

## Problem Set 5 Polymer physics

### 1 Gaussian chain and beyond

#### 1.1 Freely jointed chain (FJC) model

We consider a succession of rigid monomers of length  $a$  represented by vectors  $\mathbf{a}_i$  ( $i \in \{1, \dots, N\}$ ), see Fig. 1. The orientation of  $\mathbf{a}_i$  is given by the usual spherical angles ( $\theta_i \in [0, \pi]$ ,  $\phi_i \in [0, 2\pi]$ ). The polymer chain is in solution in a solvent of volume  $V$  (such a solvent can be considered as a heat reservoir).

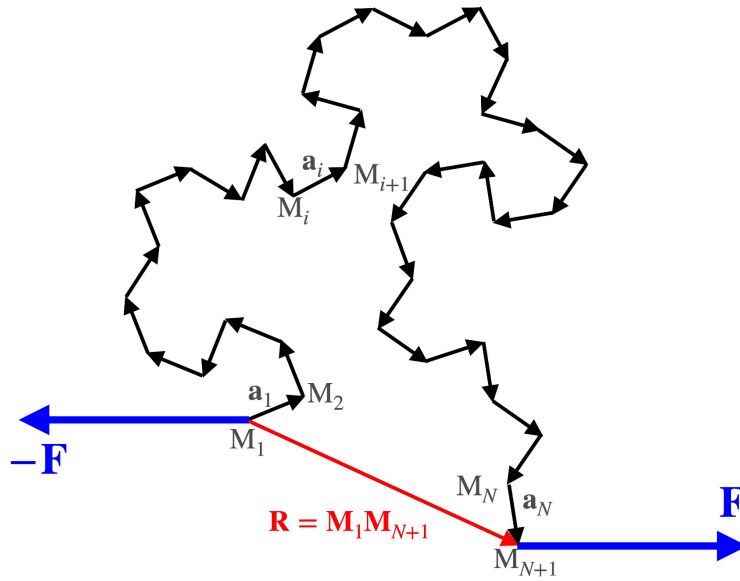


Figure 1: Sketch of a polymer chain (represented in 2d for simplicity) subject to external forces  $\mathbf{F}$  applied at its two ends, and composed of  $N$  monomers  $\mathbf{a}_i = \mathbf{M}_i \mathbf{M}_{i+1}$ , with  $|\mathbf{a}_i| = a$ . The end-to-end vector  $\mathbf{R} = \mathbf{M}_1 \mathbf{M}_{N+1}$  is shown in red.

1. Assuming that all orientations have equal probabilities, give the probability  $dP(\theta_i, \phi_i, d^2\Omega)$  of finding the monomer  $i$  in the direction  $(\theta_i, \phi_i)$  up to the infinitesimal solid angle  $d^2\Omega = \sin \theta_i d\theta_i d\phi_i$ . Deduce the probability density  $\rho(\mathbf{a}_1, \dots, \mathbf{a}_N)$  to have a given configuration  $\{\mathbf{a}_1, \dots, \mathbf{a}_N\}$  of the chain.
2. Give (without any calculation) the average values  $\langle \mathbf{a}_i \rangle$  and  $\langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle$ ? What do they represent?
3. Calculate the (canonical) partition function of the chain. One defines the end-to-end vector  $\mathbf{R} = \mathbf{M}_1 \mathbf{M}_{N+1}$ , where  $M_1$  (resp.  $M_{N+1}$ ) is the first (resp. the last) monomer of the chain (see Fig. 1). Calculate  $\langle \mathbf{R} \rangle$  and  $\langle \mathbf{R}^2 \rangle$ . Give a physical interpretation of  $\sqrt{\langle \mathbf{R}^2 \rangle}$ .
4. The chain is now submitted to a constant force  $\mathbf{F} = F_x \mathbf{u}_x + F_y \mathbf{u}_y + F_z \mathbf{u}_z$  acting on both ends. Show that the chain can be considered as having the potential energy  $U_p = -\mathbf{F} \cdot \mathbf{R}$ .
5. Compute the partition function of the chain experiencing the tensile force  $\mathbf{F}$ . Deduce an expression of  $\langle \mathbf{R} \rangle$  as a function of  $\mathbf{F}$ .

## 6. Derivation of the equation of state:

- 6.1 We assume that mechanical work can be done on the chain only via the force  $\mathbf{F}$  acting on the last monomer  $M_\ell$ .
  - 6.1.1 Express the first principle of thermodynamics as an expression for the internal energy differential  $dU$  in the variables  $(dS, d\mathbf{R} = \{dR_x, dR_y, dR_z\})$ .
  - 6.1.2 Deduce an expression for the free energy differential  $d\mathcal{F}$  in the variables  $(dT, d\mathbf{R})$ .
  - 6.1.3 Which quantity is analogous to the pressure in this context?
- 6.2 In the limit of small forces  $\beta Fa \ll 1$ , compute the equation of state of the chain. Give a corresponding expression for the free energy  $\mathcal{F}$ .

## 1.2 Taking into account interactions between monomers

### 1.2.1 Excluded volume effect

We take for granted that the free energy of an ideal chain in a solvent is given by

$$\mathcal{F}_{\text{Gauss}} = \mathcal{F}_0 + \frac{3}{2} \frac{k_B T}{Na^2} \mathbf{R}^2,$$

where  $\mathbf{R}$ , the end-to-end vector is a convenient measure of the polymer coil size, and  $\mathcal{F}_0$  is independent of  $\mathbf{R}$ . We try to improve the model by taking into account the intramolecular interactions between monomers (also known as the “excluded volume effect” if the repulsion dominates).

1. The 2nd order virial expansion

$$\frac{PV}{Nk_B T} \simeq 1 + \frac{v_2}{2} \frac{N}{V} \quad \text{with} \quad v_2 = \int d^3\mathbf{r} \left( 1 - e^{-u(\mathbf{r})/k_B T} \right)$$

describes the first correction to the ideal gas equation of state due to interactions, where  $u(\mathbf{r})$  is the pair potential. Deduce the contribution of the interactions to the free energy  $\mathcal{F}$  within this approximation. By inspection of  $\mathcal{F}$ , explain why this approach is akin to a mean-field approximation.

2. For the isolated polymer in solution, we can model the possible *effective* interactions between monomers by a pair potential  $u(r)$ . We assume furthermore that the polymer free energy can be written as

$$\mathcal{F}(R, T, N) \simeq \mathcal{F}_{\text{Gauss}} + \frac{1}{2} k_B T v_2 \int d^3\mathbf{r} c^2(r), \quad (1)$$

where  $c(r)$  is the monomer concentration and  $v_2 = v_2(T)$  is the second (effective) virial coefficient.

2.1 Why are the interactions between monomers called “effective”?

2.2 With Question 1, justify the expression (1).

3. We now assume the following form for  $u(r)$ :

$$u(r) = \begin{cases} +\infty & \text{if } r < a, \\ -\varepsilon & \text{if } a < r < 2a, \\ 0 & \text{if } 2a < r. \end{cases}$$

Plot  $u(r)$  as a function of  $r$ . Would you call this potential an attractive potential? A repulsive one? Something else? Calculate the corresponding  $v_2(T)$  and discuss in particular its sign.

4. Assuming that the first monomer  $M_f$  is pinned at  $\mathbf{r} = \mathbf{0}$ , express approximately the monomer concentration  $c(r)$  as a function of  $N$  and  $R$ . By minimizing the free energy with respect to  $R$ , calculate the radius of the polymer coil and show that  $R \sim N^\nu$ , with  $\nu$  a rational number to be determined. Discuss the different temperature regimes. Conclusions?

### 1.2.2 Fully charged polyelectrolyte

In this paragraph we consider a simple model for a charged polymer (polyelectrolyte).

1. The electrostatic energy of a charge distribution  $\rho(\mathbf{r})$  is  $E_{\text{el}} = \frac{1}{2} \int d^3\mathbf{r} \rho \mathcal{V}$  where  $\mathcal{V}(\mathbf{r})$  is the electrostatic potential (that is set to zero for  $|\mathbf{r}| \rightarrow \infty$ ). Using Gauss' theorem, show that for a charge distribution  $\rho$  constant in a sphere of radius  $R$ , one has

$$E_{\text{el}} = \frac{4\pi}{15\epsilon_0} \rho^2 R^5,$$

where  $\epsilon_0$  is the vacuum permittivity.

2. We assume that a fraction  $f$  of monomers bears an electric charge  $+e$ . Justify the following expression for the free energy:

$$\mathcal{F}(R, T, N) \simeq \mathcal{F}_{\text{Gauss}} + A \frac{(Nfe)^2}{\epsilon_0 \epsilon_r R},$$

where  $\epsilon_r$  is the relative dielectric permittivity of the solvent, and  $A$  a dimensionless constant.

3. Let us define the quantity  $\ell_B = e^2/4\pi\epsilon_0\epsilon_r k_B T$ .

- 3.1 What is the dimension of  $\ell_B$ ? Give an estimate of  $\ell_B$  for a polymer in water ( $\epsilon_r = 80$ ) at ambient temperature.
- 3.2 Show that at equilibrium, the theory predicts  $R \propto N (f^2 \ell_B a^2)^{1/3}$ , the proportionality factor being a dimensionless number or order 1.
- 3.3 With the above result, compute the average volume per monomer within the sphere of radius  $R$ .
- 3.4 Is this result compatible with the fact that two monomers are a length  $a$  apart?
- 3.5 Conclusion: the theory fails somewhere. Try to find where.

## 2 Kratky–Porod model and worm-like-chain (WLC) model

### 2.1 Kratky–Porod discrete model

We develop here a more refined model of elastic filament by taking into account the energy cost to have an angle  $\theta_i < 180^\circ$  between 2 monomers  $\mathbf{a}_i$  and  $\mathbf{a}_{i+1}$  (bending energy). We define the Kratky–Porod Hamiltonian of the chain by

$$\mathcal{H}_{\text{KP}} = -\frac{K}{a^3} \sum_{i=1}^{N-1} \mathbf{a}_i \cdot \mathbf{a}_{i+1} - \mathbf{F} \cdot \sum_{i=1}^N \mathbf{a}_i = -\frac{K}{a} \sum_{i=1}^N \cos \theta_i - \mathbf{F} \cdot \sum_{i=1}^N \mathbf{a}_i, \quad (2)$$

with  $K > 0$ .

1. Justify that  $K$  is usually written as  $K = k_B T \ell_p$ . What is the dimension of  $\ell_p$ ? Discuss briefly the effect of both terms in the Hamiltonian (2) on the chain length.
2. We denote  $\mathbf{t}_i$  the unit vector parallel to  $\mathbf{a}_i$  and pointing toward the  $(i+1)$ th monomer. Demonstrate the following expression for the average end-to-end distance  $\langle \mathbf{R} \rangle$  and its quadratic mean value  $\langle \mathbf{R}^2 \rangle$ :

$$\begin{aligned} \langle \mathbf{R} \rangle &= Na \langle \mathbf{t}_i \rangle, \\ \langle \mathbf{R}^2 \rangle &= a^2 \sum_{i,j} \langle \mathbf{t}_i \cdot \mathbf{t}_j \rangle. \end{aligned}$$

3. What is the typical value of  $\theta_i$  if  $\ell_p$  is “large” (in a sense to be precised)?

It is mathematically difficult to proceed further within the Kratky–Porod discrete model. In such a case, the *continuum limit* allows to simplify somewhat the maths, at the price of sacrificing the description of the short lengthscales, which are anyway already poorly described by the original model...

## 2.2 Worm-like-chain (WLC) continuous model

The worm like chain (WLC) is obtained as the continuum limit of the discrete Kratky–Porod model:  $a \rightarrow 0$  and  $N \rightarrow +\infty$  while keeping the contour length  $L = Na$  constant. In such a model, the filament is described as a continuous curve  $\mathbf{OM} = \mathbf{r}(s)$  where  $s$  measures the contour length along the chain (see Fig. 2). We denote  $\mathbf{t}(s)$  the tangent unit vector at point  $M$  and  $\theta(s)$  the angle between  $\mathbf{t}(s)$  and  $\mathbf{t}(s + ds)$ .

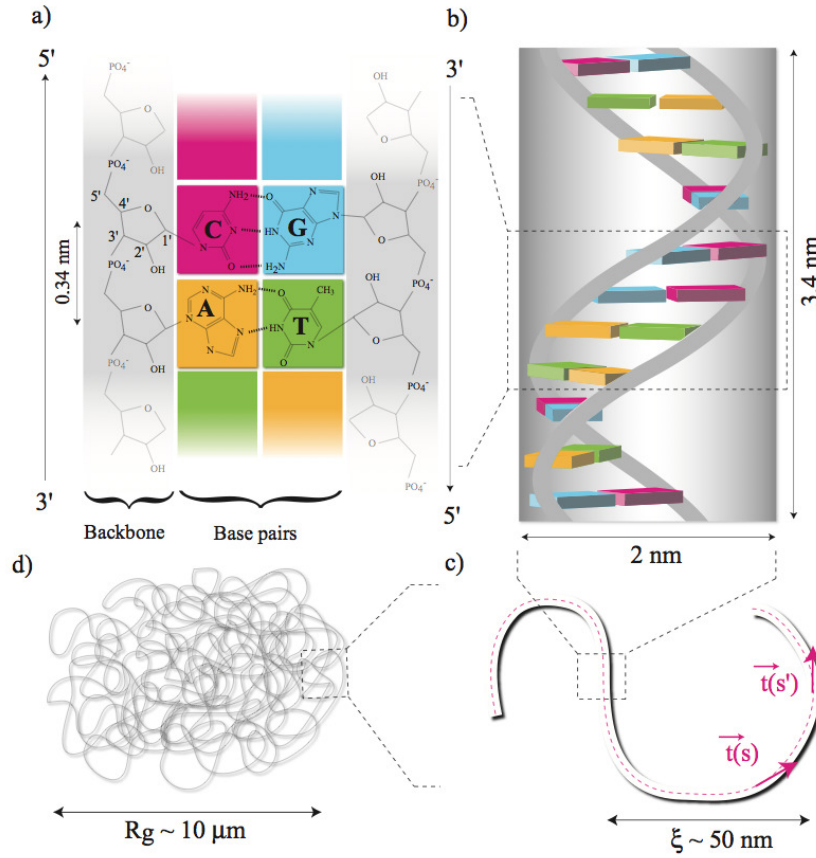


Figure 2: (a) Primary structure: each strand is made of a sugar-phosphate backbone where the four base pairs [Adenin (A), Guanin (G), Cytosin (C) and Thymin (T)] are attached. For the standard form of DNA (“DNA-B”), the distance between base pair is 3.4 Å. (b) Secondary structure: the two strand are wrapped around each other forming an helix of pitch 3.5 nm (10.5 base pairs). (c) At large scale, DNA behaves as a semiflexible polymer with a persistence length  $\ell_p = 50$  nm. (d) Long DNA chains ( $L \gg \ell_p$ ) behave as a statistical polymer coil with a giration radius  $R_g$ . [Reproduced from T.R. Strick, J.-F. Allemand, D. Bensimon, V. Croquette, *Behavior of supercoiled DNA*, Biophys. J. **74**, 2016 (1998).]

1. Show that

$$\mathbf{t}_i \cdot \mathbf{t}_{i+1} = 1 - \frac{1}{2} (\mathbf{t}_i - \mathbf{t}_{i+1})^2.$$

2. Without elaborating a rigorous mathematical demonstration, justify that in the continuous limit the first term of the chain energy in Eq. (2) can be written as

$$\mathcal{H}_{\text{WLC}}(\mathbf{r}(s)) = \frac{1}{2}k_{\text{B}}T\ell_{\text{p}} \int_0^L ds \left( \frac{\partial \mathbf{t}}{\partial s} \right)^2.$$

3. Express the end-to-end distance  $\mathbf{R}$  as an integral. How is transformed the last term of Eq. (2) in the continuum limit?
4. In absence of external force it is possible to show that

$$g(s) = \langle \mathbf{t}(s_0) \cdot \mathbf{t}(s_0 + s) \rangle = \exp \left( -\frac{|s|}{\ell_{\text{p}}} \right). \quad (3)$$

Give a physical interpretation of this expression and of the quantity  $\ell_{\text{p}}$ .

5. Calculate the mean square end-to-end distance  $R_{\text{g}} = \sqrt{\langle \mathbf{R}^2 \rangle}$ . Obtain a simplified relation in the long chain limit  $L \gg \ell_{\text{p}}$ .
6. **To go further.** We define  $d\theta(s)$  as the angle between  $\mathbf{t}(s)$  and  $\mathbf{t}(s+ds)$  and  $\theta(s) = \int_0^s \frac{d\theta}{ds} ds$ . Briefly justify that the bending energy can be written as

$$\mathcal{H}_{\text{WLC}}(\theta(s)) = \frac{1}{2}k_{\text{B}}T\ell_{\text{p}} \int_0^L ds \left( \frac{\partial \theta(s)}{\partial s} \right)^2.$$

Assuming that  $g(s) = e^{-\frac{1}{2}\langle \theta(s)^2 \rangle}$ , and using the Fourier expansion along the chain (also known as the Rouse expansion)

$$\theta(s) = \sum_{n=1}^{\infty} \theta_n \sin \left( \frac{\pi n s}{L} \right) \quad \text{with} \quad \theta_n = \frac{2}{L} \int_0^L ds \theta(s) \sin \left( \frac{\pi n s}{L} \right),$$

demonstrate the relation (3). [Hint to speed up: if  $x$  is a zero-mean Gaussian variable, its distribution is proportional to  $\exp(-x^2/2\langle x^2 \rangle)$ ]. Note that  $\sum_{n \geq 1} \frac{1}{n^2} \cos(nx) = \frac{\pi^2}{6} - x(\pi - x)$ .

### 3 Discussion

1. Orders of magnitude: Fill the table below.
2. When a force is applied to the chain in the WLC model, it is not possible to calculate an exact solution for the equation of state. Some approximate relations may be derived and are plotted in Fig. 3, together with a Monte-Carlo simulation of the WLC model and with the FJC relation. Comment the figure. Justify that orders of magnitude are correct.

organism type	genome size (base pair)	rise per base pair (Å)	$N_K$ base pair per $2\ell_p$	$\ell_p$	contour length	$R_g$ WLC model	container size
ssDNA virus STMV	1063	6.4	3				capside 7 nm
dsDNA virus	150,000	3.4	300				capside 100 nm
prokaryote E. coli	$4.6 \times 10^6$	3.4	300				cell $1 \mu\text{m}$
eukaryote human	$3.2 \times 10^9$	3.4	300				nucleus $6 \mu\text{m}$

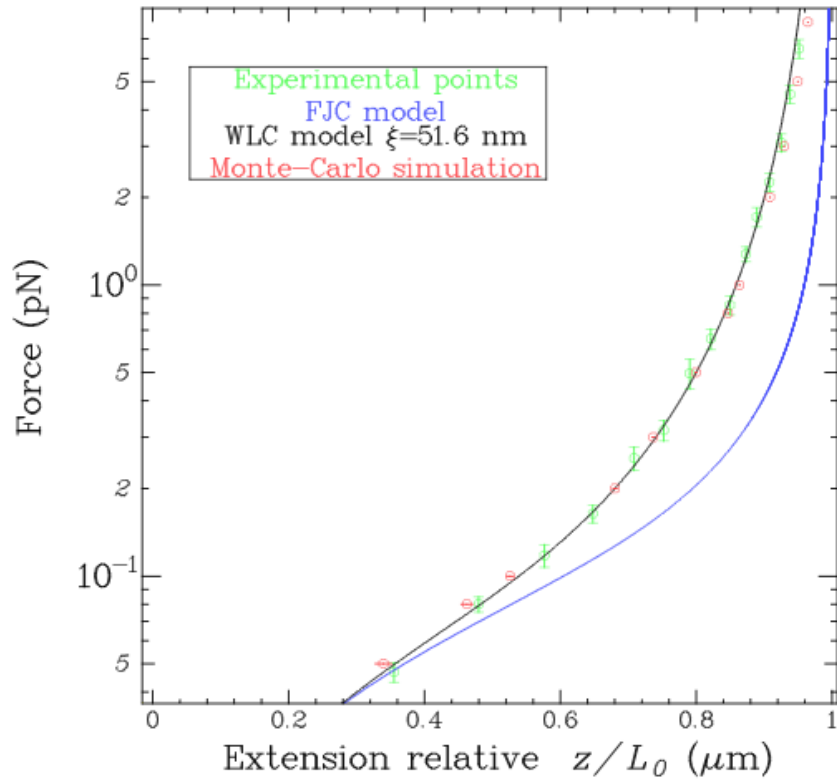


Figure 3: Force extension of a DNA molecule: comparison between experimental data and theory. (Green) experimental data; (Black) fit using a WLC model with  $\ell_p = 51.6 \pm 2 \text{ nm}$ ; (Blue) fit using a FJC model using  $a = 2\ell_p$ ; (Red) Monte-Carlo simulation of a semiflexible chain. [Reproduced from G. Chardin, *Études des topoisomérases de type II par micromanipulation d'ADN*, PhD thesis, Université Paris VII (2004)].