1) Consider the equilibrium between molecule A and molecule B, pictured at the right. We represent the energies of molecule A and molecule B as energy ladders. As shown in the diagram, the ground state energies are related by

\[ \varepsilon_{B,0} + \Delta \varepsilon = \varepsilon_{A,0} \]

For energy ladder A the spacing between energy levels is \( \varepsilon_A \) and for energy ladder B the spacing between energy levels is \( \varepsilon_B \)

\[ \varepsilon_A \quad \varepsilon_B \]

a) Using energy ladder expressions for the partition functions, write out the expression for the equilibrium constant in terms of \( \varepsilon_A \), \( \varepsilon_B \), \( \Delta \varepsilon \), and T. The constant \( k_B \) will also be in the expression. Hint: see Lecture 8.

\[ \varepsilon_{A,0} \quad \varepsilon_{B,0} \quad \Delta \varepsilon \]

b) Using your result in part a, calculate the equilibrium constant at \( T=10K \). Calculate also the standard molar Gibbs energy change \( \Delta G^0 \). Does the equilibrium lie toward A or B in this case? Calculate the standard molar enthalpy \( \Delta H^0 \), and the standard molar entropy \( \Delta S^0 \) and determine whether the equilibrium is determined mainly by the enthalpy change or the entropy change. Assume \( \Delta \varepsilon=1.00 \times 10^{-20} J \). Also assume \( \varepsilon_B = 1.00 \times 10^{-20} J \) and \( \varepsilon_A = 1.00 \times 10^{-21} J \).

\[ \varepsilon_{A,0} \quad \Delta \varepsilon \quad \varepsilon_{B,0} \]

c) Raise the temperature to \( T=1000K \) and repeat the calculation. Is A or B favored now, and is this due mainly to the entropy term or the enthalpy term?

2) For a polypeptide composed of N monomers that undergo C to H transitions non-cooperatively, the structural state of each monomer can be treated as a two level system. The energy of the C structure will be \( \varepsilon_C = 0 \) and the energy of the H structure will be
\[ \varepsilon_H = \varepsilon . \] Then the partition function for a single monomer is  
\[ q = 1 + e^{-\varepsilon / k_BT} = 1 + s , \]
where  
\[ s = e^{-\varepsilon / k_BT} \]  
The partition function for a polypeptide composed of \( N \) distinguishable monomers is  
\[ Q = \left(1 + e^{-\varepsilon / k_BT}\right)^N = \left(1 + s\right)^N. \]

a) Calculate the Internal Energy \( U \) divided by \( T \) i.e.  
\[ \frac{U}{T} \]  for this peptide if  
\( N=100. \) and \( s=0.500. \) Hint: Use the expression for the internal energy of a two level system and substitute  
\[ \varepsilon = -k_BT \ln s \]

b) Using your result from part a, calculate the entropy \( S \) for this peptide if  
\( N=100. \) and \( s=0.500. \)

c) Suppose \( s \) changes from 0.500 to 1.50. Calculate the change in helical fraction \( \Delta f_H \), and the change in entropy \( \Delta S \) when one mole of proteins, each composed of 100 monomers, has this change in helical fraction. Explain these changes.

3) As shown in Lecture 9, the Zipper model has a simple equation for the partition function that can be used to determine helicity \( f_H \):  
\[ q = q_0 \left(1 + \sigma \sum_{k=1}^{N} (N-k+1) s^k \right) \]  
where the term \( N-k+1 \) is the number of way you can arrange \( k \) contiguous H monomers in a peptide chain \( N \) monomers long.

a) From the partition function equation given above for the zipper model, it is easily shown that the probability of observing a helical sequence of length \( k \) in a peptide \( N \) monomers long is:  
\[ p_k = \frac{q_0 \sigma}{q} (N-k+1) s^k \]

For \( N=30, s=1.0, \) and \( \sigma=0.0001, \) determine the relative probability of observing a helical sequence of length \( k=10 \) versus \( k=25. \) Repeat the calculation for \( s=5.0. \) Explain these results.

b) For \( N=30 \) and \( s=1.5, \) and \( \sigma=0.001, \) what is the most probable helical length \( k \) in a protein with \( N \) monomers? What is the most probable helical length \( k \) if \( s \) changes to 5? Explain these results. Hint: Determine the maximum probability \( k \) by differentiating the expression for \( p_k \) with respect to \( k. \) Then solve  
\[ \frac{\partial p_k}{\partial k} = 0 \]  for \( k^* \), the \( k \) for which the probability is maximum.

c) In Lecture 9, we reviewed various ways to determine the fractional helicity \( f_H \) using the Zipper model. Using the information provided in Lecture 9, determine \( q \) and \( f_H \) for \( N=30, s=1.5, \sigma=0.001. \) Assume \( q_0=1. \) Hint: Use the closed form expressions for \( q \) in equation 9.12 and for \( f_H \) in 9.13. How can these expressions be simplified to make your calculations easier?
4) In the lecture notes we did not obtain a general expression for the partition function for the Bragg-Zimm model. As explained in Lecture 10, the Bragg-Zimm partition function is calculated using a 2x2 matrix \( \mathcal{M} = \begin{pmatrix} 1 & \sigma s \\ 1 & s \end{pmatrix} \). To obtain the partition function for a peptide \( N \) monomers long we use the expression:

\[
\frac{q}{q_0} = (1, 0) \mathcal{M}^N (1, 1)
\]

where \((1, 0)\) is a row vector with elements 1 and 0 and \((1, 1)\) is a column vector.

a) Using statistical matrix approach, obtain the partition function for a Bragg-Zimm trimer (\( N=3 \)).

b) Using your expression for a Bragg-Zimm trimer from part a, calculate the fractional helicity \( f_H \) for \( s=1.00 \) and \( \sigma=0.001 \).

5) As shown in lecture 10, for very large values of \( N \), there is a simple form for the Bragg-Zimm partition function: \( \ln q \approx N \ln \lambda_i \), where \( \lambda_i = \frac{1 + s + \sqrt{(1-s)^2 + 4\alpha s}}{2} \).

a) Assuming \( N=10000 \), \( s=1 \), and \( \sigma=0.001 \), calculate \( \lambda_i \).

b) Calculate the average number of helical monomers \( \langle n \rangle \) and the fractional helicity \( f_H \) assuming, \( N=10000 \), \( s=1.0 \), \( \sigma=0.001 \).

6) For a protein with four ligand binding sites the general expression for the binding polynomial \( Q \) is:

\[
Q = \left[ P \right] \left( 1 + 4k_1 [L] + 6k_1k_2 [L]^2 + 4k_1k_2k_3 [L]^3 + k_1k_2k_3k_4 [L]^4 \right)
\]

where the microscopic equilibrium constants \( k_1, k_2, k_3, \) and \( k_4 \) correspond to equilibria between the ligand \( L \) and the four partially filled or completely filled polymers.

a) In lecture we showed that if \( k_1=k_2=k_3=k_4=k \) we obtain the expression for non-cooperative binding. Assuming non-cooperative binding calculate the average number of sites bound \( \langle \nu \rangle \) for \( k=100 \) and \([L]=0.01M\). Repeat for \( k=100, [L]=0.001M \) and \( k=100, [L]=0.0001M \).

b) Repeat the calculation in part a only now assume fully cooperative binding. Explain any differences in your results for part a and b.