PHYS 328
HOMEWORK #11

Due : Tuesday, 4 Dec. 2012

1. Verify that the chemical potential used in the hemoglogibin example on p. 259 of the text is in fact approximately - 0.6 eV. You will need to review the results of section 6.2 to calculate the value of Z_{int}. State expliclitly all values/approximations you are using.

Solution : We need to determine numerical values for each of the terms in eq. 7.9 from the text :

$$\mu = -kT\ln\left(\frac{V Z_{\text{int}}}{N v_Q}\right)$$

For k we use the known value of the Boltzmann constant; T for the human body is 310 K, the quantum volume, v_Q is given by:

$$v_Q = \left(\frac{h}{\sqrt{2\pi m k T}}\right)^3$$

We know the values of h (Planck' s constant), k (Boltzmann' s constant), T (temperature), and m is the mass of an oxygen molecule (32 times the mass of a proton). Thus, we can easily compute the value of the quantum value. (In question 2 we need to find the temperature dependence of μ; note that the quantum volume appears in the denominator of the ln so contributes a term of ln $T^{3/2}$ to the chemical potential.

We are not given direct information regarding N or V, but we know that oxygen comprises approximately 20% of the atmosphere, so setting the partial pressure of oxygen to 0.2 atm is reasonable. We can use the ideal gas law to obtain an expression for the ratio V/N:

$$PV = NkT \Rightarrow \frac{V}{N} = \frac{kT}{P}$$

Finally, we need to compute Z_{int}. The internal partition function sums over all rotational and vibrational states; as we studied in Chapter 1, the vibrational modes of diatomic molecules are frozen out at room temperatures (and body temp is close enough so we expect the vibrational modes to be frozen out), so Z_{int} is the same as Z_{rot}. Section 6.2 in the text (pp. 234-236) show you how to determine the rotational partition function when $kT \gg \epsilon$ (where ϵ is a constant determined by the moment of inertia of the molecule. For a homonuclear diatomic molecule,

$$Z_{\text{rot}} \approx \frac{kT}{2\epsilon}$$

As a quick aside, we have all the information we need to answer question 2. The V/N term is proportional to T, $1/v_Q$ is proportional to $T^{3/2}$, and Z_{rot} is proportional to T. It is now easy to combine these to determine the dependence of μ on T.

To complete our calculation, we need to look up, determine, or estimate the value of ϵ for O_2. If you look through the book, you will see that ϵ(CO) = 0.00024eV (p. 235 and problem 6.23 on p. 236), so you could assume the that $\epsilon(O_2)$ might not be too different from this. You could try to compute ϵ from basic principles, using the results of section A.4. This section shows that the energy of an allowed rotational level is

$$E_j = \frac{j(j+1)\hbar^2}{2I}$$

where j is the quantum number of the rotational level, $\hbar$ is h/2 π, and I is the moment of inertia of the molecule. Compare this expression with eq. 6.29 and recognize that: given by :

$$\epsilon = \frac{\hbar^2}{2I}$$

The moment of inertia of a diatmoic molecule is given by :

$$I = \mu r_e^2$$

where μ (in this equation) is the reduced mass of the molecule and r_e is the equilibrium distance between the two oxygen atoms. (You may recall from classical mechanics that the reduced mass is:

$$\mu_{\text{reduced mass}} = \frac{m_1 m_2}{m_1 + m_2} \text{ where } m_1,\ m_2 \text{ represent the masses of the atoms.}$$

In the case of O_2, $m_1 = m_2$ so that μ_{O_2} = 8 a.m.u = 8 * mass of a proton. The equilibrium distance for O_2 can be looked up in various references (I used the classic “Spectra of Diatomic Molecules by Herzberg), which lists r_e for the ground state of oxygen as $1.21 * 10^{-10}$m. Combining all these values into a short *Mathematica* program:

```
In[13]:= Clear[h, k, temp, moment, reducedmass, m, mass, mproton, vq, zint, ϵ, p, re]
h = 6.62 × 10^-34; k = 1.38 × 10^-23; temp = 310; mproton = 1.67 × 10^-27;
p = 0.2 × 1.01 × 10^5; re = 1.21 × 10^-10; mass = 32;
vq = (h / Sqrt[2 π (mass mproton) k temp]) ^3;
moment = 8 mproton re^2;
ϵ = (h / (2 π)) ^2 / (2 moment);
zint = k temp / (2 ϵ);
chempotential = - k temp Log[(k temp / p) zint / vq] / (1.6 × 10^-19);
Print["the value of the chemical potential in eV is: = ", chempotential, " eV"]
```

```
the value of the chemical potential in eV is: = -0.583425 eV
```

Which is close enough to -0.6eV for government work.

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2. In eq. 7.10 in the text, identify all terms that have a temperature dependence and then determine the temperature dependence of the chemical potential. Does this dependence make sense given

what you know about chemical potential? Explain your reasoning.

Solution : Using the results of the problem above, and omitting all constants and factors that have no T dependence, we can write :

$$\mu \propto -T \ln\left(T \cdot T \cdot T^{3/2}\right) = -T \ln T^{7/2}$$

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3. Text problem 7.8

Solution : a) We start with the definition of the partition function :

$$Z = \Sigma e^{-\beta E_s}$$

where β = 1/k T and E represents the energy of the s^{th} state; in this case, we are told that s=10 and that E_s = 0 for each of the 10 states. Thus, our partition function is simply:

$$Z = \sum_{s=1}^{10} e^{-\beta(0)} = \sum_{s=1}^{10} 1 = 10$$

b) If there are two distinguishable particles, the total partition function of the system is :

$$Z_{total} = Z_1 \cdot Z_2 = 10 \cdot 10 = 100$$

c) If there are two bosons, we know that we can either zero, one or two bosons in one energy state. There are 10 ways of arranging 2 bosons into ten states (2 bosons in the first state, or 2 bosons in the second state ...). There are 45 ways of arranging 2 bosons into 10 states with only one boson per state (there are 10 choices for the energy state of the first boson, and 9 choices for the second state). Thus, the total number of states available is 55. Since the energy of each state is zero, the partition function is also equal to 55.

d) If there are two fermions, there are no states with two fermions in the same energy level; we can not have more than one fermion per energy level, and as shown in part c), there are 45 ways of arranging two particles in ten levels. Again, since the energy of the states is zero, the partition function equals 45.

e) We have :

$$Z_{total} = \frac{1}{N!} Z_1^N = \frac{1}{2!} 10^2 = 50$$

(midway between the values for fermions and bosons).

f) There are 100 system states for the case two distinguishable particles in 10 states; of these 100 ways, 10 of them (2 particles in level 1, 2 particles in level 2 ...) include both particles in the same state. Therefore, the probability of finding two distinguishable particles in the same single particle state is 10/100 = 1/10.

For bosons, we computed a total of 55 system states, of which 10 have both particles in the same particle state, therefore the probability of finding both particles in the same single particle state is 10/55.

Two fermions can never exist in the same particle state, so the probability of finding two fermions in the same state is zero.

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4. Text problem 7.9

Solution : Not having cleared out our data from question 1 allows us to adjust the values of temperature and molecular mass for this problem and compute simply :

```
mass = 28; temp = 300;
vq = (h / Sqrt[2 π mass mproton k temp]) ^3;
Print["The quantum volume for a nitrogen molecule = ", vq, " m³"]
```

```
The quantum volume for a nitrogen molecule = 6.83899 × 10^-33 m³
```

Boltzmann statistics are valid as long as the volume per molecule, V/N, is much greater than the quantum volume. At room temperature, we know (and you might recall from high school chem) that one mole of a gas at STP occupies a volume of 22.4 L. This is equivalent to a volume of 2.24 10^{-2} m^3, so for an Avogadro number of molecules, we have:

$$\frac{V}{N} = \frac{2.24 \times 10^{-2}\ \mathrm{m}^3}{6.02 \times 10^{23}\ \mathrm{molecules}} \sim 3 \times 10^{-26}\ \mathrm{m}^3 \big/ \mathrm{molecule}$$

This is a tiny number, but still almost 7 orders of magnitude greater than the quantum volume, so the use of Boltzmann statistics clearly holds. To find the temperature at which quantum statistics must be used, we note that the temperature has to decrease to cause the value of the quantum volume to increase by a factor of approximately 5*10^6. Since $v_Q \sim T^{-3/2}$, the temperature would have to decrease by a factor of about 30,000 (since $30,000^{3/2} \sim 5*10^6$). This means the new temperature would be approximately 300K/30,000 ~ 0.01K. This shows that Boltzmann's statistics work fine for the range of temperatures you will almost always encounter ideal gases. Alternately, you could set v_Q to $3 * 10^{-26}$ m^3 and solve for T, but that would be boring.

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5. Text problem 7.11

Solution : For fermions, the Fermi - Dirac distribution tells us the probability of finding a particle in a single particle state :

$$\bar{n}_{\mathrm{FD}} = \frac{1}{e^{(\epsilon-\mu)/kT} + 1}$$

Thus, all calculations will use this expression; we need not know ϵ and μ separately, rather, we only need to know how ϵ compares to μ. I will set x = ϵ - μ, recall that k T at room temperature is approximately 1/40 eV (more accurately it is 0.026 eV so that 1/k T = 38.46) and solve all parts at once using a short Mathematica program :

```
Clear[nfd, x]
nfd = 1 / (Exp[38.46 x] + 1) /. x → {-1.0, -0.01, 0.0, 0.01, 1.0}
```

```
{1., 0.594982, 0.5, 0.405018, 1.98168 × 10^-17}
```

The output statement lists the answers in the order requested by the text, the probability of a single particle state being occupied. Notice that when the energy is less than the chemical potential, the state is likely to be occupied (and certain to be occupied when the energy is much less than the chemical potential). When the energy exceeds the chemical potential, the occupancy number decreases, becoming vanishingly small when the energy is much greater than the potential.

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6. Text problem 7.13

Solution : For this problem, we need to use the Bose - Einstein distribution to find the average occupancy, and recall the definition of probability in quantum statistics to .find the probabilities of 0, 1, 2 or 3 bosons in the single particle state.

First, we find the average occupancy by writing a program (similar to the one used above). Again, we only care about the difference between ϵ and μ, and I will estimate k T at room temperature as 0.026eV (such that 1/ k T = 38.46 eV). Therefore, setting x = ϵ - μ, the argument of the exponential in the Bose - Einstein distribution :

$$\bar{n}_{\mathrm{BE}} = \frac{1}{e^{(\epsilon-\mu)/kT} - 1}$$

can be written as 40 x. The probability of finding exactly n particles in the state is :

$$P(n) = \frac{\text{Gibbs factor}(n)}{\text{Grand Partition function}} = \frac{e^{-n(\epsilon-\mu)/kT}}{1\big/\left(1-e^{-(\epsilon-\mu)/kT}\right)} = \frac{e^{-38.46\,n\,x}}{1\big/\left(1-e^{-38.46\,x}\right)} = \left(e^{-38.46\,x}\right)^n \left(1-e^{-38.46\,x}\right)$$

With these two equations, we can solve for occupancy numbers and probabiilties. In the program below, nbe will be the occupancy number (average number of bosons expected) per state, and prob[n,z] will compute the probability of finding exactly n bosons in a particular single particle state. The first two lines compute and print the occupancy numbers; nbe[z] is the occupancy number for bosons as a function of z, a parameter related to energy. Since we are given four energies to consider at logarithmic intervals, I index z from 0 to 3; the denominator 10^z converts the index of the do loop into the correct energy value.

The last two lines compute and print the probability of finding exactly 0, 1, 2 or 3 bosons in each of the four energy states requested. Notice that I use a double loop to do all 12 calculations with one command.

```
In[27]:= Clear[nbe, z, prob]
         nbe[z_] := 1 / (Exp[38.46 / 10^z] - 1)
         Do[Print["The average expected number of bosons when ϵ-μ = ",
           10^(-z), " eV = ", nbe[z]], {z, 3.0, 0.0, -1}]
         Print["                "]
         prob[n_, z_] := Exp[-38.46 n / 10^ z] (1 - Exp[-38.46 / 10^ z])

         Do[Print[ "If ϵ-μ = ", 1 / 10^z, " eV, then P(", n, ") = ", prob[n, z]],
          {z, 3.0, 0.0, -1}, {n, 0, 3}]
```

```
The average expected number of bosons when ϵ-μ = 0.001 eV = 25.5042
The average expected number of bosons when ϵ-μ = 0.01 eV = 2.13208
The average expected number of bosons when ϵ-μ = 0.1 eV = 0.0218315
The average expected number of bosons when ϵ-μ = 1. eV = 1.98168×10^-17
```

Notice how the expected number of bosons per particle state decreases as ϵ exceeds μ by greater amounts.

Below are the output for the probability of finding n bosons per energy state as a function of (ϵ-μ).

```
If ϵ-μ = 0.001 eV, then P(0) = 0.0377298
If ϵ-μ = 0.001 eV, then P(1) = 0.0363063
If ϵ-μ = 0.001 eV, then P(2) = 0.0349364
If ϵ-μ = 0.001 eV, then P(3) = 0.0336183
If ϵ-μ = 0.01 eV, then P(0) = 0.319277
If ϵ-μ = 0.01 eV, then P(1) = 0.217339
If ϵ-μ = 0.01 eV, then P(2) = 0.147948
If ϵ-μ = 0.01 eV, then P(3) = 0.100711
If ϵ-μ = 0.1 eV, then P(0) = 0.978635
If ϵ-μ = 0.1 eV, then P(1) = 0.0209086
If ϵ-μ = 0.1 eV, then P(2) = 0.000446712
If ϵ-μ = 0.1 eV, then P(3) = 9.54401×10^-6
If ϵ-μ = 1. eV, then P(0) = 1.
If ϵ-μ = 1. eV, then P(1) = 1.98168×10^-17
If ϵ-μ = 1. eV, then P(2) = 3.92707×10^-34
If ϵ-μ = 1. eV, then P(3) = 7.78221×10^-51
```

Notice that the probabilities for (ϵ - μ) = 0.001 eV are all very close to 0.03 so that the sum of P (0) through P (3) is much less than 1. Why does this make sense for this case? (Think about $\overline{n}$ for this energy.) Note also for ϵ-μ = 1 eV, the probability of finding any bosons in that level is exceedingly small at room temperature; the temperature would have to increase significantly to provide sufficient energy to populate this state.

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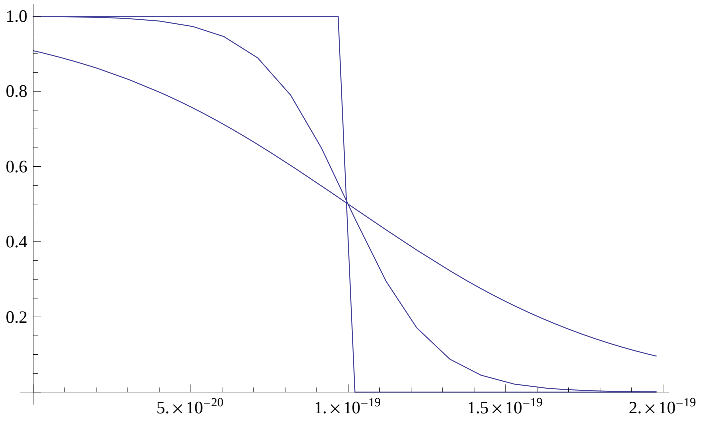
7. Write a short Mathematica program to verify the plot in Fig. 7.6 of the text. Assume that μ is constant (even though it will vary with temp); choose representative values for μ as you let ϵ vary from 0 to values greater than μ. Plot all three graphs (for high, low, and intermediate values of T) on one set of axes. Submit your output and your program with your homework.

Solution : We will use the Fermi - Dirac distribution :

$$\bar{n}_{\mathrm{FD}} = \frac{1}{e^{(\epsilon-\mu)/k\,T}+1}$$

I will set the chemical potential to about 0.6 eV and let ϵ be a free parameter. My program is :

```
Clear[nfd, ϵ, μ, k, p]
k = 1.38 × 10^-23; μ = 10^-19;
nfd = 1 / (Exp[(ϵ - μ) / (10^p k)] + 1);
Plot[nfd /. p → {1, 3, 3.5}, {ϵ, 0, 5 × 10^-19}, PlotRange → All]
```



Notice that I write the temperature as 10^p and vary the value of p. I use the *Mathematica* “slash-dot” command to allow me to print out three separate values of temperature on the same graph. When p=1, the temperature is: 10^1 = 10 K; p=3 ⇒ T =1000 K and p=3.5 ⇒ T=3160K. Notice that all three curves intersect at an occupancy of 0.5 when $\epsilon = \mu$.