

Homework 8 Solutions – Thermodynamics of Materials

PHYS 324, Spring 2008, Longwood University

Due: March 24th

1. For large values of N the most-probable value is practically identical to the mean value. To show that this is indeed the case, calculate the probability of finding one mole of paramagnetic material with a number of \uparrow states (\hat{n}_\uparrow) which differs by:
 - (a) one part in one billion from the most probable value,
 - (b) one part in one-hundred billion from the most-probable value,
 - (c) one part in one trillion from the most-probable value.

This is very similar to (actually, exactly like) the example we worked in class. One mole of material is $N = 6 \times 10^{23}$ molecules. A necessary condition for equilibrium is that for each molecule being in an \uparrow state is just as probable as being in a \downarrow state. Therefore,

$$n_\uparrow = n_\downarrow = \frac{N}{2} = 5 \times 10^{22}.$$

To determine the probability of finding the system with some differing number of \uparrow molecules from the most-probable number, we have to consider the imbalance parameter and use the Stirling approximation to the binomial distribution:

$$\frac{f_N(j)}{f_{max}} = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} e^{-\frac{j^2}{2N}} = e^{-\frac{j^2}{2N}},$$

where j is found via:

$$j = 2(n_\uparrow - \hat{n}_\uparrow).$$

For (a), $j = 1 \times 10^{14}$ and:

$$\frac{f_N(j)}{f_{max}} = e^{-\frac{j^2}{2N}} = e^{-\frac{(1 \times 10^{14})^2}{12 \times 10^{23}}} = e^{-8333} = 0.$$

For (b), $j = 1 \times 10^{12}$ and:

$$\frac{f_N(j)}{f_{max}} = e^{-\frac{j^2}{2N}} = e^{-\frac{(1 \times 10^{12})^2}{12 \times 10^{23}}} = e^{-0.8333} = 0.435.$$

For (c), $j = 1 \times 10^{11}$ and:

$$\frac{f_N(j)}{f_{max}} = e^{-\frac{j^2}{2N}} = e^{-\frac{(1 \times 10^{11})^2}{12 \times 10^{23}}} = e^{-8.333 \times 10^{-3}} = 0.992.$$

Tab. 1: Microstates for 3 atoms with three values \uparrow , \downarrow and \leftrightarrow .

$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\leftrightarrow$	$\leftrightarrow\uparrow\uparrow$
$\uparrow\uparrow\downarrow$	$\downarrow\downarrow\leftrightarrow$	$\leftrightarrow\downarrow\downarrow$
$\uparrow\downarrow\uparrow$	$\uparrow\downarrow\leftrightarrow$	$\leftrightarrow\uparrow\downarrow$
$\downarrow\uparrow\uparrow$	$\downarrow\uparrow\leftrightarrow$	$\leftrightarrow\downarrow\uparrow$
$\uparrow\downarrow\downarrow$	$\uparrow\leftrightarrow\uparrow$	$\uparrow\leftrightarrow\leftrightarrow$
$\downarrow\uparrow\downarrow$	$\downarrow\leftrightarrow\downarrow$	$\downarrow\leftrightarrow\leftrightarrow$
$\downarrow\downarrow\uparrow$	$\uparrow\leftrightarrow\downarrow$	$\leftrightarrow\leftrightarrow\uparrow$
$\downarrow\downarrow\downarrow$	$\downarrow\leftrightarrow\uparrow$	$\leftrightarrow\leftrightarrow\downarrow$
$\leftrightarrow\uparrow\leftrightarrow$	$\leftrightarrow\downarrow\leftrightarrow$	$\leftrightarrow\leftrightarrow\leftrightarrow$

Tab. 2: Microstates for $N = 3$ grouped by measurable quantity ξ .

$\xi = n_{\uparrow} - n_{\downarrow}$	$\Omega_N(\xi)$	$f_N(\xi)$
+3	1	$\frac{1}{27}$
+2	3	$\frac{3}{27}$
+1	6	$\frac{6}{27}$
0	7	$\frac{7}{27}$
-1	6	$\frac{6}{27}$
-2	3	$\frac{3}{27}$
-3	1	$\frac{1}{27}$

2. Consider a system consisting of N distinguishable atoms which may have one of three values: \uparrow , \downarrow and \leftrightarrow . The measurable quantity is ξ , which equals $n_{\uparrow} - n_{\downarrow}$. The n_{\leftrightarrow} atoms in the \leftrightarrow state do contribute to ξ .
- List all the possible microstates and the corresponding value of ξ for $N = 3$. (Hint: make a table similar to fig. 8.2 in *Intro to Thermophysics*.)
 - Make a table of ξ , $\Omega_N(\xi)$ and $f_N(\xi)$ for $N = 3$. (Hint: make a table similar to fig. 8.3 in *Intro to Thermophysics*.)

For (a), the 27 possible microstates are listed in tab. 1. For (b), see tab. 2. Notice that ξ is calculated using only n_{\uparrow} and n_{\downarrow} , where n_{\leftrightarrow} contributes in as much as it takes up a space that could have otherwise gone to an \uparrow or \downarrow atom. To determine $\Omega_N(\xi)$ just add up all of the microstates that give that value of ξ . The probability of the system being in a microstate described by ξ is equal to number of possible states for that value divided by the number of states in the entire ensemble.

3. Consider a system consisting of N identical but distinguishable harmonic oscillators. Each oscillator has an energy of $(n + \frac{1}{2})hv$. Since energy may be added to the system only in quanta of hv , we may consider the internal energy of the system as:

$$U = \frac{N}{2}hv + qhv$$

where q is the number of quanta of energy in the system.

- List all the possible microstates for $N = 3$ and $q = 2$.
- Repeat for $N = 3$ and $q = 4$.
- Do your results agree with the general result:

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

Tab. 3: Microstates for 3 harmonic oscillators with $2\hbar\nu$ added quanta of energy.

oscillator 1	oscillator 2	oscillator3
$1\hbar\nu$	$1\hbar\nu$	$0\hbar\nu$
$1\hbar\nu$	$0\hbar\nu$	$1\hbar\nu$
$0\hbar\nu$	$1\hbar\nu$	$1\hbar\nu$
$2\hbar\nu$	$0\hbar\nu$	$0\hbar\nu$
$0\hbar\nu$	$2\hbar\nu$	$0\hbar\nu$
$0\hbar\nu$	$0\hbar\nu$	$2\hbar\nu$

Tab. 4: Microstates for 3 harmonic oscillators with $4\hbar\nu$ added quanta of energy.

oscillator 1	oscillator 2	oscillator3
$4\hbar\nu$	$0\hbar\nu$	$0\hbar\nu$
$0\hbar\nu$	$4\hbar\nu$	$0\hbar\nu$
$0\hbar\nu$	$0\hbar\nu$	$4\hbar\nu$
$3\hbar\nu$	$1\hbar\nu$	$0\hbar\nu$
$3\hbar\nu$	$0\hbar\nu$	$1\hbar\nu$
$1\hbar\nu$	$3\hbar\nu$	$0\hbar\nu$
$0\hbar\nu$	$3\hbar\nu$	$1\hbar\nu$
$0\hbar\nu$	$1\hbar\nu$	$3\hbar\nu$
$1\hbar\nu$	$0\hbar\nu$	$3\hbar\nu$
$2\hbar\nu$	$1\hbar\nu$	$1\hbar\nu$
$1\hbar\nu$	$2\hbar\nu$	$1\hbar\nu$
$1\hbar\nu$	$1\hbar\nu$	$2\hbar\nu$
$2\hbar\nu$	$2\hbar\nu$	$0\hbar\nu$
$2\hbar\nu$	$0\hbar\nu$	$2\hbar\nu$
$0\hbar\nu$	$2\hbar\nu$	$2\hbar\nu$

Again, this is very similar to one of the examples worked in class. First, energy can only be added in quanta $\hbar\nu$, and we cannot split up $\hbar\nu$ into fractions. Therefore, each oscillator can only receive whole number values of $\hbar\nu$ and all of the added $\hbar\nu$ must go into the system.

For (a), the possible microstates are listed in tab. 3.

This agrees with the general result:

$$\Omega_N(q) = \frac{(3+2-1)!}{2!(3-1)!} = 6.$$

For (b), the possible microstates are listed in tab. 4.

This agrees with the general result:

$$\Omega_N(q) = \frac{(3+4-1)!}{4!(3-1)!} = 15.$$

- Write a computer program (Matlab, Maple, Maxima, etc.) to calculate the probability of having n_\uparrow spin \uparrow atoms in a system of N spin $\frac{1}{2}$ atoms (either \uparrow or \downarrow). The values N and n should be inputs. The program should calculate the probability three ways: (1) with no approximation, (2) using the Gaussian approximation and (3) using the Stirling approximation. Print the code and turn in with the rest of this assignment. Also, use this program to find the probability for each of the following cases:

- (a) $n_{\uparrow} = 10, N = 20$
 (b) $n_{\uparrow} = 5, N = 20$
 (c) $n_{\uparrow} = 75, N = 200$
 (d) $n_{\uparrow} = 15, N = 200$

I wrote two simple programs, one in Matlab and one in Maxima. The Maxima code is as follows:

```
(%i1) n:2$
(%i2) N:3$
(%i3) bin = bfloat((N!/(n!(N-n)!))*(1/2)^N);
(%i4) gau = bfloat((N!/((N/2)!*(N/2)!))*(1/2)^N*exp(-(2*(n-(N/2))^2)/(N)));
(%i5) sti = bfloat((2/(3.1415*N))^(1/2)*exp(-((2*(n-(N/2)))^2)/(2*N)));
```

The Matlab program is as follows:

```
##
## Script for calculating the probability of having n spin up atoms in a system
## of N spin 1/2 atoms.
##
clear
disp ("This script will calculate the probability of having n spin up atoms
in a system of N spin 1/2 atoms.")
disp ("You must enter a value for n and N.")
##
## Get user input
##
n = input ("n = ");
N = input ("N = ");
##
## Evaluate probability without approximation. Notice I used the command
## "factorial()" instead of !.
##
a = factorial(N);
b = factorial(n);
c = factorial(N-n);
out_binom = (a/(b*c))*(1/2)^N;
disp ("Probability from binomial distribution (no approximation)")
disp (out_binom)
##
## Evaluate probability using Gaussian approximation.
##
d = factorial(N/2);
out_gauss = (a/(d*d))*(1/2)^N*exp(-(2*(n-(N/2))^2)/(N));
disp ("Probability from binomial distribution (Gaussian approximation)")
disp (out_gauss)
##
## Evaluate probability using Stirling approximation.
##
out_stir = (2/(3.1415*N))^(1/2)*exp(-((2*(n-(N/2)))^2)/(2*N));
disp ("Probability from binomial distribution (Stirling approximation)")
disp (out_stir)
```

The results obtained from each code are practically the same. The results are shown in tab. 5.

Tab. 5: Results for no approximation, Gaussian approximation and Stirling approximation for the binomial distribution.

	Binomial	Gaussian	Stirling
$n_{\uparrow} = 10, N = 20$	0.17620	0.17620	0.17842
$n_{\uparrow} = 5, N = 20$	0.014786	0.014463	0.014645
$n_{\uparrow} = 75, N = 200$	1.050756×10^{-4}	1.087781×10^{-4}	1.089158×10^{-4}
$n_{\uparrow} = 15, N = 200$	9.103908×10^{-39}	2.361053×10^{-33}	2.364041×10^{-33}

5. Use whatever means you have available (such as a computer algebra system) and the Stirling approximation to the binomial distribution to plot the following:

- Plot $\frac{f_N(j)}{f_{max}}$ versus $\frac{j}{N}$ for $N = 100, 1,000$ and $10,000$. Use an x -range of $\frac{j}{N} = \pm 0.3$. Comment on the result, specifically addressing the relative widths of the distributions with N .
- Plot $f_N(n)$ versus n for $N = 100, 1,000, 2,000$ and $3,000$. Comment on the result, specifically addressing the heights and relative widths of the distributions with N .

For (a) the distribution is shown in fig. 1. I plotted this distribution using Maxima and the following function (Stirling approximation) for the various values of N :

$$\frac{f_N(j)}{f_{max}} = e^{-\frac{j^2}{2N}}.$$

To get the left-hand-side as a function of $\frac{j}{N}$ i did the following:

$$\frac{f_N(j)}{f_{max}} = e^{-\frac{j^2}{2N}} = e^{-\frac{j^2 N}{2N^2}} = e^{-\frac{\alpha^2 N}{2}},$$

where $\alpha = \frac{j}{N}$.

The Maxima code that I used is as follows:

```
(%i1) f100(a):=exp(-(100*a^2)/2)$
(%i2) f1000(a):=exp(-(1000*a^2)/2)$
(%i3) f10000(a):=exp(-(10000*a^2)/2)$
(%i4) plot2d([f100(a), f1000(a), f10000(a)], [a, -0.3, 0.3]);
```

For (b) the distribution is shown in fig. 2. The Maxima code that I used is as follows:

```
(%i1) f100(n):=(2/(3.1415*100))^(1/2)*exp(-2*(n-100/2)^2/100);
(%i2) f1000(n):=(2/(3.1415*1000))^(1/2)*exp(-2*(n-1000/2)^2/1000);
(%i3) f2000(n):=(2/(3.1415*2000))^(1/2)*exp(-2*(n-2000/2)^2/2000);
(%i4) f3000(n):=(2/(3.1415*3000))^(1/2)*exp(-2*(n-3000/2)^2/3000);
(%i5) plot2d([f100(n), f1000(n), f2000(n), f3000(n)], [n,-50,1700]);
```

Although the widths appear to get larger with increasing N in fig. 2, keep in mind that the relative width is defined as $\frac{\Delta A}{\langle A \rangle}$. We see this more directly in fig. 1.

Fig. 1: Probability of finding a system of N particles with imbalance j normalized for the maximum probability of j . Plotted for $N = 100, 1,000$ and $10,000$.

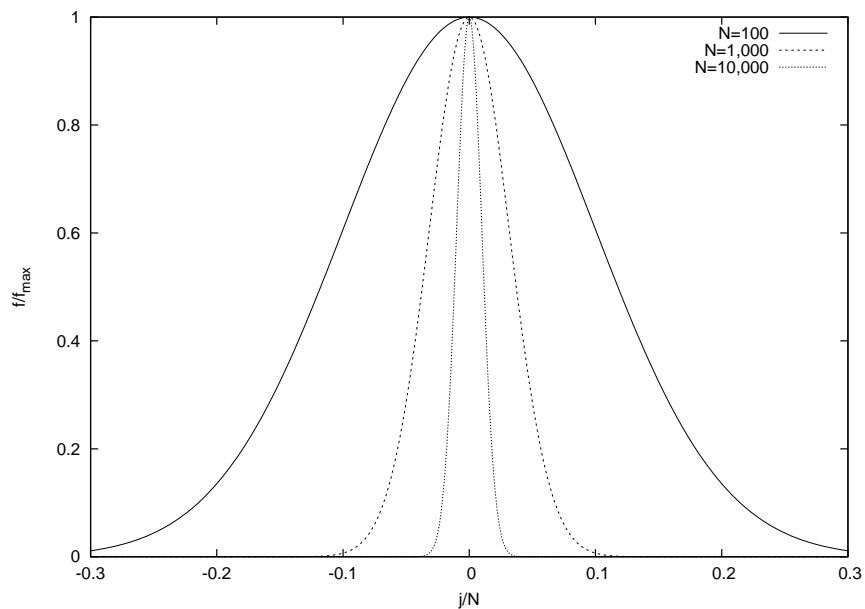


Fig. 2: Probability of finding a system of N particles with $n \uparrow$ atoms as a function of n . Plotted for $N = 100, 1,000, 2,000$ and $3,000$.

