

CH352 Assignment 1. Due: Tuesday, February 11, 2014.

Prof. David F. Coker

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 $\langle v_x \rangle$

Q2 Consider a group of unbiased coin flipping, random walkers. Each time interval they flip their coins and if one gets a head he 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

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

Lets 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:

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

Compute the values of the derivative functions appearing in the above result, 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

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

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.

Q3 Polymer length distribution. In class we used a simple monomer binding (probability p) and chain termination (probability $1 - p$) model to explore polymer growth. We found that the fraction of chains of length k , *i.e.* the probability $P(k)$ of finding a polymer chain of length k monomer units in the final reaction mixture, was

$$P(k) = \frac{n_k}{\sum_{k=1}^{\infty} n_k} \quad (4)$$

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

$$S_{\infty} = \sum_{k=1}^{\infty} x^{k-1} = \frac{1}{1 - x}, \quad |x| < 1 \quad (5)$$

to compute the average polymer chain length as

$$\langle k \rangle = \sum_{k=1}^{\infty} kP(k) = \frac{1}{1 - p} \quad (6)$$

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

$$\sigma_k^2 = \langle(k - \langle k \rangle)^2\rangle = \langle k^2 \rangle - \langle k \rangle^2 \quad (7)$$

Using the same techniques for manipulating geometric series results we employed in class 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.

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 Figure 1 below.

X		X
	X	

Figure 1: Configuration of $n=3$ gas molecules (displayed as “X” filling the cells) in 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 let's 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 the top layer completely filled for a wider 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.

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.* $p_n = \frac{1}{4}$, $p_e = \frac{1}{4}$, $p_w = \frac{1}{4}$, and $p_s = \frac{1}{4}$. 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 $p_n^f = \frac{7}{16}$, $p_e^f = \frac{1}{4}$, $p_w^f = \frac{1}{4}$, $p_s^f = \frac{1}{16}$

- (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?