Problem Set 1: Chemistry 175/273

This homework is due on Gradescope by class time on Jan. 15, 2025.

1. *The central limit theorem*
   Consider an experiment in which we measure the spontaneous magnetization of a small magnet in the absence of any external field. In ideal conditions, as we learned from the microcanonical postulate, the probability of all states with the same energy are equal, meaning the probability of observing + and − are both $1/2$.

   (a) In `python`, write a simple function to make n measurements of the magnetization (i.e., a function that returns n samples from a distribution that gives ± 1 with equal probability).

   (b) Define $\bar{x}_n = \frac{1}{n}\sum_{i=1}^{n} x_i$, which we call the sample mean of x, a random variable taking values ± 1 representing + and − spins. Generate 1000 observations of $\bar{x}_n$ with $n = 10, 100, 1000, 10000$ using the function you wrote and plot a normalized histogram of the data separately for each value of n.

   (c) Using the data that you collected to make the histograms, compute an estimate of the variance of the sample means $\mathrm{var}(\bar{x}) = \langle \bar{x}^2 \rangle - \langle \bar{x} \rangle^2$ and plot $\mathrm{var}(\bar{x}_n)$ vs. n on a log-log plot for the same n as above. Recall that the notation $\langle \cdot \rangle$ just means average.

   (d) Fit a linear function to this data to predict the scaling of $\mathrm{var}(\bar{x}_n)$ with n. Note: if the slope of the line is α, this means that the variance scales like n^{α}. What do you obtain for α from the fit?

   (e) A probability density function $p(x)$ is really a "density". Multiplying by an infinitesimal $p(x)dx$ tells you the probability that x is in the region $[x, x + dx]$. What are the units of $p(x)$? If you want to extract a probability from a histogram, explain why you need to multiply by the bin width.

   (f) Plot the histograms differently: plot $n^{\alpha} \log p(\bar{x}_n)$ for $n = 10, 100, 1000, 10000$ on a single plot. Here p is the probability density function. Make sure to shift the max values of the functions so that all the plots are aligned at $x = 0$. Here (and always in this course) the notation log means the natural logarithm. Plot $-x^2/2$ on this plot as well.

2. *Tools of the trade: the Gaussian distribution*
   One of the probability distributions that you will encounter over and over again in your life is the Gaussian distribution. We will see it many times in this course (on homework and exams, too!). The probability density function of the Gaussian distribution is

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}, \qquad (1)$$

   where the parameters μ and $\sigma > 0$ are real numbers.

   (a) Plot this function with $\mu = 0$ and $\sigma^2 = n^{-1}$ for $n = 10, 100, 1000, 10000$. Compare with the histograms you obtained in problem 1 (b).

(b) The normalization constant is determined by $Z = \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} dx$. First, let's square this integral

$$\left(\int_{-\infty}^{\infty} e^{-\frac{(x-\mu)^2}{2\sigma^2}}\right)^2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{x^2+y^2}{2\sigma^2}} dxdy, \quad (2)$$

when $\mu = 0$. Convert this integral to polar coordinates and solve it. Don't forget the Jacobian term!

(c) The mean of a distribution is

$$\langle x\rangle = \int_{-\infty}^{\infty} x\rho(x)dx. \quad (3)$$

Compute the mean of the Gaussian.

(d) The variance of a distribution is

$$\mathrm{var}(x) = \langle x^2\rangle - \langle x\rangle^2. \quad (4)$$

This requires that you compute the integral

$$\int_{-\infty}^{\infty} x^2\rho(x)dx. \quad (5)$$

Let's use a little trick. Define

$$\mathcal{I}(\alpha) = \int_{0}^{\infty} e^{-\alpha x^2} dx. \quad (6)$$

You can evaluate this integral by comparing with the answer you've already determined in (b). What is $\frac{d\mathcal{I}}{d\alpha}$? Use this to compute the variance of the Gaussian.

3. *Analyzing the numerical results*
Let's return to system in problem 1.

(a) Compute the probability that you will observe a particular sequence of length M, i.e., $p(+,-,+,+,+,-,-,\ldots)$.

(b) Find an explicit formula for the probability that you observe M_+ +'s in a measurement of M total observations.

(c) Using Stirling's approximation, compute

$$\log p(M_+).$$

How does this probability scale with M?

(d) Let $m_+ = M_+/M$. You can now express the probability $p(m_+)$ as the exponential of a function which depends on the "intensive" variable m_+ times the "extensive" number M.* In the following expression, identify $I(m_+)$:

$$p(m_+) \propto e^{MI(m_+)}. \quad (7)$$

(e) Using $I(m_+)$ determine the most likely value of m_+.

(f) Assume now that $M \approx 10^{23}$. Compute the relative probability of a small deviation $\delta m = 5 \times 10^{-8}$ from the most likely value. *Hint:* Small perturbations invite Taylor expansions.

(g) Expand $I(m_+)$ to second order to obtain a Gaussian distribution. Is this consistent with the distribution you obtained in Problem 1? What are the mean and variance of the resulting distribution?

** Intensive* means that the quantity does not scale with system size, e.g., temperature, pressure. *Extensive* quantities do scale with system size, e.g., energy, volume.