Chemistry 60641 Spring 2011
Professor J. Daniel Gezelter Due Weds. 2/16/2011

Problem Set 2

1. Your statistical mechanics class has twenty students. What is the probability that at least two classmates have the same birthday? How many people must be in the class for this probability to be greater than 50%?

2. According to the kinetic theory of gases, the energies of molecules moving along the x-direction are given by $\epsilon_x = mv_x^2/2$ where m is the mass of the molecule and v_x is the velocity in the x-direction. The distribution of particles with a given velocity is given by the Boltzmann law,
$$p(v_x) = e^{-mv_x^2/2k_BT}$$
(This is sometimes called the Maxwell-Boltzmann distribution). Given that velocities can range from $-\infty$ to ∞,
   a) Write the probability distribution $p(v_x)$ so that it is correctly normalized,
   b) Compute the average energy, $\langle mv_x^2/2 \rangle$,
   c) Find the average velocity $\langle v_x \rangle$, and
   d) Find the average momentum $\langle mv_x \rangle$.

3. A biological membrane contains N ion-channel proteins. The fraction of time that any one protein is open to allow ions to flow through is q. Express the probability $P(m, N)$ that m of the channels will be open at any given time.

4. The relative populations (a_1 and a_2) of two states (1 and 2) can be expressed as a function of the energies of the two states:
$$\frac{a_1}{a_2} = f(E_1, E_2)$$
Since the zero of the energy scale is always an arbitrary fixed value, this function must depend only on the *difference* in energies between the two states:
$$f(E_1, E_2) = f(E_1 - E_2)$$
If we consider a third state and use the same ideas, we have:
$$\tfrac{a_3}{a_2} = f(E_2 - E_3), \text{and} \quad \tfrac{a_3}{a_1} = f(E_1 - E_3)$$
while the ratio of populations must agree:
$$\frac{a_3}{a_1} = \frac{a_2}{a_1} \cdot \frac{a_3}{a_2}$$
.

a) Prove that the unknown function f must satisfy

$$f(x+y) = f(x)f(y)$$

b) Use the result of part a) to prove that the following is true:

$$\frac{d\ln f(x)}{dx} = \frac{d\ln f(y)}{dy}$$

c) For this relation to be true for all values of x and all values of y, each side must equal a constant, c. Prove that:

$$\begin{aligned} f(x) &\propto e^{cx} \\ f(y) &\propto e^{cy} \end{aligned}$$

5. A statistical mechanics puzzle: Consider the Maxwell-Boltzmann distribution of velocities in 1-D,

$$p(v_x) = e^{-mv_x^2/2k_BT}$$

In problem 2, you computed the average energy, $\langle mv_x^2/2 \rangle$, using the normalized version of this distribution. Now, consider the Boltzmann distribution of *energies*,

$$p(E) = e^{-E/k_BT}$$

If we compute the average energy, $\langle E \rangle$, by integrating over the proper domain in energies $(0, \infty)$, with a normalized distribution, we get a different answer. Why does this happen?

6. Extra credit: The Central Limit Theorem

a) Write a simple computer program (in whatever language you'd like) which generates the sum

$$X_N = \sum_{i=1}^{N} \frac{x_i}{\sqrt{N}}$$

where $\{x_1, ..., x_i, ...x_N\}$ are independent random numbers which are uniformly distributed on the interval $-1/2 < x_i < 1/2$. Your program should compute X_N at least one million times and then construct a histogram of the X_N values you observe.

b) What are the maximum and minimum possible values for X_N?

c) Show (numerically) that for large N the distribution of X_N values looks Gaussian.

d) Where does the Gaussian approximation work best? Where does it fail?