

**Department of Physics  
University of Maryland  
College Park, MD 20742-4111**

**Physics 603**

**HOMEWORK ASSIGNMENT #6**

Spring 2012

Due date for problems on Thursday, April 5 [deadline on April 10].

1. Statistics of deuterium.

- a) Discuss the wave functions needed to describe molecules of ortho-deuterium (o-D<sub>2</sub>) and para-deuterium (p-D<sub>2</sub>).
- b) Write down the partition functions for a system of N molecules of i) o-D<sub>2</sub>, ii) p-D<sub>2</sub>, iii) equilibrium D<sub>2</sub>, iv) “normal” D<sub>2</sub> (assuming a fraction x of para at high T).
- c) Find expressions for the equilibrium ratios of o-D<sub>2</sub> to p-D<sub>2</sub> at i) very high T and ii) low T.
- d) Use the Euler-MacLaurin approximation to calculate the leading quantal corrections to the behavior of i) o-D<sub>2</sub>) and ii) p-D<sub>2</sub> at high T.

2. PB 6.1 and part of 6.2:

6.1. Show that the entropy of an ideal gas in thermal equilibrium is given by the formula

$$S = k \sum_{\epsilon} [(n_{\epsilon} + 1) \ln(n_{\epsilon} + 1) - n_{\epsilon} \ln(n_{\epsilon})]$$

in the case of *bosons* and by the formula

$$S = k \sum_{\epsilon} [-(1 - n_{\epsilon}) \ln(1 - n_{\epsilon}) - n_{\epsilon} \ln(n_{\epsilon})]$$

in the case of *fermions*. Verify that these results are consistent with the general formula

$$S = -k \sum_{\epsilon} \left\{ \sum_n p_{\epsilon}(n) \ln p_{\epsilon}(n) \right\},$$

where  $p_{\epsilon}(n)$  is the probability that there are exactly  $n$  particles in the energy state  $\epsilon$ .

6.2. For BE and FD statistics show that  $\langle n_{\epsilon}^2 \rangle - \langle n_{\epsilon} \rangle^2 = \langle n_{\epsilon} \rangle \pm \langle n_{\epsilon} \rangle^2$ , respectively. Show then that in

both cases the right-hand side is  $k_B T \left( \frac{\partial \langle n \rangle}{\partial \mu} \right)_T$ .

3. PB 6.32

Derive an expression for the equilibrium constant  $K(T)$  for the reaction  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$  in terms of the ground state energy change  $\Delta \epsilon_0 = 2\epsilon_{\text{NO}} - \epsilon_{\text{N}_2} - \epsilon_{\text{O}_2}$  and the vibrational and rotational partition functions of the diatomic molecules, using results from Section 6.5. Give predictions for the ranges of temperatures where the rotational modes are classically excited but the vibration modes are suppressed and for higher temperatures where both the rotational and vibrational models are classically excited.

4. Old qualifier problem, to follow.

# Problem 4

## 1.3 In honor of the Gibbs sesquicentennial:

Consider a total number of  $N$  noble gas molecules (monatomic) confined in a cubical box of volume  $V$ , area  $A$ , and length  $L$ . The density of the gas can be described by figure 1.

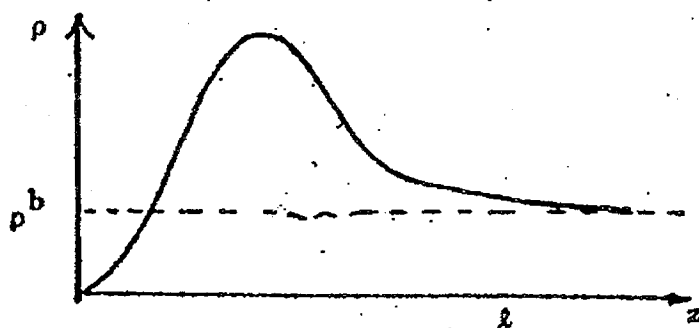


Fig. 1

The gas density  $\rho(z)$  differs from the bulk density  $\rho^b$  only over a distance  $\ell \ll L$  from a wall.

1. What is the physical origin of the peak in  $\rho$ ? On figure 1, indicate roughly an estimate of the radius  $R$  of a gas atom.
2. One can divide the box into bulk and surface regions, as depicted in figure 2, with  $V = V^b + V^s$  and  $V^s$  arbitrarily defined, similarly  $N = N^b + N^s$ . By definition  $N^b = \rho^b V^b$ . Show that if the dotted line is moved,  $\Delta N^s = \rho^b \Delta V^s$ , i.e. independent of the details of figure 1.

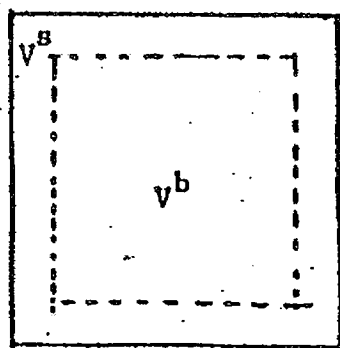


Fig. 2

Suppose there is a surface tension  $\sigma$  such that

$$dU = Tds - pdV + \sigma dA + \mu dN$$

Where  $\mu$  is the chemical potential per atom. Also,  
 $dU = dU^b + dU^s$ ,  $dN = dN^b + dN^s$  etc.

Show that  $dU^s = TdS^s - pdV^s + \mu dN^s + \sigma dA$  for an adiabatic, reversible expansion or contraction that conserves  $N$ .

One can show that the surface portion of the Gibbs potential  $G = U + pV - TS$  satisfies

$$dG^s = -S^s dT + V^s dp + \sigma dA + \mu dN^s.$$

Derive (in the Gibbs convention  $V_g = 0$ ) from this the Maxwell relation

$$\left(\frac{\partial S^s}{\partial N^s}\right)_{T,A} = -\left(\frac{\partial \mu}{\partial T}\right)_\Gamma \text{ where } \Gamma \equiv N^s/A \text{ is the surface gas}$$

density

(Possible Hint: Take a partial of  $dG^s$  with respect to  $N^s$ .)

*Another Qual Problem, not assigned, trivial after class discussion*

- (a) An atom has only one excited state, with excitation energy  $2\Delta$ . Both the ground and excited states are non-degenerate. If the atom is made part of a large system which is in thermal equilibrium, how much will the atom contribute to the total specific heat? (Ignore translational motion of the atom.) Plot your result vs. temperature.
- (b) Instead of an atom, consider a diatomic molecule composed of two atoms whose internal excitation levels are sufficiently high to be neglected. The masses and interatomic binding are, however, such that the spacing of the vibrational energy levels of the molecule is  $2\Delta$ . If this molecule is made part of a large system in thermal equilibrium, how much will it contribute to the total specific heat? (Neglect translational and rotational degrees of freedom). Plot your result vs. temperature.
- (c) Compare the plots in (a) and (b) at low temperature and show that they agree. Why? Also explain why they are different at high temperature.