Chem 534: Problem Set #1

Due in class: Thursday, Sept. 3rd

(1) Show that the Poisson distribution $P(m) = a^m \frac{e^{-a}}{m!}$ is normalized. Then calculate $\bar{m}$ and the variance. (hint: directly calculating $\langle m^2 \rangle$, which is needed for the variance, can be a bit tricky. Think about calculating $\langle x(x-1) \rangle$ instead)

(2) Assume that the probability of occupying a given energy state is given by the distribution $P(\varepsilon) = Ae^{-\varepsilon/kT}$, where k is Boltzmann's constant.

(a) Consider a collection of three total states with the first state located at $\varepsilon = 0$ and others at kT and $2kT$, respectively, relative to this first state. What is the normalization constant for this distribution?

(b) How would your answer change if there are five states with $\varepsilon = kT$ in addition to the single states at 0 and $2kT$?

(c) Determine the probability of occupying the energy level $\varepsilon = kT$ for the cases in which one and five states exist at this energy.

(3) Use the method of Lagrange undetermined multipliers to show that the function

$$-\sum_{j=1}^{N} P_j \ln P_j$$

subject to the condition $\sum_{j=1}^{N} P_j = 1$ is a maximum when P_J equals a constant.

(4) Consider a particle to be constrained to lie along a one-dimensional segment 0 to a. Quantum mechanics tells us that the particle is found to lie between x and $x + dx$ given by

$$p(x)dx = \frac{2}{a} \sin^2 \frac{n\pi x}{a} dx$$

where n = 1, 2, 3, ...

(a) Show that $p(x)$ is normalized.

(b) Calculate the average position of the particle along the line segment.