PROBLEM SET 7

1) **(10 pts)** A closed, thermally isolated container contains 100 moles of argon gas at a pressure of 1 atm and temperature 300 K. Given that argon is a monatomic gas and that the mass of an argon atom is 6.63 X 10^{-26} kg, calculate the following quantities:

   a) The average energy per argon atom in eV.

   b) The single-particle partition function of the gas

   c) The entropy of the gas.

   d) The average chemical potential per atom in eV.

2) **(5 pts) Text Problem 6.10** – the exact partition function is $Z = e^{-\alpha/2}/(1 - e^{-\alpha})$, where $\alpha = hf/\mathrm{k_B T}$, so there is no need to approximate it as suggested in part a), but you can still verify it agrees with the formula given.

3) **(20 pts)** According to the Einstein model, a crystal lattice of N atoms can be treated as a system of 3N *distinguishable* oscillators. At temperature T, the partition function for the lattice can be expressed as $Z = e^{-\alpha/2}/(1 - e^{-\alpha})$ with $\alpha \equiv \mathrm{T_E/T}$, where $\mathrm{T_E}$ is a constant with the dimensions of a temperature.

   a) Determine the internal energy U of the system.

   b) Determine the Helmholtz free energy of the system.

   c) Show that the entropy of the system is given by
   $S = 3\mathrm{Nk_B}[\alpha/(e^{\alpha} - 1) - \ln(1 - e^{-\alpha})]$

d) Show that $S \rightarrow 0$ as $T \rightarrow 0$, and that at very high temperatures, $S \approx 3Nk_B[1 - \ln(\alpha)]$

4) **(25 pts)** The vibrational partition function for N diatomic molecules is given by : $Z_{vib} = 1/(1 - e^{-T_{vib}/T})^N$, where the constant T_{vib} is a characteristic vibrational temperature

a) For a general partition function Z, show that the average energy can be expressed as $\bar{U} = k_B T^2(\partial \ln Z/\partial T)$ *Hint:* Use the definition $\beta \equiv 1/k_B T$, and the relation $\bar{U} = -\partial \ln Z/\partial \beta$,

b) Using the formula for $\bar{U}$ derived in part a), show that the average internal energy for the partition function Z_{vib} is given by: $\bar{U} = Nk_B T_{vib} e^{-T_{vib}/T} \big/ (1 - e^{-T_{vib}/T})$

c) Using the result derived in part b), show that the vibrational specific (per mole) heat capacity is given by: $c_{vib} \equiv C_{vib}/n = R(T_{vib}/T)^2 e^{-T_{vib}/T}/(1 - e^{-T_{vib}/T})^2$

5) **(10 pts)** Calculate the volume heat capacity per mole for a collection of H_2 molecules at temperature T = 2000 K. Note that the heat capacity has translational, rotational, and *vibrational* contributions. At the given temperature, the equipartition theorem can be used for the first two contributions, but for the *vibrational* contribution, one has to use the exact expression derived in problem 4 part c). For H_2 molecules, T_{vib} = 6140 K.

6) **(5 pts) Text Problem 6.25**

7) **(5 pts) Text Problem 6.45**

8) **(10 pts) Text Problem 6.48** – in part a, note that $Z_{rot} = k_B T/(2\epsilon)$ with ε given in problem 6.24. Your numerical result in this part should be close to the value given on p. 405. In part b, recall that the chemical potential

per molecule is just G/N, where G, the Gibbs free energy, is given by G=U-TS+PV.

9) **(10 pts) Text Problem 6.52** – note that in one dimension, there is only one energy per value of n, so the system is non-degenerate. First write E_n in terms of n, then determine Z by approximating the sum over n by an integral over n, as was done for the non-relativistic case. You should find that Z is directly proportional to T.