Comment on problem #3. Note that I present the result where lamda was not also expanded as a Taylor series. As discussed in class, one needs to do this to get the correct sign for the correction to the ideal gas pressure.

HW #4 Answers.

1. Show that the probability distribution p_i that maximizes the entropy for die rolls subject to a constant value of the 2^{nd} moment is a gaussian.

$S = -k \sum p_i \ln p_i$

constraints $\sum_{i=1}^{6} p_i = 1$, $\sum_{i=1}^{6} i^2 p_i = \text{const}$

$\frac{\partial S}{\partial p_i} - \alpha - \gamma i^2 = 0 \quad \forall i$ | k has been incorporated into α and γ.

$-1 - \ln p_i - \alpha - \gamma_i^2 = 0$

$\ln p_i = -1 - \alpha - \gamma_i^2 \rightarrow p_i = e^{(-1-\alpha-\gamma_i^2)} = a e^{-\gamma_i^2}$

$a \sum_{i=1}^{6} e^{-\gamma_i^2} = 1 \Rightarrow p_i = \frac{e^{-\gamma_i^2}}{\sum e^{-\gamma_i^2}}$

2.

n	0	1	2	3	4
f_n/f_0	1.0	0.2	0.04	0.008	0.002

$f_n = \frac{e^{-\beta h\nu(n+\frac{1}{2})}}{q}$, $q = \frac{e^{-\beta h\nu/2}}{(1-e^{-\beta h\nu})}$

$f_1/f_0 = e^{-\beta h\nu}$

$f_2/f_0 = e^{-2\beta h\nu}$

$f_3/f_0 = e^{-3\beta h\nu}$

$f_4/f_0 = e^{-4\beta h\nu}$

$e^{-\beta h\nu} = 0.2 \Rightarrow \beta h\nu = \ln 5 = 1.602$

$e^{-2\beta h\nu} = 0.04 \Rightarrow 2\beta h\nu = \ln 25 \Rightarrow \beta h\nu = 1.602$ etc, Since there is a constant ratio between successive population values, the distribution is at thermal distribution.

What is the temperature, if the molecule is N_2?

$$\Theta_v = \frac{h\nu}{k} = 3374\ K$$

$$\beta h\nu = \frac{h\nu}{kT} = 1.602 \Rightarrow T = 2089K$$

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3. Problem 4-9 from McQuarrie

The problem asked one to show that

$pV \geq \langle N \rangle kT$ for fermions and $pV \leq \langle N \rangle kT$ for bosons

$$\beta pV = \pm \sum_j \ln\left[1 \pm \lambda e^{-\beta \epsilon_j}\right]$$

Develop this in a Taylor series keeping the first two terms. [Note the text considers the case where only the leading term is kept.]

$$\ln(1+x) \sim x - \frac{x^2}{2} \ ; \ \ln(1-x) \sim -x - \frac{x^2}{2}$$

fermions: $pV = kT \sum_j \left[\lambda e^{-\beta\epsilon_j} - \frac{1}{2}(\lambda e^{-\beta\epsilon_j})^2 \right]$

$$pV = NkT - \underbrace{\frac{kT}{2} \sum_j \lambda^2 e^{-2\beta\epsilon_j}}_{+\ \text{quantity.}}$$

We have actually shown the opposite of what was stated in the text.

bosons: $pV = kT \sum_j \left[\lambda e^{-\beta\epsilon_j} + \frac{1}{2}(\lambda e^{-\beta\epsilon_j})^2 \right]$

$$pV = NkT + \frac{kT}{2} \sum_j \lambda^2 e^{-2\beta\epsilon_j}$$

Again, this is opposite from what we were asked to prove.

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4. A thermodynamic system with three states has $P_1 = 0.9$, $P_2 = 0.09$, and $P_3 = 0.01$ at $T = 300K$. What are the energies of states 2 and 3 relative to the ground state (1)?

Take the ground state to be the zero of energy

$$P_1 = \frac{1}{1 + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}} = .9 \quad , \; q = 1/.9$$

$$P_2 = 0.09 = .9 e^{-\beta\epsilon_2} \quad , \; P_3 = 0.01 = .9 e^{-\beta\epsilon_3}$$

$$.1 = e^{-\beta\epsilon_2} \quad , \; \beta\epsilon_2 = 2.30$$

$$\epsilon_2 = 2.30\,(300K)(1.38 \times 10^{-23}\,J/K) = 9.52 \times 10^{-21}\,J$$

similarly

$$\epsilon_3 = 4.5\,(300K)(1.38 \times 10^{-23}\,J/K) = 1.86 \times 10^{-20}\,J$$