force-extension experiment on the real chain: the two ends of the polymer are pulled by a pair of forces \vec{f} in opposite directions along, say, axis X .

First we demonstrate that for any model of the chain (ideal, real or anything else), for small enough forces such that $fR_{ee} \ll T$, the following relation holds for the resulting extension:

$$\langle x \rangle = \frac{\langle R_{ee}^2 \rangle}{3T} f \quad (2.14)$$

Generally speaking, this is one of the consequences of the fluctuation-dissipation theorem in the Statistical Mechanics that connects between the system fluctuations in thermodynamic equilibrium ($\langle R_{ee}^2 \rangle$ in this case) with the system susceptibility to external force, very much like the connection between a spring elasticity and its fluctuations (equipartition theorem is one of the partial cases of the fluctuation-dissipation theorem). We have seen the applicability of this expression for the ideal chain already (although there it works in a much wider range, also for $fR_{ee} \gg T$, but $fL \ll T$, where L is the polymer contour length).

Let's derive it now for a general case. Assume the energy of the chain conformations without external force are described by a Hamiltonian $H_0(\{\vec{r}_i\}_N)$, where $\{\vec{r}_i\}_N$ are the

monomers' locations. All of the interactions between the monomers like excluded volume, the constraints of the polymer backbone etc go into H_0 . Then the Hamiltonian H under the external force is:

$$H(\{\vec{r}_i\}_N) = H_0(\{\vec{r}_i\}_N) - fx, \quad (2.15)$$

where $x = (\vec{r}_N - \vec{r}_1) \cdot \hat{x}$.

Then the average extension is calculated in the framework of the Canonical ensemble as:

$$\langle x \rangle = \frac{\int x \cdot e^{-\beta H} d\vec{r}_1 \dots d\vec{r}_N}{\int e^{-\beta H} d\vec{r}_1 \dots d\vec{r}_N} = \frac{\int x \cdot e^{-\beta(H_0 - fx)} d\vec{r}_1 \dots d\vec{r}_N}{\int e^{-\beta(H_0 - fx)} d\vec{r}_1 \dots d\vec{r}_N} \approx \frac{\int (x + \beta fx^2) \cdot e^{-\beta H_0} d\vec{r}_1 \dots d\vec{r}_N}{\int (1 + \beta fx) \cdot e^{-\beta H_0} d\vec{r}_1 \dots d\vec{r}_N}, \quad (2.16)$$

where we expanded the exponent into a Taylor series since we are looking at the weak force limit and thus expect $x \ll R_{ee}$ and so $\beta fx \ll 1$.

The linear in x terms under the integrals in the equation essentially average x in the situation with no external force (under H_0 Hamiltonian). Because of isotropicity this average is 0, and we are left with:

$$\langle x \rangle = \beta f \frac{\int x^2 \cdot e^{-\beta H_0} d\vec{r}_1 \dots d\vec{r}_N}{\int e^{-\beta H_0} d\vec{r}_1 \dots d\vec{r}_N} = \beta f \langle x^2 \rangle_0 = \frac{\langle R_{ee}^2 \rangle}{3T} f, \quad (2.17)$$

where $\langle x^2 \rangle_0$ labels the mean square component x of the end-to-end vector in the conditions of no external force, that is then replaced by $\langle R_{ee}^2 \rangle / 3$ due to isotropicity ($\langle R_{ee}^2 \rangle$ is taken without the external force as well, of course).

This proves our statement for the weak forces in general case. For the real chains we can replace $\langle R_{ee}^2 \rangle$ by R_F , so that:

$$\langle x \rangle = \frac{R_F^2}{3T} f. \quad (2.18)$$

To some degree this expression reminds of a dipole polarizability for molecules: there the interaction energy of a dipole with the external field has been $U = -\vec{d}\vec{E}$ vs. $U = -\vec{r}_{1N}\vec{f}$ in the current case, and the resulting polarizability $\alpha = d^2/3T$ for the molecules vs. polymer spring compliance $K^{-1} = \langle R_{ee}^2 \rangle / 3T$.

We can suggest that the Eq. 2.18 is valid more or less up to the extensions $\langle x \rangle \approx R_F$, i.e. $fR_F \approx 3T$. Beyond that limit the coil obviously undergoes a significant deformation and the forces can no longer be assumed weak.

This brings us to the strong force-extension limit: $fR_F \gg 3T$ (but still $fL \ll T$). This case can be treated in the framework of Pincus' blob model. The idea is to split the

polymer into segments (blobs) of size ξ_b small enough so that at their scale the external influence can be considered as weak, or rather at the limit of switching to strong. In the current case then the blob size can be determined from $f\xi_b \approx 3T$. Within the blob the force does not change the statistics much, so we can use Flory's formula relating the size of the blob to the number of monomers g within it: $\xi_b = ag^\nu$ and $g = (\xi_b/a)^{1/\nu}$, where a is some proportionality coefficient.

At the scale of the whole chain the force is large and we can expect the blobs to be lined up along the force direction. Then the extension is expected to be:

$$x = \frac{N}{g}\xi_b = Na^{1/\nu}\xi_b^{1-1/\nu} = (aN^\nu)^{1/\nu} \left(\frac{f}{3T}\right)^{1/\nu-1} = R_F^{1/\nu} \left(\frac{f}{3T}\right)^{1/\nu-1} = R_F \left(\frac{fR_F}{3T}\right)^{1/\nu-1}. \quad (2.19)$$

Substituting into the Eq. 2.19 the Flory exponent for the real polymer in 3D $\nu = 3/5$, we obtain:

$$x = R_F \left(\frac{fR_F}{3T}\right)^{2/3}. \quad (2.20)$$

Thus the force-extension dependence is no longer linear (although the forces remain elastic in the sense that the situation is fully reversible): greater extensions require more forces than those that would have been expected under a simple Hookean law. Notice, that again the result does not depend on the polymer model details (Kuhn length, polymer length, excluded volume etc) just on the overall size of the polymer coil R_F : again a feature of a system with the scaling property.

Notice also, that the substitution into the Eq. 2.19 of the exponent for the ideal chain $\nu = 1/2$ and ideal chain size R_0 instead of R_F gives the correct result:

$$x = \frac{R_0^2}{3T}f \quad (2.21)$$

i.e. the weak force extension formula holds also for strong forces in the case of the ideal chain, as expected. This confirms our approach to treating the strong force limit.

We can now check how much energy is needed to separate a real chain ends by a distance x . Expressing force f through x from the Eq. 2.20, we obtain:

$$f = \frac{3T}{R_F} \left(\frac{x}{R_F}\right)^{3/2}. \quad (2.22)$$

The free energy change is then obtained by integrating this expression over x :

$$\Delta F \approx T \left(\frac{x}{R_F}\right)^{5/2}. \quad (2.23)$$

2.2.2. Confinement of a Real Chain in a Tube

The estimation of the free energy change to confine a *real* chain to a tube is superficially similar to that of the *ideal* chains. In terms of the calculation, the main difference is that for the number of Kuhn segments between the chain collisions with the tube in the Eq. 2.12 we use the Flory statistics instead of the ideal chain statistics:

$$D \approx an^{3/5} \Rightarrow n \approx \left(\frac{D}{a}\right)^{5/3}, \quad (2.24)$$

and then the free energy change is again just the number of collisions multiplied by the temperature:

$$\Delta F \approx \frac{N}{n}T = N \left(\frac{a}{D}\right)^{5/3} T = \left(\frac{aN^{3/5}}{D}\right)^{5/3} T = \left(\frac{R_F}{D}\right)^{5/3} T. \quad (2.25)$$

I assume it goes without saying that the result does not depend on the microscopic details of the polymer model (polymer contour length, excluded volume, Kuhn length etc).

Although for this problem the calculations appear similar for ideal and real chains, there is a significant qualitative difference between the two cases: the parts of the real polymer in between the collisions with the tube walls we would call *blobs*, the same way as in the force-extension problem. The point is not in the naming of course, but in the fact that the structure of the polymer within the blobs is not affected by the external forces and so follows the statistics of the free chain. Different blobs do not occupy the same space: this would increase the monomer-monomer interaction energy and affect the coil structure (unlike for an ideal chain where there are no monomer interactions). Thus different blobs line up along the tube. Interestingly, the same extension of a polymer along the tube requires roughly the same energy as in the force-extension experiment.

Let's check this. The length of the tube occupied by a real chain can be obtained just lining up the blobs, each of D size:

$$x = \frac{N}{n}D = \left(\frac{a}{D}\right)^{5/3} ND = \left(\frac{R_F}{D}\right)^{5/3} D = R_F \left(\frac{R_F}{D}\right)^{2/3} \quad (2.26)$$

Expressing from here R_F/D through x and substituting into the Eq. 2.25 we get:

$$\Delta F = T \left(\frac{x}{R_F}\right)^{5/2}. \quad (2.27)$$

As we see this coincides with the Eq. 2.23 for the force-extension setup.

Problem Set 2

1. Find relation between R_g and R_{ee} in the case of freely jointed chain. How does it compare with Eq. 2.1.

Hint: While this problem can be attacked in a straightforward manner directly from definitions, a more elegant way is by starting with a proof that

$$R_g^2 = \frac{1}{2(N+1)^2} \sum_{n=0}^N \sum_{m=0}^N \langle (\vec{r}_n - \vec{r}_m)^2 \rangle. \quad (2.28)$$

2. Gaussian chain is defined as a limit of an ideal chain such that distances between any two points on the chain are normally distributed, i.e. probability density for the vector \vec{r}_{nm} connecting any two monomers n and m is

$$P(\vec{r}_{nm}) = \left(\frac{3}{2\pi \langle r_{nm}^2 \rangle} \right)^{3/2} \exp \left(-\frac{3r_{nm}^2}{2 \langle r_{nm}^2 \rangle} \right) \quad (2.29)$$

with $\langle r_{nm}^2 \rangle = |n - m|b^2$. Derive the structure factor of such a chain (Debye formula). Express it as a function of wave vector q and chain gyration radius R_g . Check the expression behaviour in the limit of $qR_g \gg 1$ and explain the result.

Hint: You might find it useful to show first that $\langle \exp(ikx) \rangle = \exp\left(-\frac{q^2 \langle x^2 \rangle}{2}\right)$ holds for a 1D Gaussian distributed variable x . For a 3D Gaussian distributed variable r we respectively have $\langle \exp(i\vec{q}\vec{r}) \rangle = \exp\left(-\frac{q^2 \langle r^2 \rangle}{6}\right)$. If you want to use these expressions, derive them first.

3. Consider a chain of $N \gg 1$ links of length b . There are small springs in the joints between the consecutive links which attempt to preserve the direction of the links, i.e. the energy in the joint is minimal when the angle θ_i between consecutive links $[i, i + 1]$ is zero (links point in the same direction). Otherwise, the energy in the joint is $\epsilon_i = K\theta_i^2/2$. Thermal fluctuations, of course, lead to $\theta_i \neq 0$. (with a minor modification this is Kratky-Porod model of the Worm Like Chain).
 - How large should be the stiffness K of the springs, so that $\theta_i \ll 1$ is kept.
 - For the case of stiff springs, what is the persistence length, R_{ee} and Kuhn length of such a chain.

- show that the continuous limit of such a chain is the worm like chain. What is the relation between the parameters of the chain N, b, K and the respective parameters of the worm-like chain.
4. DNA has rather large Kuhn length of $b \approx 100$ nm. Its effective diameter can be estimated as $d \approx 4$ nm (including hard-core and electric repulsion in physiological conditions). Use the results of your calculation of rods' excluded volume to estimate the DNA length at which collisions within the chain starts. Below this length DNA can be thought of as an ideal chain.
 5. Worm-like chain with length $L \ll l_p$ is rather stiff and has a reasonably well-defined direction. We can align X-axis along the chain (for example along the line connecting the chain ends). In this case s in Eq. 2.8 can be replaced with x and it is convenient to replace $\vec{r}(s)$ with $\vec{r}_\perp(x)$, describing the deviation of the point on the chain from X-axis:

$$H = \frac{1}{2} \kappa \int_0^L dx \left(\frac{\partial^2 \vec{r}_\perp(x)}{\partial x^2} \right)^2, \quad (2.30)$$

- Why are we allowed to make these substitutions?
- Find the mean-square displacement $\langle \vec{r}_\perp^2 \rangle$ of the point in the center of the chain.

Note: The result depends somewhat on the boundary conditions. Use conditions of the ends of the polymer stack on the X-axis, i.e. $r_\perp(0) = r_\perp(L) = 0$. This is of course consistent with drawing the direction of X-axis as a line passing through the polymer ends.

6. Consider a semiflexible polymer of length L and persistence length l_p : L can be either larger or smaller than l_p . Consider this polymer to be confined within the long tube of diameter D . The tube diameter is much smaller than both L and l_p . Estimate (estimate! no exact derivation) the number of collision points between the tube and the polymer. Estimate the increase in the free energy due to confinement.
7. A great experimental breakthrough in the mid-1990s was a capability to stretch single DNA polymers (see works of Chu, Bustamante, Chatenay, Bensimon and their coworkers). For example, one end of DNA polymer is attached to an immobile surface and another to some kind of a handle which is used to pull the end of DNA and measure

the extension (displacement of that end). At about the same time an exact theoretical expression was derived by Marko&Siggia relating the applied force \vec{f} to the extension x and to DNA length L and persistence length l_p (for $L \gg l_p$). Nevertheless, they suggested to use an approximate expression, which is simpler than the exact one and is almost as precise:

$$\frac{fl_p}{k_B T} = \frac{x}{L} + \frac{1}{4 \left(1 - \frac{x}{L}\right)^2} - \frac{1}{4} \quad (2.31)$$

This expression is in fact a combination of two limiting cases: those of small forces and of large forces (how small and how large?). Explain these limiting cases: the case of small forces you can treat exactly and the case of large forces up to a numeric coefficient so far (you'll treat it exactly in the next problem). For the large forces you might find it possible to use the result of the previous problem. Explain the way they are combined in a single expression.

8. Semiflexible polymer (e.g. DNA) with length $L \gg l_p$ is stretched along axis x with rather large force f , such that $fl_p > k_B T$.

- We define the *projected length* L_{\parallel} of a polymer as, well, the length of its projection onto x axis: say, if the one end of the polymer is hold at $x = 0$ then the projected length of the polymer will be just the x -coordinate of the other end. Show that under strong stretching as defined above, the projected length can be expressed as:

$$L_{\parallel} \approx L - \frac{1}{2} \int_0^L dx \left(\frac{\partial \vec{r}_{\perp}(x)}{\partial x} \right)^2, \quad (2.32)$$

where \vec{r}_{\perp} is defined in the same way as in Problem 5.

- Show that the Hamiltonian of the chain under large force can be expressed as:

$$H = \frac{\kappa}{2} \int_0^L dx \left(\frac{\partial^2 \vec{r}_{\perp}(x)}{\partial x^2} \right)^2 + \frac{f}{2} \int_0^L dx \left(\frac{\partial \vec{r}_{\perp}(x)}{\partial x} \right)^2, \quad (2.33)$$

where as before $\kappa = k_B T l_p$

- Write the Hamiltonian in terms of spatial Fourier modes and find the mean square values of mode amplitudes.
- Calculate average projected length $\langle L_{\parallel} \rangle$ as a function of force f . Notice that $\langle L_{\parallel} \rangle$ is the same as extension x in the Problem 7. Verify that the expression you get is equivalent to Eq. ?? in the limit of high forces (including the numeric coefficient.)