Section A

1.

$$dG = \mu_1 dN_1 + \mu_2 dN_2 = 0$$

and

$$dN_1 + dN_2 = 0$$

we have that $\mu_1 = \mu_2$.
Also,

$$\begin{aligned} d\mu_1(T,P) &= d\mu_2(T,P) \\ \Rightarrow \frac{1}{N_1}\left(\frac{\partial G_1}{\partial T}dT + \frac{\partial G_1}{\partial P}dP\right) &= \frac{1}{N_2}\left(\frac{\partial G_2}{\partial T}dT + \frac{\partial G_2}{\partial P}dP\right) \end{aligned}$$

$$\Rightarrow (s_2 - s_1)dT = (v_2 - v_1)dP \quad s_i = \frac{S_i}{N_i}; v_i = \frac{V_i}{N_i}$$

and

$$\left.\frac{dP}{dT}\right|_\gamma = \frac{s_1 - s_2}{v_1 - v_2}$$

With

$$\begin{aligned} s &= \frac{1}{T}\left(\frac{U + PV}{N}\right) - \frac{\mu}{T} \\ &= \frac{1}{T}\frac{H}{N} - \frac{\mu}{T} \\ \Rightarrow s_1 - s_2 &= \frac{1}{T}\left(\frac{H_1}{N_1} - \frac{H_2}{N_2} - \mu_1 + \mu_2\right) \\ &= \frac{1}{T}\mathcal{L} \text{ since } \mu_1 = \mu_2. \end{aligned}$$

Then

$$\left.\frac{dP}{dT}\right|_\gamma = \frac{1}{T}\frac{\mathcal{L}}{v_1 - v_2}$$

as required.
For this equation to be meaningful we require a volume change, a signal for a first order phase transition.

2.

$$\begin{aligned} Z_\Omega &= \sum_N \frac{1}{N!}\left(\frac{zV}{\lambda^3}\right)^N \\ &= \exp\left(\frac{Vz}{\lambda^3}\right) \end{aligned}$$

$$\Rightarrow = -\frac{1}{\beta}\ln Z_\Omega = -\frac{1}{\beta}\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right)$$

And

$$-\frac{\partial\Omega}{\partial\mu} = N = \frac{1}{\beta}\frac{V}{\lambda^3}\beta e^{\beta\mu}$$

yields,

$$\mu = \frac{1}{\beta} \ln \left(\frac{N\lambda^3}{V} \right)$$

3.

$$\begin{aligned} F(T,M,B) &= F_0(T) + \int d^3x \left\{ a(T)\vec{M}(x) \cdot \vec{M}(x) + b(T) \left(\vec{M}(x) \cdot \vec{M}(x) \right)^2 + \ldots \right. \\ &\left. + c(T) \sum_{ij} (\nabla_j M_i(x) \cdot \nabla_j M_i(x) + ldots) - \vec{B} \cdot \vec{M}(x) \right\} \end{aligned}$$

Equilibrium implies $\frac{dF}{dM} = 0$ and $\vec{x}$-independence implies $\nabla() = 0$. Then, considering the z-direction only

$$2a(t)M_z(x) + 4b(T)M_z^3(x) = B_z(x)$$

Need a solution with $B_z = 0$ and $M_z \neq 0$ and $T < T_c$.

$$\begin{aligned} M_z &= 0 \\ M_z &= \pm\sqrt{\frac{-a(t)}{2b(T)}} \end{aligned}$$

4. Consider 2 ideal gases, A and B with V_A, N_A, T and V_B, N_B, T respectively. Compare gases before and after mixing with $S = S_A + S_B$ and S_{A+B}.
Write entropy, $S(U(V,T),V,N)$. Then $\frac{dS}{dV}|_T = \frac{P}{T} = \frac{1}{T}\frac{NRT}{V} = \frac{NR}{V}$ and

$$S(T,V) = NR\ln V + S_0(T)$$

Before mixing

$$S = S_A + S_B = N_A R \ln V_A + N_B R \ln V_B + S_0(T)$$

and $S_0(T)$ is an irrelevant constant that can be set to zero.
After mixing

$$\begin{aligned} S_{A+B} &= (N_A + N_B)R\ln V_A + V_B \\ &= (N_A + N_B)R\ln V \end{aligned}$$

Then subtracting the entropies we have the change in entropy after mixing

$$S_{A+B} - (S_A + S_B) = N_A R \ln \frac{V}{V_A} + N_B R \ln \frac{V}{V_B} > 0$$

but if gas A and gas B are the same then removing the partition should result in zero change in entropy.

$$\Rightarrow \text{ PARADOX}$$

5. For a Bose-Einstein (BE) system

$$N = A\int_0^\infty d\epsilon\sqrt{\epsilon}n(\epsilon) \quad n(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}-1}$$

If $\mu > 0$ then $n(0) < 0$ which is not physically meaningful. Therefore BE $\Rightarrow \mu < 0$ and $\Rightarrow z = e^{\beta\mu} \leq 1$. Then

$$\begin{aligned} 0 < n(\epsilon) &= \frac{z}{e^{\beta\epsilon}-z} \\ \Rightarrow z &\geq 0 \end{aligned}$$

and putting this together $0 \leq z \leq 1$ as required.

6. The expectation value of f is written $\bar{f} = \frac{1}{Z}\sum_N f(N)\rho_N$.
Decompose the system into R large subsystems (R is also large). Then write $\bar{f}_a$ is the expectation value of f in a, with $a = 1, 2\ldots R$.

$$\Rightarrow \bar{f} = \overline{\sum_{a=1}^{R} f_a} = \sum_{a=1}^{R} \bar{f}_a \sim R * \bar{f}_{a^*}$$

where $\bar{f}_{a^*}$ is a typical value of $\bar{f}_a$. Fluctuations of the system are $\Delta f \equiv f - \bar{f}$. Then

$$\overline{(\Delta f)^2} = \overline{(\sum_{a=1}^{R} \Delta f_a)^2} = \sum_{a=1}^{R}\overline{(\Delta f_a)^2} + \sum_{a\neq b}\Delta f_a \Delta f_b$$

and the last term is zero by statistical independence. So,

$$\overline{(\Delta f)^2} = R\overline{(\Delta f_a)^2}$$

Then, the RMS fluctuation

$$\frac{\sqrt{\overline{(\Delta f_a)^2}}}{\bar{f}} \propto \frac{1}{\sqrt{R}} \stackrel{R\to\infty}{\longrightarrow} 0$$

If $f = E$ then $\bar{E} = U$ and

$$\frac{\sqrt{\overline{(E-U)^2}}}{U} \propto \frac{1}{\sqrt{R}} \longrightarrow 0$$

As $N \longrightarrow \infty \Rightarrow$ the canonical and microcanonical ensembles are equivalent.

Section B

1.

$$\begin{aligned} Z_\Omega &= \sum_N \sum_{E_N} e^{-\beta(E_N-\mu)} \\ &= \sum_N z^N Z_N \\ &= \sum_N \frac{z^N}{N!} V^N \lambda^{-3N} \\ &= e^{\frac{Vz}{\lambda^3}} \end{aligned}$$

Then

$$\Omega = -PV = -\frac{1}{\beta}\ln Z_\Omega = -\frac{1}{\beta}\left(\frac{Vz}{\lambda^3}\right)$$

For the reaction $2H_2 + O_2 \leftrightarrow 2H_2O$, need μ

$$\begin{aligned}\Omega &= -\frac{1}{\beta}\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right)\\ -\frac{\partial\Omega}{\partial\mu} &= \frac{1}{\beta}\frac{V}{\lambda^3}\beta e^{\beta\mu}\\ &= N\end{aligned}$$

Then

$$\Rightarrow \mu = \frac{1}{\beta}\ln\frac{N\lambda^3}{V}.$$

For chemical equilibrium, $dG = \sum \mu_i dN_i = 0$. Consider the reaction represented by $\sum \nu_i A_i$ and with $\sum \nu_j \mu_j = 0$. Treating the constituents in the perfect gas model

$$\mu_j = \frac{1}{\beta}\ln\frac{N_j\lambda_j^3}{V}$$

with $P_jV = N_jkT$ and $P = \sum_j P_j = NkT$ os that

$$\mu_j = kT\ln c_jP + f_j(k,T) \;\; ; \;\; \text{with } c_j = N_j/N \quad \text{and } f_j = kT\ln\frac{\lambda^3}{kT}$$

Therefore

$$\prod c_j^{\nu_j} = P^{-\sum \nu_j} e^{-\mu\nu_j f_j/kT}$$

Substitute $\nu_1 = 2, \nu_2 = 1, \nu_3 = -2$ and $N_1 = 2, N_2 = 1, N_3 = 2$ and simplify to get

$$\frac{1}{V} = \frac{m_1}{m_3}\frac{\sqrt{2\pi m_2 kT}}{h}$$

2. Recall from the notes,

$$\mathcal{H} = -J\sum_{n,\mu}\sigma_n\sigma_{n+\mu} - h\sum_n \sigma_n$$

and in D dimensions there are $q = 2D$ nearest neighbours. In mean field theory

$$\sigma_n\sigma_{n'} = -M^2 + M(\sigma_n + \sigma_{n'}) + \partial\sigma_n\partial\sigma_{n'}$$

and the last term is neglected. The doing the sum, $\sum_{n,\mu}$

$$\begin{aligned}H &= \frac{1}{2}qJNM^2 - (qJM + h)\sum_n \sigma_n\\ Z &= e^{-\frac{1}{2}\beta qJNM^2}\sum_{\{\sigma\}} e^{\beta(qJM+h)\sum_n \sigma_n}\\ &= e^{-\frac{1}{2}\beta qJNM^2}\left[2\cosh\beta(qJM+h)\right]^N\end{aligned}$$

Then,

$$\begin{aligned} A = F/N &= -kT \ln Z \\ &= -kT \ln 2\cosh\beta(qJM + h) + \frac{1}{2}qJM^2 \end{aligned}$$

and $\partial A/\partial M = 0 \Rightarrow M = \tanh\beta(qJM+h)$. This equation can be solved (eg. graphically) for $h = 0$ and $M \neq 0$ and you find a stable solution for $\beta qJM = M \Rightarrow \beta qJ = 1$, which gives

$$T_c = qJ/k$$

In mean field theory, F can be expanded in powers of M. Then, $\frac{\partial F}{\partial M}|_{B=0} = 0$ at equilibrium which can be solved for M and hence χ ... see notes for details.

Note that the susceptibility diverges at the critical point ie at $T = T_c$.

3. Given $U(T,V) = V\int_0^\infty d\omega u(\omega, T)$, find $u(\omega, T)$. In the notes this corresponds to

$$dE_\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$$

(see lecture notes for this derivation).

To find S/V recall $\mu = 0 \Rightarrow F = \Omega$ and $\Omega = -\frac{1}{\beta}\ln Z_\Omega$. We know that $Z = (1 - e^{-\beta\epsilon})$ for 1 state so

$$F = kT\ln(1 - e^{-\beta\epsilon}) \quad \text{for 1 quantum state}$$

and the number of quantum states of photons with frequency in range $\omega \to \omega d\omega = \frac{V\omega^2 d\omega}{\pi^2 c^3}$. Then

$$\begin{aligned} F_{total} &= \int_0^\infty kT\frac{V\omega^2 d\omega}{\pi^2 c^3}\ln(1 - e^{-\beta\epsilon}) \\ &= \frac{kTV}{\pi^2 c^3}\int_0^\infty \omega^2 \ln(1 - e^{-\frac{\hbar\omega}{kT}})d\omega \end{aligned}$$

Writing $x = \frac{\hbar\omega}{kT}$ and integrating by parts

$$\begin{aligned} F_{total} &= \frac{kTV}{\pi^2 c^3}\frac{(kT)^3}{\hbar^3}\int_0^\infty x^2\ln(1 - e^{-x})dx \\ &= \frac{(kT)^4 V}{\pi^2 c^3 \hbar^3}\left\{-\frac{1}{3}\int_0^\infty \frac{x^3}{e^x - 1}dx\right\} + C \\ &= -\frac{V(kT)^4}{3\pi^2 c^3\hbar^3}\int_0^\infty \frac{x^3}{e^x - 1}dx \\ &= -\frac{V\pi^2 (kT)^4}{45(\hbar c)^3} \\ &= -\frac{4\sigma}{3c}VT^4 \end{aligned}$$

where the constant term (independent of T) is ignored. Then

$$S = \frac{\partial F}{\partial T} = \frac{16\sigma}{3c} V T^3$$

and $S/V = \frac{16\sigma}{3c}T^3$. Note above that in the integration by parts:

$$dv = x^2 dx \quad \text{and } u = \ln(1 - e^{-x})$$

4. Calculate $P(N/V)$ as $T \to 0$ and c_V as $T \to 0$. Have that

$$n(\epsilon) = \frac{1}{e^{\beta(\epsilon-1)} + 1} \begin{cases} 1 & \epsilon < \mu \\ \mu, \epsilon > \mu & \end{cases} \tag{1}$$

Then,

$$N \to A \int_0^\mu \epsilon^{1/2} d\epsilon = \frac{2}{3} A \mu^{3/2}$$

and

$$\Omega \to -\frac{2}{3} A \int_0^\infty \epsilon^{3/2} d\epsilon = -\frac{2}{3} \left(\frac{2}{5} \mu^{5/2} \right)$$

Then

$$\begin{aligned} \Omega = -PV &= -\frac{4}{15} \left(\frac{3N}{A} \right)^{5/3} \\ PV &= \frac{4}{15} \left(\frac{3}{A} \right)^{5/3} \left(\frac{N}{V^{3/5}} \right)^{5/3} \end{aligned}$$

For c_V, recall $S = -\frac{\partial \Omega}{\partial T}$ and $c_V = T \frac{\partial S}{\partial T}$. Use

$$I = \int_0^\infty \frac{f(\epsilon) d\epsilon}{e^{\beta(\epsilon-\mu)} + 1} \sim \int_0^\mu d\epsilon f(\epsilon) + 2(kT)^2 f'(\mu) \int_0^\infty \frac{x}{e^x + 1} dx + \ldots$$

and $\int_0^\infty \frac{x}{e^x+1} dx = \pi^2/12$ to re-write Ω as

$$\begin{aligned} \Omega &= -\frac{2}{3} A \left[\int_0^\mu \epsilon^{3/2} d\epsilon + 2(kt)^2 \left(\frac{d}{d\mu} \mu^{3/2} \right) \frac{\pi^2}{12} + \ldots \right] \\ &= -\frac{4}{15} A \mu^{5/2} + \frac{\pi^2}{4} (kT)^2 \mu^{1/2} \left(-\frac{2}{3} A \right) + \ldots \end{aligned}$$

and also $\mu = \mu_0 + (kT)^2 \mu_1 + \mathcal{O}(kT)^2$ with $\mu_0 = \left(\frac{3N}{2A} \right)^{2/3}$ and $\mu_1 = -\frac{\pi^2}{12} \frac{1}{\mu_0}$. Then

$$\Omega = -\frac{4}{15} A \mu_0^{5/2} - \frac{\pi}{9} (kT)^2 A \mu_0^{1/2} + \ldots$$

and

$$S = -\frac{\partial \Omega}{\partial T} = \frac{2\pi^2}{9} k^2 T A \mu_0^{1/2} + \ldots$$

and

$$c_V = T \frac{\partial \Omega}{\partial T} = T \left(\frac{2\pi^2}{9} k^2 A \mu_0^{1/2} \right) = aT$$

and $c_V \to 0$ like $T \to 0$.