

1. Imagine flipping an unbiased coin  $N$  times. Let  $N_H$  be the number of heads results, and  $f = N_H/N$  be the fraction of such results.
  - (a) What is the probability of observing a particular sequence of heads (H) and tails (T) results, e.g., H H T H H T H T T H...?
  - (b) How many possible flip sequences yield exactly  $N_H$  results? Your answer should involve the factorial function,  $M! \equiv M \times (M - 1) \times (M - 2) \times \dots \times 3 \times 2 \times 1$ .
  - (c) Write an exact equation for the probability  $P(N_H)$  of observing  $N_H$  heads results when the coin is flipped  $N$  times.
  - (d) Stirling's approximation

$$\ln(M!) \approx M \ln(M) - M \text{ for large } M$$

allows you to simplify your result in part (c). Show that  $P(N_H)$  can be written in the large deviation form

$$P(N_H) = e^{-NI(f)}$$

when  $N$  is sufficiently large to justify Stirling's approximation. Identify and plot  $I(f)$  as a function of  $f$ .

- (e) Now imagine the physical scenario of  $N \gg 1$  noninteracting spin-1/2 particles. In a particular measurement, the observed  $z$ -component of each spin is up or down with equal probability. What is the probability of observing a number  $N_{up}$  of up spins in a given observation? Write your answer in terms of the fraction  $f = N_{up}/N$ .
  - (f) Although  $N_{up} = N/2$  is the most likely observation, a typical measurement will not yield *exactly* half of the spins point up. For Avogadro's number of spins,  $N \approx 10^{24}$ , estimate the relative probability of a deviation  $\delta = 0.0000001$  from the ideal fraction, i.e., calculate  $P(f = 0.5 + \delta)/P(f = 0.5)$ . Your final answer need not be highly accurate; just determine the order of magnitude. (For this purpose, Taylor expansion of  $\ln P$  about  $\delta = 0$  is both permitted and a good idea).
  - (g) What does your result imply about the reproducibility of measurements on macroscopic systems?
2. In class we introduced the one definition of the entropy, due to Boltzmann:

$$S_B = k_B \ln \Omega$$

Another definition due to Gibbs is given by:

$$S_G = -k_B \sum_{\nu} P(\nu) \ln P(\nu)$$

where  $P(\nu)$  is the probability to find the system is a microstate  $\nu$ .

- (a) For an isolated system (with fixed energy  $E$ , number of molecules  $N$ , and volume  $V$ ) show that  $S_B$  and  $S_G$  are identical. Recall that in such a system, all allowed microstates are equally likely.

- (b) For the remaining parts of this problem, consider a collection of  $N$  indistinguishable particles arranged on a lattice of  $M$  cells. Each cell can be occupied by at most one particle, and particles in different cells do not interact. Derive the expression for the total number of possible configurations for this system given by:  $\Omega(M, N) = \frac{M!}{(M-N)!N!}$ .
- (c) Assuming  $M$ ,  $N$ , and  $M - N$  are all very large, use Stirling's approximation to write the Boltzmann entropy per cell,  $S_B/M$  as a function of  $f \equiv N/M$  alone.
- (d) The occupation state of one cell in this lattice system is not affected by that of any other cell. As a result, the total entropy can be written as  $S = M s_{\text{cell}}$  where  $s_{\text{cell}}$  is the entropy of a single cell. Using Gibbs' definition of entropy, calculate  $s_{\text{cell}}$  in terms of  $p_1$  and  $p_0$ , the probabilities of finding a particular cell occupied or unoccupied, respectively.
- (e) Write the average number  $\langle n \rangle$  of particles in a given cell in terms of  $p_1$  and  $p_0$ .
- (f) Finally, by relating  $\langle n \rangle$  to the fraction  $f$  of occupied cells, demonstrate the equivalence of  $S_B$  and  $S_G$  for this non-interacting lattice gas.
3. Consider a dilute gas in a container with density  $\rho$ . Suppose we observe a part of this system with volume  $V$  and we want to understand the behavior of the number of particles in this region. Let's divide the volume  $V$  into smaller cells with volume  $v$ , where each cell can be occupied by only one gas particle. Thus, for cell  $i$ , the number of particles in the cell  $n_i = 0$  or 1. Thus,

$$N = \sum_{i=1}^M n_i$$

where  $M = V/v$ . Additionally, since the gas is dilute, different cells are uncorrelated.

- (a) Show that the average number of particles in volume  $V$  is  $\langle N \rangle = Mv\rho$ . Hint: you will need to find an expression for the average number of particles in a cell,  $\langle n_i \rangle$ .
- (b) Let's define  $\delta N \equiv N - \langle N \rangle$ . Show that  $\sigma = \sqrt{\langle (\delta N)^2 \rangle} = \sqrt{Mv\rho(1 - v\rho)}$  (Hint: what is  $n_i^2$  when  $n_i = 0$  or 1?)  
What happens to  $\sigma$  in the dilute limit, i.e.,  $v\rho \ll 1$ ? Compare  $\sigma$  to  $\langle N \rangle$  in this dilute limit for macroscopic systems, where  $N \sim 10^{24}$ .
- (c) Now let's take a different take and find the probability of finding the particles in the region  $V$  in a specific configuration  $(n_1, n_2, \dots, n_M)$ . Given that  $n_i = 0$  or 1, what is the probability  $p_1$  that a single cell is occupied?
- (d) Out of the  $M$  cells in the observable volume,  $N$  of them are occupied. Hence, what is the probability  $P(n_1, n_2, \dots, n_M)$  of observing a specific configuration? Remember that different cells are uncorrelated, i.e., independent.
- (e) If  $\Omega(N)$  is the number of configurations of the entire system where  $N$  particles are present in the volume  $V$ , what is the probability  $P(N)$  of  $N$  particles occupying the volume  $V$ ?

- (f) Like in Problem 2, we can find  $\Omega(N)$  by counting the total possible configurations. Assuming both  $M$  and  $N$  are big (Stirling's approximation applies), find an expression for  $\ln \Omega(N)$  in terms of  $M$  and  $\phi = N/M$ .
- (g) Now that you have  $\ln \Omega(N)$ , you can find an expression for  $\ln P(N)/M$  in terms of  $M, p_1$  and  $\phi$ . Using this, plot  $P(N)$  as a function of  $\phi$  for  $p_1 = 0.2$  and  $M = 10, 100, 1000$  and  $10000$ . What is happening? What would you expect for  $M = 1$  mole of gas particles?