Chemistry 60641 Fall 2023
Professor J. Daniel Gezelter Due Friday, September 22, 2023

Problem Set 2

1. Consider the Gaussian probability density $P(x)$ for the continuous variable x,

$$P(x)dx = Ae^{-a(x-x_0)^2}dx$$

Determine the normalization constant A.

2. Using $P(x)$ from the previous problem, compute $\langle x \rangle$, $\langle x^2 \rangle$, and σ_x

3. Do the same operations as in problems 1 and 2, but for the Exponential distribution,

$$p(x)dx = ce^{-\lambda x}dx, \quad x \geq 0$$

4. Compute the quantity $\left\langle (x - \langle x \rangle)^4 \right\rangle$ for both the normalized Gaussian distribution and the normalized Exponential distribution. Use this quantity to evaluate the *non-Gaussian parameter* for both distributions:

$$\alpha_2 = \frac{\left\langle (x - \langle x \rangle)^4 \right\rangle}{5 \left\langle (x - \langle x \rangle)^2 \right\rangle^2} - \frac{3}{5}$$

5. 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 $\langle mv_x \rangle$.

6. 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.

7. 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:

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

8. 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 5, 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?

9. 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?