Chemistry 20262 Spring 2018
Professor J. Daniel Gezelter Due Fri. 4/27/2018

Problem Set 10
Deeper problems on probability & entropy

1. Consider a small protein which is composed of 101 amino acids chained together in sequence to make 100 peptide bonds. In our Avogadro lab, we saw that peptide bonds have two dihedral angles (ϕ and ψ) that describe the local structure around that bond.

   - If each of the 200 angles has 3 configurations or "states" it can explore (e.g. 0°, 120° and 240°), how many unique configurations are there for this protein?
   - If the protein visits all of these configurations, and takes approximately 1 femtosecond (1 fs = 10^{-15} s) to visit each one, how long should it take for it to find the absolute lowest energy configuration through an exhaustive search?
   - Most small proteins fold to their low energy configurations in around 1 ms. Explain how it is possible for proteins to find their lowest energy configuration. (This is sometimes called *Levinthal's paradox*.)

2. Suppose we have two connected flasks with N_a molecules of A in the left flask and N_b molecules of B in the right. There's only one way of arranging the molecules in the two flasks (or one *microstate*) that segregates A in one flask and B in the other. The *entropy*, S, of a particular *macroscopic* state can be defined as

$$S = k_B \ln W$$

   where W is the number of *microstates* that belong to that macrostate. Consider the macroscopic state which has $N_a/2$ molecules of A in both flasks and $N_b/2$ molecules of B in both flasks.

   - Write down an expression for the number of microstates, W, that correspond to this particular macrostate.
   - Use Stirling's approximation,

$$\ln N! \approx N \ln N - N$$

     to predict an entropy of mixing (ΔS_{mix}) when $N \to \infty$.

3. The entropy of money: Suppose that someone tells you that he has a total of 25 cents in his pocket. There are only a few different combinations of coins which could add up to 25 cents.

   a) What is the entropy of 25 cents? Give your answer in terms of k_B.

b) If you were told that one of the coins was a dime, would the entropy increase or decrease? Why?

4. Numbers can have an information or *Shannon* entropy. If we had a sequence of N digits that were randomly chosen, one way to write the entropy of those digits is:

$$S = -\sum_{i=1}^{N} P(s_i) \log_2 (P(s_i))$$

where $P(s_i)$ is the relative frequency (or probability) of each character in the digit string.

Some numbers are very predictable. The first 100 digits of $\frac{1}{9}$ are all the same, so $P(1) = 1$ while $P(2) = \cdots = P(0) = 0$. What's the Shannon entropy of $\frac{1}{9}$? What is the Shannon entropy of the first 100 digits of π? What is the Shannon entropy of the first 100 digits of $\frac{41}{29}$?

5. Consider a square lattice of $N \times N$ points. A closed contour of length ℓ is one which starts at one lattice point and traverses ℓ steps before returning to the original point (without crossing itself along the way).

- On a 3×3 lattice, how many closed contours of length 4 can be drawn?
- On a 4×4 lattice, how many closed contours of length 8 can be drawn?
- Extra credit (Very hard!) Can you come up with a general formula for the number of closed contours of length ℓ on a $N \times N$ lattice? A formula for the *upper bound* of the number of contours in terms of ℓ and N would also be one way to answer this question.

(Although it may seem quite abstract, the answer to this question is related to why some materials become permanent magnets.)