Post-Lecture Question 2

(a) (i)

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N \quad \Rightarrow \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}\,,\ \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}\,.$$

$$\begin{aligned}
S_{\text{bath}} &= k_B \ln \Omega_{\text{bath}}(N - N_S, E - E_S) \\
&= k_B \left[\ln \Omega_{\text{bath}}(N,E) - N_S \left(\frac{\partial \ln \Omega_{\text{bath}}}{\partial N}\right)_{E,V}(N,E) - E_S \left(\frac{\partial \ln \Omega_{\text{bath}}}{\partial E}\right)_{N,V}(N,E)\right] \\
&= k_B \left[\ln \Omega_{\text{bath}}(N,E) - \frac{N_S}{k_B} \left(\frac{\partial S_{\text{bath}}}{\partial N}\right)_{E,V}(N,E) - \frac{E_S}{k_B} \left(\frac{\partial S_{\text{bath}}}{\partial E}\right)_{N,V}(N,E)\right] \\
&= S_{\text{bath}}(N,E) - \frac{\mu_{\text{bath}N_S}}{T_{\text{bath}}} - \frac{E_S}{T_{\text{bath}}}
\end{aligned}$$

$$\Rightarrow \quad S_{\text{total}} = S_{\text{bath}}(N,E) + S_{\text{sys}}(N_S,E_S) + \frac{1}{T_{\text{bath}}}(\mu_{\text{bath}}N_S - E_S)$$

When S_{total} is maximised,

$$\begin{aligned}
\frac{\partial S_{\text{total}}}{\partial N_S} &= \frac{\partial S_{\text{sys}}}{\partial N_S} + \frac{\mu_{\text{bath}}}{T_{\text{bath}}} \\
&= -\frac{\mu_{\text{sys}}}{T_{\text{sys}}} + \frac{\mu_{\text{bath}}}{T_{\text{bath}}} = 0 \\
\frac{\partial S_{\text{total}}}{\partial E_S} &= \frac{\partial S_{\text{sys}}}{\partial E_S} - \frac{1}{T_{\text{bath}}} \\
&= \frac{1}{T_{\text{sys}}} - \frac{1}{T_{\text{bath}}} = 0
\end{aligned}$$

$$\Rightarrow \quad \begin{cases} T_{\text{sys}} = T_{\text{bath}} = T \\ \mu_{\text{sys}} = \mu_{\text{bath}} = \mu \end{cases}$$

$$\begin{aligned}
\Phi_{\text{sys}}(N_S,E_S) &= E_S - TS_{\text{sys}}(N_S,E_S) - N_S\mu \\
&= -T\left[S_{\text{sys}}(N_S,E_S) + \frac{1}{T}(N_S\mu - E_S)\right] \\
&= -TS_{\text{total}} + TS_{\text{bath}}(N,E)\,,
\end{aligned}$$

where $TS_{\text{bath}}(N,E)$ is a constant. As $T > 0$, maximum $S_{\text{total}} \Rightarrow$ minimum Φ_{sys}.

(ii) At fixed T, μ, $\mathrm{d}\Phi = -P\,\mathrm{d}V \Rightarrow \Phi = -PV$. As V_{sys} fixed and $V, P > 0$, Φ_{sys} is minimised by maximum P_{sys}.

(b) (i)

$$\begin{aligned}
\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} &= \frac{\partial}{\partial \beta}\sum_i e^{-\beta E_i} = -\sum_i E_i e^{-\beta E_i} \\
&= -\sum_i e^{-\beta E_i} \frac{\sum_j E_j e^{-\beta E_j}}{\sum_k e^{-\beta E_k}} \\
&= -Q\,\langle E\rangle_N
\end{aligned}$$

(ii) Have

$$\Xi = \sum_i \sum_j e^{-\beta E_i} z^{N_j} \,.$$

$$\begin{aligned}
\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{z,V} &= \frac{1}{\Xi}\left(\frac{\partial \xi}{\partial \beta}\right)_{z,V} \\
&= \frac{1}{\Xi}\sum_i \sum_j \frac{\partial}{\partial \beta} e^{-\beta E_i} z^{N_j} \\
&= -\frac{1}{\Xi}\sum_i \sum_j E_i e^{-\beta E_i} z^{N_j}
\end{aligned}$$

$$\begin{aligned}
\langle E \rangle &= \sum_i \sum_j E_i P(E_i, N_j) \\
&= \sum_i \sum_j E_i \frac{e^{-\beta E_i} z^{N_j}}{\sum_p \sum_q e^{-\beta E_p} z^{N_q}} \\
&= \frac{1}{\Xi}\sum_i \sum_j E_i e^{-\beta E_i} z^{N_j} \\
&= -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{z,V}
\end{aligned}$$

(iii)

$$\Xi = \sum_i \sum_j e^{-\beta E_i} e^{\beta \mu N_j}$$

$$\begin{aligned}
\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\mu,V} &= \frac{1}{\Xi}\left(\frac{\partial \xi}{\partial \beta}\right)_{\mu,V} \\
&= \frac{1}{\Xi}\left(\sum_i \sum_j -E_i e^{-\beta E_i} e^{\beta \mu N_j} + \sum_i \sum_j \mu N_j e^{-\beta E_i} e^{\beta \mu N_j}\right) \\
&= -\frac{1}{\Xi}\sum_i \sum_j E_i e^{-\beta E_i} e^{\beta \mu N_j} + \mu \frac{1}{\Xi}\sum_i \sum_j N_j e^{-\beta E_i} e^{\beta \mu N_j} \\
&= -\langle E \rangle + \mu \langle N \rangle
\end{aligned}$$

(iv)

$$\begin{aligned}
\left(\frac{\partial (\Phi/T)}{\partial (1/T)}\right)_{\mu,V} &= \frac{1}{T}\left(\frac{\partial \Phi}{\partial (1/T)}\right)_{\mu,V} + \Phi \left(\frac{\partial (1/T)}{\partial (1/T)}\right)_{\mu,V} \\
&= \frac{1}{T}\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V}\left[\frac{\partial}{\partial T}\frac{1}{T}\right]^{-1} + \Phi \\
&= -TS + E - TS - \mu N \\
&= E - \mu N
\end{aligned}$$

(v) In the thermodynamic limit, $E = \langle E \rangle$ and $N = \langle N \rangle$, so

$$\left(\frac{\partial (\beta \Phi)}{\partial \beta}\right)_{\mu,V} = \left(\frac{\partial (\Phi/T)}{\partial (1/T)}\right)_{\mu,V} = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\mu,V}$$

$$\Rightarrow \beta \Phi = -\ln \Xi + c$$

Set $c = 0$, get $\Phi = -k_B T \ln \Xi$.