Post-Lecture Question 3

(a) (i) $U(\{\mathbf{r}_i\}) = 0$

$$Q = \frac{1}{\Lambda^{3N} N!} \int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i = \frac{V^N}{\Lambda^{3N} N!}$$

(ii) (α)

$$\begin{aligned} A &= -k_B T \ln Q \\ &= -N k_B T \ln V + 3N k_B T \ln \Lambda + k_B T \ln N! \\ &\approx -N k_B T \ln V + 3N k_B T \ln \Lambda + N k_B T \ln N - N k_B T \\ &= N k_B T \left[\ln \frac{N\Lambda^3}{V} - 1 \right] \end{aligned}$$

(β)

$$\ln Q = N \ln V - 3N \ln \Lambda - \ln N!$$

$$E = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = 3N \left(\frac{\partial \ln \Lambda}{\partial \beta} \right)_{N,V}$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{2\pi m}} \beta^{\frac{1}{2}} \quad \Rightarrow \quad \left(\frac{\partial \ln \Lambda}{\partial \beta} \right)_{N,V} = \frac{1}{2\beta}$$

$$E = \frac{3}{2} N k_B T$$

(γ)

$$S = \frac{E - A}{T} = N k_B \left[\frac{5}{2} + \ln \frac{V}{N\Lambda^3} \right]$$

(δ)

$$\begin{aligned} P &= -\left(\frac{\partial A}{\partial V} \right)_{T,\mu} \\ &= N k_B T \frac{\partial}{\partial V} \ln V = \frac{N k_B T}{V} \end{aligned}$$

(iii)

$$S = N k_B \left(\frac{5}{2} + \ln \frac{V}{N} - 3 \ln \Lambda \right)$$

$$\lim_{T \to 0} \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} = \infty$$

$$\Rightarrow \quad \lim_{T \to 0^+} S = -\infty$$

(iv)

$$\begin{aligned} \mu &= \left(\frac{\partial A}{\partial N} \right)_{V,T} = k_B T \left[\ln \frac{N\Lambda^3}{V} - 1 \right] + N k_B T \frac{V}{N\Lambda^3} \frac{\Lambda^3}{V} \\ &= k_B T \ln \frac{N\Lambda^3}{V} - k_B T + k_B T \\ &= k_B T \ln \rho \Lambda^3 \end{aligned}$$

(b)

$$\begin{aligned}
PV &= k_B T \ln \Xi \\
&= k_B T \ln \sum_{N=0}^{\infty} \frac{z^N V^N}{\Lambda^{3N} N!} \\
&= k_B T \ln \sum_{N=0}^{\infty} \frac{1}{N!} (\frac{zV}{\Lambda^3})^N \\
&= k_B T \frac{zV}{\Lambda^3}
\end{aligned}$$

Have

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial \beta\mu} \right)_{V,T} = \frac{\partial}{\partial \beta\mu} \frac{zV}{\Lambda^3} = \frac{zV}{\Lambda^3} \, .$$

Therefore,

$$PV = \langle N \rangle \, k_B T \, ,$$

consistent with (a)(ii)(δ).

(c) (i)

$$\begin{aligned}
\Delta &= \beta P \int_0^{\infty} \frac{1}{\Lambda^{3N} N!} V^N e^{-\beta PV} \, \mathrm{d}V \\
&= \frac{1}{\Lambda^{3N} N! (\beta P)^N} \int_0^{\infty} (\beta PV)^N e^{-\beta PV} \, \mathrm{d}(\beta PV) \\
&= \frac{1}{\Lambda^{3N} N! (\beta P)^N} \Gamma(N+1) \\
&= \frac{1}{\Lambda^{3N} (\beta P)^N}
\end{aligned}$$

(ii)

$$\begin{aligned}
G &= -k_B T \ln \Delta \\
&= k_B T \ln \Lambda^{3N} (\beta P)^N \\
&= N k_B T \ln \beta P \Lambda^3
\end{aligned}$$

$$\begin{aligned}
\mu &= \left(\frac{\partial G}{\partial N} \right)_{P,T} \\
&= k_B T \ln \beta P \Lambda^3
\end{aligned}$$

Result from (a) and (b):

$$\begin{aligned}
\mu &= k_B T \ln \frac{N}{V} \Lambda^3 \\
&= k_B T \ln \frac{P}{k_B T} \Lambda^3 \\
&= k_B T \ln \beta P \Lambda^3 \, ,
\end{aligned}$$

which is consistent.