Home work week 3

1. In the lecture we derived the direction of flow of energy between two compartments using the Clausius principle. Use the same derivation to find the equilibrium conditions, when the wall separating the two compartments is movable, but does not allow heat to flow through (a movable adiabatic wall). At equilibrium, any change in volume of the compartments should not change the total entropy of the combined systems:

$$\left(\frac{\partial S_{AB}}{\partial V_A}\right)_{E_A,N_A,E_B,N_B} = 0 \tag{1}$$

   We know from common sense that at equilibrium the pressures are the same on both sides $p_a = p_B$. Can you use this information to derive an expression for the pressure in terms of a derivative of the entropy?

2. Consider 1,000,000 two-level systems (e.g. 1,000,000 spin-$\frac{1}{2}$ nuclei in a magnetic field), with an energy gap of 3 10^{-20} J between the levels. How many of these system are in the lower energy level and in the upper level at

   (a) 0 K?

   (b) 10 K?

   (c) 100 K?

   (d) 1000 K?

   (e) 10,000 K?

   Assume that these N nuclei are not interacting with one another. $k = 1.3806\ 10^{-23}$ JK^{-1}

3. Write down the partition function for a quantum harmonic oscillator. If you don't recall the solution, check your books, or wikipedia. For this exercise

it suffices, however, to know that the discrete eigenvalues (energies) of the Schrödinger equation are

$$E_i = (i + \frac{1}{2})\hbar\omega \tag{2}$$

and integer i runs from 0 (ground state) to infinity. If the angular frequency $\omega = \sqrt{\frac{k}{m}} = 125\ 10^{12}$ Hz (vibrational frequency of hydrogen molecule, H_2) what is the ratio between the occupation (*i.e.* probability) of the ground state ($i = 0$) and of the first vibrationally excited state ($i = 1$) at

(a) 1 K?

(b) 10 K?

(c) 100 K?

(d) 1,000 K?

(e) 10,000 K?

use that $\hbar = 1.0546\ 10^{-34}$ Js and $k = 1.3806\ 10^{-23}$ JK^{-1}

Next, compute the average energy at these temperatures. What do you notice when you plot the average energies versus temperature?

Hint 1: $e^{abc} = (e^{ab})^c = (e^{ac})^b = (e^{bc})^a$

Hint 2: $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ if $|x| < 1$.

Hint 3: The program Mathematica makes hint 1 & 2 obsolete...