

CH352 Assignment 1: Due Tuesday, 6 February 2017

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Tuesday, 31 January 2017

Q1 The Maxwell-Boltzmann velocity probability distribution function

According to the kinetic theory of gases, the energies of molecules of mass m moving with velocity v_x in the x -direction are given by $\epsilon_x = \frac{1}{2}mv_x^2$. The Maxwell-Boltzmann velocity distribution gives that the fraction of particles, $p(v_x)$, moving with velocity v_x is proportional to $\exp[-\epsilon_x/k_B T] = \exp[-mv_x^2/2k_B T]$.

- (i) Write down the normalized Maxwell-Boltzmann velocity probability distribution.
- (ii) Use your normalized velocity distribution to compute the average kinetic energy, $\langle \frac{1}{2}mv_x^2 \rangle$.
- (iii) Compute the average velocity $\langle v_x \rangle$.

(i) Normalized Maxwell-Boltzmann velocity probability distribution

We are trying to find α s.t.

$$p(v_x) = \alpha e^{-mv_x^2/2k_B T} \quad (\text{Q1.1})$$

is normalized. Because v_x is defined on the whole real number line, we need to integrate over $[-\infty, \infty]$:

$$\frac{1}{\alpha} = \int_{-\infty}^{\infty} e^{-mv_x^2/2k_B T} dv_x. \quad (\text{Q1.2})$$

As was given in class:

$$\int_{-\infty}^{\infty} e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad (\text{Q1.3})$$

where in this case $a = m/2k_B T$.

$$\frac{1}{\alpha} = \sqrt{\frac{2\pi k_B T}{m}} \quad (\text{Q1.4})$$

$$\boxed{p(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T}} \quad (\text{Q1.5})$$

(ii) Average kinetic energy, $\langle \frac{1}{2}mv_x^2 \rangle$

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \int_{-\infty}^{\infty} \frac{1}{2}mv_x^2 \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T} dv_x \quad (\text{Q1.6})$$

Let $m/2k_B T = \gamma$

$$= \sqrt{\frac{m^2\gamma}{4\pi}} \int_{-\infty}^{\infty} v_x^2 e^{-\gamma v_x^2} dv_x \quad (\text{Q1.7})$$

$$= -\sqrt{\frac{m^2\gamma}{4\pi}} \int_{-\infty}^{\infty} \frac{d}{d\gamma} e^{-\gamma v_x^2} dv_x \quad (\text{Q1.8})$$

$$= -\sqrt{\frac{m^2\gamma}{4\pi}} \frac{d}{d\gamma} \sqrt{\frac{\pi}{\gamma}} \quad (\text{Q1.9})$$

$$= \frac{m}{4\gamma} \quad (\text{Q1.10})$$

$$\boxed{\left\langle \frac{1}{2}mv_x^2 \right\rangle = \frac{k_B T}{2}} \quad (\text{Q1.11})$$

Interestingly, this does not depend on the mass of the gas, but it does depend on the temperature.

Also, this might not match with the normal $\frac{3}{2}k_B T$ for the average kinetic energy of a gas that you've heard; that is because we calculated only the average kinetic energy in the x -direction, but y and z will have the same kinetic energy contributions.

(iii) Average velocity $\langle v_x \rangle$

If you did a lot of work for this question, that's unfortunate. There are two ways the answer can be found easily.

First, thinking physically, the $+x$ -direction is not special (in the absence of an external force) nor is the $-x$ -direction. Therefore, because there is no average motion, the integrals in the negative and positive directions will cancel, and the average velocity is zero.

Second, thinking more mathematically, v_x is an odd function and $e^{-\gamma v_x^2}$ is an even function. An even function multiplied by an odd function will give an odd function. Then, the integral over all space of an odd function is always zero, by symmetry (the area under the x -axis is the same as the area above the x -axis).

$$\boxed{\langle v_x \rangle = 0}$$

Q2 Unbiased coin-flipping random walkers

Consider a group of unbiased coin-flipping, random walkers. At each time interval they flip their coins, and if one gets a head she takes a step to the right, while if a walker gets a tail he takes a step to the left. After

N time intervals the fraction of random walkers that have taken m steps to the right, and thus $N - m$ steps to the left, is given by the binomial distribution

$$P(m, N) = \left(\frac{1}{2}\right)^N \frac{N!}{m!(N-m)!} \quad (\text{Q2.1})$$

Let's get an idea of what this distribution looks like by Taylor series expanding $\ln P(m, N)$ as a function of m (for fixed N) in displacements, $[m - m^*]$, from its peak value which occurs at say $m = m^*$.

- (i) Use Stirling's approximation, $\ln n! \sim n \ln n - n$ to find the value of $m = m^*$ where $\ln P(m, N)$ has its maximum value for a given fixed number of time intervals, N .
- (ii) The Taylor series expansion in terms of m for fixed N we are looking for has the following form, keeping only terms to second order, $[m - m^*]^2$, in displacements of m from its value m^* at the peak of the distribution:

$$\ln P(m, N) \sim \ln P(m^*, N) + \frac{d \ln P}{dm}(m^*, N)[m - m^*] + \frac{1}{2} \frac{d^2 \ln P}{dm^2}(m^*, N)[m - m^*]^2. \quad (\text{Q2.2})$$

Compute the values of the derivative functions appearing in the above results, for fixed N at the point $m = m^*$ you determined in part (i).

- (iii) Let $P(m^*, N) = P^*(N)$ and exponentiate both sides of the above result using your derivative values and obtain an approximate expression for $P(m, N)$
- (iv) If you have done things correctly in the above steps your result should be a normalized Gaussian distribution which has the general form

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp[-x^2/2\sigma^2] \quad (\text{Q2.3})$$

where σ is the width of the Gaussian and x is the displacement from the peak of the distribution. By comparing your result with this general form obtain an expression for the width σ_m of your distribution of displacements, $[m - m^*]$ (number of steps from the peak), and then use your width to determine the normalization constant, $P^*(N)$, of your distribution. Your results will depend on N , the number of time intervals for which the random walkers have been flipping and stepping. Comment on how the shape of the distribution changes as N increases.

- (v) Use your distribution to compute the root-mean-square (rms) displacement $\sqrt{\langle(m - m^*)^2\rangle}$ of the group of random walkers.

Note: This random walk model provides a very realistic description of how particles are kicked around by collisions with solvent molecules that cause Brownian motion and diffusion.

(i) Value m^* that maximizes P

$$\begin{aligned} \ln P(m, N) &= -N \ln 2 + \ln N! - \ln m! - \ln(N - m)! \\ \frac{\partial}{\partial m} \ln P(m, N) &= -\frac{\partial}{\partial m} m \ln m - \frac{\partial}{\partial m} (N - m) \ln(N - m) \\ &= 1 + \ln m - 1 + \ln(N - m) \\ &= -\ln \frac{m}{N - m} \\ 0 &= \ln \frac{m^*}{N - m^*} \end{aligned}$$

$$\boxed{m^* = N/2}$$

Note: while this initially may not seem to depend on the "fairness" of the coin, if the coin were not fair, there would be a p_H^m term that would not cancel immediately.

(ii) The Taylor series expansion of P in terms of m for fixed N

$$\boxed{\frac{d \ln P}{dm}(m^*, N) = 0}$$

by definition because the maximum is a zero of the first derivative (see above).

$$\begin{aligned} \frac{d^2 \ln P}{dm^2} &= -\frac{d}{dm} \ln m + \frac{d}{dm} \ln(N - m) \\ &= -\frac{1}{m} - \frac{1}{N - m} \end{aligned}$$

$$\boxed{\frac{d^2 \ln P}{dm^2}(m^*, N) = -\frac{4}{N}}$$

(iii) Second order approximation of P

$$\ln P(m, N) \sim \ln P^* + 0 - \frac{2}{N} [m - N/2]^2$$

$$\boxed{P(m, N) \sim P^* e^{-2(m-N/2)^2/N}}$$

(iv) Normalized Gaussian distribution

Let $x = m - m^* = m - N/2$, then

$$P(m, N) = P^* e^{-2x^2/N}$$

and $\boxed{\sigma_m^2 = N/4}$.

$$P(m, N) = \sqrt{\frac{2}{N\pi}} e^{-2x^2/N}$$

is the normalized second order approximation of $P(m, N)$ around the maximum of the function.

Because σ_m^2 is linearly dependent on N , the distribution gets wider (and flatter) as the number of steps increases. This can also be seen by the inverse relationship of the second derivative to N .

(v) Root-mean-square displacement

We are looking for $\sqrt{\langle(m - m^*)^2\rangle} = \sqrt{\langle x^2\rangle}$:

$$\begin{aligned}\langle x^2 \rangle &= \int_{-\infty}^{\infty} x^2 \sqrt{\frac{2}{N\pi}} e^{-2x^2/N} dx \\ &= -\sqrt{\frac{2}{N\pi}} \frac{\partial}{\partial(2/N)} \int_{-\infty}^{\infty} e^{-2x^2/N} dx \\ &= -\sqrt{\frac{2}{N\pi}} \frac{\partial}{\partial(2/N)} \sqrt{\frac{N\pi}{2}} \\ &= \frac{1}{2} \sqrt{\frac{2}{N\pi}} \frac{N^3\pi}{8} \\ \boxed{\sqrt{\langle x^2 \rangle} = \sqrt{\frac{N}{4}}}\end{aligned}$$

which, as expected, is the same as σ_m .

Q3 Polymer Length Distribution

We can use a simple monomer binding (probability p) and chain termination (probability $1 - p$) model to explore polymer growth. We can find that the fraction of chains of length k , that is the probability $P(k)$ of finding a polymer chain of length k monomer units in the final reaction mixture, is

$$P(k) = \frac{n_k}{\sum_{k=1}^{\infty} n_k} \quad (\text{Q3.1})$$

where $n_k = p^{k-1}(1 - p)$. We can use this probability distribution, together with the geometric series result that

$$S_{\infty} = \sum_{k=1}^{\infty} x^{k-1} = \frac{1}{1 - x}, \quad |x| < 1 \quad (\text{Q3.2})$$

to compute the average polymer chain length as

$$\langle k \rangle = \sum_{k=1}^{\infty} kP(k) = \frac{1}{1 - p}. \quad (\text{Q3.3})$$

When working with polymer beads like polystyrene it is often important to know the polydispersity of your sample. A useful measure of polydispersity is the root mean square fluctuation from the average chain length, or variance, σ_k , of the chain length distribution defined as

$$\sigma_k^2 = \langle (k - \langle k \rangle)^2 \rangle = \langle k^2 \rangle - \langle k \rangle^2. \quad (\text{Q3.4})$$

Using the same techniques for manipulating geometric series results, obtain an expression for σ_k in terms of p for our polymer growth model. Suppose $p = 0.001$; compute the mean polymer chain length and its variance.

We are given

$$\langle k \rangle = \frac{1}{1 - p}.$$

This means we just need to find $\langle k^2 \rangle$. This is given by

$$\begin{aligned}\langle k^2 \rangle &= \sum_{k=1}^{\infty} k^2 P(k) \\ &= \frac{1}{\sum_{k=1}^{\infty} p^{k-1} (1-p)} \sum_{k=1}^{\infty} k^2 p^{k-1} (1-p) \\ &= 1 \times \frac{1-p}{p} \sum_{k=1}^{\infty} k^2 p^k\end{aligned}$$

Then, using the result shown below (or a table of series results),

$$\begin{aligned}&= \frac{1-p}{p} \times \frac{p(1+p)}{(1-p)^3} \\ \langle k^2 \rangle &= \frac{1+p}{(1-p)^2}\end{aligned}$$

Then, to get σ_k , we can use these results to find

$$\sigma_k^2 = \frac{1+p}{(1-p)^2} - \frac{1}{(1-p)^2}$$

$$\sigma_k^2 = \frac{p}{(1-p)^2}$$

For $p = 0.001$, $\langle k \rangle = 1.001$ and $\sigma_k^2 = 0.001002$.

A few other notes: first,

$$\begin{aligned}\sum_{k=1}^{\infty} p^{k-1} (1-p) &= \sum_{k=1}^{\infty} p^{k-1} - p^{k+1} \\ &= \sum_{k=1}^{\infty} p^{k-1} - \sum_{k=1}^{\infty} p^k \\ &= \sum_{k=0}^{\infty} p^k - \sum_{k=1}^{\infty} p^k \\ &= p^0 + \sum_{k=1}^{\infty} p^k - \sum_{k=1}^{\infty} p^k \\ &= 1\end{aligned}$$

and second,

$$\sum_{k=1}^{\infty} k p^k = p + 2p^2 + 3p^3 + 4p^4 + \dots$$

and

$$\sum_{k=1}^{\infty} k^2 p^k = p + 4p^2 + 9p^3 + 16p^4 + \dots$$

They obviously look fairly similar, but also notice that

$$\frac{d}{dp} \sum_{k=1}^{\infty} k p^k = 1 + 4p + 9p^2 + 16p^3 + \dots$$

This is even more similar, and they only differ by a factor of p . We also know the value of the infinite sum of p^k (from eq. (Q3.2)), which can be seen to be related in the same manner. Using this,

$$\begin{aligned} \sum_{k=1}^{\infty} k^2 p^k &= p \frac{d}{dp} \sum_{k=1}^{\infty} k p^k \\ &= p \frac{d}{dp} p \frac{d}{dp} \sum_{k=1}^{\infty} p^k \\ &= p \frac{d}{dp} p \frac{d}{dp} \left(\frac{p}{1-p} \right) \\ \sum_{k=1}^{\infty} k^2 p^k &= \frac{p(1+p)}{(1-p)^3}. \end{aligned}$$

This gives the sum of the series needed above.

Q4 Probability to partially fill a nanotube

Consider the injection of a small amount of gas ($n = 3$ gas molecules) into a short length (5 molecular units) of carbon nanotube. Suppose initially that the cross-section of the nanotube is 3 molecular units and that only one molecule can occupy a cell at any one time. A typical configuration of the initial system is depicted schematically in fig. 1.

×		×
	×	

Figure 1: Configuration of $n = 3$ gas molecules (displayed as a “×” filling the cells) in a small nanotube with width 3 molecular units and length 5 molecular units

- (i) What is the probability that all the gas molecules are found just in the top layer of cells?
- (ii) What is the probability that all the gas molecules will be found in only the top three layers of cells?
- (iii) Now lets make the nanotube wider, so the cross-section of the tube is 4 molecular units. Keeping everything else fixed, what is the probability that the 3 gas molecules are now found in the top layer of the wider tube? Is it more or less probable to find all three molecules in the top layer for a wider tube?

(i) Probability of all in top row, p_{top}

$$\begin{aligned} p_{\text{top}} &= \frac{n_{\text{top}}}{n_{\text{total}}} \\ &= \frac{\binom{3}{3}}{\binom{15}{3}} \\ p_{\text{top}} &= \frac{1}{455} \end{aligned}$$

(ii) Probability of all in the top three rows

$$\begin{aligned} p_{\text{top}} &= \frac{n_{\text{top}}}{n_{\text{total}}} \\ &= \frac{\binom{9}{3}}{\binom{15}{3}} \\ p_{\text{top}} &= \frac{84}{455} \\ p_{\text{top}} &= \frac{12}{65} \end{aligned}$$

(iii) p_{top} for a wider tube

$$\begin{aligned} p_{\text{top}} &= \frac{\binom{4}{3}}{\binom{20}{3}} \\ p_{\text{top}} &= \frac{1}{285} \end{aligned}$$

It is more likely (not quite twice as likely) to find all three molecules in the top row of the wider tube as compared to all the molecules in the top row of the narrower tube.

Q5 Extrema of multivariate functions with constraints

- (i) Find the maximum of the function $f(x, y) = -(x - a)^2 - (y - b)^2$ subject to the constraint that $y = kx$.
- (ii) Find the minimum of the paraboloid $f(x, y) = (x - x_0)^2 + (y - y_0)^2$ subject to the constraint that $y = 2x$.
- (iii) Release the constraint in (ii) and find the absolute minimum of the paraboloid.

(i) $f(x, y) = -(x - a)^2 - (y - b)^2, y = kx$

Defining $g(x, y) = y - kx = 0$ as the constraint,

$$\begin{aligned} \nabla f(x, y) &= \lambda \nabla g(x, y) \\ (-2(x - a), -2(y - b)) &= \lambda (-k, 1) \\ x &= \frac{\lambda k}{2} + a \quad \text{and} \quad y = -\frac{\lambda}{2} + b \end{aligned}$$

Then using the constraint,

$$0 = -\lambda \left(\frac{1}{2} + \frac{k^2}{2} \right) + b - ak$$

$$\lambda = \frac{2(b - ak)}{1 + k^2}$$

$$\boxed{x = \frac{a + kb}{1 + k^2} \quad \text{and} \quad y = k \frac{a + kb}{1 + k^2}}$$

$$f_{\max}(x, y) = - \left(\frac{a + kb}{1 + k^2} - a \right)^2 - \left(k \frac{a + kb}{1 + k^2} - b \right)^2$$

$$\boxed{f_{\max}(x, y) = - \frac{(b - ak)^2}{k^2 + 1}}$$

We know this is a maximum because $f(x, y)$ is concave down.

(ii) $f(x, y) = (x - x_0)^2 + (y - y_0)^2, y = 2x$

Again, $g(x, y) = y - 2x = 0$, and

$$\mathcal{L}(x, y, \lambda) = f(x, y) - \lambda g(x, y)$$

$$= (x - x_0)^2 + (y - y_0)^2 - \lambda y + 2\lambda x$$

$$\nabla \mathcal{L}(x, y, \lambda) = (2(x - x_0) + 2\lambda, 2(y - y_0) - \lambda, -y + 2x)$$

$$0 = (2(x - x_0) + 2\lambda, 2(y - y_0) - \lambda, -y + 2x)$$

$$\left(x = -\lambda + x_0, y = \frac{\lambda}{2} + y_0, y = 2x \right)$$

$$\lambda = \frac{2}{5}(2x_0 - y_0)$$

$$\boxed{x = \frac{1}{5}(x_0 + 2y_0) \quad \text{and} \quad y = \frac{2}{5}(x_0 + 2y_0)}$$

$$f_{\max}(x, y) = \left(\frac{x_0 + 2y_0}{5} - x_0 \right)^2 + \left(\frac{2x_0 + 4y_0}{5} - y_0 \right)^2$$

$$\boxed{f_{\max}(x, y) = \frac{(y_0 - 2x_0)^2}{5}}$$

This is guaranteed to be a minimum because this function is concave up.

(iii) $f(x, y) = (x - x_0)^2 + (y - y_0)^2$

$$\boxed{x = x_0, y = y_0, \text{ and } f_{\max}(x, y) = 0}$$

Q6 Calculating the entropy of dipoles in a field

You have a solution of dipolar molecules with a positive charge at the head and a negative charge at the tail. When there is no electric field applied to the solution, the dipoles point north (n), east (e), west (w),

and south (s) with equal probabilities (i.e., $p_n = \frac{1}{4}$, $p_e = \frac{1}{4}$, $p_s = \frac{1}{4}$, and $p_w = \frac{1}{4}$). However when a field is applied to the solution, we find a different distribution with more positive head groups pointing north so that the probabilities are now $p_n^f = \frac{7}{16}$, $p_e^f = \frac{1}{4}$, $p_w^f = \frac{1}{4}$, and $p_s^f = \frac{1}{16}$.

- (i) What is the polarity of the applied field (i.e., in which direction does the field have its most positive pole)?
- (ii) Calculate the entropy of the system in the absence of the field.
- (iii) Calculate the entropy of the system in the presence of the field.
- (iv) Does the system become more ordered or less ordered when the field is applied?

(i) Polarity of field

Since more positive head groups are pointing north, the most positive pole of the field is to the south.

(ii) Entropy with no external field, S_0

Using eq. (5.2) on page 82 of Dill and Bromberg,

$$\begin{aligned} S_0 &= -k_B \sum_i p_i \ln p_i \\ &= -k_B (p_n \ln p_n + p_e \ln p_e + p_w \ln p_w + p_s \ln p_s) \\ &= k_B \ln 4 \end{aligned}$$

$$S_0 = 1.386 k_B = 1.913 \times 10^{-23} \text{ J K}^{-1}$$

(iii) Entropy in the external field,

$$S_f = -k_B \left(\frac{7}{16} \ln \frac{7}{16} + \frac{1}{4} \ln \frac{1}{4} + \frac{1}{4} \ln \frac{1}{4} + \frac{1}{16} \ln \frac{1}{16} \right)$$

$$S_f = 1.228 k_B = 1.695 \times 10^{-23} \text{ J K}^{-1}$$

(iv) Change in ordering

The system becomes more ordered. The entropy decreases because they are more likely to be facing in one direction as opposed to the anisotropy in the absence of the field.