Problem Set 3: Chemistry 175/273

This homework is due on Gradescope by class time on Jan. 29, 2025.

1. *Reversibly unfolding RNA*

In a 2001 paper in *Science*, Jan Liphardt, now a professor at Stanford, performed a set of difficult and interesting measurements on a single molecule of RNA. Using a technique called "optical trapping", Liphardt and coworkers were able to study the strength of the folded state by mechanically unfolding the RNA molecule. In their experiment, schematically depicted in Fig. 1, they attached an individual molecule to a pair of polystyrene beads. Using the radiation pressure of the laser, the beads can be trapped in a harmonic potential, meaning that if the position of the laser is changed, a force is applied to the bead and hence the RNA molecule is pulled on.

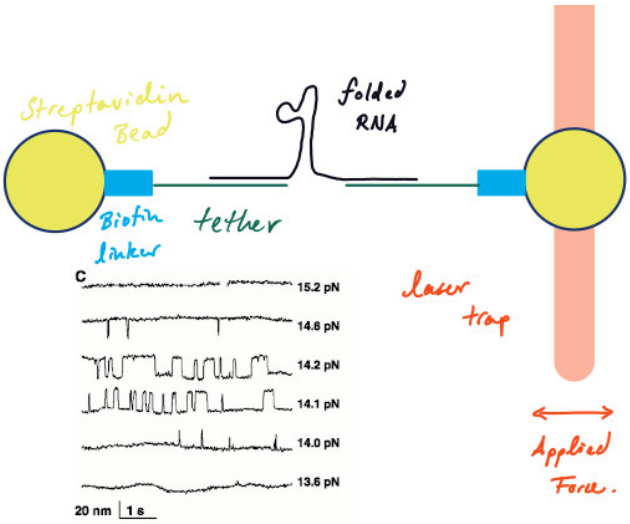

Figure 1: Experimental apparatus and time traces of the length of the RNA molecule under different applied forces. The curves plot the length of the RNA as a function of time. At small forces, the RNA maintains the length of the folded state l_0. Under larger forces, the RNA unfolds rapidly and has a longer length l_1. In these experiments, $\Delta l = 22\text{nm}$.

(a) Let's assume that we can model the system reductively; in the absence of an applied force, we will assume that there are only two states. The folded state has energy that depends on the length of the RNA, $E(l_0) = \epsilon_0$ and the unfolded state has an energy $E(l_1) = \epsilon_1$. Write an expression for the probability of the folded state and the unfolded state. Compute the relative probability of the folded state compared to the unfolded (again, there is no applied force in this part); write your answer in terms of $\Delta\epsilon = \epsilon_1 - \epsilon_0$.

(b) When there is a constant applied force f_{ext} the energy depends on the length of the RNA molecule l. Suppose we set the center of the optical trap so that there is no force on the unfolded state, but the energy of the system increases by $(l_1 - l_0)f_{\text{ext}}$ in the folded state. Physically, you can think of this as the RNA molecule doing work to pull the optical bead away from the position in which it is trapped. Compute the ratio of probability of the folded state to the probability of unfolded state in the presence of an applied force.

(c) The experimental measurements (inset in the figure) show that at about 14.2 pN, the system spends occupies the folded and unfolded states with equal probability. Using your calculation from (b) and the fact that $k_B T = 4.114$ pN·nm at 298K, calculate $\Delta\epsilon$. Experimentally, $\Delta l = 22$nm.

(d) Plot the fraction unfolded as a function of f_{ext}.

2. *Thermal de Broglie Breakdown*

We derived the translational partition function z_{trans} at temperatures of interest for many applications in Chemistry. However, the approximation we made can fail. Consider a hydrogen atom in a one-dimensional box of length 1nm.

(a) Derive an expression for the translational entropy using the translation partition function we derived in lecture 5. Plot this function S/k_B from 0-10 K. What happens below $K = 1$?

(b) Why does the expression give a non-physical result for low temperatures? What approximations did you use when writing your expression for S.

(c) At low temperature, the partition function can be approximated by considering only the ground state and first excited state. With this approximation, derive an expression for S and plot S/k_B from 0-10 K.

(d) What is the asymptotic value of this function as a function of T? Why does this expression break down at $T \to \infty$?

3. *A two state metal ion*

Some metal ions form solids in which one unpaired electron is isolated. For example, $RbTi(SO_4)_2 \cdot 12\,H_2O$ has $Ti(H_{2O})_6^{3+}$ ions with one unpaired electron spin. To a good approximation, these spins are independent, isolated, and distinguishable. In the presence of an external magnetic field B, each spin has either energy

$$\epsilon_1 = -\mu B \qquad \text{or} \qquad \epsilon_2 = +\mu B \tag{1}$$

where μ is the magnetic moment of the electron, a constant.

(a) What is the canonical partition function q for a single spin? Express your answer in terms of a hyperbolic trigonometric function.

(b) The magnetic moment of the entire system, which we will call M, is given by $\mu(n_1 - n_2)$ where n_1 is the average number of spins with energy ϵ_1 and n_2 is the average number of spins with energy ϵ_2. Derive an expression for M using the fact that spins are distinguishable and independent.

(c) As the magnetic field $B \to 0$ show that the expression in (b) can be written as

$$M = C\frac{B}{T}. \tag{2}$$

This is Curie's law. Write the constant C (Curie's constant) in terms of n, μ, and k_B.

Hyperbolic functions

$$\sinh x = \frac{e^x - e^{-x}}{2}$$
$$\cosh x = \frac{e^x + e^{-x}}{2}$$
$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$