Physics 4251 / Fall 2013
Problem Set 7, Nov. 4
Due: Monday, Nov. 17 before class

Problem 1: Energy from ATP using ΔG and the standard state

We want to show that the energy from ATP hydrolysis depends on the concentration of the final products, [ADP] and [Pi]. For the reaction A + B ↔ C + D, the equilibrium constant is:

$$K_{\text{eq}} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}, \tag{1}$$

where [A] means the concentration of A and $K_{\text{eq}} = \exp[(\Delta G - \Delta G^\circ)/kT]$, i.e.,

$$\Delta G = \Delta G^\circ + kT \ln K_{\text{eq}}. \tag{2}$$

Note that we have added in a constant, ΔG°, called the standard free energy change, to the usual equation relating K_{eq} and ΔG. Why do we need this? At equilibrium, $\Delta G = 0$, i.e. the net "force" = 0, or, in other words, the sum of the energetic and entropic terms equals zero. There is no net force (due to energy or entropy) which will tend to change one species into another (A + B going into C + D, for example). But, of course, the equilibrium constant is non-zero. With $\Delta G = 0$, the amount of concentrations of A, B, C, D will determine ΔG°, i.e., $K_{\text{eq}} = \exp(-\Delta G^\circ/kT)$. It is important that this is at some fixed temperature and fixed concentration of A, B, C, D. For convenience we take the concentration to be 1 Moles/Liter. Then ΔG° is just a number, which you measure.

Finally, if you are dealing with moles, you use $R = N_A k$, where R is the "gas constant", i.e., 8.31432 J/mol·K. (You may remember for an ideal gas, $PV = nRT$ where n is the number of moles, or equivalently, $PV = NkT$, where N is the number of molecules and $N = N_A$ if you're dealing with 1 mole). So,

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}\right) \tag{3}$$

Now let's focus on ATP hydrolysis.

$$\text{ATP} + \text{H}_2\text{O} \leftrightarrow \text{ADP} + \text{inorganic phosphate (Pi)} \tag{4}$$

Note that since H_2O is the solvent, we take [H_2O] to be 1 M. While technically, the molarity of water is 55.5 M, because it is effectively constant, we absorb it into our standard state and, thus, it does not factor into the righthand term of Eq. 3. The body temperature is 37°C.

(a) After an equilibrium experiment at body temperature, we find that $K_{\text{eq}} = 130{,}000$. What is ΔG°?

(b) Let's say that [ATP] = 10 mM, [ADP] = 100 μM, and [Pi] = 1 mM. What is the free energy, or the energy available from the hydrolysis of 1 mole of ATP? For an individual ATP?

(c) Now let [ATP] = 2 mM, [ADP] = 1 mM, and [Pi] = 2 mM. What is the free energy, or the energy available from the hydrolysis of an individual ATP?

(d) Express 100 pN-nm (roughly the amount of energy released with splitting one ATP) in units that allow you to compare this value to the free energy. Are they consistent?
As you can see, the amount of energy released by ATP depends on the cells [ADP] and [Pi], which vary from cell to cell; hence, ATP is 80-100 pN-nm.

Problem 2: Variational approach to deformation induced by MscL

In the lecture, the membrane free energy was determined by using variational calculus to solve for the function $u(x)$ that minimizes it. As an alternative, we will try the technique of adopting a variational solution at the outset. As a reminder, the free energy is given by

$$G_h[u(x)] = \frac{K_b}{2}\int_0^\infty \left(\frac{\mathrm{d}^2 u}{\mathrm{d}x^2}\right)^2 \mathrm{d}x + \frac{K_t}{2w_0^2}\int_0^\infty u(x)^2 \mathrm{d}x. \tag{5}$$

where we have let the lower limit of integration go from $R \to 0$ simply by redefining $x = x - R$.

(a) As a first try, assume the function for the deformation induced by the membrane protein is $u(x) = Ae^{-x/x_0}$ and plug this "trial solution" directly into the free energy $G_h[u(x)]$ given above. Carry out the integration and then minimize G_h with respect to x_0. Determine A by setting $u(0) = u_0$. What is the value of x_0 that minimizes G_h? What is the minimum G_h?

(b) Now we can compare our trial solution with the exact solution, namely

$$G_h^{\mathrm{exact}} = \frac{K_t u_0^2}{\sqrt{2}\lambda w_0^2} \tag{6}$$

where $\lambda = (K_t/K_b w_0^2)^{1/4}$. What is $G_h^{(\mathrm{a})}/G_h^{\mathrm{exact}}$? Provide the exact result. As a check, it should be, numerically, 0.62 (I think).

Problem 3: Membrane case study

As a further exploration of the properties of lipids, you'll work on the Membrane Case Study this week. It can be downloaded from http://www.ks.uiuc.edu/Training/CaseStudies/ (see "Lipid Bilayers").

(a) Do Exercise 4.

(b) Do Exercise 6.