University of Washington
Department of Chemistry
Chemistry 355
Spring Quarter 2005

Homework Assignment 7: Due no later than 5:00 pm on 5/14/04
8.3, 8.6, 8.13

8.3) According to text equation 16, after N jumps the probability of a displacement m places from the origin is $P(m) \propto \frac{N!}{[(N+m)/2]![(N-m)/2]!}$. Then the relative probability of observing after 8 total jumps four displacements from the origin versus two displacements is

$$\frac{P(4)}{P(2)} = \frac{8!}{[(8+4)/2]![(8-4)/2]!} \cdot \frac{[(8+2)/2]![(8-2)/2]!}{8!}$$

$$= \frac{[(8+2)/2]![(8-2)/2]!}{[(8+4)/2]![(8-4)/2]!} = \frac{5! \times 3!}{6! \times 2!} = \frac{1}{2}$$

8.6) Consider the fact that for spherical molecules the frictional coefficient f is proportional to the radius R (Stokes' Law). Consider also that the volume is proportional to the mass and the volume of a sphere is proportional to the radius cubed. Then f is proportional to the cube root of volume and thus is also proportional to the cube root of mass. Take that proportionality (i.e. f proportional to the cube root of mass) and determine how s and D depend on mass when the molecule is spherical.

Solution: Suppose the molecule is spherical. The easiest case to study is if the molecule is unhydrated in solution…i.e. has no waters of hydration attached. Then the volume of one mole of spherical molecules is $\bar{V} = M_2\bar{V}_2 = N_0\left(\frac{4}{3}\pi R^3\right)$ where N_0 is Avagadro's number.

Then $R = \left(\frac{3}{4\pi}\frac{M_2\bar{V}_2}{N_0}\right)^{1/3}$.

- From the statement $D_2 = \frac{k_B T}{6\pi\eta R} = \frac{RT}{6\pi\eta N_0 R}$ we get

$$D_2 = \frac{RT}{6\pi\eta N_0 R} = \frac{RT}{6\pi\eta N_0}\left(\frac{4\pi N_0}{3M_2\bar{V}_2}\right)^{1/3} \Rightarrow D_2 \propto \frac{1}{M_2^{1/3}}$$

- From the statement $s = \frac{m(1-\bar{V}_2\rho)}{6\pi\eta R} = \frac{M_2}{N_0}\frac{(1-\bar{V}_2\rho)}{6\pi\eta}\left(\frac{4\pi N_0}{3M_2\bar{V}_2}\right)^{1/3} \Rightarrow s \propto M_2^{2/3}$

8.13) Calculate the molecular radii for myoglobin and hemoglobin. The ratio of the radii equals the cube root of the ratio of the volumes.

$$D = \frac{k_B T}{6\pi\eta R} \Rightarrow R = \frac{k_B T}{6\pi\eta D}$$

Myoglobin: $R = \frac{k_B T}{6\pi\eta D} = \frac{(1.38\times10^{-23}\,J/K)(293K)}{6\pi(0.00102kg/m\cdot s)(11.3\times10^{-11}m^2/s)} = 1.86nm$

Hemoglobin: $R = \frac{k_B T}{6\pi\eta D} = \frac{(1.38\times10^{-23}\,J/K)(293K)}{6\pi(0.00102kg/m\cdot s)(6.9\times10^{-11}m^2/s)} = 3.05nm$

$\therefore \frac{r_{Hb}}{r_{Mb}} = \frac{3.05}{1.86} = 1.64$

If Hb were a tetramer, its volume would be four times that of Mb:

$\frac{r_{Hb}}{r_{Mb}} = \left(\frac{V_{Hb}}{V_{Mb}}\right)^{1/3} = \left(\frac{4V_{Mb}}{V_{Mb}}\right)^{1/3} = (4)^{1/3} = 1.59$. The experimental ratio is close to the theoretical ratio

2) A 200 base pair DNA may be modeled as a rigid rod that is $6.8\text{x}10^{-8}$ m in length and has a radius of 10^{-9} m.

a) Calculate the axial ratio and the volume of a 200 base pair DNA molecule.

Solution:

$$P = \frac{L}{d} = \frac{L}{2R} = \frac{68}{2} = 34.$$

$$V = \pi R^2 L = (3.14)(10^{-9}m)^2(68\times10^{-9}m) = 2.14\times10^{-25}m^3$$

b) Calculate the radius of a sphere which has an equal volume to the rod-shaped DNA in part a.

Solution:

$$V = \frac{4}{3}\pi R_0^3 = 214\times10^{-27}m^3 \Rightarrow R_0 = \left(\frac{3\cdot 214\times10^{-27}m^3}{4\pi}\right)^{1/3} = 3.7\times10^{-9}m$$

c) Assuming the 200 base pair DNA may be modeled as a rigid rod, calculate the frictional coefficient f. Assume the solvent viscosity is 0.01 gm cm^{-1} s^{-1}.

$$f = f_0\frac{(2/3)^{1/3}P^{2/3}}{\ln(2P)-0.3} = 6\pi\eta R_0\frac{(2/3)^{1/3}P^{2/3}}{\ln(2P)-0.3}$$

$$= (6\pi)(0.01gm/cm\cdot s)(3.7\times10^{-7}cm)\frac{(2/3)^{1/3}(34)^{2/3}}{\ln(68)-0.3}$$

$$= 69.71\times10^{-9}g/s\left(\frac{.873\cdot 10.5}{3.92}\right) = 1.63\times10^{-7}g/s$$

d) Calculate the diffusion coefficient of a 200 base pair DNA. Assume T=298K.

$$D = \frac{k_B T}{f} = \frac{(1.38\times10^{-16}\,ergs/K)(293K)}{1.63\times10^{-7}\,g/s} = 2.48\times10^{-7}\,cm^2\,/\,s$$

2) A 200 base pair fragment of DNA is 680 Angstroms long and 20 Angstroms in diameter. It has a molecular weight of 135,000 grams/mole.

a) Calculate the frictional coefficient of this DNA fragment, assuming it can be treated as a rod of length L=680 Angstoms and diameter d=20 Angstroms.

Solution: From Lecture 26… a rod-like particle has a length 2a and radius b. Its volume is given by the formula: $V_{rod} = 2\pi ab^2$. The axial ratio P is defined as $P = \frac{a}{b}$.

the frictional coefficient is defined as $f = f_0 \frac{(2/3)^{1/3} P^{2/3}}{\ln(2P) - 0.30}$.

The term f_0 in the equation above is defined as $f_0 = 6\pi\eta R_0$. R_0 is defined as the radius of a sphere which has a volume equal to the volume of the rod with axial ratio P=a/b. R_0 is determined as follows: $V_{sphere} = V_{rod} \Rightarrow \frac{4\pi}{3}R_0^3 = 2\pi ab^2 \Rightarrow R_0^3 = \frac{3ab^2}{2} \Rightarrow R_0 = \left(\frac{3ab^2}{2}\right)^{1/3}$

So P=a/b=680/20=34…Note 1 Angstrom is 10^{-10}m. Then 2a=680 Ang. And 2b=20 Ang. Then

$$f = f_0\frac{(2/3)^{1/3}P^{2/3}}{\ln(2P)-0.30} = (6\pi\eta R_0)\left(\frac{(2/3)^{1/3}P^{2/3}}{\ln(2P)-0.30}\right)$$

$$= 6\pi(0.001Pa\cdot s)\left(\frac{3}{2}(340\times10^{-10}m)(10\times10^{-10}m)^2\right)^{1/3}$$

$$\times\left(\frac{(2/3)^{1/3}(34)^{2/3}}{\ln(68)-0.30}\right) = (0.0188Pa\cdot s)(51\times10^{-27}m^3)^{1/3}(2.38)$$

$$= 0.165\times10^{-9}kg/s = 1.65\times10^{-7}g/s$$

b) Calculate the sedimentation coefficient of the DNA assuming the gram specific volume of DNA is 0.51 mL/gram.

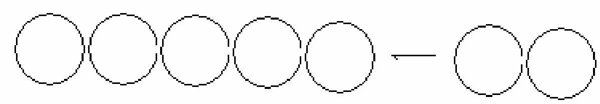
Solution:

$$s = \frac{m(1-\overline{V}_2\rho)}{f} = \frac{M_2(1-\overline{V}_2\rho)}{N_A f}$$

$$= \frac{(135{,}000gm/mole)(1-(0.51mL/gm)(1gm/mL))}{(6.02\times10^{23}/mole)(1.65\times10^{-7}g/s)}$$

$$= 6.66\times10^{-13}\sec^{-1} = 6.66S$$

c) For the purpose of calculating the frictional coefficient f, a rod-like, linear polymer can be more accurately treated as a string of N touching beads, each spherical bead has a diameter δ. The rod is therefore of length Nδ.



For such a polymer the frictional coefficient is $f = \frac{3\pi\eta N\delta}{\ln N}$ where η is the viscosity of the solvent, assumed here to be water. Calculate the bead diameter and number of beads required to have the same total volume and length as the DNA described in part a.

Solution: The length of the string of beads is 680 Angstroms=Nδ. The volume of the DNA cylinder is

$$V = 2a\pi b^2 = (2)(3.14)\left(340\times10^{-10}m\right)\left(10^{-9}m\right)^2$$
$$= 2.14\times10^{-25}m^3$$

Te volume of the string of beads is the volume of the bead $\frac{4}{3}\pi\left(\frac{\delta}{2}\right)^3 = \frac{\pi\delta^3}{6}$ times the number of beads N or $\frac{N\pi\delta^3}{6}$. So we have two unknowns…N and d…but two equations …

$$N\delta = 680\times10^{-10}m$$
$$\frac{N\pi\delta^3}{6} = 2.14\times10^{-25}m^3$$
$$\therefore \frac{N\pi\delta^3}{6} = \frac{(N\delta)\pi\delta^2}{6} = \frac{\left(680\times10^{-10}m\right)\pi\delta^2}{6} = 2.14\times10^{-25}m^3$$
$$\delta^2 = \frac{(6)\left(2.14\times10^{-25}m^3\right)}{\left(680\times10^{-10}m\right)\pi} = 6.01\times10^{-18}m^2 \Rightarrow \delta = 2.45\times10^{-9}m$$
$$N = \frac{680\times10^{-10}m}{24.5\times10^{-10}m} \approx 28$$

Comment: The rise between adjacent base pairs is about 4 Angstroms in B form DNA, so these beads are of dimension much larger than a single base pair.It means that for the purposes of calculating friction coefficients, the minimal unit in DNA is about 5-6 base pairs…at least according to this model.

d) Calculate the frictional coefficient and the sedimentation coefficient of the DNA described in part c.

$$f = \frac{3\pi\eta N\delta}{\ln N} = \frac{(3)(3.14)(0.001 Pa\cdot s)(28)\left(24.5\times10^{-10} m\right)}{\ln(28)}$$

$$= \frac{5.64\times10^{-10} kg/s}{3.33} = 1.69\times10^{-10} kg/s = 1.94\times10^{-7} g/s$$

e) .

3) Chromatin is the complex of DNA and proteins (mostly histones) found in all eukaryotic cells. The fundamental repeating unit of chromatin is the nucleosome particle. The properties of the DNA and the protein in nucleosome particles were determined using a combination of velocity sedimentation, dynamic light scattering, and gel electrophoresis.

- Dynamic light scattering studies determined the diffusion coefficient of the nucleosome particle in solution at 293K to be $4.37\text{x}10^{-7}$ cm^2/s.
- In the same solution velocity sedimentation performed at 18,100 revolutions per minute, obtained the following data:

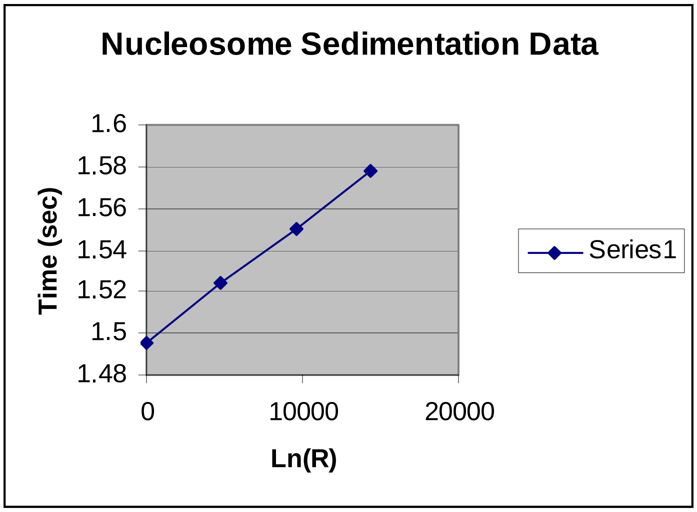
Time (minutes)	Boundary Position r (cm)
0	4.460
80	4.593
160	4.713
240	4.844

- Gel electrophoresis showed that the DNA molecule associated with a single nucleosome protein complex is 200 base pairs in length.

a) What is the molecular weight of the nucleosome particle? Assume the solution has a density of $1.02 g/cm^3$ and the specific volume of the nucleosome particle is $0.66 cm^3/g$.

$$s = \frac{m\left(1-\overline{V}_2\rho\right)D}{k_B T} = \frac{M\left(1-\overline{V}_2\rho\right)D}{N_A k_B T}$$

Obtain s from a plot of lnR versus time



The slope is

$$s\omega^2 = 5.70 \times 10^{-6}\ \sec^{-1} \Rightarrow s = \frac{\left(5.70 \times 10^{-6}\ \sec^{-1}\right)\left(60\ \sec/\min\right)^2}{\left(2\pi \times 18{,}100\ \min^{-1}\right)^2} = 1.58 \times 10^{-12}\ \sec = 15.8S$$

Then $M = N_A \dfrac{s k_B T}{\left(1 - \bar{V}_2 \rho\right) D}$

$$= \frac{\left(6.02 \times 10^{23}\ mole^{-1}\right)\left(1.38 \times 10^{-16}\ ergs/K\right)\left(1.58 \times 10^{-12}\ \sec\right)\left(293K\right)}{\left(1 - (0.66)(1.02)\right)\left(4.37 \times 10^{-7}\ cm^2/s\right)} = 2.70 \times 10^5\ g/mole$$

b) Assuming the nucleosome particle is spherical, calculate its Stokes radius. Assume the viscosity of the solution is 0.01 gm cm^{-1} s^{-1}.

$$D = \frac{k_B T}{6\pi\eta R} \Rightarrow R = \frac{k_B T}{6\pi\eta D} = \frac{\left(1.38 \times 10^{-16}\ ergs/K\right)\left(293K\right)}{6\pi\left(0.01 g/cm \cdot s\right)\left(4.37 \times 10^{-7}\ cm^2/s\right)} = 4.91 \times 10^{-7}\ cm$$

c) Assuming each base pair in DNA is separated from the adjacent base pairs by about 3.4×10^{-10} m, approximately how long is a piece of DNA 200 base pairs in length? Based on this result, and the result from part b, comment on how tightly packed the DNA is in the nucleosome.

Length of DNA $\left(200\ base\ pairs\right)\left(3.4 \times 10^{-8}\ cm/base\ pair\right) = 68 \times 10^{-7}\ cm$

Because the length of the DNA is much greater than the diameter of the nucleosome particle we assume the DNA must be tightly folded in the nucleosome.

d) Other evidence suggests that the protein component of the nucleosome is composed of a complex of eight protein molecules. Assuming that a single DNA base pair weighs 660g/mole, estimate the total weight of the protein in the nucleosome and the weight of each component protein.

Weight Protein Complex = Weight Nucleosome – Weight DNA=270,000g/mole-(660g/mole)(200)=138,000g/mole

Weight Protein Monomer=138,000/8=17,250g/mole

e) How are the proteins and DNA packed in the nucleosome? To answer this question, assume the eight proteins form a unhydrated, spherical complex with specific volume 0.74 cm^3/g. Calculate the radius of this hypothetical protein sphere. Assume the 200 base pair DNA behaves as a random coil polymer. Calculate the root mean square (rms) end-to-end distance. Comparing the protein sphere radius with the rms end-to-end distance for the DNA, is most of the DNA packed outside or inside the protein core of the nucleosome? Explain.

$$R_{protein} = \left(\frac{3}{4\pi}\frac{M\bar{V}_2}{N_A}\right)^{1/3} = \left(\frac{3}{4\pi}\frac{(138{,}000g/mole\,of\ complex)(0.74cc/g)}{(6.02\times10^{23}mole^{-1})}\right) = 3.5\times10^{-7}cm$$

$$\sqrt{R_{DNA}^2} = \ell\sqrt{N} = (3.4\times10^{-8}cm)(200)^{1/2} = 4.8\times10^{-7}cm$$

Note because $\sqrt{R_{DNA}^2} >> R_{protein}$, the DNA occupies a larger volume than the protein and is thus largely located outside the protein core particle.