Chemistry 60641 Professor J. Daniel Gezelter Fall 2025 Due Friday, February 14, 2025

## 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  $\sigma_x$
- 3. Do the same operations as in problems 1 and 2, but for the Exponential distribution,

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

4. Compute the quantity  $\langle (x - \langle x \rangle)^4 \rangle$  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  $\infty$ ,

- 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:

$$\frac{a_3}{a_2} = f(E_2 - E_3)$$
, and  $\frac{a_3}{a_1} = f(E_1 - E_3)$ 

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:

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

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*,

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

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?