## PART I

### Question 1

Adiabatic, $đQ = 0, \quad \Rightarrow đW = P\,dV$

$PV^\gamma = k, \qquad P_1V_1^\gamma = P_2V_2^\gamma$

$$\therefore W = \int_{V_1}^{V_2} \frac{k}{V^\gamma} dV$$
$$= \left[\frac{k}{\gamma - 1}\frac{1}{V^{\gamma-1}}\right]_{V_1}^{V_2}$$
$$= \frac{k}{\gamma - 1}\left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right)$$
$$= \frac{P_1}{\gamma - 1}\left(\frac{V_1^\gamma}{V_2^{\gamma-1}} - \frac{V_1^\gamma}{V_1^{\gamma-1}}\right)$$
$$= \frac{P_1}{\gamma - 1}\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right]$$

### Question 2

$$F = E - TS = n\varepsilon - Tk\ln\left[\frac{N!}{n!\,(N-n)!}\right]^2$$
$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial E} = \varepsilon\frac{\partial S}{\partial n}$$
$$S = 2k[\ln N! - \ln n! - \ln(N-n)!]$$

$$\frac{\partial S}{\partial n} = 2k\left[-\frac{\partial}{\partial n}\ln n! - \frac{\partial}{\partial n}\ln(N-n)!\right]$$
$$= -2k\left[\frac{\partial}{\partial n}(n\ln n - n) + \frac{\partial}{\partial n}\big((N-n)\ln(N-n) - N + n\big)\right]$$
$$= -2k[\ln n + 1 - 1 - 1 - \ln(N-n) + 1]$$
$$= -2k\ln\left(\frac{n}{N-n}\right)$$
$$\frac{\varepsilon}{2kT} = \ln\left(\frac{N-n}{n}\right)$$
$$e^{\frac{\varepsilon}{2kT}} = \frac{N}{n} - 1$$
$$\frac{n}{N} = \frac{1}{e^{\frac{\varepsilon}{2kT}} + 1}$$

### Question 3

$$Z = \sum_r (2r+1) e^{-\beta\left[\varepsilon_r^{tr} + \frac{\hbar}{2I} r(r+1)\right]} = \sum_r e^{-\beta\varepsilon_r^{tr}} \sum_r (2r+1) e^{\beta\varepsilon_r^{rot}} = Z_{trans} Z_{rot}$$

$$Z_1^{trans} = \int_0^\infty f(p) e^{-\beta\left(\frac{p^2}{2m}\right)} dp = \int_0^\infty \frac{V4\pi p^2}{h^3} e^{-\beta\left(\frac{p^2}{2m}\right)} dp = V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$$

$$Z_1^{rot} = 1 + 3e^{-\beta\frac{\hbar^2}{I}} + 5e^{-\beta\frac{3\hbar^2}{I}} + \cdots$$

Let $x = r(r+1)$, $\quad dx = (2r+1)\,dr$

$$Z_1^{rot} \approx \int_0^\infty (2r+1)\, e^{-\beta\frac{\hbar^2}{2I} r(r+1)} dr = \int_0^\infty e^{-\beta\frac{\hbar^2}{2I} x}\, dx \Rightarrow \frac{2I}{\beta\hbar^2}$$

for $\frac{\varepsilon_r}{kT} \ll 1$.

$$\therefore Z = V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \left(\frac{2I}{\beta\hbar^2}\right) = V\left(\frac{2\pi m}{h^2}\right)\left(\frac{2I}{\hbar^2}\right)\beta^{-\frac{5}{2}}$$

$$\bar{E} = -\frac{\partial(\ln Z)}{\partial\beta} = -\frac{\partial}{\partial\beta}\left[\ln\left(\frac{V2I}{\hbar^2}\right) + \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{5}{2}\ln\beta\right] = \frac{5}{2}kT$$

$$C = N\frac{\partial\bar{E}}{\partial T} = \frac{5}{2}Nk$$

### Question 4(i)

$$\begin{aligned} Z(V,T) &= \sum_{n_1}\sum_{n_2} \ldots \left(e^{-\beta n_1\varepsilon_1} e^{-\beta n_2\varepsilon_2} e^{-\beta n_3\varepsilon_3} \ldots\right) \\ &= \sum_{n_1} e^{-\beta n_1\varepsilon_1} \sum_{n_2} e^{-\beta n_2\varepsilon_2} \sum_{n_3} e^{-\beta n_3\varepsilon_3} \ldots \\ &= \frac{1}{1-e^{-\beta\varepsilon_1}}\ \frac{1}{1-e^{-\beta\varepsilon_2}} \frac{1}{1-e^{-\beta\varepsilon_3}} \ldots \\ &= \prod_{r=1}^{\infty} \frac{1}{1-e^{-\beta\varepsilon_r}} \end{aligned}$$

### Question 4(ii)

$$\begin{aligned} \bar{n}_r &= -\frac{1}{\beta}\frac{\partial(\ln Z)}{\partial\varepsilon_r} \\ &= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_r}\left[\ln\left(\frac{1}{1-e^{-\beta\varepsilon_1}}\frac{1}{1-e^{-\beta\varepsilon_2}}\frac{1}{1-e^{-\beta\varepsilon_3}}\ldots\right)\right] \\ &= \frac{1}{\beta}\frac{\partial}{\partial\varepsilon_r}\sum_i \ln\left(1-e^{-\beta\varepsilon_i}\right) \\ &= \frac{1}{\beta}\frac{\beta e^{-\beta\varepsilon_r}}{1-e^{-\beta\varepsilon_r}} \\ &= \frac{1}{e^{\beta\varepsilon_r}-1} \end{aligned}$$

**Question 5(i)**

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1}$$

where + is for Fermions, - is for Bosons.

$$\frac{1}{\beta}\left(\frac{\partial \bar{n}_i}{\partial \mu}\right) = \frac{e^{\beta(\varepsilon_i-\mu)}}{(e^{\beta(\varepsilon_i-\mu)} \pm 1)^2} = (\Delta n_i)^2$$

$$\therefore \Delta n_i = \frac{e^{\frac{\beta(\varepsilon_i-\mu)}{2}}}{e^{\beta(\varepsilon_i-\mu)} + 1}, \qquad (FD)$$
$$= \frac{e^{\frac{\beta(\varepsilon_i-\mu)}{2}}}{e^{\beta(\varepsilon_i-\mu)} - 1}, \qquad (BE)$$

**Question 5(ii)**

Fluctuation is $\frac{\Delta n_i}{\bar{n}_i}$, actually almost the same for both statistic, since $e^{\frac{\beta(\varepsilon_i-\mu)}{2}}$ is quite large. Except the case of an extremely degenerate FD gas for which the energetically lowest lying single particle states are occupied, $\bar{n}_i \approx 1$.

**Question 6**

**PART II**

**Question 1(i)**

$$S = k \ln \Omega$$
$$= k \ln\left(\frac{N!}{n!\,(N-n)!}\right)$$
$$= k[\ln N! - \ln n! - \ln(N-n)!]$$
$$= k[N \ln N - n \ln n - (N-n)\ln(N-n)]$$

$$E = -n\mu B + (N-n)\mu B = (N-2n)\mu B$$
$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial E} = -\frac{k}{2\mu B}\ln\left(\frac{N-n}{n}\right)$$

**Question 1(ii)**

$$\mu B = \frac{E}{N-2n}$$
$$\therefore \frac{1}{T} = \frac{k}{2E}(N-2n)\ln\left(\frac{n}{N-n}\right)$$
$$E = kT\left(\frac{N}{2} - n\right)\ln\left(\frac{n}{N-n}\right)$$

**Question 1(iii)**

$$Z_1 = e^{-\beta\mu B} + e^{\beta\mu B} = 2\cosh\beta\mu B = 2\cosh\frac{\mu B}{kT}$$

$$E = N\frac{\partial(\ln Z_1)}{\partial\beta} - \frac{N\sinh\frac{\mu B}{kT}}{\cosh\frac{\mu B}{kT}} = N\mu B\tanh\frac{\mu B}{kT}$$

It is very different. For energy of 1 particle, it depends on $\mu B$. When there are many particles, it depends on $kT$.

**Question 2(i)**

Consider a system immersed in a heat bath. We assume particle number N and volume V are fixed. The system microstates in equilibrium labeled $1,2,\dots,r$ and energies $E_1, E_2, \dots, E_r$. We let $E_0$ be the total energy of the system. The probability,

$$\begin{aligned} p_r &= \frac{\Omega_2(E_0 - E_r)}{\sum_r \Omega_2(\mathrm{E_0 - E_r})} \\ &= \text{const.}\, e^{\frac{S_2(E_0-E_r)}{k}} \\ &= \text{const.}\, e^{\frac{1}{k}\left[S_2(E_0) - \frac{\partial S_2(E_0)}{\partial E_0}E_r\right]} \\ &= \text{const.}\, e^{\frac{1}{k}S_2(E_0) - \beta E_r} \\ &= \frac{e^{-\beta E_r}}{Z} \\ &= \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \end{aligned}$$

$$\therefore Z = \sum_r e^{-\beta E_r}$$

$$\bar{E} = \sum_r p_r E_r = \sum_r \frac{e^{-\beta E_r}}{Z}E_r = -\sum_r p_r\left[\frac{\partial(\ln Z_r)}{\partial\beta}\right] = -\frac{\partial(\ln Z)}{\partial\beta}$$

$$(\Delta E)^2 = \overline{E^2} - \bar{E}^2 = \frac{\partial^2\ln Z}{\partial\beta^2} - \left(\frac{\partial\ln Z}{\partial\beta}\right)^2 + \left(\frac{\partial\ln Z}{\partial\beta}\right)^2 = \frac{\partial^2\ln Z}{\partial\beta^2}$$

**Question 2(ii)**

$$\bar{E} = -\frac{\partial\ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\left[-\ln N! + N\ln V - \frac{3}{2}N\ln\left(\frac{\hbar\beta}{2\pi m}\right)\right] = \frac{3}{2}NkT$$

$$(\Delta E)^2 = \frac{\partial}{\partial\beta}\left(\frac{\partial\ln Z}{\partial\beta}\right) = \frac{\partial}{\partial\beta}\left(-\frac{3}{2}\frac{N}{\beta}\right) = \frac{3}{2}Nk^2T^2$$

$$\frac{\Delta E}{\bar{E}} = \frac{\sqrt{\frac{3N}{2}}kT}{\frac{3}{2}kT} = \sqrt{\frac{2}{3}}\frac{1}{\sqrt{N}} \propto \frac{1}{\sqrt{N}}$$

Relative fluctuation is inversely proportional to the root of its size. $N\sim10^{23}$, fluctuation is extremely small, so the energy of macroscopic body in heat bath, for practical purposes, is completely determined.

**Question 3(i)**
At equilibrium,
$2\mu_{CO_2} = 2\mu_{CO} + \mu_{O_2}$

**Question 3(ii)**
$dN_i \propto v_i$
Where $v_i$ is the stoichiometric coefficient.
$\therefore dN(CO_2): dN(CO): dN(O_2) = 2: -2: -1$

**Question 3(iii)**
Law of mass action,

$$\prod_i (c_i)^{v_i} = K_c(T)$$

$$c_i = \frac{N_i}{V}$$

$$K_c(T) = \frac{c_{CO}^2 c_{O_2}}{c_{CO_2}^2}$$

$$2(1-f)CO_2 \rightleftharpoons f(2CO + O_2)$$
$$\rightleftharpoons 2fCO + fO_2$$

At a fixed, temperature, the total pressure P,

$$P = P_{CO_2} + P_{CO} + P_{O_2}$$

$$P_{CO_2} = \frac{2(1-f)}{2(1-f) + 2f + f} P = \frac{2(1-f)}{2+f} P$$

$$P_{CO} = \frac{2f}{2+f} P$$

$$P_{O_2} = \frac{f}{2+f} P$$

$$K_P(T) = \prod_i (P_i)^{v_i} = \frac{\left(\frac{2f}{2+f}\right)^2 \left(\frac{f}{2+f}\right) P^3}{\left[\frac{2(1-f)}{2+f}\right] P^2} = \frac{f^3}{2(1-f)^2} P$$

$$P = 2K_P \frac{(1-f)^2}{f^3} = 2K_P \left(\frac{1}{f^3} - \frac{2}{f^2} + \frac{1}{f}\right)$$

When P increases, f decreases.

---

Solutions done by: John Soo