CH352 Assignment 2. Due: in class in Thursday or at the latest Friday, February 28, 2014.

Prof. David F. Coker

Q1 Ideal gas partition functions and thermodynamic quantities. The energy levels of a particle of mass m in a 1D box of length L_x are $E_{n_x} = n_x^2 h^2/(8mL_x^2)$. Using the fact that the partition function for a particle moving in the x-direction is $q_x = \sum_{n_x} \exp[-\beta E_{n_x}]$, where $\beta = 1/(k_B T)$ and for a large box the energy levels are closely spaced so the sum can be replaced by an integral over a continuous version of the counter n, so that, $q_x = \sum_{n_x} e^{-\beta E_{n_x}} \sim \int_0^\infty dn e^{-\beta E_{n_x}}$.

(i) Compute the partition function for a particle moving in the x-direction.

(ii) Use the fact that the energy levels of a particle moving in a three dimensional box are given by $E_{n_x,n_y,n_z} = E_{n_x} + E_{n_y} + E_{n_z}$ and your result from (i) to obtain an expression for the partition function, q, of a single particle moving in a three dimensional box, giving your final answer in terms of the volume of the box $V = L_x L_y L_z$.

(iii) If particles moving in three dimensions don't interact with one another, as in the case of an ideal gas, the partition function, Q, of N non-interacting, identical particles can be shown to be the product of the partition functions of the individual particles thus, $Q = q^N/N!$ where the $N!$ factor accounts for the different possible ways of labeling the identical particles. Use your result from (ii) to obtain an expression for the N particle partition function of an ideal gas.

(iv) Generalizing the result we found in class we can show that the internal energy of a system of N particles each moving in three dimensions can be obtained from the result

$$U = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} \tag{1}$$

Using this result and your findings from (iii) obtain an expression for the internal energy of an ideal gas.

Q2 Entropy of an ideal gas. In class we showed that

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \tag{2}$$

Use this result to compute the entropy of an ideal gas.

Q3 Chemical potentials in mixtures. Consider a lattice model of a two component mixture. Suppose all lattice sites are occupied by either type A molecules or type B molecules and the system contains N_A molecules of type A and N_B molecules of type B so the total number of lattice sites is $N_A + N_B$.

(i) Compute the entropy of the system.

(ii) Compute the chemical potential of species A expressing your result in terms of N_A and N_B and in terms of the mole fraction $X_A = N_A/(N_A + N_B)$

Q4 Entropy changes are independent of process pathway. Using your result for the entropy of an ideal gas from Q2:

(i) Express $\Delta S_V = S_2(V_2) - S_1(V_1)$, the entropy change upon changing the volume from V_1 tp V_2 at fixed particle number N.

(ii) Express $\Delta S_N = S_2(N_2) - S_1(N_1)$, the entropy change upon changing the particle number from N_1 to N_2, at fixed volume V.

(iii) Write an expression for the entropy change, ΔS, for a two step process $(V_1, N_1) \rightarrow (V_2, N_1) \rightarrow (V_2, N_2)$ in which the volume changes first at fixed particle number then the particle number changes at fixed volume. Be sure to indicate the component entropy change for each step of the process.

(iv) Show that the entropy change, ΔS, above is exactly the same as for the two step process in reverse order: changing the particle number first, then the volume.

Q5 Mechanical equilibrium equalizes density. Consider a volume divided into M equal size cells. The volume contains a movable piston that separates that the left region, A, from the right region, B, so that at any instant the number of cells in the left region, M_A, and the number of cells in the right region, M_B, sum to give the total volume, $M_A + M_B = M$, which is fixed. Suppose the left region contains N_A particles and the right regions contains N_B particles and that once a cell is occupied by a particle it can't be occupied by any others (excluded volume!!). Note that as the piston is moved to the right, expanding M_A, the shrinking size of region B can always be written in terms of M_A as $M_B = M - M_A$ using the constant total volume constraint.

(i) Give general expressions for the multiplicities of states in regions A and B, *i.e.* W_A and W_B respectively and write the total multiplicity $W = W_A W_B$ in terms of M_A alone using the above observation.

(ii) To simplify the above results lets assume that the number of particles in any region, N, is always MUCH less that the number of cells in the volume, M, *i.e.* $N << M$. Your multiplicities in (i) should contain terms like $M!/(M - N)!$. Show that these terms can be simplified under these conditions and approximated as

$$\lim_{N<<M} \frac{M!}{(M-N)!} \sim M^N \tag{3}$$

(iii) Use the result from (ii) to simplify your expression from (i) and obtain an approximate expression for the entropy $S = k_B \ln W$ written in terms of M_A. Find the value of $M_A = M_A^*$ that maximizes S and show that at equilibrium the piston will move to equalize the density of particles on each side.