Problem III.3

① Taking account of constraints, we have to maximize

$$-w_{i,v}\sum_{i,v}\ln w_{i,v}-\lambda\sum_{i,v}w_{i,v}-\lambda_E\sum_{i,v}w_{i,v}E_{i,v}-$$
$$-\lambda_V\sum_{i,v}w_{i,v}V$$

(Lagrangian multipliers method).

Set $\frac{\partial}{\partial w_{i,v}}(\text{"})=0$

$$\therefore\ -[\ln w_{i,v}+1]-\lambda-\lambda_E E_{i,v}-\lambda_V V=0$$
$$\therefore\ w_{i,v}=e^{-(\lambda+1)}e^{-(\lambda_E E_{i,v}+\lambda_V V)}$$

set $\beta=\lambda_E$, $\gamma=\lambda_V$ (For those who use k_B: $\beta=\frac{\lambda_E}{k_B}$; $\gamma=\frac{\lambda_V}{k_B}$)

$$\therefore\ w_{i,v}=C\,e^{-(\beta E_{i,v}+\gamma V)}$$

Solving for C from the normalization condition:

$$\sum_{i,v}w_{i,v}=1 \Rightarrow$$

$$w_{i,v}=\frac{e^{-(\beta E_{i,v}+\gamma V)}}{\sum_{i,v}e^{-(\beta E_{i,v}+\gamma V)}}=$$

$$=\frac{1}{Z_0}e^{-(\beta E_{i,v}+\gamma V)}$$

Problem III.3 | Sheet 2

(2) $S = -\sum_{i,V} w_{i,V} \ln w_{i,V} =$

$$= \sum_{i,V} w_{i,V} \left[\beta E_{i,V} + \gamma V + \ln Z_0 \right] =$$

$$= \beta \langle E \rangle + \gamma \langle V \rangle + \ln Z_0$$

Take the total differential of this:

$$dS = \beta\, d\langle E \rangle + \langle E \rangle\, d\beta + \gamma\, d\langle V \rangle + \langle V \rangle\, d\gamma + d(\ln Z_0)$$

$$d(\ln Z_0) = \left(\frac{\partial \ln Z_0}{\partial \beta}\right)_\gamma d\beta + \left(\frac{\partial \ln Z_0}{\partial \gamma}\right)_\beta d\gamma$$

But $\left(\frac{\partial \ln Z_0}{\partial \beta}\right)_\gamma = -\langle E \rangle$

$$\left(\frac{\partial \ln Z_0}{\partial \gamma}\right)_\beta = -\langle V \rangle$$

Hence

$$dS = \beta\, d\langle E \rangle + \gamma\, d\langle V \rangle$$

Compare this with the 1st & 2nd law

$(E \to \langle E \rangle, \ V \to \langle V \rangle)$

$$d\langle E \rangle = T\, dS - p\, d\langle V \rangle, \text{ or}$$

$$dS = \frac{1}{T}\left[d\langle E \rangle + p\, d\langle V \rangle \right]$$

This implies that

$$\boxed{\begin{aligned} \beta &= \frac{1}{T} \\ \gamma &= \frac{p}{T} = p\beta \end{aligned}}$$

③ From part ②:

NOTE

$$\ln Z_0 = S - \beta\langle E\rangle - \gamma\langle V\rangle$$

$$\ln Z_0 = S - \frac{\langle E\rangle}{T} - \frac{P\langle V\rangle}{T} \Rightarrow$$

$$-T\ln Z_0 = \langle E\rangle - TS + P\langle V\rangle = G$$

Now $\langle(\Delta V)^2\rangle = \langle V^2\rangle - \langle V\rangle^2$

$$\langle V^{x}\rangle = \frac{\sum_{i,V} V^{x} e^{-(\beta E_{i,V} + \gamma V)}}{\sum_{i,V} e^{-(\beta E_{i,V}+\gamma V)}}$$

Note:

$$\left(\frac{\partial\langle V\rangle}{\partial\gamma}\right)_\beta = -\frac{1}{Z_0}\sum_{i,V} V^2 e^{-(\beta E_{i,V}+\gamma V)} -$$

$$- \frac{1}{Z_0^2}\left(\frac{\partial Z_0}{\partial\gamma}\right)_\beta \left(\sum_{i,V} V e^{-(\beta E_{i,V}+\gamma V)}\right) =$$

$$= -\langle V^2\rangle - \langle V\rangle\left(\frac{\partial \ln Z_0}{\partial\gamma}\right)_\beta =$$

$$= -\left[\langle V^2\rangle - \langle V\rangle^2\right]$$

$$\therefore \langle(\Delta V)^2\rangle = -\left(\frac{\partial\langle V\rangle}{\partial\gamma}\right)_\beta = -T\left(\frac{\partial\langle V\rangle}{\partial P}\right)_T =$$

$$= T\langle V\rangle \underbrace{\kappa_T}_{\text{isothermal compressibility}}$$