## **Homework Assignment 3**

PHYSICS 314 - THERMODYNAMICS & STATISTICAL PHYSICS (Spring 2018) *Due Friday, February 16<sup>th</sup>, by noon, Noyce 1135* 

I cannot award full credit for work that I am unable to read or follow. For my benefit and for yours, please:

- Write neatly
- Show and EXPLAIN all steps
- Make diagrams large and clearly-labeled

You are welcome to collaborate with others on this assignment. However, the work you turn in should be your own. Please cite collaborators and outside sources. See the syllabus for details.

Regardless of the number of parts, all homework problems are weighted equally. Regardless of the number of questions, all homework assignments are weighted equally.

- 1) A box is separated by a partition that divides its volume into the ratio 3:1. The larger portion of the box contains 1,000 molecules of Ne gas. The smaller portion contains 100 molecules of He gas. A small hole is punctured in the partition, and one waits until equilibrium is attained.
  - a) Find the mean number of molecules of each type on either side of the partition.

The hole allows the gasses reach diffusive equilibrium, which means that both gasses are distributed evenly throughout the volume. Thus, the mean number of molecules per unit volume is the same everywhere.

The larger side of box has ¾ the total volume, and thus ¾ the total of each type of molecule on average.

$$\overline{N_{Ne}} = Ne \; molecules_{total} \times \frac{3}{4} = 1,000 \; Ne \; molecules \times \frac{3}{4}$$

$$\overline{N_{Ne}} = 750 \text{ molecules}$$

$$\overline{N_{He}} = He \ molecules_{total} \times \frac{3}{4} = 100 \ He \ molecules \times \frac{3}{4}$$

$$\overline{N_{He}} = 75 \ molecules$$

The smaller side of box has ¼ the total volume, and thus ¼ the total of each type of molecule on average.

$$\overline{N_{Ne}} = Ne \; molecules_{total} \; \times \frac{1}{4} = 1,000 \; Ne \; molecules \; \times \frac{1}{4}$$

$$\overline{N_{Ne}} = 250 \ molecules$$

$$\overline{N_{He}} = He \ molecules_{total} \times \frac{1}{4} = 100 \ He \ molecules \times \frac{1}{4}$$

$$\overline{N_{He}} = 25 \text{ molecules}$$

b) After a long time, what is the probability of finding 1,000 molecules of Ne gas in the larger portion and 100 molecules of He gas in the smaller portion (*i.e.*, the same distribution as in the initial system)?

Examine the probability for each molecule. Note that the probabilities are the same for either type of molecule.

Probabilty of finding a molecule on the bigger side =  $\frac{3}{4}$ 

Probabilty of finding a molecule on the smaller side =  $\frac{1}{4}$ 

The probability for the whole system is the product of the probabilities for each molecule since they are independent.

Probabilty of 1,000 Ne molecules on the bigger side =  $3/4 \times 3/4 \times 3/4 = (3/4)^{1000}$ 

Probabilty of 100 He molecules on the smaller side =  $\frac{1}{4} \times \frac{1}{4} \times \frac{1}{4} \times \dots = \left(\frac{1}{4}\right)^{100}$ 

Probabilty of both of the above = 
$$(1/4)^{100} \times (3/4)^{1000} \approx 7 \times 10^{-186}$$

That's extremely unlikely, even for a relatively low number of molecules.

2) Use Sterling's approximation to show that the multiplicity of an Einstein solid, for any large values of N (number of oscillators) and q (number of energy units) is roughly equal to the expression shown below.

$$\Omega pprox rac{\left(rac{q+N}{q}
ight)^q \left(rac{q+N}{N}
ight)^N}{\sqrt{2\pi q rac{q+N}{N}}}$$

(The square root in the denominator in the final expression shown above is merely large. Often it can be neglected.) Hint: Do not neglect the  $\sqrt{2\pi N}$  in Stirling's approximation, and first show the following equality.

$$\Omega = \frac{N}{q+N} \frac{(q+N)!}{q!\,N!}$$

Begin with general expression for an Einstein solid with N oscillators and q units of energy.

$$\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!}$$

Rewrite the factorials by multiplying by 1 = N/N as follows.

$$(q+N-1)! = (q+N-1)! \times \frac{N}{N} = \frac{(q+N)!}{q+N}$$

$$(N-1)! = (N-1)! \times \frac{N}{N} = \frac{N!}{N}$$

Sub these expressions into the multiplicity expression to get the expression from the hint.

$$\Omega(N,q) = \left(\frac{N}{q+N}\right) \frac{(q+N)!}{q!\,N!}$$

Apply the Stirling approximation to the three factorial terms.  $x! \approx x^x e^{-x} \sqrt{2\pi x}$ 

$$\Omega(N,q) \approx \left(\frac{N}{q+N}\right) \frac{(q+N)^{(q+N)} e^{-(q+N)} \sqrt{2\pi(q+N)}}{\left(q^q e^{-q} \sqrt{2\pi q}\right) \left(N^N e^{-N} \sqrt{2\pi N}\right)}$$

Cancel the exponential terms and one factor of  $\sqrt{2\pi}$ .

$$\Omega(N,q) \approx \left(\frac{N}{q+N}\right) \frac{(q+N)^{(q+N)} \sqrt{(q+N)}}{\left(q^q \sqrt{q}\right) \left(N^N \sqrt{2\pi N}\right)}$$

Rearrange by collecting like powers.

$$\Omega(N,q) \approx \frac{(q+N)^{(q+N)}}{q^q N^N} \left(\frac{N}{q+N}\right) \sqrt{\frac{q+N}{2\pi Nq}}$$

Separate by powers again, and absorb the fraction in parentheses into the radical.

$$\Omega(N,q) \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \sqrt{\frac{N}{2\pi q(q+N)}}$$

Take the reciprocal of the radical to match the given form.

$$\Omega \approx \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{2\pi q \, \frac{q+N}{N}}}$$

3) For a single large two-state paramagnet, the multiplicity function is very sharply peaked about N<sub>↑</sub> = N / 2. Use Stirling's approximation to estimate the height of the peak in the multiplicity function, that is, to approximate  $\Omega\left(N_{\uparrow} = \frac{N}{2}\right)$ . Do not neglect the  $\sqrt{2\pi N}$  in Stirling's approximation. For full credit, simplify to the following form. (Each box represents a single number or variable.)

$$\Omega\left(N_{\uparrow} = \frac{N}{2}\right) \approx \blacksquare \P \sqrt{\frac{\blacksquare}{\blacksquare \blacksquare}}$$

Hint: Use the In manipulation technique for very large numbers.

Begin with the expression from class for the multiplicity of a two-state paramagnet.

$$\Omega(N_{\uparrow}) = \frac{N!}{N_{\uparrow}! \, N_{\downarrow}!}$$

In the most probable macrostate, the dipoles are evenly split between the two orientations.

$$N_{\uparrow} = N_{\downarrow} = \frac{N}{2}$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) = \frac{N!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!} = \frac{N!}{\left[\left(\frac{N}{2}\right)!\right]^{2}}$$

Use Stirling's Approximation to rewrite the factorials.  $x! \approx x^x e^{-x} \sqrt{2\pi x}$ 

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx \frac{N^{N} e^{-N} \sqrt{2\pi N}}{\left[\left(\frac{N}{2}\right)^{\frac{N}{2}} e^{-\frac{N}{2}} \sqrt{\pi N}\right]^{2}}$$

Instead of simplifying directly (see end of solution\*), get practice with dealing with big numbers. To deal with these numbers, take the natural log of the multiplicity. (Later, exponentiate to get back to multiplicity.)

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx \ln \left( \frac{N^{N} e^{-N} \sqrt{2\pi N}}{\left[ \left( \frac{N}{2} \right)^{\frac{N}{2}} e^{-\frac{N}{2}} \sqrt{\pi N} \right]^{2}} \right)$$

Use log properties to rewrite this.

$$\ln A/_B = \ln A - \ln B$$

$$\ln A^B = B \ln A$$

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx \ln \left[ N^N e^{-N} \sqrt{2\pi N} \right] - 2 \ln \left[ \left( \frac{N}{2} \right)^{\frac{N}{2}} e^{-\frac{N}{2}} \sqrt{\pi N} \right]$$

$$\ln A \times B = \ln A + \ln B$$

$$\ln A^B = B \ln A$$

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx \left[ N \ln N - N + \frac{1}{2} \ln(2\pi N) \right] - 2 \left[ \frac{N}{2} \ln \left( \frac{N}{2} \right) - \frac{N}{2} + \frac{1}{2} \ln(\pi N) \right]$$

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx N \ln N + \frac{1}{2} \ln(2\pi N) - N \ln \left( \frac{N}{2} \right) - \ln(\pi N)$$

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx N \left( \ln N - \ln \left( \frac{N}{2} \right) \right) + \frac{1}{2} \ln(2\pi N) - \ln(\pi N)$$

Use log properties again.

$$\ln A/B = \ln A - \ln B$$

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx N \ln \left( \frac{N}{N/2} \right) + \frac{1}{2} \ln(2\pi N) - \ln(\pi N)$$

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx N \ln(2) + \frac{1}{2} \ln(2\pi N) - \ln(\pi N)$$

$$\ln A^{B} = B \ln A$$

$$\ln \Omega \left( N_{\uparrow} = N_{\downarrow} = \frac{N}{2} \right) \approx \ln(2^{N}) + \ln(\sqrt{2\pi N}) + \ln\left(\frac{1}{\pi N}\right)$$

Now exponentiate to get back to multiplicity.

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) = e^{\ln\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right)}$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx e^{\ln(2^{N}) + \ln(\sqrt{2\pi N}) + \ln\left(\frac{1}{\pi N}\right)}$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx e^{\ln(2^{N})} e^{\ln(\sqrt{2\pi N})} e^{\ln\left(\frac{1}{\pi N}\right)}$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx 2^{N} \sqrt{2\pi N} \left(\frac{1}{\pi N}\right)$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx 2^{N} \sqrt{2\pi N} \left(\frac{1}{\pi N}\right)$$

\*More direct method:

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx \frac{N^{N} e^{-N} \sqrt{2\pi N}}{\left[\left(\frac{N}{2}\right)^{\frac{N}{2}} e^{-\frac{N}{2}} \sqrt{\pi N}\right]^{2}}$$

Square denominator.

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx \frac{N^{N} e^{-N} \sqrt{2\pi N}}{\left(\frac{N}{2}\right)^{N} e^{-N} \pi N}$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx \frac{N^{N} \sqrt{2\pi N}}{\left(\frac{N}{2}\right)^{N} \pi N}$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx \frac{\sqrt{2\pi N}}{\left(\frac{1}{2}\right)^{N} \pi N}$$

$$\Omega\left(N_{\uparrow} = N_{\downarrow} = \frac{N}{2}\right) \approx 2^{N} \sqrt{\frac{2}{N\pi}}$$

The same as above.

- 4) This is a continuation of problem 3). Follow the steps to derive a formula for the multiplicity function in the vicinity of the peak, in terms of  $x \equiv N_{\uparrow} (N/2)$ .
  - a) First show that the multiplicity can be written as shown.

$$\Omega(N_{\uparrow}) \approx \frac{N^{N}}{\left( \left( N/_{2} \right)^{2} - x^{2} \right)^{N/_{2}} \left( N/_{2} + x \right)^{x} \left( N/_{2} - x \right)^{-x}} \sqrt{\frac{N}{2\pi \left[ \left( N/_{2} \right)^{2} - x^{2} \right]}}$$

Use a similar method as in a).

$$\Omega(N_{\uparrow}) = \frac{N!}{N_{\uparrow}! \, N_{\downarrow}!}$$

Use Stirling's Approximation to rewrite the factorials.  $x! \approx x^x e^{-x} \sqrt{2\pi x}$ 

$$\Omega(N_{\uparrow}) \approx \frac{N^{N} e^{-N} \sqrt{2\pi N}}{\left[N_{\uparrow}^{N_{\uparrow}} e^{-N_{\uparrow}} \sqrt{2\pi N_{\uparrow}}\right] \times \left[N_{\downarrow}^{N_{\downarrow}} e^{-N_{\downarrow}} \sqrt{2\pi N_{\downarrow}}\right]}$$

Cancel one factor of  $\sqrt{2\pi}$  and combine terms on the bottom.

$$\Omega(N_{\uparrow}) \approx \frac{N^N e^{-N} \sqrt{N}}{{N_{\uparrow}}^{N_{\uparrow}} {N_{\downarrow}}^{N_{\downarrow}} e^{-(N_{\uparrow} + N_{\downarrow})} \sqrt{2\pi N_{\downarrow} N_{\uparrow}}}$$

Note  $N=N_{\uparrow}+N_{\downarrow}$ , and so the exponential terms also cancel.

$$\Omega(N_{\uparrow}) \approx \frac{N^{N} \sqrt{N}}{N_{\uparrow}^{N_{\uparrow}} N_{\downarrow}^{N_{\downarrow}} \sqrt{2\pi N_{\downarrow} N_{\uparrow}}}$$

Now bring in the definition of x to replace  $N_{\uparrow}$  and  $N_{\downarrow}$ .

$$x \equiv N_{\uparrow} - N_{/2}$$

$$N_{\uparrow} = N_{/2} + x$$

$$N = N_{\uparrow} + N_{\downarrow} \rightarrow N_{\uparrow} = N - N_{\downarrow}$$

$$N - N_{\downarrow} = x + N_{/2}$$

$$N_{\downarrow} = N_{/2} - x$$

$$\Omega(N_{\uparrow}) \approx \frac{N^{N} \sqrt{N}}{\left(N_{/2} + x\right)^{N_{/2} + x} \left(N_{/2} - x\right)^{N_{/2} - x} \sqrt{2\pi(N_{/2} - x)(N_{/2} + x)}}$$

Separate out the x in the exponents.

$$\Omega(N_{\uparrow}) \approx \frac{N^{N}\sqrt{N}}{\left(N_{/2} + x\right)^{N/2}\left(N_{/2} - x\right)^{N/2}\left(N_{/2} + x\right)^{x}\left(N_{/2} - x\right)^{-x}\sqrt{2\pi\left[\left(N_{/2}\right)^{2} - x^{2}\right]}}$$

$$\Omega(N_{\uparrow}) \approx \frac{N^{N}\sqrt{N}}{\left[\left(N_{/2} + x\right)\left(N_{/2} - x\right)\right]^{N/2}\left(N_{/2} + x\right)^{x}\left(N_{/2} - x\right)^{-x}\sqrt{2\pi\left[\left(N_{/2}\right)^{2} - x^{2}\right]}}$$

$$\Omega(N_{\uparrow}) \approx \frac{N^{N}}{\left(\left(N_{/2}\right)^{2} - x^{2}\right)^{N/2}\left(N_{/2} + x\right)^{x}\left(N_{/2} - x\right)^{-x}}\sqrt{\frac{N}{2\pi\left[\left(N_{/2}\right)^{2} - x^{2}\right]}}$$

b) To deal with these numbers, take the natural log of the multiplicity. Show the following.

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - \frac{N}{2} \ln \left[ \binom{N}{2}^2 - x^2 \right] - x \ln \left[ \binom{N}{2} + x \right] + x \ln \left[ \binom{N}{2} - x \right] + \frac{1}{2} \ln \left( \frac{N}{2\pi} \right) - \frac{1}{2} \ln \left( \binom{N}{2}^2 - x^2 \right)$$

$$\ln \Omega(N_{\uparrow}) \approx \ln \left( \frac{N^{N}}{\left( \left( \frac{N}{2} \right)^{2} - x^{2} \right)^{N/2} \left( \frac{N}{2} + x \right)^{x} \left( \frac{N}{2} - x \right)^{-x}} \sqrt{\frac{N}{2\pi \left[ \left( \frac{N}{2} \right)^{2} - x^{2} \right]}} \right)$$

Use log properties to rewrite this.

$$\ln A \times B = \ln A + \ln B$$

$$\ln \Omega(N_{\uparrow}) \approx \ln \left( \frac{N^{N}}{\left( \left( \frac{N}{2} \right)^{2} - x^{2} \right)^{N/2} \left( \frac{N}{2} + x \right)^{x} \left( \frac{N}{2} - x \right)^{-x}} \right) + \ln \left( \sqrt{\frac{N}{2\pi \left[ \left( \frac{N}{2} \right)^{2} - x^{2} \right]}} \right)$$

$$\ln A/B = \ln A - \ln B$$

$$\ln \Omega(N_{\uparrow}) \approx \ln(N^{N}) - \ln \left[ \left( (N/_{2})^{2} - x^{2} \right)^{N/_{2}} (N/_{2} + x)^{x} (N/_{2} - x)^{-x} \right] + \ln(\sqrt{N})$$
$$- \ln \left( \sqrt{2\pi \left[ (N/_{2})^{2} - x^{2} \right]} \right)$$

$$\ln A \times B = \ln A + \ln B$$

$$\begin{split} \ln \Omega(N_{\uparrow}) &\approx \ln(N^{N}) - \ln \left[ \left( \binom{N}{2}^{2} - x^{2} \right)^{N/2} \right] - \ln \left[ \binom{N}{2} + x \right]^{x} - \ln \left[ \binom{N}{2} - x \right]^{-x} + \ln \left( \sqrt{N} \right) \\ &- \ln \left( \sqrt{2\pi \left[ \binom{N}{2}^{2} - x^{2} \right]} \right) \end{split}$$

$$\ln A^B = B \ln A$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - \frac{N}{2} \ln \left[ \left( \binom{N}{2}^2 - x^2 \right) \right] - x \ln \left[ \binom{N}{2} + x \right] + x \ln \left[ \binom{N}{2} - x \right] + \frac{1}{2} \ln(N) - \frac{1}{2} \ln \left( 2\pi \left[ \binom{N}{2}^2 - x^2 \right] \right)$$

$$\ln A \times B = \ln A + \ln B$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - \frac{N}{2} \ln \left[ \left( \binom{N}{2}^2 - x^2 \right) \right] - x \ln \left[ \binom{N}{2} + x \right] + x \ln \left[ \binom{N}{2} - x \right] + \frac{1}{2} \ln(N) - \frac{1}{2} \ln \left( 2\pi \left[ \binom{N}{2}^2 - x^2 \right] \right)$$

$$\ln A \times B = \ln A + \ln B$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - \frac{N}{2} \ln \left[ \left( \binom{N}{2}^2 - x^2 \right) \right] - x \ln \left[ \binom{N}{2} + x \right] + x \ln \left[ \binom{N}{2} - x \right] + \frac{1}{2} \ln(N) - \frac{1}{2} \ln(2\pi) - \frac{1}{2} \ln \left( \binom{N}{2}^2 - x^2 \right)$$

$$\ln A - \ln B = \ln^A/_B$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - \frac{N}{2} \ln \left[ \left( \frac{N}{2} \right)^{2} - x^{2} \right] - x \ln \left[ \left( \frac{N}{2} + x \right) \right] + x \ln \left[ \left( \frac{N}{2} - x \right) \right] + \frac{1}{2} \ln \left( \frac{N}{2\pi} \right) - \frac{1}{2} \ln \left( \left( \frac{N}{2} \right)^{2} - x^{2} \right)$$

c) In the vicinity of the peak,  $N \gg x$ . Use this fact to rewrite some of the terms in the multiplicity. Show the following.

$$\ln\left[\binom{N}{2}^2 - x^2\right] \approx 2\ln\left[\frac{N}{2}\right] - \left(\frac{2x}{N}\right)^2$$

$$\ln\left[\frac{N}{2} \pm x\right] \approx \ln\left[\frac{N}{2}\right] \pm \frac{2x}{N}$$

$$\ln\left[\binom{N}{2}^2 - x^2\right] = \ln\left[\binom{N}{2}^2 \left(1 - \left(\frac{2x}{N}\right)^2\right)\right]$$

$$\ln A \times B = \ln A + \ln B$$

$$\ln\left[\binom{N}{2}^2 - x^2\right] = \ln\left[\binom{N}{2}^2\right] + \ln\left[1 - \left(\frac{2x}{N}\right)^2\right]$$

In the vicinity of the peak,  $N \gg x$ , so  $\left(\frac{2x}{N}\right)^2 \ll 1$ . Use this fact and  $\ln(1+y) \approx y$  for  $y \ll 1$ .

$$\ln\left[\binom{N/2}{2}^2 - x^2\right] \approx \ln\left[\binom{N/2}{2}^2\right] - \left(\frac{2x}{N}\right)^2$$

$$\ln A^B = B \ln A$$

$$\ln\left[\left(\frac{N}{2}\right)^2 - x^2\right] \approx 2\ln\left[\frac{N}{2}\right] - \left(\frac{2x}{N}\right)^2$$

Use the same method for the similar terms.

$$\ln[N/2 \pm x] = \ln\left[N/2\left(1 \pm \frac{2x}{N}\right)\right]$$
$$\ln A \times B = \ln A + \ln B$$

$$\ln[N/2 \pm x] = \ln[N/2] + \ln[(1 \pm \frac{2x}{N})]$$

In the vicinity of the peak,  $N \gg x$ , so  $\frac{2x}{N} \ll 1$ . Use this fact and  $\ln(1+y) \approx y$  for  $y \ll 1$ .

$$\ln[N/2 \pm x] \approx \ln[N/2] \pm \frac{2x}{N}$$

d) Plug the approximations from c) into the multiplicity term from b) and get an expression for the multiplicity. Check that your formula agrees with your answer to problem 3) when x = 0.

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - \frac{N}{2} \left( 2 \ln \left[ \frac{N}{2} \right] - \left( \frac{2x}{N} \right)^{2} \right) - x \left[ \ln \left[ \frac{N}{2} \right] + \frac{2x}{N} \right] + x \left[ \ln \left[ \frac{N}{2} \right] - \frac{2x}{N} \right] + \frac{1}{2} \ln \left( \frac{N}{2\pi} \right) - \frac{1}{2} \left( 2 \ln \left[ \frac{N}{2} \right] - \left( \frac{2x}{N} \right)^{2} \right)$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - N \ln \left[\frac{N}{2}\right] + \frac{N}{2} \left(\frac{2x}{N}\right)^{2} - x \ln \left[\frac{N}{2}\right] - \frac{2x^{2}}{N} + x \ln \left[\frac{N}{2}\right] - \frac{2x^{2}}{N} + \frac{1}{2} \ln \left(\frac{N}{2\pi}\right) - \ln \left[\frac{N}{2}\right] + \frac{2x^{2}}{N^{2}}$$

The  $x \ln[N/2]$  terms cancel. Multiply the  $\frac{N}{2}$  term.

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - N \ln \left[ \frac{N}{2} \right] + \frac{2x^2}{N} - \frac{2x^2}{N} - \frac{2x^2}{N} + \frac{1}{2} \ln \left( \frac{N}{2\pi} \right) - \ln \left[ \frac{N}{2} \right] + \frac{2x^2}{N^2}$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln N - N \ln \left[ \frac{N}{2} \right] - \frac{2x^2}{N} + \frac{1}{2} \ln \left( \frac{N}{2\pi} \right) - \ln \left[ \frac{N}{2} \right] + \frac{2x^2}{N^2}$$

Combine the terms with an N in front.

$$\ln A - \ln B = \ln^A/B$$

$$\ln \Omega(N_\uparrow) \approx N \ln \left[\frac{N}{N/2}\right] - \frac{2x^2}{N} + \frac{1}{2} \ln \left(\frac{N}{2\pi}\right) - \ln \left[\frac{N}{2}\right] + \frac{2x^2}{N^2}$$

$$\ln \Omega(N_\uparrow) \approx N \ln 2 - \frac{2x^2}{N} + \frac{1}{2} \ln \left(\frac{N}{2\pi}\right) - \ln \left[\frac{N}{2}\right] + \frac{2x^2}{N^2}$$

Get rid of the leading 1/2, and combine the last two log terms.

$$B \ln A = \ln A^{B}$$

$$\ln A - \ln B = \ln \frac{A}{R}$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln 2 - \frac{2x^2}{N} + \ln \left( \sqrt{\frac{N}{2\pi}} \right) - \ln \left[ \frac{N}{2} \right] + \frac{2x^2}{N^2}$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln 2 - \frac{2x^2}{N} + \ln \left( \frac{\sqrt{\frac{N}{2\pi}}}{N/2} \right) + \frac{2x^2}{N^2}$$

$$\ln \Omega(N_{\uparrow}) \approx N \ln 2 - \frac{2x^2}{N} + \ln \sqrt{\frac{2}{N\pi}} + \frac{2x^2}{N^2}$$

In the vicinity of the peak,  $N \gg x$ , so the N<sup>2</sup> in the denominator means last term is much smaller than the others. Ignore it.

$$\ln \Omega(N_{\uparrow}) \approx N \ln 2 + \ln \sqrt{\frac{2}{N\pi}} - \frac{2x^2}{N}$$

$$B \ln A = \ln A^B$$

$$\ln \Omega(N_{\uparrow}) \approx \ln 2^{N} + \ln \sqrt{\frac{2}{N\pi}} - \frac{2x^{2}}{N}$$

Exponentiate to get back to the multiplicity.

$$\Omega(N_{\uparrow}) = e^{\ln \Omega(N_{\uparrow})}$$

$$\Omega(N_{\uparrow}) \approx e^{\ln 2^{N} + \ln \sqrt{\frac{2}{N\pi}} - \frac{2x^{2}}{N}}$$

$$\Omega(N_{\uparrow}) \approx e^{\ln 2^{N}} e^{\ln \sqrt{\frac{2}{N\pi}}} e^{-\frac{2x^{2}}{N}}$$

$$\Omega(N_{\uparrow}) \approx 2^{N} \sqrt{2\pi N} \left(\frac{1}{\pi N}\right)$$

$$\Omega(N_{\uparrow}) \approx 2^{N} \sqrt{\frac{2}{N\pi}} e^{-\frac{2x^{2}}{N}}$$

Check x = 0.

$$\Omega(N_{\uparrow}) \approx 2^N \sqrt{\frac{2}{N\pi}} e^{-0}$$

$$\Omega(N_{\uparrow}) \approx 2^N \sqrt{\frac{2}{N\pi}}$$

This is the answer from problem 3) for the peak height of the multiplicity function.

e) What is the half-width half-max of the multiplicity function from b)? (That is, at what value of x will it reach ½ its maximum value?)

The maximum value is at x = 0. (This is the result from a).)

$$\Omega\left(N_{\uparrow}=N_{\downarrow}=\frac{N}{2}\right)\approx 2^{N}\sqrt{\frac{2}{N\pi}}$$

Thus, the value is half of this when the exponential term equals ½.

$$e^{-\frac{2x^2}{N}} = \frac{1}{2}$$

Solve for x.

$$-\frac{2x^2}{N} = \ln\frac{1}{2}$$

$$-\ln A = \ln A^{-1}$$

$$-\frac{2x^2}{N} = -\ln 2$$

$$x^2 = \frac{N}{2} \ln 2$$

$$x = \sqrt{\frac{N}{2} \ln 2}$$

- 5) The mathematics of the previous problems can also be applied to a one-dimensional random walk a journey consisting of N steps, all the same size, each chosen randomly to be either forward or backward.
  - a) Where are you most likely to find yourself after the end of a very long random walk? (Did you assume N was even? If so, what happens if N is odd?)

Treat this like the other two-state problems. The total number of steps is the number of steps backward plus the number of steps forward.

$$N = N_{\leftarrow} + N_{\rightarrow}$$

Let the starting place is position 0. Let position be x.

$$x = N_{\perp} - N_{\perp}$$

From problem 3), the peak of the probability function, and thus the most probable outcome is when the total *N* is split between the two states.

$$N_{\rightarrow} = N_{\leftarrow} = N/2$$

In this most probable state, calculate the position.

$$x = N_{\rightarrow} - N_{\leftarrow} = N/2 - N/2$$
$$x = 0$$

The most likely ending location is the starting location if N is even. But what if N isn't even? The probability would be that x = 0 for N-1 steps, and then the most probable location would be the result of the next step: either one step forward or one step backward from the starting place.

b) Suppose you take a random walk of 10,000 steps. Roughly what is the half-width half-max (in steps) of the multiplicity function of possible ending positions for your random journey? This gives you an idea of where you can expect to end up. (Follow Schroeder's advice and ignore the weird unit problem.)

Use the result from 4e) for the half-width half-max of a two-state system.

$$x = \sqrt{\frac{N}{2} \ln 2}$$

$$x = \sqrt{\frac{10,000}{2} \ln 2}$$

$$x \approx 59 steps$$

6) A good example of a random walk in nature is the diffusion of a molecule through a gas. The average step length is then referred to as the mean free path (I), given by Schroeder in Equation 1.62:

$$l = \frac{1}{4\pi r^2} \frac{V}{N}$$

(where r is the radius of the molecule in question). Assume this model is correct, and treat the situation as one-dimensional, neglecting any small numerical factors that might arise from the varying step size and the multi-dimensional nature of the path. Assume the gas is a diatomic ideal gas.

a) Volume *V* and number of molecules *N* are sometimes tough to estimate in an open area. Find the mean free path in terms of the molecular radius *r*, the temperature *T*, and the pressure *P*.

$$l = \frac{1}{4\pi r^2} \frac{V}{N}$$

Use the ideal gas law.

$$l = \frac{1}{4\pi r^2} \frac{kT}{P}$$

b) Estimate the average speed of a gas molecule in terms of temperature T, number of degrees of freedom f, and molecular mass m.

Use the equipartition theorem to find the energy per molecule.

$$\frac{U}{N} = \frac{f}{2}kT$$

Energy per molecule is also given by the usual kinetic energy expression. The overbar indicates an average.

$$\frac{U}{N} = \frac{1}{2}m\overline{v^2}$$

Set the two equations equal to one another, and solve for the square root of the average velocity squared.

$$\frac{U}{N} = \frac{f}{2}kT = \frac{1}{2}m\overline{v^2}$$

$$\frac{fkT}{m} = \overline{v^2}$$

$$\sqrt{\overline{v^2}} = \sqrt{\frac{fkT}{m}}$$

c) Find the average time between collisions t<sub>avg</sub> in terms of f, k, T, m, r, and P.

The average time between collisions is the mean path length divided by the average speed.

$$t_{avg} = \frac{l}{\sqrt{\overline{v^2}}}$$

$$t_{avg} = \frac{\frac{1}{4\pi r^2} \frac{kT}{P}}{\sqrt{\frac{fkT}{m}}}$$

$$t_{avg} = \frac{1}{4\pi r^2} \frac{1}{P} \sqrt{\frac{mkT}{f}}$$

d) Show that the following expression is a (half-width half-max) estimate of the expected net displacement D of an air molecule traveling through air in a time  $\Delta t$ .

$$D = \frac{1}{r} \sqrt{\frac{\Delta t \ln 2}{8\pi P}} \left(\frac{f}{m}\right)^{1/4} k^{3/4} T^{3/4}$$

The half-width half-max net displacement is given by the half-width half-max of the net number of steps  $N_{1/2}$  multiplied by the length per step (mean free path). Use the half-width half-max expression from part b) of the previous problem.

$$D = N_{1/2}l$$

$$D = \sqrt{\frac{N}{2} \ln 2 l}$$

The number of steps is given by the total time divided by the average time per step.

$$N = \frac{\Delta t}{t_{avg}}$$

$$D = \sqrt{\frac{\Delta t}{2t_{avg}} \ln 2 l}$$

Note: It is easier to plug in the first expression for tavg.

$$D = \sqrt{\frac{\Delta t}{2 l / \sqrt{\overline{v^2}}} \ln 2 l}$$

$$D = \sqrt{\frac{\Delta t \sqrt{\overline{v^2}}}{2l}} \ln 2 l$$

$$D = \sqrt{\frac{l\Delta t\sqrt{\overline{v^2}}}{2}\ln 2}$$

$$D = \sqrt{\frac{\left(\frac{1}{4\pi r^2} \frac{kT}{P}\right) \Delta t \sqrt{\frac{fkT}{m}}}{2} \ln 2}$$

$$D = \sqrt{\frac{\left(\frac{1}{4\pi r^2} \frac{k^{3/2} T^{3/2}}{P}\right) \Delta t \sqrt{\frac{f}{m}}}{2} \ln 2}$$

$$D = \frac{1}{r} \sqrt{\frac{\Delta t \ln 2}{8\pi P}} \left(\frac{f}{m}\right)^{1/4} k^{3/4} T^{3/4}$$

e) Assume T = 298 K and atmospheric pressure. Assume an air molecule has  $r \approx 1.5 \times 10^{-10} \ m$  and  $m = 46 \times 10^{-27} \ kg$ . Let the total time be one second. Find a numerical answer for the expression in d).

Plug in the values. f= 5 for a diatomic gas.

$$D \approx \frac{1}{1.5 \times 10^{-10} \, m} \sqrt{\frac{1 \, s \times \ln 2}{8\pi \times 1 \, atm}} \left(\frac{5}{46 \times 10^{-27} \, kg}\right)^{1/4} \left(1.3 \times 10^{-23} \, J/_K\right)^{3/4} (298 \, K)^{3/4}$$

$$D \approx .006 \, m = 0.6 \, cm$$

- 7) A coin is flipped 400 times. Find the probability (as a percentage) of getting 215 heads in these 400 flips. Use the following two methods:
  - a) Use Stirling's approximation for the factorials in the equation for  $\Omega(n)$ . Hint: The  $\sqrt{2\pi N}$  term cannot be neglected here.

The probability of getting the macrostate of 215 heads in 400 flips is given by the number of microstates in that macrostate divided by the number of overall microstates.

$$\Omega(N = 400, N_H = 215) = \frac{N!}{N_H! (N - N_H)!}$$

$$\Omega(N = 400, N_H = 215) = \frac{400!}{215! (400 - 215)!}$$

$$\Omega(N = 400, N_H = 215) = \frac{400!}{215! 185!}$$

The total number of microstates is the product of the number of microstates for each coin (2).

$$\Omega_{all} = 2 \times 2 \times 2 \times ... = 2^{400}$$

$$Prob(N = 400, N_H = 215) = \frac{\Omega(N = 400, N_H = 215)}{\Omega_{all}}$$

$$Prob(N = 400, N_H = 215) = \frac{400!}{215! \cdot 185!}$$

Use the technique of taking the log and manipulating. (Later exponentiate to return to probability.)

$$\ln[\text{Prob}(N = 400, N_H = 215)] = \ln\left(\frac{\frac{400!}{215! \, 185!}}{2^{400}}\right)$$

Use log properties.

$$\ln A/_B = \ln A - \ln B$$

$$\ln A \times B = \ln A + \ln B$$

$$\ln[\text{Prob}(N = 400, N_H = 215)] = \ln(400!) - \ln(215!) - \ln(185!) - \ln(2^{400})$$

$$\ln A^B = B \ln A$$

$$\ln[\text{Prob}(N = 400, N_H = 215)] = \ln(400!) - \ln(215!) - \ln(185!) - 400\ln(2)$$

Use Stirling Approximation.  $x! \approx x^x e^{-x} \sqrt{2\pi x}$  (Note the following equation takes up multiple lines.)

$$\begin{split} \ln[\operatorname{Prob}(N=400,N_H=215)] \\ &\approx 400\ln(400) - 400 + \frac{1}{2}\ln(2\pi\times400) - \left[215\ln(215) - 215 + \frac{1}{2}\ln(2\pi\times215)\right] \\ &- \left[185\ln(215) - 185 + \frac{1}{2}\ln(2\pi\times185)\right] - 400\ln2 \end{split}$$

$$\ln[\text{Prob}(N=400,N_H=215)]\approx 2000.5-943.291-784.295-277.259$$

$$ln[Prob(N = 400, N_H = 215)] \approx -4.3447$$

Exponentiate to get the probability.

$$Prob(N = 400, N_H = 215) \approx e^{-4.3447}$$

$$Prob(N = 400, N_H = 215) \approx 1.3\%$$

b) Approximate the probability distribution for number of heads as a Gaussian distribution. *Hint: Use the result from 4d*).

The probability is the multiplicity of the macrostate of interest (215 heads) divided by the total multiplicity. The total multiplicity is just the number of possible states for each coin (2) raised to the power of the number of coins (N = 400) because the flips are independent.

From 4d), we have expression for the multiplicity that is a Gaussian distribution.

$$\Omega(N,x) \approx 2^N \sqrt{\frac{2}{N\pi}} e^{-\frac{2x^2}{N}}$$

x here is defined to be the difference from the most probable macrostate, N/2. For the current problem, N = 400, and x = 215 - 400 / 2 = 15.

$$Prob(N = 400, N_H = 215) = \frac{\Omega(N = 400, x = 15)}{\Omega_{all}}$$

$$Prob(N = 400, N_H = 215) \approx \frac{2^{400} \sqrt{\frac{2}{400\pi}} e^{-\frac{2(15)^2}{400}}}{2^{400}}$$

$$Prob(N = 400, N_H = 215) \approx \sqrt{\frac{2}{400\pi}} e^{-\frac{2(15)^2}{400}}$$

$$Prob(N = 400, N_H = 215) \approx \sqrt{\frac{2}{400\pi}} e^{-\frac{2(15)^2}{400}}$$

$$Prob(N = 400, N_H = 215) \approx 1.3\%$$

c) Do you answers match? Hint: They should!

Yes, both are ≈1.3%. Hurray!

- 8) List <u>three</u> main ideas from this homework assignment. For example, you could write a few-sentence explanation of a concept, or list an equation and explain the variables and in what circumstances the equation applies.
  - The goal is for you to review and to reflect on the big picture. Think about what you might want to remember when you look back at this homework before the test. I hope that this will be useful for your studying. I am not looking for anything specific here; you will be graded on effort and completion.