

# CH352 Assignment 1: Due Tuesday, 6 February 2017

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## 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 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  $\sigma$  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  $\sigma_m$  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

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,  $\sigma_k$ , 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  $\sigma_k$  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 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?

## 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.,  $p_n = \frac{1}{4}$ ,  $p_e = \frac{1}{4}$ ,  $p_s = \frac{1}{4}$ , 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?