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PART 1

Question 1 (i)

The energy of dipole aligned to B field is $-\mu B$ while anti-parallel alignment results in energy of μB. So,

$$E = -n\mu B + (6-n)\mu B$$
$$= 6\mu B - 2n\mu B$$
$$= 2\mu B(3-n)$$

Question 1 (ii)

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

$\Omega(0) = 1$

$\Omega(1) = 6$

$\Omega(2) = 15$

$\Omega(3) = 20$

$\Omega(4) = 15$

$\Omega(5) = 6$

$\Omega(6) = 1$

The largest multiplicity occurs for $n = 3$, so the most likely macrostate of the system has 3 dipoles parallel and 3 anti-parallel to the B field. For this configuration, the energy associated with the B field for the system will be zero. The least likely states are where $n = 0$ or $n = 0$, meaning all dipoles are anti-parallel or parallel to the B field.

Question 2

Take ε_1 to be the zero energy level and let $\varepsilon = \varepsilon_2 - \varepsilon_1$ so $\varepsilon_2 = \varepsilon$. Then, $Z_1 = 1 + e^{-\beta\varepsilon}$ which is partition function for 1 particle.

$$\ln Z_1 = \ln\left(1 + e^{-\beta\varepsilon}\right)$$

$$E_1 = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} = \frac{\varepsilon}{e^{\beta\varepsilon} + 1}$$

$$E(T, V, N) = \frac{N\varepsilon}{e^{\beta\varepsilon} + 1}$$

For very low T, $T \ll 1, \beta \gg 1$,

$E = N\varepsilon e^{-\beta\varepsilon} \Rightarrow 0$, meaning that most particles have energy ε_1.

For very high T, $T \gg 1, \beta \ll 1$, then

$e^{\beta\varepsilon} + 1 \approx 1 + \beta\varepsilon + 1 = 2 + \beta\varepsilon$, so,

$$E = \frac{N\varepsilon}{e^{\beta\varepsilon} + 1} \Rightarrow \frac{N}{2}\varepsilon$$

So about half are in state with energy ε_1, half in state with energy ε_2.

Question 3 (i)

$$Z_1 = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh\frac{\mu B}{kT} = 2\cosh x$$

$$\bar{\varepsilon}_1 = -\frac{\partial \ln Z_1}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln(2\cosh x) = -\frac{\sinh x}{\cosh x}\mu B = -\mu B \tanh x$$

$$E(T) = -N\mu B \tanh x$$

$$\bar{\mu} = \mu\frac{1}{Z_1}e^{\beta\mu B} - \mu\frac{1}{Z_1}e^{-\beta\mu B} = \frac{\mu}{2\cosh x}2\sinh x = \mu\tanh x$$

$$M = N\mu\tanh x$$

The heat capacity of a system due to magnetic field is

$$C_H = \left(\frac{đQ}{dT}\right)_H$$

And energy is $E = -\mu HM$ excluding mutual field energy.

$$dE = đQ - M\mu_0 dH$$

$$C_H = \left(\frac{\partial E}{\partial T}\right)_H = -\mu_0 H\left(\frac{\partial M}{\partial T}\right)_H = -\mu_0 H\frac{\partial}{\partial T}N\mu\tanh x = N\mu\mu_0 H\,\mathrm{sech}^2 x\,\frac{\mu B}{kT^2}$$

Assuming applied magnetic field $\mu_0 H$ and local field B is the same, $C_H = Nkx^2\,\mathrm{sech}^2\,x$.

Question 3 (ii)

$$\lim_{T\to 0} E = \lim_{x\to\infty} -N\mu\beta\tanh x = -N\mu\beta$$

So all atoms are aligned.

$$\lim_{T\to\infty} E = \lim_{x\to 0} -N\mu\beta\tanh x = 0$$

The atoms are randomly aligned.

For the heat capacities,

$$\lim_{T\to 0} C_H = \lim_{x\to\infty} Nkx^2\,\mathrm{sech}^2\,x = \lim_{x\to\infty}\frac{Nkx^2}{\cosh^2 x}$$

By L'Hôpital's rule,

$$\lim_{x\to\infty}\frac{Nkx^2}{\cosh^2 x} = Nk\lim_{x\to\infty}\frac{x}{\cosh x\sinh x} = Nk\lim_{x\to\infty}\frac{1}{\sinh^2 x + \cosh^2 x} = Nk\lim_{x\to\infty}\frac{1}{1 + 2\sinh^2 x} = 0$$

In agreement with 3rd Law.

Question 4 (i)

Energy gained by A = Energy lost by B.

$$\int_{T_A}^{T} C_A\,dT = -\int_{T_B}^{T} C_B\,dT$$

$C_A(T - T_A) = C_B(T_B - T)$

$T(C_A + C_B) = C_A T_A + C_B T_B$

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B}$$

Question 4 (ii)

Using a reversible path,

$$\Delta S_A = \int_{T_A}^{T} \frac{C_A}{T} dT = C_A \ln \frac{T}{T_A}$$

Similarly,

$$\Delta S_B = C_B \ln \frac{T}{T_B}$$

$$\Delta S = C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B}$$

Question 4 (iii)

If $T_A = T_B, T = T_A$, then

$$\Delta S = C_A \ln \frac{T_A}{T_A} + C_B \ln \frac{T_A}{T_B} = 0$$

Otherwise,

$$\Delta S = C_A \ln \frac{C_A T_A + C_B T_B}{T_A(C_A + C_B)} + C_B \ln \frac{C_A T_A + C_B T_B}{T_B(C_A + C_B)}$$

We are given $\ln x \leq x - 1$

$1 - x \leq -\ln x$

$$1 - x \leq \ln \frac{1}{x}$$

$$\Delta S \geq C_A \left[1 - \frac{T_A(C_A + C_B)}{C_A T_A + C_B T_B}\right] + C_B \left[1 - \frac{T_B(C_A + C_B)}{C_A T_A + C_B T_B}\right]$$

$$= C_A \frac{C_B T_B - C_B T_A}{C_A T_A + C_B T_B} + C_B \frac{C_A T_A - C_A T_B}{C_A T_A + C_B T_B}$$

$$= 0$$

Question 5 (i)

Question 5 (ii)

Question 5 (iii)

Question 6 (i)

$$\lim_{T\to 0}\beta = \lim_{T\to 0}\frac{1}{kT} = \infty$$

So, at $T = 0K$,

$$dN(\varepsilon) = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}\,d\varepsilon \text{ for } \varepsilon < \mu(0) = \varepsilon_F. \text{ So,}$$

$$N = \int_0^{\varepsilon_F}\frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}\,d\varepsilon = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\frac{2}{3}\varepsilon_F^{\frac{3}{2}}$$

$$E = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\int_0^{\varepsilon_F}\varepsilon^{\frac{3}{2}}\,d\varepsilon = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\frac{2}{5}\varepsilon_F^{\frac{5}{2}} = \frac{4\pi V}{h^3}(2m)^{\frac{3}{2}}\frac{2}{3}\varepsilon_F^{\frac{3}{2}}\frac{3}{5}\varepsilon_F = \frac{3}{5}N\varepsilon_F$$

Question 6 (ii)

At $T = 0K$, $F = E - TS = E$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \left(\frac{\partial E}{\partial V}\right)_{T,N}$$

$$E = \frac{3}{5}N\frac{h^2}{2m}\left(\frac{3}{8\pi}\frac{N}{V}\right)^{\frac{2}{3}} = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}}\frac{N^{\frac{5}{3}}}{V^{\frac{2}{3}}}$$

$$P = \frac{2h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}}\left(\frac{N}{V}\right)^{\frac{5}{3}} = \frac{4}{10}\frac{h^2}{2m}\left(\frac{3}{8\pi}\frac{N}{V}\right)^{\frac{2}{3}}\frac{N}{V} = \frac{2}{5}\varepsilon_F n$$

Question 6 (iii)

$$1\text{erg} = 10^{-7}\text{J}$$

$$P = \frac{2}{5}(10^{-18}J)(5\times 10^{28}\text{m}^{-3}) = 2\times 10^{10}\text{Pa}$$

PART 2

Question 1 (a)

Clasius-Clapeyron Equation:

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

Since volume of gas V_2 far larger than volume of liquid/solid V_1, $\Delta V \approx V_2$. Also, we assume a perfect classical gas so $PV_2 = nRT$.

$$\frac{d\ln P}{dT} = \frac{1}{P}\frac{dP}{dT} \approx \frac{1}{P}\frac{L}{TV_2} = \frac{1}{P}\frac{L}{T}\frac{P}{nRT} = \frac{L}{nRT^2}$$

$$d\ln P = \frac{L}{nRT^2}dT$$

For 1 mol, we get

$$d\ln P = \frac{L}{RT^2}dT$$

$$\ln P = -\frac{L}{RT} + k$$

$$P = P_0 e^{-\frac{L}{RT}}$$

Where k is a constant and $P_0 = P(T = 0)$.

Question 1 (b) i)

At the triple point,

$$23.03 - \frac{3754}{T} = 1.949 - \frac{3063}{T}$$

$$23.03T - 3754 = 19.49T - 3063$$

$$3.54T = 691$$

$$T = 195.2\text{K}$$

Question 1 (b) ii)

To find L_{sub}, we use C-C equation on the equation given:

$$\frac{L_{sub}}{RT^2} = \frac{d}{dT}\left(23.03 - \frac{3754}{T}\right) = \frac{3754}{T^2}$$

$$L_{sub} = 31210\text{J mol}^{-1}$$

To find L_{vap}, similarly

$$\frac{L_{vap}}{RT^2} = \frac{d}{dT}\left(19.49 - \frac{3063}{T}\right) = \frac{3063}{T^2}$$

$$L_{vap} = 25466\text{J mol}^{-1}$$

Since we are talking about state functions,

$$\Delta S_{sub} = \Delta S_{vap} + \Delta S_{melt}$$

$$L_{melt} = 57455\text{ mol}^{-1}$$

Question 2 (i)

$$E(T) = uV = aT^4V, \qquad P = \frac{a}{3}T^4, \qquad (1)$$

$$dE = 4aT^3V\,dT + aT^4\,dV, \qquad (2)$$

Substitute (1) and (2) into the fundamental thermodynamic relation,

$$T\,dS = 4aT^3V\,dT + aT^4\,dV + \frac{a}{3}T^4\,dV$$

$$dS = 4aT^2V\,dT + \frac{4}{3}aT^3\,dV$$

$$\text{Now,} \qquad dS = d\left(\frac{4}{3}aT^3V\right), \text{so}$$

$$S = \frac{4}{3}aT^3V + A$$

where A is a constant. But by third law, $S(T = 0) = 0$, so $A = 0$ and therefore $S = \frac{4}{3}aT^3V$.

Question 2 (ii)

$$H = E + PV = aT^4V + \frac{a}{3}T^4V = \frac{4}{3}aT^4V$$

$$F = E - TS = aT^4V - \frac{4}{3}aT^4V = -\frac{1}{3}aT^4V$$

$$G = E + PV - TS = \frac{4}{3}aT^4V - \frac{4}{3}aT^4V = 0$$

Question 2 (iii)

$$\mu = \left(\frac{\partial G}{\partial H}\right)_{T,P} = 0$$

So $\varepsilon_F = 0$ and at $T = 0\text{K}$, all particles are at the zero energy level.

Question 3 (a)

We begin from the definition of the grand potential, which is

$$\Omega = -kTln\,\mathcal{Z}, \text{with } \mathcal{Z}(T,V,\mu) = \sum_{N_r} e^{\beta(\mu N - E_{N_r})}$$

$$\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = -\frac{kT}{\mathcal{Z}}\sum_{N_r}\beta N e^{\beta(\mu N - E_{N_r})} = -\sum_{N_r} N P_{N_r} = -\bar{N}$$

So $\bar{N} = -\frac{\partial\Omega}{\partial\mu}$

$$\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{T,V} = -\left(\frac{\partial\bar{N}}{\partial\mu}\right)_{T,V} = -\sum_{N_r} N\left(\frac{\partial P_{N_r}}{\partial\mu}\right)_{T,V}, \qquad (1)$$

Observe that

$$\frac{1}{P_{N_r}}\left(\frac{\partial P_{N_r}}{\partial\mu}\right)_{T,V} = \left(\frac{\partial \ln P_{N_r}}{\partial\mu}\right)_{T,V}$$

$$= \frac{\partial}{\partial\mu}\left[\beta\mu N - \beta E_{N_r} - \ln\mathcal{Z}\right]_{T,V}$$

$$= \beta N - \frac{\partial\ln\mathcal{Z}}{\partial\mu}$$

$$= \beta N - \beta\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}$$

$$= \beta N - \beta\bar{N}, \qquad (2)$$

Sub (2) into (1),

$$\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{T,V} = -\sum_{N_r} N P_{N_r}(\beta N - \beta\bar{N}) = -\beta\sum_{N_r} N^2 P_{N_r} + \beta\sum_{N_r} N\bar{N}P_{N_r} = -\beta\overline{N^2} + \beta\bar{N}^2$$

$$(\Delta N)^2 = \overline{N^2} + \overline{N}^2 = -kT\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{T,V}, \qquad \Delta N = \sqrt{-kT\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{T,V}}$$

Question 3 (b)

$$\mathcal{Z} = \sum_{Nr} e^{\beta(\mu N - E_{N_r})} = \sum_N e^{\beta\mu N} \sum_r e^{-\beta E_{N_r}} = \sum_\mu e^{\beta\mu N} Z(T, VN)$$

For a perfect classical gas,

$$Z(T,V,N) = \frac{1}{N!}[Z_1(T,V)]^N$$

$$\mathcal{Z}(T,V,\mu) = \sum_N \frac{1}{N!}\left[e^{\beta\mu}Z_1(T,V)\right]^N = e^{e^{\beta\mu}Z_1(T,V)}$$

$$\Omega = -PV = -kT\ln\mathcal{Z} = -kTe^{\beta\mu}Z_1(T,V)$$

But $N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = e^{\beta\mu}Z_1(T,V)$

$\therefore PV = NkT$

[Answer incomplete…]

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