PHY 410 Homework 6 Solutions

1. K + K. Ch. 5, # 6 Gibbs sum for a 2-level system

3 states: $N=0$, $\varepsilon_s = 0$ $\quad$ $N=1$, $\varepsilon_s = 0$ $\quad$ $N=1$, $\varepsilon_s = \varepsilon$ $\quad$ $\lambda \equiv e^{\mu/\tau}$

a) $$\mathcal{Z} = \sum_N \sum_{s(N)} e^{(N\mu - \varepsilon_s)/\tau} = \sum_N \sum_{s(N)} \lambda^N e^{-\varepsilon_s/\tau}$$

$$\underline{\underline{\mathcal{Z} = 1 + \lambda + \lambda e^{-\varepsilon/\tau}}}$$

b) $$\langle N \rangle = \frac{\sum_{N,s} N \lambda^N e^{-\varepsilon_s/\tau}}{\mathcal{Z}} = \underline{\underline{\frac{\lambda + \lambda e^{-\varepsilon/\tau}}{\mathcal{Z}}}}$$

c) $$\langle N(\varepsilon) \rangle = \frac{\lambda e^{-\varepsilon/\tau}}{\mathcal{Z}}$$ ← Only the 3rd state with energy ε contributes to the numerator for these.

d) $$\langle \varepsilon \rangle = \frac{\sum_{N,s} \varepsilon_s \lambda^N e^{-\varepsilon_s/\tau}}{\mathcal{Z}} = \underline{\underline{\frac{\varepsilon \lambda e^{-\varepsilon/\tau}}{\mathcal{Z}}}}$$

e) 4 states: $N=0$, $\varepsilon_s = 0$ $\quad$ $N=1$, $\varepsilon_s = 0$ $\quad$ $N=1$, $\varepsilon_s = \varepsilon$ $\quad$ $N=2$, $\varepsilon_s = \varepsilon$

$$\mathcal{Z} = \sum_{N,s(N)} \lambda^N e^{-\varepsilon_s/\tau} = 1 + \lambda + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-\varepsilon/\tau}$$

$$\underline{\underline{\mathcal{Z} = (1+\lambda)(1 + \lambda e^{-\varepsilon/\tau})}}$$

2. K. + K. Ch 5, #8 CO poisoning

3 states: $N = 0$, $\varepsilon = 0$ $N_{O_2} = 1$, $\varepsilon_s = \varepsilon_A$ $N_{CO} = 1$, $\varepsilon_s = \varepsilon_B$

a) No CO is present, so consider only the first 2 states:

$$\mathfrak{Z} = 1 + \lambda_{O_2} e^{-\varepsilon_A/\tau} \qquad \langle N_{O_2} \rangle = \frac{\lambda_{O_2} e^{-\varepsilon_A/\tau}}{\mathfrak{Z}}$$

Given: $\lambda_{O_2} = 1 \cdot 10^{-5}$, $\langle N_{O_2} \rangle = 0.9$, find ε_A:

$$\lambda_{O_2} e^{-\varepsilon_A/\tau} = \mathfrak{Z} \langle N_{O_2} \rangle = \left(1 + \lambda_{O_2} e^{-\varepsilon_A/\tau}\right) \cdot 0.9$$

$$0.1 \, \lambda_{O_2} e^{-\varepsilon_A/\tau} = 0.9$$

$$e^{-\varepsilon_A/\tau} = \frac{9}{\lambda_{O_2}} = \frac{9}{1 \cdot 10^{-5}} = 9 \cdot 10^5$$

$$-\frac{\varepsilon_A}{\tau} = \ln\left(9 \cdot 10^5\right) = 13.7$$

$$\varepsilon_A = -13.7 \cdot k_B T = -13.7 \cdot \left(8.62 \cdot 10^{-5} \frac{eV}{K}\right) \cdot 310\,K$$

$$\varepsilon_A = \underline{\underline{-0.366 \, eV}}$$

b) With CO present, all 3 states are in play:

$$\mathfrak{Z} = 1 + \lambda_{O_2} e^{-\varepsilon_A/\tau} + \lambda_{CO} e^{-\varepsilon_B/\tau}$$

$$\langle N_{O_2} \rangle = \frac{\lambda_{O_2} e^{-\varepsilon_A/\tau}}{z}$$

Given : $\lambda_{O_2} = 1 \cdot 10^{-5}$, $\lambda_{CO} = 1 \cdot 10^{-7}$, $\langle N_{O_2} \rangle = 0.1$

Find ε_B :

$$\lambda_{O_2} e^{-\varepsilon_A/\tau} = z \langle N_{O_2} \rangle = \left(1 + \lambda_{O_2} e^{-\varepsilon_A/\tau} + \lambda_{CO} e^{-\varepsilon_B/\tau}\right) \cdot 0.1$$

$$0.9 \lambda_{O_2} e^{-\varepsilon_A/\tau} - 0.1 = 0.1 \cdot \lambda_{CO} e^{-\varepsilon_B/\tau}$$

From part (a), $e^{-\varepsilon_A/\tau} = 9 \cdot 10^{5}$, $\lambda_{O_2} e^{-\varepsilon_A/\tau} = 9$

$$0.9 \cdot 9 - 0.1 = 0.1 \cdot \lambda_{CO} e^{-\varepsilon_B/\tau}$$

$$e^{-\varepsilon_B/\tau} = \frac{8.1 - 0.1}{0.1 \cdot 1 \cdot 10^{-7}} = 8 \cdot 10^{8}$$

$$-\frac{\varepsilon_B}{\tau} = \ln\left(8 \cdot 10^{8}\right) = 20.5$$

$$\varepsilon_B = -20.5 \cdot k_B T = -20.5 \cdot 0.0267\,\text{eV} = \underline{\underline{-0.548\,\text{eV}}}$$

3. K. + K. Ch 6, # 3 $\quad f(\varepsilon)$ allowing for double occupancy

3 states: $\quad N=0 \quad N=1 \quad N=2$

$\qquad\qquad \varepsilon_s = 0 \quad \varepsilon_s = \varepsilon \quad \varepsilon_s = 2\varepsilon$

a) $$\mathcal{Z} = \sum_N \sum_{s(N)} \lambda^N e^{-\varepsilon} = 1 + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-2\varepsilon/\tau}$$

$$\langle N \rangle = \frac{\sum_N \sum_{s(N)} N \lambda^N e^{-\varepsilon_s/\tau}}{\mathcal{Z}} = \frac{\lambda e^{-\varepsilon/\tau} + 2\lambda^2 e^{-2\varepsilon/\tau}}{\mathcal{Z}}$$

b) 2 orbitals with same energy: $N = N_1 + N_2$

4 states: $\quad N=0 \quad N_1 = 1 \quad N_2 = 1 \quad N = 2$

$\qquad\qquad \varepsilon_s = 0 \quad \varepsilon_s = \varepsilon \quad \varepsilon_s = \varepsilon \quad \varepsilon_s = 2\varepsilon$

$$\mathcal{Z} = 1 + \lambda e^{-\varepsilon/\tau} + \lambda e^{-\varepsilon/\tau} + \lambda^2 e^{-2\varepsilon/\tau}$$

$$\langle N \rangle = \frac{\lambda e^{-\varepsilon/\tau} + \lambda e^{-\varepsilon/\tau} + 2\lambda^2 e^{-2\varepsilon/\tau}}{\mathcal{Z}}$$

$$= \frac{2\lambda e^{-\varepsilon/\tau}\left(1 + \lambda e^{-\varepsilon/\tau}\right)}{\left(1 + \lambda e^{-\varepsilon/\tau}\right)^2} = \frac{2\lambda e^{-\varepsilon/\tau}}{1 + \lambda e^{-\varepsilon/\tau}}$$

Notice:

$$\langle N \rangle = 2\,\frac{1}{\lambda^{-1} e^{\varepsilon/\tau} + 1} = 2\,\frac{1}{e^{(\varepsilon-\mu)/\tau} + 1} = 2 f_{FD}(\varepsilon)$$

Fermi-Dirac

4. K. + K. Ch 6, #12 Ideal gas in 2D

Follow the approach of Ch. 6 (which I did in class) using the Grand Canonical Ensemble to get the Classical distribution function:

$$f(\varepsilon) = e^{(\mu - \varepsilon)/\tau}$$

a) Sum over all orbitals s to get the average number of particles:

$$\langle N \rangle = \sum_s f(\varepsilon_s) = \sum_s e^{(\mu - \varepsilon_s)/\tau} = e^{\mu/\tau} \sum_s e^{-\varepsilon_s/\tau}$$

$$\langle N \rangle = e^{\mu/\tau} Z_1$$

I will calculate Z_1 using periodic boundary conditions. You can also use hard-wall boundary conditions if you prefer.

$$Z_1 = \sum_s e^{-\varepsilon_s/\tau} = \frac{A}{(2\pi)^2} \int d^2k \, e^{-\varepsilon(k)/\tau}$$

A ← area of box

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$$

$$= \frac{A}{(2\pi)^2} \int_0^\infty 2\pi k \, dk \, e^{-\frac{\hbar^2 k^2}{2m\tau}}$$ polar coordinates

$$Z_1 = \frac{A}{2\pi} \cdot \frac{-m\tau}{\hbar^2} e^{-\frac{\hbar^2 k^2}{2m\tau}} \Big|_0^\infty = \frac{A m \tau}{2\pi \hbar^2}$$

Replace $\langle N \rangle$ with N

$$e^{\mu/\tau} = \frac{N}{Z_1} = \frac{N}{A} \frac{2\pi\hbar^2}{m\tau} = \frac{n}{n_Q^{2D}}$$

where the quantum concentration in 2D is defined by

$$n_Q^{2D} = \frac{m\tau}{2\pi\hbar^2}$$

$$\underline{\underline{\mu = \tau \ln\left(n/n_Q\right)}} \quad \text{where} \quad n = \frac{N}{A}$$

b) $$F = \sum_{N'=1}^{N} \mu(N', \tau, A) = \sum_{N'=1}^{N} \left[\tau \ln N' - \tau \ln(n_Q A)\right]$$

$$= \tau \ln N! - N\tau \ln(n_Q A)$$

$$= \tau\left(N \ln N - N\right) - N\tau \ln(n_Q A)$$

$$F = N\tau\left[\ln \frac{N}{n_Q A} - 1\right] = N\tau\left[\ln \frac{n}{n_Q} - 1\right]$$

$$U = -\tau^2 \frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right) = -\tau^2 \frac{\partial}{\partial \tau}\left\{N \ln\left(\frac{N}{A}\frac{2\pi\hbar^2}{m\tau}\right) - N\right\}$$

$$U = N\tau^2 \frac{\partial}{\partial \tau}\left[\ln \tau + \text{constants}\right] = \underline{\underline{N\tau}}$$

c) $$F = U - \tau\sigma \Rightarrow \sigma = \frac{U - F}{\tau}$$

$$\sigma = \frac{1}{\tau}\left\{N\tau - N\tau\left(\ln n/n_Q - 1\right)\right\}$$

$$\underline{\underline{\sigma = N\left[\ln \frac{n_Q}{n} + 2\right]}}$$

You could also use $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N}$

5. K. + K. Ch. 5, #10

a) $$\langle N^2 \rangle = \frac{\sum_N \sum_{s(N)} N^2 e^{(N\mu - \varepsilon_{s(N)})/\tau}}{\mathcal{Z}}$$

$$\text{numerator} = \sum_N \sum_{s(N)} \tau^2 \frac{\partial^2}{\partial \mu^2} e^{(N\mu - \varepsilon_s)/\tau} = \tau^2 \frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

$$\Rightarrow \langle N^2 \rangle = \frac{\tau^2}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

b) $$\langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \frac{\tau^2}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \left(\frac{\tau}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \right)^2$$

using $\langle N \rangle = \frac{\tau}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu}$

$$\frac{\partial \langle N \rangle}{\partial \mu} = \frac{\tau}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} + \tau \frac{\partial \mathcal{Z}}{\partial \mu} \cdot \left(-\frac{1}{\mathcal{Z}^2} \frac{\partial \mathcal{Z}}{\partial \mu} \right)$$ product rule and chain rule

Compare with formula for $\langle (\Delta N)^2 \rangle$ to see that

$$\langle (\Delta N)^2 \rangle = \tau \frac{\partial \langle N \rangle}{\partial \mu}$$