Chem 440
Spring 2022

Hour Exam 2

Useful numbers and formulas you may need are given at the end.
You must turn in (or upload PDF or JPEG on Moodle if remote) your answer by 10:55 to get full credit.

1. (10 pts) Let's think about averages over microstates, using the coins-in-a-bag example:

a. (1+1) A bag contains one 1-dollar coin and 4 quarters. If you draw a single coin from the bag many times in a row, **what is** the average value of a draw? **Could you** ever draw that amount in a single attempt?

Solution: $P(X = \$1) = \frac{1}{5}$ and $P(X = \$0.25) = \frac{4}{5}$

Average draw $E = \sum X_i\, P_i = 1 * \frac{1}{5} + 0.25 * \frac{4}{5} = \frac{2}{5} = 0.4$

No, there is no 40 cent coin.

b. (1+1) If the bag contained one 1-dollar coin, 4 quarters, and 10 dimes, what would be the answer to the **same two questions**?

Solution: $P(X = \$1) = \frac{1}{15}$, $P(X = \$0.25) = \frac{4}{15}$, and $P(X = \$0.10) = \frac{10}{15} = \frac{2}{3}$

The average draw is $E = \sum X_i\, P_i = 1 * \frac{1}{15} + 0.25 * \frac{4}{15} + 0.10 * \frac{2}{3} = \frac{1}{5} = 0.2$

No, there is no 20 cent coin.

c. (1+2) If the bag from part **a.** contains twice as many dollar coins, **how much** does the probability of drawing a dollar coin **increase**? **How much** does the average value of a draw increase over **a.**?

Solution: $P(X = \$1) = \frac{2}{6} = \frac{1}{3}$, and $P(X = \$0.25) = \frac{4}{6} = \frac{2}{3}$; the probability of a dollar coin goes up from 1/5 to 1/3, changing by +2/15≈13%.

The average draw is $E = \sum X_i\, P_i = 1 * \frac{1}{3} + 0.25 * \frac{2}{3} = \frac{1}{2}$. The average draw increases from 0.4 to 0.5.

a. (1+2) If the bag from part **b.** contains twice as many dollar coins, **how much** does the probability of drawing a dollar coin <u>increase</u>? **Could you** draw that amount in a single attempt?

Solution: Average draw $E = \sum X_i\, P_i = 1 * \frac{2}{16} + 0.25 * \frac{4}{16} + 0.10 * \frac{10}{16} = \frac{1}{4}$

Yes, there is a \$0.25 coin (1 quarter)

The moral of the story: just because the average of a measurement has a certain value, don't expect that you can necessarily ever obtain that value from any given measurement.

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2. (10 pts) Let's think about the free energy G of a protein folding reaction as a function of temperature.

a. (2) **Write down** a formula for $G(T)$ in terms of H, T and S. [Hint: intercept as a function of slope.]

$$G = H - \frac{dH}{dS}S = H - TS$$ [Full credit for just $G = H - TS$.]

b. (2+1) **Write down** an integral for $S(T)$ in terms of $S^{(0)}$, C_P, T and T_0. Assuming C_P is independent of T, pull it out of the integral and **do the integral** to get a simple formula for $S(T)$. [Hint: the integral should start at $T^{(0)}$ and go to T.]

Solution:

$$C_P = T\left(\frac{dS}{dT}\right)_P \rightarrow dS = C_P\frac{dT}{T}$$

$\int_{S(0)}^{S(T)} dS = S(T) - S^0 = \int_{T(0)}^{T} C_P\frac{dT}{T}$; pull out to integrate the $1/T$ into a logarithm, and

$$S(T) = S^0 + C_P(ln(T) - ln(T^0))$$

Interesting fact: not only does S depend on $\ln(V)$, it also depends on $\ln(T)$ if the heat capacity is constant.

c. (2+1) **Write down** an integral for $H(T)$ in terms of $H^{(0)}$, C_P, T and T_0. Assuming C_P is independent of T, pull it out of the integral and **do the integral** to get a simple formula for $H(T)$.

Solution:

$$C_P dT = dH \rightarrow H(T) = H^0 + \int_{T(0)}^{T} C_P dT = H^0 + C_P(T - T_0)$$

d. (2) **Insert** b. and c. into your formula from a to obtain G as a function of $S^{(0)}$, $H^{(0)}$, C_P, T and T_0. Note that this formula has a minimum where $\partial G/\partial T$=0. So there is a temperature at which a protein is the most stable, and it will unfold at lower and higher temperature!

Solution:

$$G = H^0 + C_P(T - T_0) - TS^0 - TC_P(ln(T) - ln(T^0))$$

Interesting fact: if you were to plot this, the curve looks like a bowl: there is a minimum in the free energy. Thus a protein can be unfolded both by heating it to increase G, but also by cooling it! We call the latter cold denaturation. You can stick an egg in the freezer, and after a couple of months (things go slower at low temperature), it will begin to look hard-boiled!

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3. (10 pts) Let's think about the partition function for the two spin states of an electron, $m_s = \pm\frac{1}{2}$, which has some interesting features.

a) (2) When there's no applied magnetic field, the two spin states are microstates of the electron, both with the same energy *E=0*. **What is** the microcanonical partition function *W*(*E=0*) in that case?

Solution: *W*=2 (spin up and spin down)

Note: this is unusual; for most systems *W*=1 in the lowest energy state.

b) (1+1) When a magnetic field is turned on, the two $m_s = \pm\frac{1}{2}$ states now have <u>different</u> energies, *E*=0 and *E*=ε. **What is** *W*(*E*=0)? **What is** *W*(*E*=ε)?

Solution: Now *W*(*E*=0) = 1, and *W*(*E*=ε)=1

Note: this is a more normal case. In practice, there is almost always a stray field or something that causes the degeneracy of the ground state to be 1.

c) (2+1+1) Now let's assume the electron spin in the magnetic field is at some temperature *T*. **Write down** its canonical partition function Z in terms of k_B, *T*, and ε, using the sum formula for *Z*. [Hint: the summation should only have two terms.] **What is** the value of *Z* as *T* goes to 0? **What is** the value of *Z* as *T* goes to ∞?

Solution: $Z = \sum_k e^{-\beta E_k}$, where $\beta = \frac{1}{K_B T}$, and thus $Z = e^0 + e^{-\beta\varepsilon} = 1 + e^{-\beta\varepsilon}$

As *T* goes to 0, *β* goes to ∞, and so *Z* goes to 1. Thus at low temperature, only one microstate is populated. As *T* goes to ∞, *β* goes to 0, and so *Z* goes to 2. Thus at high temperature, both microstates are populated. Higher *T* gives access to more microstates.

d) (2+2) The average energy is given by $E = \sum_k E_k \rho_k$. In our case, this sum only has two terms. **Write down** the formula for *E*(*T*) in terms of k_B, *T*, and ε. [Hint: replace ρ_k by the Boltzmann factor and *Z* from part (c).] **What is** the highest value *E* can go to? [Hint: take the limit as *T* goes to ∞.]

Solution:

$E = 0\frac{e^{-\beta 0}}{1+e^{-\beta\varepsilon}} + \varepsilon\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$. I

If *T* goes to ∞ (*β* goes to 0), then $e^{-\beta\varepsilon}$=1 and *E*=*ε*/2.

Interesting facts:

So, no matter how much you heat the electron, its energy can only go to *ε*/2, never to *ε*. By heating stuff, you can't get the system completely into the excited state, no matter how hard you try!

Once you have the formula for *F*, you can calculate any thermodynamic property of the electron spin, such as *E*=*F*+*TS*, heat capacity, and so on!

4) (10 pts) Let's think about diffusion of molecules through the axon of a neuron. The axon is 1 cm long, a typical length in the brain. Tip: don't forget that 1 cm = 10,000 μm.

a) (2+1) A protein in the axon has a diffusion coefficient D=10 $\mu m^2/s$. On average **how long** does the protein take to diffuse in one dimension down the length of the axon? What is that time in units of years?

Solution:

$$< x^2 >= 10{,}000^2 = 2Dt$$

$$\frac{100{,}000{,}000}{2 * 10} = t = \mathbf{5,000,000}\ \boldsymbol{seconds}$$

$$t = \frac{5{,}000{,}000}{60 * 60 * 24 * 365} = \mathbf{0.159}\ \boldsymbol{years}$$

b) (2) Based on your result in (a), **do you think** that nerve signals are transmitted by protein diffusion along the axon? [Hint: yes/no answer is good enough.]

Solution: **No.**

c) (2+1) Calcium ions in the axon have a diffusion coefficient D=5000 $\mu m^2/s$. On average **how long** does the ion take to diffuse in one dimension down the length of the axon? **What is** that time in units of hours?

Solution:

$$< x^2 >= 10{,}000^2 = 2Dt$$

$$\frac{100{,}000{,}000}{2 * 5000} = t = \mathbf{10,000}\ \boldsymbol{seconds}$$

$$t = \frac{5{,}000{,}000}{60 * 60} = \mathbf{2.78}\ \boldsymbol{hours}$$

d) (2) Based on your result in (b), **do you think** that nerve signals are transmitted by ion diffusion along the axon? [Hint: yes/no answer.]

Solution: **No.**

Indeed, nerve impulses are transmitted by electrostatic waves due to ion channels in the membrane, which propagate much faster (milliseconds) than anything that diffuses over 1 cm in a cell.

In science, it is often useful to be able to rule out a mechanism, like you did above: "When you have eliminated all which is impossible, then whatever remains, however improbable, **must be the truth**." – Sherlock Holmes, channeled by Sir Arthur Conan Doyle.