Problem Set 4: Solutions

1) a)

$$Z = \int_{-\infty}^{\infty} \frac{dp\ dx}{2\pi\hbar} \exp\left(-\frac{p^2}{2\mu kT} - \frac{Kx^2}{2kT} - \frac{bx^4}{kT}\right) \approx \tag{1}$$

$$\approx \int_{-\infty}^{\infty} \frac{dp\ dx}{2\pi\hbar} \exp\left(-(1/2kT)(\frac{p^2}{\mu} + Kx^2)\right)(1 - \frac{bx^4}{kT}) = \tag{2}$$

$$= \frac{kT}{\hbar\omega}(1 - \frac{b < x^4 >}{kT}) \tag{3}$$

where,

$$< x^4 >= (\frac{kT}{K})^2 \int_{-\infty}^{\infty} \frac{dy}{\sqrt{2\pi}} e^{-y^2/2} y^4 = 3(\frac{kT}{K})^2$$

Therefore, $Z = \frac{kT}{\hbar\omega}(1 - \frac{3bkT}{K^2})$.

b)

$$Z = Tr\ \left[e^{-\beta[H_0 + b<x^4>]}\right] = ... = Z_0(1 - \beta b < x^4 >)$$

where,

$$< x^4 >= \frac{\hbar^2}{4K\mu} < (a + a^\dagger)^4 >= \frac{\hbar^2}{4K\mu} < (a^\dagger)^2 a^2 + a^2 (a^\dagger)^2 + aa^\dagger aa^\dagger + a^\dagger aa^\dagger a + aa^\dagger a^\dagger a + a^\dagger aaa^\dagger >$$

using $[a, a^\dagger] = aa^\dagger - a^\dagger a = 1$ and $\hat{n} = a^\dagger a$ we get $(a^\dagger)^2 a^2 = a^\dagger(aa^\dagger - 1)a = \hat{n}^2 - \hat{n}$,

$$a^2(a^\dagger)^2 = a(a^\dagger a + 1)a^\dagger = (a^\dagger a + 1)^2 + (a^\dagger a + 1) = (\hat{n} + 1)^2 + \hat{n} + 1 = \hat{n}^3 + 3\hat{n} + 2$$

and $aa^\dagger aa^\dagger = (\hat{n}+1)^2 = \hat{n}^2 + 2\hat{n} + 1$, $a^\dagger aa^\dagger a = \hat{n}^2$, $aa^\dagger a^\dagger a = (\hat{n}+1)\hat{n} = \hat{n}^2 + \hat{n}$, $a^\dagger aaa^\dagger = \hat{n}(\hat{n}+1) = \hat{n}^2 + \hat{n}$.
Therefore,

$$< x^4 >= \frac{\hbar^2}{4K\mu} < (\hat{n}^2 - \hat{n}) + (\hat{n}^3 + 3\hat{n} + 2) + (\hat{n}^2 + 2\hat{n} + 1) + \hat{n}^2 + \hat{n}^2 + \hat{n} + \hat{n}^2 + \hat{n} >= \tag{4}$$

$$= \frac{\hbar^2}{4K\mu} < 6\hat{n}^2 + 6\hat{n} + 3 >= \frac{3\hbar^2}{4K\mu} < 2\hat{n}^2 + 2\hat{n} + 1 > \tag{5}$$

Now, $< \hat{n} >= \frac{1}{e^{\beta\omega\hbar} - 1}$ and

$$< \hat{n}^2 >= \frac{1}{Z} \sum_{n=0}^{\infty} n^2 e^{-n\beta\hbar\omega} = \tag{6}$$

$$= -\frac{1}{Z} \sum_{n=0}^{\infty} \frac{d}{d(\beta\hbar\omega)} \sum_{n=0}^{\infty} n e^{-n\beta\hbar\omega} = \tag{7}$$

$$= -\frac{d}{d(\beta\hbar\omega)} < \hat{n} > + < \hat{n} >^2 = \tag{8}$$

$$= \frac{e^{\beta\omega\hbar}}{(e^{\beta\omega\hbar} - 1)^2} + \frac{1}{(e^{\beta\omega\hbar} - 1)^2} = \tag{9}$$

$$= \frac{e^{\beta\omega\hbar} + 1}{(e^{\beta\omega\hbar} - 1)^2} \tag{10}$$

therefore,

$$< x^4 >= \frac{3\hbar^2}{4K\mu}\left[\frac{2(e^{\beta\omega\hbar}+1)}{(e^{\beta\omega\hbar}-1)^2}+\frac{2}{e^{\beta\omega\hbar}-1}+1\right]= \tag{11}$$

$$= \frac{3\hbar^2}{4K\mu}\frac{(e^{\beta\omega\hbar}+1)^2}{(e^{\beta\omega\hbar}-1)^2} \tag{12}$$

Finally,

$$Z = \frac{e^{-\frac{\beta\omega\hbar}{2}}}{1-e^{-\beta\omega\hbar}}\left[1-b\beta\frac{3\hbar^2}{4K\mu}\frac{(e^{\beta\omega\hbar}+1)^2}{(e^{\beta\omega\hbar}-1)^2}\right]$$

c) If $\beta\omega\hbar \to 0$ then

$$Z \to \frac{1}{\beta\omega\hbar}\left[1-b\frac{3\beta\hbar^2}{(\beta\omega\hbar)^2K\mu}\right]= \tag{13}$$

$$= \frac{kT}{\omega\hbar}\left[1-\frac{3bkT}{\omega^2K\mu}\right]=\frac{kT}{\omega\hbar}\left[1-\frac{3bkT}{K^2}\right]. \tag{14}$$

This agrees with the classical result, in the high T limit.

2) It depends on the component of $\vec{v}$ directed toward the observer,

$$P(v_x) \propto e^{-\frac{mv_x^2}{2kT}}$$

Because $\frac{\delta\lambda}{\lambda_0}=\frac{v_x}{c}$, we have

$$P(\delta\lambda) \propto e^{-\frac{mc^2}{2kT}\left(\frac{\delta\lambda}{\lambda_0}\right)^2}$$

For $T = 6000$ K,

$$\sqrt{(\delta\lambda)^2}/\lambda_0 = \sqrt{\frac{kT}{mc^2}} = \sqrt{\frac{1.38\ 10^{-23}\ 6000}{1.67\ 10^{-27}\ (3\ 10^8)^2}} = 2.3\ 10^{-5}$$

3) $A_{final} = -kTN\ln\frac{3Z_0+Z_e}{N}+...$, where we include the $-kTN\ln(1/N)$ term arising from $1/N!$ factors in Z....is translational part which does not change.

$$A_{initial} = -\frac{kTN}{4}\ln(\frac{Z_e}{N/4})-kT\frac{3N}{4}\ln(\frac{3Z_0}{3N/4})= \tag{15}$$

$$= \frac{kTN}{4}\ln(\frac{Z_e}{N/4})-3\frac{kTN}{4}\ln(\frac{Z_0}{N/4}) \tag{16}$$

Here we regard the gas as a mixture of $S=0$ and $S=1$ components assuming each $S=1$ molecule can go into any of the 3 spin-states in (15), or we consider a mixture of 4 spin state components (N/4 particles of each type) in (16).

In the second interpretation,

$$Z = \frac{Z_e^{N/4}}{(N/4)!}\left[\frac{Z_0^{N/4}}{(N/4)!}\right]$$

We divide by $(N/4)!$ because 4 groups of $N/4$ particles are indistinguishable but we can distinguish between groups.

$$\frac{\Delta A}{kT} = -N\ln\left(\frac{3Z_0+Z_e}{N}\right) + \frac{N}{4}\ln\left(\frac{Z_e}{N/4}\right) + \frac{3N}{4}\ln\left(\frac{Z_0}{N/4}\right) = -N\ln\left(\frac{(3Z_0+Z_e)/4}{Z_e^{1/4}Z_0^{3/4}}\right)$$

where $\frac{(3Z_0+Z_e)/4}{Z_e^{1/4}Z_0^{3/4}} \geq 1$ for all Z_e, Z_0.

Proof.: let $X = Z_0/Z_e$, then we must prove $\frac{(3X+1)}{4X^{3/4}} \geq 1$ or $3X^{1/4} + X^{-3/4} \geq 4$. The minimum is at $\frac{3}{4}(X^{-3/4} - X^{-7/4}) = 0$, implying $X = 1$. At $X = 1$ the ratio is 1, therefore $\Delta A \leq 0$. This proves that $\Delta A \leq 0$ for any Z_e, Z_0. Here we have $Z_e \approx 1$ and $Z_0 \approx 0$, then $\frac{\Delta A}{kT} \approx -N\ln\left(\frac{3/4}{Z_0^{3/4}}\right)$, where $Z_0 = \exp(-2T_0/T)$ ($T_0 \approx 85K$ for H_2). Then

$$\frac{\Delta A}{kT} = -N\ln\left[\frac{1}{4}\exp(-\frac{3T_0}{2T})\right] = -\frac{3NT_0}{2T} + N\ln 2 \tag{17}$$

$$\Delta A = -\frac{3NkT_0}{2} + NkT\ln 2 < 0 \tag{18}$$

Furthermore,

$$\Delta S = -\frac{\partial(\Delta A)}{\partial T} = -Nk\ln 2 < 0$$

Both A and S decrease, and $\Delta A/N = -1.38\ 10^{-21}$ J and $\Delta S/N = -9.6\ 10^{-24}$ J/K. Since the system is in equilibrium with a heat bath, A must decrease but S may decrease also. The entropy of the heat bath can increase by more so the total entropy increases.

4) As shown in class,

$$\frac{n_e n_p}{n_H} = e^{E_0/kT}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$$

but $n_e = n_p$, then

$$n_p = e^{E_0/2kT}\sqrt{n_H}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/4} = \exp\left(-\frac{13.6}{2\cdot 8.617\ 10^{-5}\ 6000}\right)\sqrt{10^{25}}\left[\frac{1.67\ 10^{-27}\ 1.38\ 10^{-23}\ 6000}{2\pi(1.05\ 10^{-34})^2}\right]^{3/4} = 5.8\ 10^{22}.$$

$$n_{H,ex} = 4n_H e^{E_{exp/kT}} = 4\ 10^{25}\exp\left(-\frac{10.2}{8.617\ 10^{-5}\ 6000}\right) = 1.08\ 10^{17}$$

$n_p > n_{H,ex}$ because there are many more states available to an ionized p-e pair than to a H-atom in first excited states.