

## Problems ideal chains

### 1. The effective freely jointed chain (Kuhn model)

(a) In the Kuhn model, the polymer chain is divided into  $N$  effective segments with an effective segment length (or Kuhn length)  $b$ . We can find  $N$  and  $b$  by demanding that the mean square end-to-end distance  $\langle R^2 \rangle$  and the maximum extension  $R_{max}$  are the same as those of the original problem. Use this to find  $b$  and  $N$  as a function of the number of chemical segments  $n$ , the bond length  $l$ , the characteristic ratio  $C_\infty$ , and the bond angle  $\theta$ .

(b) For polyethylene, the characteristic ratio is 7.4, the bond angle  $68^\circ$ , and the bond length is 0.154 nm (experimental facts). Calculate the Kuhn length.

### 2. Coil-helix transition

A certain polysaccharide exhibits a transition at temperature  $T_t$  towards a helix structure upon cooling. Above  $T_t$  (where there is no helix), the chain consists of  $N$  Kuhn segments, each of length  $b$ . Upon the transition, 16 of those Kuhn segments convert into 1 new Kuhn segment of the helix. The helix is still flexible, although much stiffer than the chain was above  $T_t$ : the Kuhn length of the helix  $b_H$  is 8 times that above  $T_t$ . By what factor does the root-mean-square end-to-end distance change upon this transition, assuming that the chain remains ideal (no excluded-volume interactions)?

### 3. The freely rotating chain and the wormlike chain

In the freely rotating chain model, we assume that the polymer consists of segments with a fixed bond angle  $\theta$ , while all torsion angles  $\phi$  are equally probable. The mean-square end-to-end distance of a polymer is given by

$$\langle R^2 \rangle = \sum_{i=1}^n \sum_{j=1}^n \langle \vec{r}_i \cdot \vec{r}_j \rangle \quad (1)$$

To find an expression for  $\langle R^2 \rangle$  we need the correlation between vectors  $\vec{r}_i$  and  $\vec{r}_j$ . The correlation between adjacent vectors is  $\langle \vec{r}_i \cdot \vec{r}_{i-1} \rangle = l^2 \cos \theta$ . Bond vector  $\vec{r}_{i-1}$  passes the correlation on to  $\vec{r}_{i-2}$ , and so on so that

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

(a) Show that equation 1 can be written as

$$\langle R^2 \rangle = l^2 \sum_{i=1}^n \left[ 1 + \sum_{k=1}^{i-1} (\cos \theta)^k + \sum_{k=1}^{n-i} (\cos \theta)^k \right] \quad (3)$$

(b) Because  $(\cos \theta)^k$  decreases rapidly with increasing  $k$ , we can replace the upper limits in both summations by  $\infty$ . Use this to evaluate the summations, and show that

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

for the freely rotating chain. (Hint: use  $\sum_{i=1}^{\infty} t^i = t/(1-t)$ ).

(c) For polyethylene,  $\theta = 68^\circ$ . Compare to the experimental value ( $C_\infty = 7.4$ ); what causes the difference?

(d) For very small values of the bond angle,  $\theta \ll 1$ , the freely jointed chain model becomes equivalent to the wormlike chain model. To see this, we write equation 2 as

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = l^2 \exp\left(-\frac{|j-i|l}{l_p}\right) \quad (4)$$

How does the persistence length  $l_p$  depend on  $\theta$ ?

(e) To evaluate equation 1 using equation 4, we replace the summations by integrals:

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

Show that the mean square end-to-end distance for the wormlike chain is given by

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

(f) Show that for  $R_{max} \gg l_p$  this converges to the ideal chain result, while for  $R_{max} \ll l_p$  it corresponds to the rigid rod limit.

#### 4. The radius of gyration.

The radius of gyration is defined as

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (\vec{R}_i - \vec{R}_{cm})^2 \quad (5)$$

with

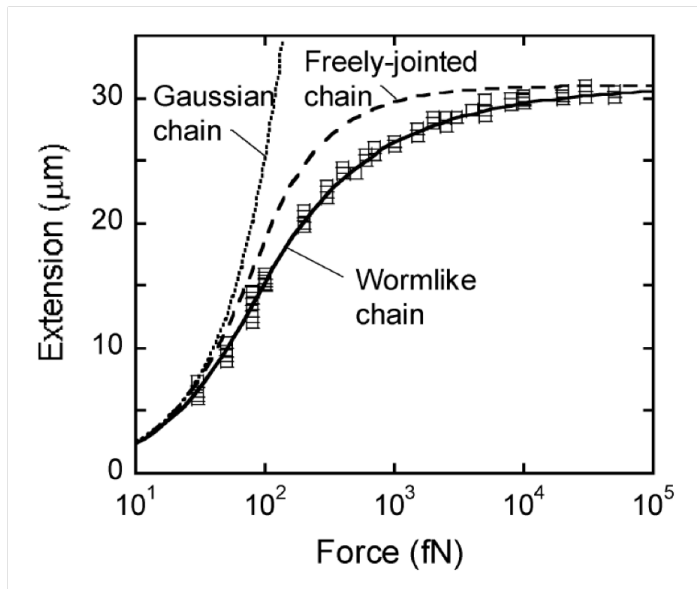
$$\vec{R}_{cm} = \frac{1}{N} \sum_{j=1}^N \vec{R}_j \quad (6)$$

the position of the center of mass of the chain. According to a theorem due to Lagrange, equation 5 can also be written as

$$R_g^2 = \frac{1}{N^2} \sum_{i=1}^N \sum_{j=i}^N (\vec{R}_i - \vec{R}_j)^2 \quad (7)$$

- (a) Give a proof of Lagrange's theorem.
- (b) Show that the radius of gyration of an ideal polymer chain equals  $\langle R_g^2 \rangle = Nb^2/6$ .  
Hint: make use of the fact that the section between  $\vec{R}_i$  and  $\vec{R}_j$  obeys the ideal chain result. Since  $N$  is large, the summations can be replaced by integrals:  $\sum_{k=1}^N \rightarrow \int_0^N du$ .
- (c) Calculate the radius of gyration of a rodlike polymer.

### 5. Stretching DNA.



The figure shows the force extension curve for DNA is given (at 298 K). From these data, estimate the persistence length of DNA.

### 6. Cyclization of polymers

The probability of a polymer to form a closed loop during polymerization is determined by the probability that the two ends of the chain are within a certain distance  $\delta$  from each other (with  $\delta$  a small distance on the order of the bond length  $l$ , so  $\delta \ll bN^{1/2}$ ). Show that for an ideal polymer chain, the looping probability decays as  $N^{-3/2}$  with the number of Kuhn segments.

### 7. Gel permeation chromatography

Gel permeation chromatography, also known as size exclusion chromatography is a

well-known technique to separate polymers based on their molar mass. The separation takes place in a chromatographic column filled with beads of a rigid porous gel. The pores in these gels are of similar size as the polymers; small polymers can enter the pores and therefore leave the column later than large polymers that cannot enter the pores. The important parameter for the separation process is the partition coefficient of the polymer between the pore and the bulk fluid  $K_M = c_{pore}/c_{bulk}$  (which depends on the molar mass  $M$ ). To find  $K_M$  we consider an ideal polymer chain of  $N$  Kuhn segments of Kuhn length  $b$  confined in a spherical cavity of diameter  $D$ .

(a) First we consider the case where  $D < R$  (with  $R$  the pore size). Estimate the free energy of the polymer by assuming that every collision with the wall costs approximately  $kT$ , and from this estimate the partition coefficient.

(b) Now, we consider the case  $D \gg R_g$ . Estimate  $K_M$  for this case by assuming that the polymer is excluded from a zone of thickness  $\delta \approx R$  from the wall of the pores.

### 8. Random walk statistics: the diffusion equation

An ideal polymer chain behaves as a random walk. The distribution function therefore obeys the same equations as those for a diffusing particle, i.e. Fick's diffusion equation (with time replaced by the coordinate along the chain  $n$ ). For polymers this equation is also known as Edwards' equation. For the  $x$ -direction this becomes

$$\frac{\partial P(n, x, x')}{\partial n} = \frac{b^2}{6} \frac{\partial^2 P(n, x, x')}{\partial x^2} \quad (8)$$

where  $x$  and  $x'$  are the position of segment  $n$  and of the beginning of the chain, respectively. Similar equations hold for the  $y$  and  $z$  directions.

(a) What is the initial condition, for  $n = 0$ ?

(b) The solution for a free ideal polymer with its origin at  $x' = 0$  can be found by Fourier transform in the  $x$ -domain,

$$\hat{P}(n, \omega) = \int_{-\infty}^{\infty} P(n, x) e^{-2\pi i \omega x} dx$$

Show that the solution of equation 8 is the Gaussian distribution and that the constant  $b^2/6$  in the diffusion equation indeed gives the correct mean square end-to-end distance. Hint: the Fourier transform of the second derivative,  $F[\partial^2 P/\partial x^2] = -4\pi^2 \omega^2 \hat{P}$ . Furthermore, the Fourier transform of a Gaussian function,

$$F[e^{-ax^2}] = \sqrt{\frac{\pi}{a}} \exp\left(-\frac{\pi^2 \omega^2}{a}\right)$$

## Solutions

### 1. The effective freely jointed chain (Kuhn model)

(a) The end-to-end distance is  $\langle R^2 \rangle = C_\infty n l^2 = N b^2$ . The maximum end-to-end distance is  $R_{max} = n l \cos(\theta/2) = N b$ . This gives two equations for two unknowns; solving gives  $b = C_\infty l / \cos(\theta/2)$  and  $N = n \cos^2(\theta/2) / C_\infty$ .

(b) Substitution of the numbers gives  $b = 1.4$  nm, about 9 time larger than the chemical bond length  $l$ .

### 2. Coil-helix transition

The size above  $T_t$  is given by  $\langle R_0^2 \rangle = N b^2$ , and below  $T_t$  it is  $\langle R_H^2 \rangle = N_H b_H^2$  with  $N_H$  the number of helical Kuhn segments. Since 16 original Kuhn units form one helical Kuhn unit, we have  $N_H = N/16$ . Also it is given that  $b_H = 8b$ . We thus find  $\langle R_H^2 \rangle = (N/16)(8b)^2 = 4N b^2$ . Hence the coil is four times bigger. Note that the maximum length is now also different, i.e.  $R_{max} = N_H b_H = (N/16)(8b) = N b/2$ . This is because due to the helical turn, the length per segment is effectively smaller.

### 3. The freely rotating chain and the wormlike chain

(a) To account for the absolute value of  $|j - i|$  we must split the sum up in three parts:  $i = j$ ,  $i < j$ , and  $i > j$ . This gives

$$\langle R^2 \rangle = \sum_{i=1}^n \left[ l^2 + \sum_{j=1}^{i-1} l^2 (\cos \theta)^{i-j} + \sum_{j=i+1}^n l^2 (\cos \theta)^{j-i} \right]$$

By replacing  $i - j = k$  in the first summation and  $j - i = k$  in the second, and taking the factor  $l^2$  out, we obtain equation 3.

(b) Replacing the summation by infinite series, we get

$$\begin{aligned} \langle R^2 \rangle &= l^2 \sum_{i=1}^n \left[ 1 + 2 \sum_{k=1}^{\infty} (\cos \theta)^k \right] \\ &= l^2 \sum_{i=1}^n \left[ 1 + \frac{2 \cos \theta}{1 - \cos \theta} \right] \\ &= l^2 \sum_{i=1}^n \left[ \frac{1 - \cos \theta}{1 - \cos \theta} + \frac{2 \cos \theta}{1 - \cos \theta} \right] \\ &= l^2 n \left[ \frac{1 + \cos \theta}{1 - \cos \theta} \right] \end{aligned}$$

So that  $C_\infty = (1 + \cos \theta) / (1 - \cos \theta)$ .

(c) For  $\theta = 68^\circ$  we get  $C_\infty \approx 2$ , which is much lower than the experimental value. The reason is that the rotation is hindered by steric repulsion between the monomers.

(d) Comparing equation 2 to 4, we see that they are the same if

$$l_p = -\frac{l}{\ln(\cos\theta)}$$

Note that expanding for  $\theta \ll 1$  gives with  $\cos\theta \approx 1 - \theta^2/2$  and  $\ln(1-x) \approx -x$  :  $l_p \approx 2l/\theta^2$ .

(e) We get (by splitting the integral to account for the absolute value of  $|u-v|$ ):

$$\begin{aligned} \langle R^2 \rangle &= \int_0^{R_{max}} \int_0^{R_{max}} \exp\left[-\frac{|u-v|}{l_p}\right] dv du \\ &= \int_0^{R_{max}} \left[ \int_0^u \exp\left(\frac{v-u}{l_p}\right) dv + \int_u^{R_{max}} \exp\left(-\frac{v-u}{l_p}\right) dv \right] du \\ &= \int_0^{R_{max}} \left[ l_p \left(1 - e^{-u/l_p}\right) + l_p \left(1 - e^{-(R_{max}-u)/l_p}\right) \right] du \\ &= 2l_p R_{max} - 2l_p^2 \left[ 1 - \exp\left(-\frac{R_{max}}{l_p}\right) \right] \end{aligned}$$

(f) For  $R_{max} \gg l_p$ , the second term vanishes, and  $\langle R^2 \rangle \approx 2l_p R_{max}$ , which is the result of the Kuhn model with  $b = 2l_p$ . For  $R_{max} \ll l_p$ , we must expand the exponential up to second order,  $e^{-R_{max}/l_p} \approx 1 - R_{max}/l_p + (1/2)(R_{max}/l_p)^2 - \dots$ . This gives  $\langle R^2 \rangle \approx R_{max}^2$ .

#### 4. The radius of gyration.

(a)

$$\begin{aligned} R_g^2 &= \frac{1}{N} \sum_{i=1}^N (\vec{R}_i - \vec{R}_{cm})^2 \\ &= \frac{1}{N} \sum_{i=1}^N (\vec{R}_i^2 - 2\vec{R}_i \cdot \vec{R}_{cm} + \vec{R}_{cm}^2) \\ &= \frac{1}{N} \sum_{i=1}^N \vec{R}_i^2 - \vec{R}_{cm}^2 \\ &= \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N (\vec{R}_i^2 - \vec{R}_i \cdot \vec{R}_j) \end{aligned}$$

where in the third step we have used equation 6 and the fact that  $\vec{R}_{cm}$  does not depend on  $i$  so it can be taken before the summation, while in the fourth step we have again

used equation 6 (with  $R_{cm}^2 = (1/N^2) \sum_i \sum_j \vec{R}_i \vec{R}_j$ ). Now, we also have

$$(\vec{R}_i - \vec{R}_j)^2 = \vec{R}_i^2 - 2\vec{R}_i \vec{R}_j + \vec{R}_j^2$$

Comparing this to the previous result, we see that

$$\begin{aligned} R_g^2 &= \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N (\vec{R}_i - \vec{R}_j)^2 \\ &= \frac{1}{N^2} \sum_{i=1}^N \sum_{j=i}^N (\vec{R}_i - \vec{R}_j)^2 \end{aligned}$$

where in the last line, the second summation runs from  $i$  to  $N$  to make each term appear only once in the summation. (b) For ideal chains,  $\langle (\vec{R}_i - \vec{R}_j)^2 \rangle = |j - i|b^2$ , so that

$$\begin{aligned} \langle R_g^2 \rangle &= \frac{1}{N^2} \sum_{i=1}^N \sum_{j=i}^N (j - i)b^2 \\ &\approx \frac{1}{N^2} \int_0^N \int_u^N (v - u)b^2 dv du \\ &= \frac{b^2}{N^2} \int_0^N \left( \frac{1}{2}N^2 - uN + \frac{1}{2}u^2 \right) du \\ &= \frac{b^2}{N^2} \left( \frac{1}{2}N^3 - \frac{1}{2}N^3 + \frac{1}{6}N^3 \right) \\ &= \frac{Nb^2}{6} \end{aligned}$$

(c) Writing equation 5 in integral form

$$R_g^2 = \frac{1}{N} \int_0^N (\vec{R}(u) - \vec{R}_{cm})^2 du$$

Since a rod only has one conformation, we don't need to average. Placing the center of mass, with coordinate  $u = N/2$  in the origin,  $\vec{R}_{cm} = 0$ , we have  $\vec{R}(u) = (u - N/2)b$ . Hence,

$$\begin{aligned} R_g^2 &= \frac{1}{N} \int_0^N (u - N/2)^2 b^2 du \\ &= \frac{b^2}{N} \int_{-N/2}^{N/2} x^2 dx \\ &= \frac{N^2 b^2}{12} = \frac{R_{max}^2}{12} \end{aligned}$$

## 5. Stretching DNA.

For small extensions, the curve follows the ideal chain model, with  $f = 3kTR/Nb^2 = 3kTR/R_{max}b$ . At large force, the extension saturates at  $R_{max}$ , with  $R_{max} = 30 \mu\text{m}$ . Taking a point on the curve at small force than yields  $b$ . E.g. for  $f = 10 \text{ fN} = 10^{-14} \text{ N}$ ,  $R \approx 2.4 \mu\text{m}$ . This gives  $b \approx 100 \text{ nm}$ , so that  $l_p = b/2 = 50 \text{ nm}$ .

## 6. Cyclization of polymers

The looping probability is the probability that the end-to-end distance is smaller than  $\delta$ :

$$\begin{aligned} p_l &= \int_0^\delta 4\pi R^2 P(R, N) dR \\ &= \int_0^\delta 4\pi R^2 \left( \frac{3}{2\pi N b^2} \right)^{3/2} e^{-3R^2/2Nb^2} dR \end{aligned}$$

Since  $\delta \ll bN^{1/2}$ , we can approximate the exponential by 1, so that

$$p_l = \int_0^\delta 4\pi R^2 \left( \frac{3}{2\pi N b^2} \right)^{3/2} dR = \left( \frac{6}{\pi N^3} \right)^{1/2} \left( \frac{\delta}{b} \right)^3 \sim N^{-3/2}$$

## 7. Gel permeation chromatography

(a) The distance between collisions is on the order of  $D$ ; between collisions the chain is deal, so  $D \approx bg^{1/2}$ , with  $g$  the number of segments between collisions. So  $g = (D/b)^2$ . The number of collisions is then  $(N/g) = N(b/D)^2$ , and the free energy is  $F = (N/g)kT = N(b/D)^2kT$ . The partition coefficient is according to Boltzmann  $K_M = \exp(-F/kT) = \exp(-Nb^2/D^2)$ .

(b) The thickness of the depletion zone is  $\delta = R = bN^{1/2}$ ; this means that in each pore a volume of  $A_{pore}\delta \approx \pi D^2 R$  is excluded (because the area is  $A_{pore} = 4\pi(D/2)^2$ ). If the concentration in the remainder of the pore is assumed to be the same as that in the bulk, we have an average pore concentration of  $c_{bulk} \times [(\pi/6)D^3 - \pi D^2 R] / [(\pi/6)D^3] = c_{bulk}(1 - 6R/D)$ . Hence,  $K_M \approx 1 - 6R/D$ .

## 8. The Edwards diffusion equation for polymer conformations

- (a) The initial condition must be  $P(0, x, x') = \delta(x - x')$ .  
(b) First, we Fourier transform the diffusion equation:

$$\frac{\partial \hat{P}(n, \omega)}{\partial n} = -(2/3)\pi^2 \omega^2 b^2 \hat{P}(n, \omega)$$

This first order differential equation (with initial condition  $\hat{P}(0, \omega) = 1$ , since  $F[\delta(x)] =$



1) is easily solved

$$\hat{P}(n, \omega) = e^{-(2/3)\pi^2\omega^2 b^2 n}$$

Comparing to the Fourier transform of  $e^{-ax^2}$ , we see that  $a = 3/2nb^2$  here. Hence, the inverse Fourier transform is

$$P(n, x) = \sqrt{\frac{3}{2\pi nb^2}} \exp\left(-\frac{3x^2}{2nb^2}\right)$$

which is indeed the distribution function of the ideal chain, with  $\langle x^2 \rangle = \frac{1}{3}nb^2$ .