Question 1 (i)

There are N atoms, N lattice, and M interstitial states. So for n atoms in the interstitial sites,

$$\Omega = \binom{N}{N-n}\binom{M}{n} = \frac{N!}{n!\,(N-n)!}\frac{M!}{n!\,(M-n)!}$$

$$\begin{aligned} S &= k\ln\Omega = k[\ln N! + \ln M! - 2\ln n! - \ln(N-n)! - \ln(M-n)!] \\ &= k[N\ln N + M\ln M - 2n\ln n - (N-n)\ln(N-n) - (M-n)\ln(M-n)] \end{aligned}$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial n}{\partial E}\frac{\partial S}{\partial n} = \frac{k}{\epsilon}[-2\ln n - 2 + \ln(N-n) + 1 + ln\,(M-n) + 1]$$

$$T = \frac{\epsilon}{k}\frac{1}{\ln\frac{(N-n)(M-n)}{n^2}}$$

Hint 1: Ω is found through combinatoric methods. Since there are n atoms in the interstitial sites, there are $\binom{M}{n}$ ways of placing those n atoms in M interstitial sites. So after filling up the n atoms, there are $N-n$ atoms left, and they are fit into the N lattice sites. Multiply these two combinations, and you get the results.

Hint 2: Use Stirling's Formula to find the final expression of S.

Question 1 (ii)

$$\frac{\epsilon}{kT} = -\ln\frac{n^2}{(N-n)(M-n)}$$

$$e^{-\frac{\epsilon}{kT}} = \frac{n^2}{(N-n)(M-n)} \quad \text{[shown]}$$

For $\epsilon \ll kT$, $e^{-\frac{\epsilon}{kT}} \approx 1$, so

$$\frac{n^2}{(N-n)(M-n)} \approx 1 \quad \Rightarrow \quad n = \frac{MN}{M+N}$$

Question 1 (iii)

If $M = N$,

$$\frac{n^2}{(N-n)^2} = e^{-\frac{\epsilon}{kT}}$$

At low T, $n = 0$; at high T, $n = \frac{N^2}{2N} = \frac{N}{2}$.

This agrees with the laws of thermodynamics, since the greatest disorder (highest entropy and temperature) should occur when $n = \frac{N}{2}$, while the lowest disorder occurs when $n = 0$.

Question 2 (i)

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

$$Z = \frac{1}{h}\int_{-\infty}^{\infty} e^{-\beta\left(\frac{p^2}{2m}+\frac{1}{2}m\omega^2 q^2\right)}\,dp\,dq = \frac{1}{h}\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}}\,dp \int_{-\infty}^{\infty} e^{-\frac{\beta m\omega^2 q^2}{2}}\,dq = \frac{1}{\beta\hbar\omega}$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{\partial}{\partial\beta}(\ln\beta\hbar\omega) = kT$$

Hint: make use of the integral formula given.

Question 2 (ii)

$$Z = \sum_n e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} = e^{-\frac{\beta\hbar\omega}{2}}\sum_n^{\infty} e^{-\beta\hbar\omega n} = \frac{1}{2}\operatorname{csch}\frac{\beta\hbar\omega}{2}$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{\partial}{\partial\beta}\left[\ln\left(e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}\right)\right] = \frac{\hbar\omega}{2}\coth\frac{\beta\hbar\omega}{2}$$

Hint: Use the sum to infinity formula for Z, and be familiar with the conversion between hyperbolic and exponential functions, as well as their differentiations.

Question 2 (iii)

For small $\frac{\beta\hbar\omega}{2}$, $\coth\frac{\beta\hbar\omega}{2} \approx \frac{2}{\beta\hbar\omega}$, thus

$$\langle E\rangle = \frac{\hbar\omega}{2}\frac{2}{\beta\hbar\omega} = kT$$

Which is the classical results. So we conclude that classical result is only valid at either high T, or small $\hbar\omega$ (energy level).

Question 3 (i)

$$\frac{\lambda^3 P}{kT} = g_{\frac{5}{2}}(\zeta), \qquad \lambda^3 n = g_{\frac{3}{2}}(\zeta)$$

$$PV = kT\ln\mathcal{Z} = g_{\frac{5}{2}}(\zeta)\frac{kTV}{\lambda^3}$$

$$\ln \mathcal{Z} = \frac{V}{\lambda^3} g_{\frac{5}{2}}(\zeta)$$
$$U = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} = \frac{3}{2} \frac{V}{\beta} \frac{1}{\lambda^3} g_{\frac{5}{2}}(\zeta) = \frac{3}{2} PV \quad \text{[shown]}$$

Question 3 (ii)

$$n\lambda^3 = g_{\frac{3}{2}}(\zeta) = \zeta + \frac{\zeta^2}{2^{\frac{3}{2}}} + \cdots$$

1st order, $\zeta = n\lambda^3$.

2nd order, $n\lambda^3 = \zeta + \frac{(n\lambda^3)^2}{2^{\frac{3}{2}}}$

$$\Rightarrow \zeta = n\lambda^3 \left(1 - \frac{n\lambda^3}{2^{\frac{3}{2}}}\right) \quad \text{[shown]}$$

Hint: substitute the 1st order term into the second term of $n\lambda^3 = \zeta + \frac{\zeta^2}{2^{\frac{3}{2}}} + \cdots$ only! This kind of substitution will be the key to solve many similar statistical mechanics problems.

Question 3 (iii)

At high temperature,

$$\frac{\lambda^3 P}{kT} = \zeta + \frac{\zeta^2}{2^{\frac{5}{2}}} + \cdots = n\lambda^3 \left(1 - \frac{n\lambda^3}{2^{\frac{3}{2}}}\right) + (n\lambda^3)^2 \left(1 - \frac{n\lambda^3}{2^{\frac{3}{2}}}\right)^2 \frac{1}{2^{\frac{5}{2}}} = n\lambda^3 \left(1 - \frac{n\lambda^3}{2^{\frac{5}{2}}}\right)$$
$$U = \frac{3}{2} PV = \frac{3}{2} \frac{VkT}{\lambda^3} \left[n\lambda^3 - \frac{(n\lambda^3)^2}{2^{\frac{5}{2}}}\right] = \frac{3}{2} NkT \left(1 - \frac{n\lambda^3}{2^{\frac{5}{2}}}\right)$$

The first term refers to the classical gas approximation, the second is the quantum correction for Bose gases.

Hint: For the first line, binomial approximation is required to get the final results.

Question 4 (i)

It is an ideal gas of N free electrons with mass m, volume V at low temperature. We also have

$$f(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}, \qquad \mu = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right]$$

$$U = \int_0^\infty \epsilon n(\epsilon) f(\epsilon)\, d\epsilon = \int_0^\infty n(\epsilon) \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{3}{2}}\, d\epsilon$$

Using Sommerfeld expansion,

$$G'(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{3}{2}}, \qquad G(\epsilon) = \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{5}{2}}, \qquad G''(\epsilon) = \frac{3V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}$$

Using the expression $N = \frac{2}{3}\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon_F^{\frac{3}{2}}$ (you can calculate yourself), we have

$$\begin{aligned} U &\approx G(\mu) + \frac{\pi^2}{6}(kT)^2 G''(\mu) + \cdots \\ &= \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \mu^{\frac{5}{2}} + \frac{\pi^2}{6}(kT)^2 \frac{3}{4}\frac{V}{\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \mu^{\frac{1}{2}} + \cdots \\ &= \frac{3}{5} N\epsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right] \quad \text{[shown]} \end{aligned}$$

Hint: $\mu^{\frac{1}{2}} \approx \epsilon_F^{\frac{1}{2}}$, while substitute $\mu^{\frac{5}{2}}$ with the expression of μ given in the question.

Question 4 (ii)

$$P = \frac{2}{3}\frac{U}{V} \approx \frac{2}{5}\frac{N}{V}\epsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right]$$

$$\Omega_G = -PV \approx -\frac{2}{5} N\epsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right]$$

$$\begin{aligned} S &= \frac{U - \Omega_G - N\mu}{T} \\ &\approx \frac{1}{T}\left\{\frac{3}{5} N\epsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2\right] + \frac{2}{5} N\epsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2\right] - N\epsilon_F \left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2\right]\right\} \\ &= \frac{1}{2} N\pi^2 k^2 \frac{T}{\epsilon_F} \end{aligned}$$

$$F = U - TS \approx \frac{3}{5} N\epsilon_F \left[1 - \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2\right]$$

Question 4 (iii)

For P, if the 2nd term is neglected, we have $PV = \frac{2}{5} NkT_F$.

For S, at very low temperature, we see that it is proportional to T, in accordance to the 3rd Law of Thermodynamics.