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Statistical Mechanics 6

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1. (i) two energy levels $E_1 = -\mu_B B$, $E_2 = \mu_B B$

Single particle Partition function

$$Z_1 = e^{+\beta \mu_B B} + e^{-\beta \mu_B B} = 2 \cosh(\beta \mu_B B)$$

$$= 2 \cosh\left(\frac{\mu_B B}{k_B T}\right) \checkmark$$

(ii) Particles are localised and distinguishable

\Rightarrow overall partition function given by

$$Z = Z_1^N = 2^N \cosh^N\left(\frac{\mu_B B}{k_B T}\right)$$

$$= \left(2 \cosh(\beta \mu_B B)\right)^N$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \left(N \ln \left(2 \cosh(\beta \mu_B B) \right) \right)$$

$$= -N \frac{\partial}{\partial \beta} \left(\ln 2 + \ln \left(\cosh(\beta \mu_B B) \right) \right)$$

$$= -N \frac{\sinh(\beta \mu_B B)}{\cosh(\beta \mu_B B)} \mu_B B$$

$$= -N \mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right)$$

keeping B constant means keeping all the energy levels E_i constant ($\because \mu_B$ is a constant)

Hence $dQ = dU - \sum_{\alpha} P_{\alpha} dE_{\alpha} = dU$

$$C_B = \left(\frac{\partial Q_{rev}}{\partial T} \right)_B = T \left(\frac{\partial S}{\partial T} \right)_B = \left(\frac{\partial U}{\partial T} \right)_B$$

$$= \frac{\partial}{\partial T} \left(-N \nu_B B \tanh \left(\frac{N \nu_B B}{k_B T} \right) \right)$$

$$= -N \nu_B B \frac{\frac{N \nu_B B}{k_B} \left(-\frac{1}{T^2} \right)}{\cosh^2 \left(\frac{N \nu_B B}{k_B T} \right)}$$

$$= \frac{N \nu_B B^2}{k_B} \frac{1}{T^2 \cosh^2 \left(\frac{N \nu_B B}{k_B T} \right)}$$

$$= N k_B \left(\frac{N \nu_B B}{k_B T} \right)^2 \frac{4}{\left(\exp \left(\frac{N \nu_B B}{k_B T} \right) + \exp \left(-\frac{N \nu_B B}{k_B T} \right) \right)^2}$$

$$= N k_B \left(\frac{2 N \nu_B B}{k_B T} \right)^2 \frac{\exp \left(\frac{2 N \nu_B B}{k_B T} \right)}{\left(\exp \left(\frac{2 N \nu_B B}{k_B T} \right) + 1 \right)^2}$$

$$= N k_B \left(\frac{\theta}{T} \right) \frac{e^{\theta/T}}{(e^{\theta/T} + 1)^2} \quad \checkmark \quad \left(\theta = \frac{2 N \nu_B B}{k_B} \right)$$

When C_B reach $C_{B, \max}$, ~~$\frac{\partial C_B}{\partial T}$~~ let $\frac{\theta}{T} = x$

then ~~$\frac{\partial C_B}{\partial T} = 0$~~ $\frac{\partial C_B}{\partial x} = 0$

$$\Rightarrow 0 = \frac{\partial}{\partial x} \left(x^2 \frac{e^x}{(e^x+1)^2} \right)$$

$$= \frac{2xe^x}{(e^x+1)^2} + x^2 \frac{e^x(e^x+1)^2 - e^x(2)(e^x+1)e^x x^2}{(e^x+1)^4}$$

$$\Rightarrow (e^x+1)^2(2x+x^2)e^x = 2e^{2x}(e^x+1)x^2$$

$$\Rightarrow (2x+x^2)(e^x+1) = 2e^x x^2$$

$$\Rightarrow 2x+x^2+2xe^x+x^2e^x = 2x^2e^x$$

$$\therefore (x^2-2x)e^x = x^2+2x$$

$$\therefore e^x = \frac{x^2+2x}{x^2-2x} = \frac{x(x+2)}{x(x-2)} = \frac{x+2}{x-2}$$

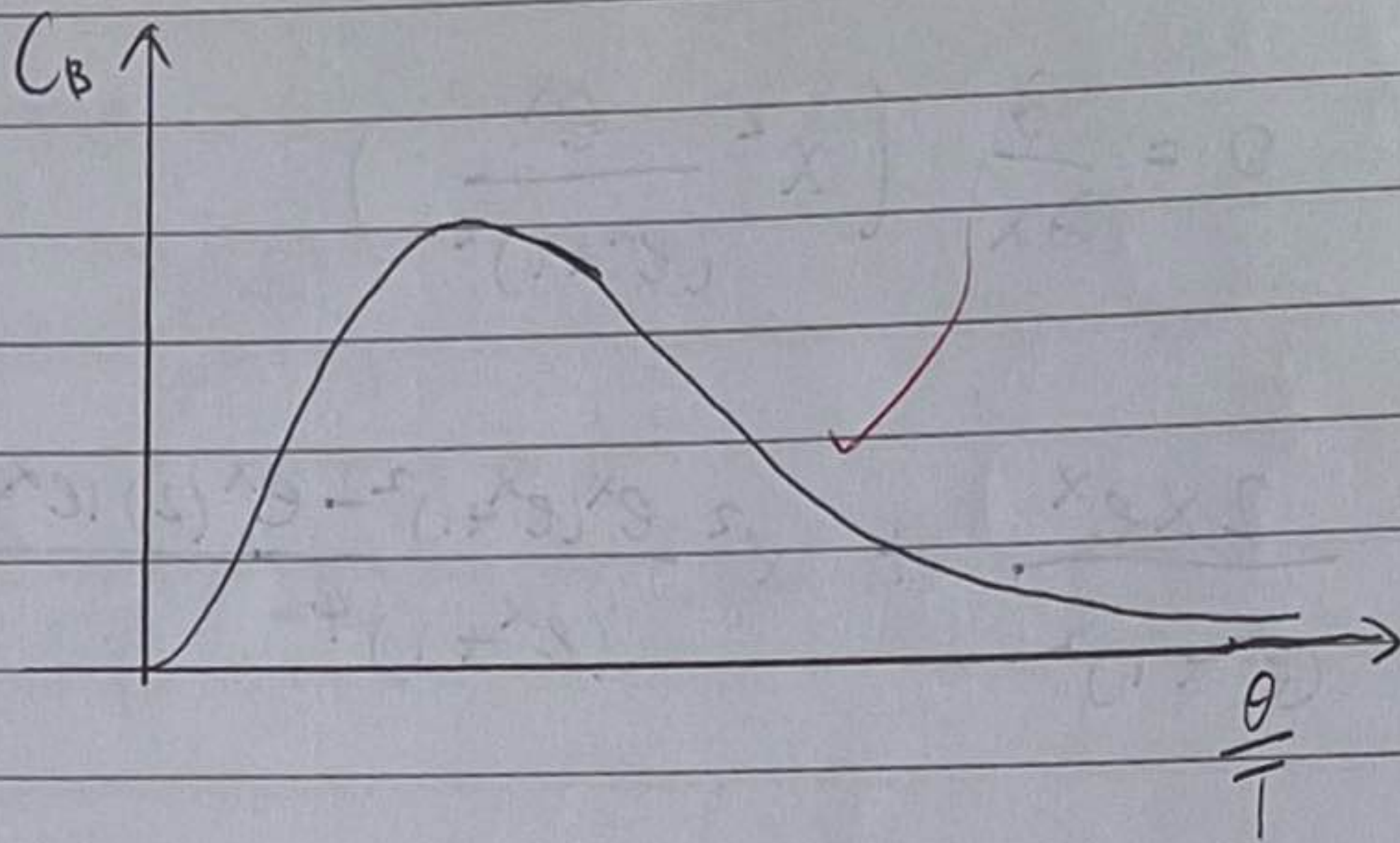
$$\Rightarrow e^x = 1 + \frac{4}{x-2}$$

$$\Rightarrow e^x - 1 = \frac{4}{x-2}$$

Solve numerically $x = 2.39936 \approx 2.4$

$$\Rightarrow \frac{0}{T_{\max}} = 2.4 \Rightarrow \frac{2N_B B}{k_B T_{\max}} = 2.4$$

$$\Rightarrow \boxed{T_{\max} = \frac{0.83 N_B B}{k_B}} \Rightarrow \boxed{A = 0.83}$$



(iii)

$$T_{max} = \frac{0.83 \mu_B B}{k_B}$$

$$\mu_B = 9.274 \times 10^{-24} \text{ J/T}$$

$$B = 10 \text{ T}$$

$$k_B = 1.38 \times 10^{-23}$$

$$\Rightarrow T_{max} = \frac{(0.83)(9.274 \times 10^{-24})(10)}{(1.38 \times 10^{-23})}$$

$$= \boxed{5.58 \text{ K}} \checkmark$$

2. Energy levels $E_n = (n + \frac{1}{2})\hbar\omega$ for a single oscillator

$$Z_1 = \sum_{n=0}^{\infty} \exp(-\beta(n + \frac{1}{2})\hbar\omega)$$

$$= \exp(-\frac{1}{2}\beta\hbar\omega) \sum_{n=0}^{\infty} \exp(-n\beta\hbar\omega)$$

$$= \exp(-\frac{1}{2}\beta\hbar\omega) \frac{1}{1 - \exp(-\beta\hbar\omega)}$$

~~$$= \exp(-\frac{1}{2}\beta\hbar\omega) \frac{1}{\exp(\frac{1}{2}\beta\hbar\omega) - \exp(-\frac{1}{2}\beta\hbar\omega)}$$~~

$$= \frac{1}{2 \sinh(\frac{1}{2}\beta\hbar\omega)}$$

$$\therefore Z = Z_1^N = \frac{1}{2^N \sinh^N(\frac{1}{2}\beta\hbar\omega)}$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} (-N \ln 2 - N \ln(\sinh(\frac{1}{2}\beta\hbar\omega)))$$

$$= N \frac{\partial}{\partial \beta} \ln(\sinh(\frac{1}{2}\beta\hbar\omega))$$

$$= N \frac{\cosh(\frac{1}{2}\beta\hbar\omega) \cdot \frac{1}{2}\hbar\omega}{\sinh(\frac{1}{2}\beta\hbar\omega)}$$

~~$$= \frac{1}{2}\hbar\omega$$~~

$$= \frac{N}{2} \hbar\omega \coth(\frac{1}{2}\hbar\beta\omega)$$

$$\Rightarrow U = \frac{N}{2} \hbar \omega \coth \left(\frac{\hbar \omega}{2k_B T} \right)$$

$$= \frac{N}{2} \hbar \omega \frac{e^{\hbar \omega / k_B T} + 1}{e^{\hbar \omega / k_B T} - 1}$$

$$= \frac{N}{2} \hbar \omega \left(1 + \frac{2}{e^{\hbar \omega / k_B T} - 1} \right)$$

when T is high i.e. $T \gg \frac{\hbar \omega}{k_B}$, then

$$e^{\hbar \omega / k_B T} \approx 1 + \frac{\hbar \omega}{k_B T}$$

$$\therefore U \approx \frac{N}{2} \hbar \omega \left(1 + \frac{2}{\frac{\hbar \omega}{k_B T}} \right)$$

$$= \frac{N}{2} \hbar \omega \left(\frac{2k_B T}{\hbar \omega} + 1 \right)$$

$$\approx N k_B T$$

let $x = \exp(\hbar \omega / k_B T)$ then.

$$\frac{U}{N} = \left(m + \frac{1}{2} \right) \hbar \omega = \frac{x+1}{x-1} \left(\frac{1}{2} \hbar \omega \right)$$

$$\Rightarrow \frac{x+1}{x-1} = 2m+1$$

$$\Rightarrow x+1 = (2m+1)x - (2m+1)$$

$$2mx = 2m+2 \Rightarrow x = \frac{m+1}{m}$$

$$S = \frac{U}{T} + k_B \ln Z$$

~~$$= \frac{k_B}{2} \frac{h\omega}{k_B T} \frac{x+1}{x-1} + k_B \left(-N \ln 2 - N \ln \left(\frac{x+1}{2} \right) \right)$$~~

$$= k_B \frac{N}{2} \frac{h\omega}{k_B T} \frac{x+1}{x-1} + k_B \left(-N \ln 2 - N \ln \left(\frac{e^{-\frac{1}{2}\beta h\omega}}{1 - \exp(-\beta h\omega)} \right) \right)$$

$\ln x$

~~$$= \frac{N k_B}{2} \frac{\ln x}{x-1} \frac{x+1}{x-1} - N k_B (\ln 2 +$$~~

$$= N k_B \frac{\ln x}{2} \frac{x+1}{x-1} + N k_B \left(-\frac{1}{2} \ln x - \ln \left(1 - \frac{1}{x} \right) \right)$$

$$= \frac{1}{2} N k_B \ln x (2m+1) - \frac{1}{2} N k_B \ln x - N k_B \ln \left(\frac{x-1}{x} \right)$$

$$= N k_B \left[m \ln \left(\frac{m+1}{m} \right) - \ln \left(\frac{1}{m+1} \right) \right]$$

$$\Rightarrow \frac{S}{N k_B} = m \ln \left(\frac{m+1}{m} \right) - \ln \left(\frac{1}{m+1} \right)$$

$$= m \ln(m+1) - m \ln m + \ln(m+1)$$

$$= \boxed{(m+1) \ln(m+1) - m \ln m}$$

QED.

When $m=0$

$$\frac{S}{Nk_B} = \lim_{m \rightarrow 0} \left(\frac{1}{m} \ln m \right) = \lim_{m \rightarrow 0} m \ln m$$

$$\lim_{m \rightarrow 0} m \ln m = \lim_{m \rightarrow 0} \frac{\ln m}{\frac{1}{m}} = \lim_{m \rightarrow 0} -\frac{\frac{1}{m}}{\frac{1}{m^2}}$$

$$= \lim_{m \rightarrow 0} -m = 0$$

$$\therefore \frac{S}{Nk_B} \rightarrow 0 \text{ as } m \rightarrow 0$$

When the average energy per oscillator is equal to the lowest energy level of a single oscillator,

each oscillator occupies its lowest energy state with no more than 1

ways of distributing probabilities

Hence entropy = 0

3 (i)

$$Z_{\text{mag}} = \sum_{m_J=-J}^J \exp\left(-\frac{m_J g_J N_B B}{k_B T}\right) \quad \left(\gamma = \frac{g_J N_B B}{k_B T}\right)$$

$$= \sum_{m_J=-J}^J \exp(-m_J \gamma) = \exp(-J\gamma) \frac{1 - \exp((2J+1)\gamma)}{1 - \exp(\gamma)}$$

$$= \frac{\exp(-J\gamma) - \exp((J+1)\gamma)}{1 - \exp(\gamma)}$$

$$= \frac{\exp(-(J+\frac{1}{2})\gamma) - \exp((J+\frac{1}{2})\gamma)}{\exp(-\frac{1}{2}\gamma) - \exp(\frac{1}{2}\gamma)}$$

$$= \frac{\cancel{2} \sinh((J+\frac{1}{2})\gamma)}{\cancel{2} \sinh(\frac{1}{2}\gamma)} = \boxed{\frac{\sinh((J+\frac{1}{2})\gamma)}{\sinh(\frac{1}{2}\gamma)}}$$

(ii) For overall system,

$$Z = Z_{\text{mag}}^N = \left(\frac{\sinh((J+\frac{1}{2})\gamma)}{\sinh(\frac{1}{2}\gamma)}\right)^N$$

$$F = -k_B T \ln Z = -k_B T N \ln \left(\frac{\sinh((J+\frac{1}{2})\gamma)}{\sinh(\frac{1}{2}\gamma)}\right)$$

magnetic moment

$$m = -\left(\frac{\partial F}{\partial B}\right)_T = +k_B T N \frac{\sinh(\frac{1}{2}\gamma)}{\sinh((J+\frac{1}{2})\gamma)} \left(\frac{(J+\frac{1}{2}) \cosh((J+\frac{1}{2})\gamma) \sinh(\frac{1}{2}\gamma)}{\sinh^2(\frac{1}{2}\gamma)}\right)$$

$$= \left(\frac{\frac{1}{2} \cosh(\frac{1}{2}\gamma) \sinh((J+\frac{1}{2})\gamma)}{\sinh^2(\frac{1}{2}\gamma)}\right) \left(\frac{\partial \gamma}{\partial B}\right)_T$$

$$= \bullet k_B T N \left(\frac{\partial Y}{\partial B} \right)_T \left[\left(J + \frac{1}{2} \right) \coth \left(\left(J + \frac{1}{2} \right) Y \right) - \frac{1}{2} \coth \left(\frac{1}{2} Y \right) \right]$$

$$= k_B T N \frac{g_J \mu_B N_B}{k_B T} \left[\left(J + \frac{1}{2} \right) \coth \left(\left(J + \frac{1}{2} \right) Y \right) - \frac{1}{2} \coth \left(\frac{1}{2} Y \right) \right]$$

$$\chi = \lim_{B \rightarrow 0} \frac{\mu_0 M}{B} = \lim_{B \rightarrow 0} \frac{\mu_0 m}{V B}$$

$$= \lim_{B \rightarrow 0} \lim_{\substack{B \rightarrow 0 \\ Y \rightarrow 0}} \frac{\mu_0 g_J \mu_B N}{B V} \left[\left(J + \frac{1}{2} \right) \coth \left(\left(J + \frac{1}{2} \right) Y \right) - \frac{1}{2} \coth \left(\frac{1}{2} Y \right) \right]$$

$$\lim_{x \rightarrow 0} \coth(x) = \frac{1}{x} + \frac{x}{3}$$

$$= \lim_{\substack{B \rightarrow 0 \\ Y \rightarrow 0}} \frac{\mu_0 g_J \mu_B N}{B} \left[\left(J + \frac{1}{2} \right) \left(\frac{1}{\left(J + \frac{1}{2} \right) Y} + \frac{\left(J + \frac{1}{2} \right) Y}{3} \right) - \frac{1}{2} \left(\frac{2}{Y} + \frac{1}{3} Y \right) \right]$$

$$= \lim_{\substack{B \rightarrow 0 \\ Y \rightarrow 0}} \frac{\mu_0 g_J \mu_B N}{B V} \left[\left(J + \frac{1}{2} \right)^2 \left(\frac{1}{3} Y \right) - \left(\frac{1}{2} \right)^2 \left(\frac{1}{3} Y \right) \right]$$

$$= \lim_{\substack{B \rightarrow 0 \\ Y \rightarrow 0}} \frac{\mu_0 g_J \mu_B N V}{3 B V} \left[\left(J + \frac{1}{2} \right)^2 - \left(\frac{1}{2} \right)^2 \right]$$

$$= \lim_{\substack{B \rightarrow 0 \\ Y \rightarrow 0}} \frac{\mu_0 g_J \mu_B N (J+1) J}{3 V} \left(\frac{Y}{B} \right) \rightarrow \frac{g_J \mu_B}{k_B T}$$

$$n = \frac{N}{V}$$

$$= \frac{\mu_0 g_J^2 \mu_B^2 n J(J+1)}{3 k_B T}$$

For spin $-\frac{1}{2}$ particles : $J = \frac{1}{2}$

$$\chi = \frac{n N_0 g_J^2 \mu_B^2 \frac{1}{2} \left(\frac{3}{2} \right)}{3 k_B T}$$

for spin $-\frac{1}{2}$, $g_J = 2$

$$= \frac{n N_0 g_J^2 \mu_B^2}{4 k_B T} = \frac{4 n N_0 \mu_B^2}{4 k_B T} = \frac{n N_0 \mu_B^2}{k_B T} \quad \checkmark$$

predicted from the above formula, which is consistent with the result derived in the lectures:

~~For spin $-\frac{1}{2}$ particles,~~

$$\chi = \left(2 \cosh \left(\frac{\mu_B B}{k_B T} \right) \right)$$

4. Based on equipartition theorem :

For monatomic gas :

3 D.o.f \rightarrow kinetic energy has 3 modes
(one in each direction of x, y, z)

For diatomic gas :

D.o.f \rightarrow 3 kinetic energy modes + 2 rotational modes (the third needs very temperature to be excited so we ignore it)
+ 2 ~~vibrant~~ possibly 2 vibrational modes (kinetic energy relative to the centre of mass and potential energy)

\therefore D.o.f = 5 (vibration not excited)
7 (vibration excited)

For solid: Each atom is connected by 6 springs and so N particles has

$$N \times \frac{6}{2} = 3N \text{ springs.}$$

Each spring has D.o.f = 2 (vibrational)

$$\therefore \text{D.o.f per particle} = \frac{2 \times 3N}{N} = 6$$

$$(R = 8.314 \text{ J/K} \cdot \text{mol})$$

Hence: for monatomic gas: $\langle E \rangle = \frac{3}{2} N k_B T$

$$C_V = \frac{3}{2} N_A k_B = \frac{3}{2} R \approx 12.47 \text{ J/K} \cdot \text{mol}$$

For diatomic gas: $\langle E \rangle = \frac{5}{2} k_B N T$

(~~or noble gas~~)

$$\text{or } \frac{7}{2} N k_B T$$

$$C_V = \frac{5}{2} R \approx 20.79 \text{ J/K} \cdot \text{mol}$$

$$\text{or } C_V = \frac{7}{2} R \approx 29.10 \text{ J/K} \cdot \text{mol}$$

For solid: $\langle E \rangle = 3 N k_B T$

$$C_V = 3R \approx 24.94 \text{ J/K} \cdot \text{mol}$$

Hence: $\therefore C_p - C_V = R$ for ~~gas~~ ideal gases

$C_p = C_V = C$ for solids

\therefore For monatomic gas:

$$C_p = \frac{5}{2} R = 20.79 \text{ J/K} \cdot \text{mol} \quad \checkmark$$

For diatomic gas:

$$C_p = \frac{7}{2} R \approx 29.10 \text{ J/K} \cdot \text{mol} \quad \checkmark \text{ (vibration not excited)}$$

$$C_p = \frac{9}{2} R = 37.415 \text{ J/K} \cdot \text{mol} \quad \text{(vibration excited)}$$

For solids:

$$C_p = 3R = 24.94 \text{ J/K} \cdot \text{mol} \quad \checkmark$$

Hence :

$$\text{Al} \rightarrow C_p = 24.35 \sim 24.94 \rightarrow \text{solid}$$

$$\text{Ar} \rightarrow C_p = 20.79 \sim 20.79 \rightarrow \text{monatomic gas}$$

$$\text{Au} \rightarrow C_p = 25.42 \sim 24.94 \rightarrow \text{solid}$$

$$\text{Cu} \rightarrow C_p = 24.44 \sim 24.94 \rightarrow \text{solid}$$

$$\text{He} \rightarrow C_p = 20.79 \sim 20.79 \rightarrow \text{solid monatomic gas}$$

$$\text{H}_2 \rightarrow C_p = 28.82 \sim 29.10 \rightarrow \text{diatomic gas}$$

$$\text{Fe} \rightarrow C_p = 25.10 \sim 24.94 \rightarrow \text{solid}$$

$$\text{Pb} \rightarrow C_p = 26.44 \sim 24.94 \rightarrow \text{solid}$$

$$\text{Ne} \rightarrow C_p = 20.79 \sim 20.79 \rightarrow \text{monatomic gas}$$

$$\text{N}_2 \rightarrow \text{~~29.13~~ } C_p = 29.13 \sim 29.10 \rightarrow \text{diatomic gas}$$

$$\text{O}_2 \rightarrow C_p = 29.36 \sim 29.10 \rightarrow \text{diatomic gas}$$

$$\text{Ag} \rightarrow C_p = 25.53 \sim 24.94 \rightarrow \text{solid}$$

$$\text{Xe} \rightarrow C_p = 20.79 \sim 20.79 \rightarrow \text{monatomic gas}$$

$$\text{Zn} \rightarrow C_p = 25.40 \sim 24.94 \rightarrow \text{solid}$$

From this we can see that monatomic gases (noble gases) agree with the equipartition theorem very well, whereas solids and ~~diatomic~~ diatomic gases do not match ~~the~~ the predictions as accurately as monatomic gases.

This is because diatomic gases and solids have energy levels that need high temperature to excite compared to energy levels of ~~diatomic~~ monatomic gases.

✓ 298 K is a temperature high enough for the equipartition theorem to be very accurate but ~~not high~~ high for monatomic gases but not high enough for it to be very accurate for diatomic gases and solids.

5. (i) For 1-D harmonic oscillator (which we use to model the vibration of N_2)

$$C_V^{570} = N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{\exp(\hbar \omega / k_B T)}{[\exp(\hbar \omega / k_B T) - 1]^2}$$

From the data we know that at $T \approx 1170 \text{ K}$

$$\frac{C_V^{570}}{R(\text{\# of moles})} = 3 - 2.5 = 0.5$$

$$\therefore C_V^{570} = 0.5 N k_B$$

$$\Rightarrow \frac{1}{2} = \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{\exp(\hbar \omega / k_B T)}{[\exp(\hbar \omega / k_B T) - 1]^2} \quad \text{for } T = 1170 \text{ K}$$

$$\Rightarrow \frac{\hbar \omega}{k_B T} = 2.98 \quad (\text{solved numerically})$$

$$\Rightarrow \omega = \frac{2.98 \times 1170 \times 1.38 \times 10^{-23}}{1.05 \times 10^{-34}} = 4.6 \times 10^{14} \text{ Hz}$$

$$\text{frequency } f = \frac{\omega}{2\pi} = 7.19 \times 10^{13} \text{ Hz}$$

(ii) moment of inertia

$$I \sim \mu S^2 = (1.15 \times 10^{-26} \text{ kg}) (1 \times 10^{-10})^2$$

$$= 1.15 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

↑
reduced
mass of
 N_2

↑
separation
between atoms

Temperature needed to ~~freeze~~ freeze the rotational degree of freedom is

$$T_R = \frac{h^2}{2Ik_B} = 3.5 \text{ K}$$

Hence it is ^{only} possible to freeze the rotational degree of freedom ~~to~~ if we can control the temperature to ~~be~~ be lower than 3.5 K, which is very difficult.

6. For a diatomic molecule, d.o.f = 5

$\therefore \theta_{rot} \ll T \ll \theta_{vib} \therefore$ We can ignore vibration and treat rotation classically (T is high enough)

\Rightarrow By equipartition theorem:

$$U = \langle E \rangle = \frac{5}{2} k_B T$$

$$\therefore U = - \frac{\partial \ln Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial T} \frac{\partial T}{\partial \beta} = - \frac{\partial \ln Z / \partial T}{\partial \beta / \partial T}$$

$$= (-k_B T^2) \left(- \frac{\partial \ln Z}{\partial T} \right)$$

$$\beta = \frac{1}{k_B T}$$

$$\frac{\partial \beta}{\partial T} = - \frac{1}{k_B T^2}$$

$$= k_B T^2 \frac{\partial \ln Z}{\partial T}$$

$$\therefore \frac{5}{2} = T \frac{\partial \ln Z}{\partial T} \Rightarrow \frac{5}{2} \frac{1}{T} = \frac{\partial \ln Z}{\partial T}$$

$$\Rightarrow \ln Z = \int \frac{5}{2} \frac{1}{T} dT = \frac{5}{2} \ln T + f_1(V)$$

$$\Rightarrow Z = \exp\left(\frac{5}{2} \ln T\right) \exp(f_1(V))$$

$$\Rightarrow Z = T^{5/2} f_2(V)$$

f_1, f_2 are function of V and independent of T

$$\Rightarrow Z \propto T^{5/2}$$

$$\text{Also, } Z = V \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \sum_{(i)} e^{-\eta_i / k_B T}$$

where η_i are the energy levels of rotation.

It is given by $\eta_{l,m} = \frac{\hbar^2}{2I} l(l+1)$ which is independent of V

$$\therefore Z \propto V$$

$$\Rightarrow Z \propto VT^{5/2} \quad \checkmark$$

$$\text{let } Z = C VT^{5/2} \quad (C = \text{const})$$

$$\text{then } F = -k_B T \ln Z = -k_B C T (\ln V + \frac{5}{2} \ln T)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -k_B \left(\ln V + \frac{5}{2} + \frac{5}{2} \ln T\right)$$

Along an adiabat $S = \text{const}$

$$\therefore \ln V + \frac{5}{2} \ln T = \text{const} \Rightarrow \exp(VT^{5/2}) = \text{const}$$

$$\Rightarrow VT^{5/2} = \text{const}$$

Ideal gas law for one molecule $PV = k_B T$

$$\therefore T = \frac{PV}{k_B} \quad \therefore V \left(\frac{PV}{k_B}\right)^{5/2} = \text{const}$$

$$\therefore P^{5/2} V^{7/2} = \text{const}$$

$$\boxed{PV^{7/5} = \text{const}} \quad \checkmark$$

7. a) For classical ideal gas, the states α are

$$\alpha = (\alpha_N, N)$$

where $\alpha_N = \{n_{k_1}, \dots, n_{k_n}\}$, $\sum_k n_k = N$

occupation numbers

The Grand Partition function:

$$Z = \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})} = \sum_{\alpha_N} \sum_N e^{-\beta(E_{\alpha_N} - \mu N)}$$

$$= \sum_N e^{\beta \mu N} \sum_{\alpha_N} e^{-\beta E_{\alpha_N}}$$

$$= \sum_N e^{\beta \mu N} Z_N$$

$$= \sum_N e^{\beta \mu N} \frac{Z_1^N}{N!} = \sum_N \frac{(e^{\beta \mu} Z_1)^N}{N!}$$

$$= \exp(Z_1 \exp(\beta \mu))$$

where $Z_1 = \frac{V}{\lambda_{th}^3} Z_{int}$, $\lambda_{th} = h \sqrt{\frac{2\pi}{m k_B T}}$

Grand Potential

$$\Phi = -k_B T \ln Z = -k_B T Z_1 e^{\beta \mu}$$

$$p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T, \mu} = -(-k_B T) e^{\beta \mu} \frac{Z_{int}}{\lambda_{th}^3} \frac{Z_1}{V}$$

$$= \frac{k_B T}{V} e^{\beta \mu} Z_1 = -\frac{\Phi}{V}$$

$$\bar{N} = - \left(\frac{\partial \Phi}{\partial N} \right)_{T,V} = k_B T Z_1 \frac{\partial}{\partial N} e^{\beta N}$$

$$= \underbrace{k_B T \beta}_{1} Z_1 e^{\beta N} = Z_1 e^{\beta N} = - \frac{\Phi}{k_B T}$$

$$\therefore -\Phi = \bar{N} k_B T = pV$$

$$\Rightarrow pV = \bar{N} k_B T \Rightarrow p = n k_B T \quad (n = \frac{\bar{N}}{V})$$

b) mass of each atom = m

$$\rightarrow \text{reduced mass} = \frac{m^2}{2m} = \frac{m}{2}$$

$$\text{moment of inertia } I = m_R r^2 = \frac{1}{2} m r^2$$

\therefore rotation levels are excited but vibrational levels are not:

$$\therefore Z_{\text{int}} = Z_{\text{rotation}} = \frac{2Ik_B T}{h^2} = \frac{m r^2 k_B T}{h^2}$$

$$\therefore \bar{N} = Z_1 e^{\beta N} = Z_1 \exp(N/k_B T)$$

$$\therefore \ln \frac{\bar{N}}{Z_1} = \frac{N}{k_B T}$$

$$\Rightarrow N = -k_B T \ln \frac{Z_1}{\bar{N}}$$

$$\therefore Z_1 = \frac{V}{\lambda_{th}^3} Z_{\text{int}}$$

$$\therefore N = -k_B T \ln \frac{Z_{\text{int}} V}{\lambda_{th}^3 \bar{N}} = -k_B T \ln \frac{Z_{\text{int}}}{n \lambda_{th}^3}$$

$$8 = k_B T \ln \frac{Z_{int}}{n} = k_B T \ln \frac{n \lambda^3}{Z_{int}}$$

$$= k_B T \ln \left(\frac{h^3 \left(\frac{2\pi}{mk_B T} \right)^{3/2}}{mr^2 k_B T} \right)$$

$$\therefore p = nk_B T \quad \therefore n = \frac{p}{k_B T}$$

$$\therefore N = k_B T \ln \left(\frac{\frac{p}{k_B T} h^3 \left(\frac{2\pi}{mk_B T} \right)^{3/2}}{mr^2 k_B T} \right)$$

$$N = k_B T \ln \left(p h^3 (2\pi)^{3/2} m^{-5/2} (k_B T)^{-7/2} r^{-2} \right)$$

~~$$N = k_B T \ln$$~~

8. System in equilibrium

$\Rightarrow T$ is constant, N is constant

$$\therefore N = -k_B T \ln \frac{Z_1}{N} = \text{const} \quad \text{because the}$$

system is composed of ideal gas

$$Z_1 = \frac{V}{\lambda_{th}^3} Z_{int} \quad \lambda_{th} = \frac{h}{\sqrt{2m k_B T}}$$

and Z_{int} here is the centrifugal potential effect Z_{cf} and the effect of rotational and vibrational degrees of freedom Z_{rv}

* Centrifugal force $F_{cf} = m\Omega^2 r$

\Rightarrow Centrifugal potential $V_{cf} = -\frac{1}{2} m \Omega^2 r^2$

$$Z_{cf} = \exp\left(+\frac{m\Omega^2 r^2}{2k_B T}\right) \quad (\text{only one energy level})$$

$$\therefore \text{const} = N = -k_B T \ln \left[\frac{V}{\lambda_{th}^3 N} Z_{rv} \exp\left(+\frac{m\Omega^2 r^2}{k_B T}\right) \right]$$

$$= -k_B T \left[\ln \frac{N(r) \lambda_{th}^3}{Z_{rv}} - \frac{1}{2} m \Omega^2 r^2 \right]$$

$$\Rightarrow \ln \frac{N(r) \lambda_{th}^3}{Z_{rv}} = \text{const} + \frac{m\Omega^2 r^2}{k_B T}$$

$$\Rightarrow n(r) = \frac{Zrv}{\lambda_{th}^3} e^{\text{constant}} \exp\left(+\frac{m\Omega^2 r^2}{2k_B T}\right)$$

constant is $n(0)$ $\because r=0, n=n(0)$

$$\Rightarrow n(r) = n(0) \exp\left(\frac{m\Omega^2 r^2}{2k_B T}\right)$$

Total number of molecules inside cylinder is unchanged $\bar{N} = \text{const}$. $\bar{N} = \bar{n}V$, $V = \pi R^2 L$

$$\text{Also } \bar{N} = \iiint n(r) d\tau = \int_0^R n(r) 2\pi r L dr$$

volume element

$$= 2\pi L \int_0^R n(0) \exp\left(\frac{m\Omega^2 r^2}{2k_B T}\right) r dr \quad (\text{let } c = \frac{m\Omega^2}{2k_B T})$$

$$= 2\pi L n(0) \int_0^R r e^{cr^2} dr$$

$$\int r e^{cr^2} dr = \frac{1}{2} \int e^{cr^2} d(r^2)$$

$$= \frac{1}{2c} e^{cr^2} + \text{const}$$

$$\Rightarrow \bar{N} = \bar{n}V = 2\pi L n(0) \frac{1}{2c} e^{cr^2} \Big|_0^R$$

$$= \frac{2\pi L n(0)}{c} [e^{cR^2} - 1]$$

$$\Rightarrow n(0) = \frac{\bar{n}cV}{\pi L [e^{cR^2} - 1]}$$

$$C = \frac{m\Omega^2}{2k_B T}, \quad \frac{V}{L} = \pi R^2$$

$$\Rightarrow n(0) = \frac{\bar{n} \frac{m\Omega^2}{2k_B T} \pi R^2}{\pi [e^{\frac{m\Omega^2 R^2}{2k_B T}} - 1]}$$

$$\Rightarrow n(0) = \frac{\bar{n} m \Omega^2 R^2}{2k_B T [e^{\frac{m\Omega^2 R^2}{2k_B T}} - 1]}$$

$$\Rightarrow n(r) = \frac{\bar{n} m \Omega^2 R^2 \exp\left(-\frac{m\Omega^2 r^2}{2k_B T}\right)}{2k_B T [e^{\frac{m\Omega^2 R^2}{2k_B T}} - 1]}$$

When $r = R$

$$n(R) = \frac{\bar{n} m \Omega^2 R^2 \exp\left(-\frac{m\Omega^2 R^2}{2k_B T}\right)}{2k_B T [e^{\frac{m\Omega^2 R^2}{2k_B T}} - 1]}$$

At high temperature, $\frac{m\Omega^2 R^2}{2k_B T}$ is small

$$n(R) \xrightarrow{\approx} \bar{n} \frac{\left(\frac{m\Omega^2 R^2}{2k_B T}\right) \exp\left(-\frac{m\Omega^2 R^2}{2k_B T}\right)}{\left[1 + \frac{m\Omega^2 R^2}{2k_B T} - 1\right]}$$

$$= \bar{n} \exp\left(-\frac{m\Omega^2 R^2}{2k_B T}\right) \approx \bar{n} \left(1 - \frac{m\Omega^2 R^2}{2k_B T}\right) \approx \bar{n}$$

Basically the density profile is uniform.
Rotation does not affect the number density distribution very much.

At low temperature, $\frac{m\Omega^2 R^2}{2k_B T}$ is large

$$\Rightarrow \exp\left(-\frac{m\Omega^2 R^2}{2k_B T}\right) - 1 \sim \exp\left(-\frac{m\Omega^2 R^2}{2k_B T}\right)$$

$$\therefore n(R) \rightarrow \bar{n} \frac{m\Omega^2 R^2}{2k_B T} \gg \bar{n}$$

\therefore Most of the particles are accumulated at the edge of the cylinder.

9. From 7 we know that for classical ideal gas the grand partition function

$$\mathcal{Z} = \exp(z_1 \exp(\beta\mu))$$

The grand potential

$$\Phi = -k_B T \ln \mathcal{Z} = -k_B T z_1 e^{\beta\mu}$$

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T, V} = z_1 e^{\beta\mu} + k_B T z_1 \beta e^{\beta\mu}$$

$$= z_1 e^{\beta\mu}$$

$$\Rightarrow \beta\mu = \ln \frac{\bar{N}}{z_1} \Rightarrow \mu = k_B T \ln \frac{\bar{N}}{z_1}$$

$$\therefore \mathcal{Z} = \exp(z_1 e^{\beta\mu}) = e^{\bar{N}}$$

The probability to find exactly N particles is

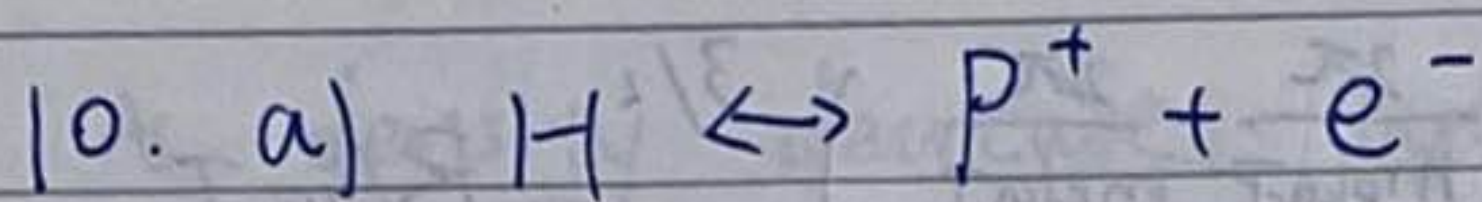
$$P_N = \sum_{\alpha_N} P_{\alpha_N} = \frac{1}{\mathcal{Z}} \sum_{\alpha_N} e^{-\beta(E_{\alpha_N} - \mu N)} = \frac{e^{\beta\mu N}}{\mathcal{Z}} \sum_{\alpha_N} e^{-\beta E_{\alpha_N}}$$

$z_N = \frac{z_1^N}{N!}$

$$= \frac{e^{\beta\mu N}}{\mathcal{Z}} z_N = \frac{z_1^N e^{\beta\mu N}}{N! \mathcal{Z}}$$

$$= \frac{(z_1 e^{\beta\mu})^N}{N!} \left(\frac{1}{\mathcal{Z}}\right) = \frac{\bar{N}^N e^{-\bar{N}}}{N!}$$

→ poisson distribution



$\nu_H = \nu_1 = 1, \nu_{P^+} = \nu_2 = -1, \nu_{e^-} = \nu_3 = -1$

$\sum_s \nu_s \mu_s = 0 \Rightarrow \nu_H \mu_H + \nu_{P^+} \mu_{P^+} + \nu_{e^-} \mu_{e^-} = 0$

$\Rightarrow \boxed{\mu_H = \mu_{P^+} + \mu_{e^-}} \checkmark$

in chemical equilibrium

b) For classical ideal gases

$\prod_s c_s^{\nu_s} = P^{-\sum_s \nu_s} \prod_s \left[\frac{k_B T}{\lambda_{th,s}^3} Z_{int,s} \right]^{\nu_s}$

where $c_s = \frac{N_s}{N} = \frac{N_s}{V} \cdot \frac{V}{N} = \frac{n_s}{n}$

$\nu_1 = 1, \nu_2 = -1, \nu_3 = -1, P = n k_B T$

sub in $\Rightarrow \frac{(n_H/n)}{(n_P/n)(n_{e^-}/n)} = P \left[\frac{k_B T}{\lambda_{th,H}^3} \cdot \frac{\lambda_{th,P}^3}{k_B T} \cdot \frac{\lambda_{th,e}^3}{k_B T} \right] \frac{Z_{int,H}}{Z_{int,P} Z_{int,e}}$

$\lambda_{th,s} = h \sqrt{\frac{2\pi}{m_s k_B T}}, Z_{int,H} = Z_{int,P} = 1, Z_{int,e} = 1$

no energy associated with internal structure

$Z_{int,H} = \sum_i \exp(-\beta E_i) \approx \exp(-\beta(-R)) = e^{BR} = e^{R/k_B T}$

ignoring all excited states

Ground state $E = -R$

$$\frac{n_H}{n_p n_e} x = x \left(\hbar^2 \frac{\frac{2\pi}{m_p k_B T} \cdot \frac{2\pi}{m_e k_B T}}{\frac{2\pi}{m_H k_B T}} \right)^{3/2} e^{-R/k_B T}$$

$$\rightarrow \frac{n_p n_e}{n_H} = \left(\frac{k_B T}{2\pi \hbar^2} \left(\frac{m_H m_e}{m_p} \right) \left(\frac{m_H}{m_p m_e} \right)^{-1} \right)^{3/2} e^{-R/k_B T}$$

$$\frac{m_H}{m_p m_e} \approx \frac{m_p + m_e}{m_p m_e} = \frac{1}{m_p} + \frac{1}{m_e} \approx \frac{1}{m_e}$$

$$m_H \approx m_p + m_e$$

$$m_p \gg m_e$$

$$\frac{1}{m_p} \ll \frac{1}{m_e}$$

$$\rightarrow \boxed{\frac{n_p n_e}{n_H} = \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T}}$$

→ The Saha Equation

(c) Conservation of charge $\Rightarrow n_e = n_p$

Conservation of nucleons $\Rightarrow n_p + n_H = n \rightarrow \text{fixed}$

$$\rightarrow \frac{n_e n_p}{n_H} = \frac{n_p^2}{n - n_p} = n \left(\frac{n_p^2/n^2}{1 - \frac{n_p}{n}} \right) = n \frac{x^2}{1-x}$$

$$\therefore \boxed{\frac{x^2}{1-x} = \frac{1}{n} \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T} = f(n, T)}$$

→ x is a function of n and T
implicit form of the function given above

↑
quadratic equation for x
can be solved.

As density decreases under constant temperature,

$F(n, T)$ increases $\rightarrow \frac{x^2}{1-x^2}$ increases

$\rightarrow x$ increases ($\approx 0 < x < 1$)

(Qualitatively why?) decreased density \Rightarrow fewer recombination events

A cloud of hydrogen with $n \sim 1 \text{ cm}^{-3} = 10^{-6} \text{ m}^{-3}$

$$p = (n_{\text{He}} + n_{\text{H}}) k_B T$$

$$\frac{x^2}{1-x^2} = \frac{1}{n} \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T} = F(n, T) = F$$

$$\frac{n_p n_e}{n_H} = \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T}$$

$$\frac{n_p n_e}{n_H} = n^2 x^2 = n^2 (1-x^2)$$

then $x^2 = (1-x^2) F \rightarrow x^2 + Fx^2 - F = 0$

$$\rightarrow x = \frac{1}{2} (\sqrt{F^2 + 4F} - F) \quad \text{or} \quad x = \frac{1}{2} (-\sqrt{F^2 + 4F} - F)$$

$$\because 0 < x < 1 \quad \therefore x = \frac{1}{2} (\sqrt{F^2 + 4F} - F)$$

$$\Rightarrow x(n, T) = \frac{1}{2} (\sqrt{F^2(n, T) + 4F(n, T)} - F(n, T))$$

$$\frac{x^2}{(1-x^2)^2}$$

$$\frac{x^2}{1-x^2} = F(n, T)$$

where $F(n, T) = \frac{1}{n} \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T}$

$$x^2 = F(1-x^2)$$

For the cloud to be mostly ionised,

$$\therefore (1-x^2) \ll 1$$

$$(1-x^2) \approx 0$$

let's assume that $x \approx \underline{0.95} \quad 0.99$

$$x = \sqrt{\frac{F}{1+F}}$$

$$\text{Then } \cancel{F(10^{-6}, T)} = F(10^{-6}, T) = \frac{0.95^2}{1-0.95} = 18.05$$

$$\text{Then } F(10^{-6}, T) \approx \frac{0.99^2}{1-0.99} \approx 98.01$$

$$\Rightarrow \left(\frac{h}{m_e k_B} \sqrt{\frac{2\pi}{m_e k_B}} \right)^3 n(98.01) = T^{3/2} e^{-R/k_B T}$$

$$= \left[(1.05 \times 10^{-34}) \sqrt{\frac{2\pi}{(9.11 \times 10^{-31})(1.38 \times 10^{-23})}} \right]^3 (10^{-6})(98.01) \approx 4 \times 10^{-26} \text{ K}^{3/2}$$

$$\frac{R}{k_B} \approx \frac{13.6 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} \approx 1.58 \times 10^5 \text{ K}$$

$$\rightarrow T^{3/2} e^{-\frac{(1.58 \times 10^5 \text{ K})}{T}} \approx 4 \times 10^{-26} \text{ K}^{3/2}$$

$$\rightarrow \boxed{T \approx 2.3 \times 10^3 \text{ K}} \quad \checkmark$$

total pressure is $p = (n_e + n_p + n_{it}) k_B T$

d) $p = n k_B T$ $\therefore \frac{1}{n} = \frac{k_B T}{p}$ $= (n_e + n) k_B T$
 $n_e + n = \frac{k_B T}{p}$

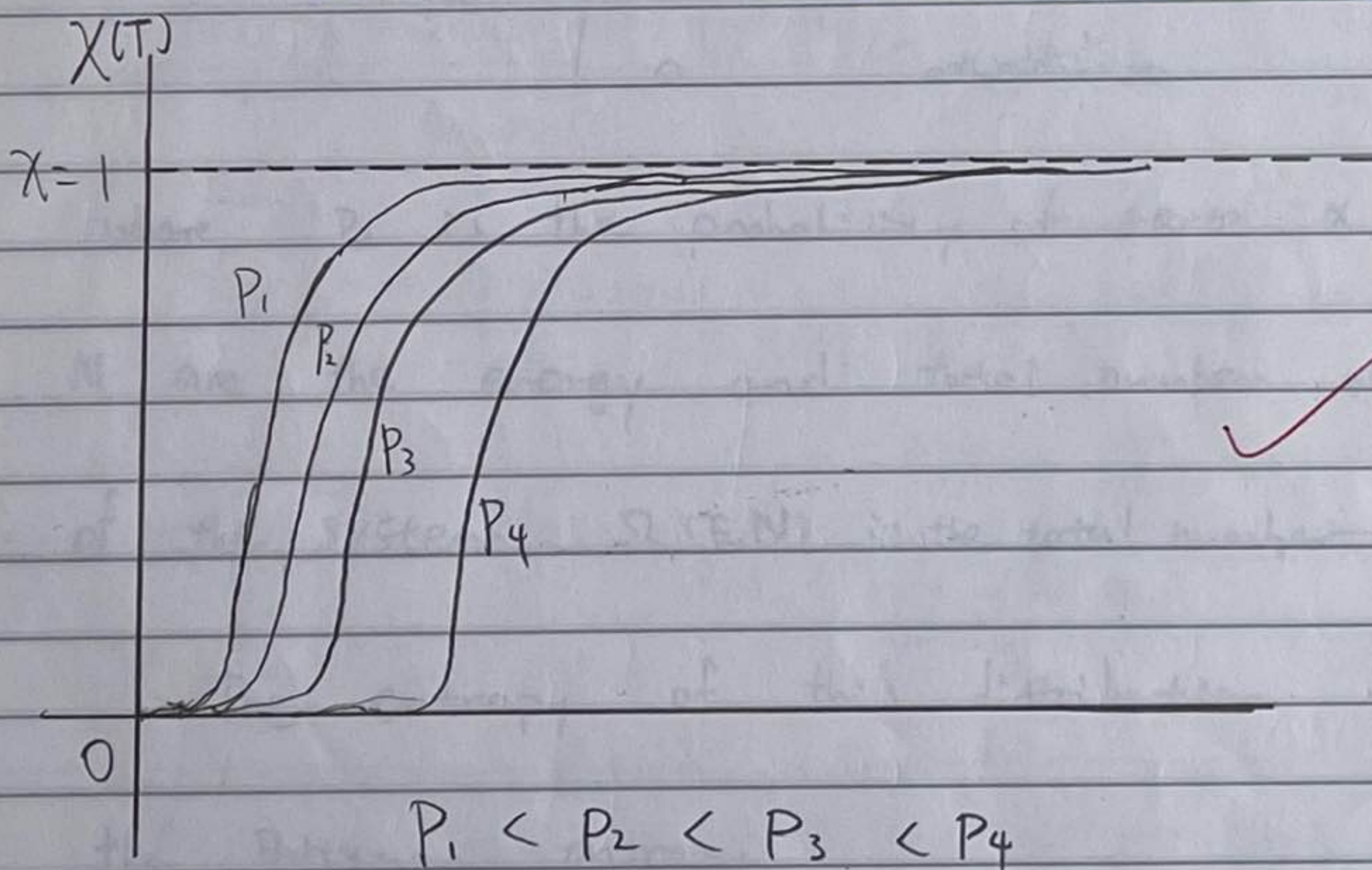
$$F(p, T) = \frac{k_B T}{p} \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T} \quad n = \left(\frac{k_B T}{p} - n_e \right)$$

$$= \frac{k_B}{p} \left(\frac{m_e k_B}{2\pi \hbar^2} \right)^{3/2} T^{5/2} e^{-\frac{R}{k_B T}} \quad n = \left(\frac{k_B T}{p} - n_e \right)$$

$$F(p, T) = \left(\frac{k_B T}{p} - n_e \right) \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T}$$

~~$\chi = \chi(p, T)$~~

$$\rightarrow \chi(p, T) = \frac{1}{2} \left(\sqrt{F^2(p, T) + 4F(p, T)} - F(p, T) \right)$$



11. For a completely isolated system the energy

is conserved and total number of particles

is fixed.

According to the postulate of equal a priori

probabilities, all states are equiprobable

$$\rightarrow P_{\alpha} = \begin{cases} \frac{1}{\Omega(E, N)} & E_{\alpha} = E, N_{\alpha} = N \\ 0 & \text{otherwise} \end{cases}$$

where P_{α} is the probability of state α , E and

N are the energy and total number of particles

of the system. $\Omega(E, N)$ is the total number of microstates

The entropy of this distribution is

the Boltzmann entropy

$$S = k_B S_G = -k_B \sum_{\alpha} P_{\alpha} \ln P_{\alpha}$$

$$= -k_B \sum_{\alpha=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k_B \ln \frac{1}{\Omega} = k_B \ln \Omega(E, N)$$

Now, pick a small part of the system

$\Omega_{\text{part}}(\epsilon, n)$ is the number of microstates of the small part that have energy ϵ and n particles

$\Omega_{\text{res}}(E-\epsilon, N-n)$ is the number of microstates of the ~~small~~ rest of the system, that have energy $E-\epsilon$ and $N-n$ particles.

$P(\epsilon, n)$ is the probability for the ^{small part of the} system to have energy ϵ and n particles. $N \gg n, E \gg \epsilon$

$$\therefore P(\epsilon, n) = \frac{\Omega_{\text{part}}(\epsilon, n) \Omega_{\text{res}}(E-\epsilon, N-n)}{\Omega(E, N)}$$

$$= \frac{\Omega_{\text{part}}(\epsilon, n)}{\Omega(E, N)} \exp\left(\frac{S_{\text{res}}(E-\epsilon, N-n)}{k_B}\right)$$

$$\approx \frac{\Omega_{\text{part}}(\epsilon, n)}{\Omega(E, N)} \exp\left(\frac{1}{k_B} [S_{\text{res}}(E, N) - \epsilon \frac{\partial S_{\text{res}}}{\partial E} + n \frac{\partial S_{\text{res}}}{\partial N}]\right)$$

~~Volume V is a fixed parameter of the system~~

~~system is isolated~~

$$\frac{\partial E}{\partial S} = T$$

$$\frac{\partial E}{\partial S} = T(\bar{E})$$

No work is done on the reservoir

$$\rightarrow d\mathcal{E}_{\text{res}} = dE_{\text{res}} = T dS_{\text{res}} \quad (T \text{ is temperature})$$

$$\rightarrow \frac{1}{T} = \frac{\partial S_{\text{res}}}{\partial E}$$

Adding a particle to the reservoir, the chemical potential μ is defined to be

$$\mu = -\frac{\partial \mathcal{E}_{\text{res}}}{\partial N} = -T \frac{\partial S_{\text{res}}}{\partial N} \rightarrow \frac{\partial S_{\text{res}}}{\partial N} = -\frac{\mu}{T}$$

$$P(\mathcal{E}, n) = \frac{\exp\left(\frac{S_{\text{res}}(\mathcal{E}, N)}{k_B}\right) \Omega_{\text{part}}(\mathcal{E}, n) \exp\left(-\frac{1}{k_B T} (\mathcal{E} - \mu n)\right)}{\Omega(\mathcal{E}, N)}$$

\hookrightarrow independent of \mathcal{E}, n

$= \frac{1}{Z}$, constant of normalisation.

$$\rightarrow P(\mathcal{E}, n) = \frac{1}{Z} \Omega_{\text{part}}(\mathcal{E}, n) \exp\left(-\frac{1}{k_B T} (\mathcal{E} - \mu n)\right)$$

$$\sum_{\mathcal{E}, n} P(\mathcal{E}, n) = 1 \rightarrow Z = \sum_{\mathcal{E}, n} \Omega_{\text{part}}(\mathcal{E}, n) \exp\left(-\frac{1}{k_B T} (\mathcal{E} - \mu n)\right)$$

$P(\mathcal{E}, n)$ = probability for the ~~sys~~ small subsystem to have energy \mathcal{E} and n particles.

$\Omega_{\text{part}}(\mathcal{E}, n)$ is the number of microstates in which the system have energy \mathcal{E} and n particles

Hence, the probability of a particular state α with energy ϵ and n particles, denoted by P_α , is given by

$$\Omega(\epsilon, n) P_\alpha = P(\epsilon, n) \quad \Omega(\bar{\epsilon}_\alpha)$$

$$\therefore P_\alpha = \frac{P(\epsilon, n)}{\Omega(\epsilon, n)}$$

$$\Rightarrow P_\alpha = \frac{1}{Z} \exp\left(-\frac{1}{k_B T} (\epsilon - \mu n)\right)$$

$$Z = \sum_{\epsilon, n} \Omega_{\text{part}}(\epsilon, n) \exp\left(-\frac{1}{k_B T} (\epsilon - \mu n)\right)$$

$$= \sum_{\alpha} P_\alpha \exp\left(-\frac{1}{k_B T} (\epsilon_\alpha - \mu N_\alpha)\right)$$

$$\Omega_{\text{part}}(\epsilon, n) P_\alpha = P(\epsilon, n) \quad \text{for } \epsilon = \epsilon_\alpha, n = N_\alpha$$

$$\therefore P_\alpha = \frac{P(\epsilon, n)}{\Omega_{\text{part}}(\epsilon, n)} = \frac{1}{Z} \exp\left(-\frac{1}{k_B T} (\epsilon - \mu n)\right)$$

$$P_\alpha = \frac{1}{Z} \exp\left(-\frac{1}{k_B T} (\epsilon_\alpha - \mu N_\alpha)\right) = \frac{1}{Z} e^{-\beta(\epsilon_\alpha - \mu N_\alpha)}$$

$$Z = \sum_{n, \epsilon} \Omega_{\text{part}}(\epsilon, n) \exp\left(-\frac{1}{k_B T} (\epsilon - \mu n)\right)$$

$$= \sum_{\alpha} \exp\left(-\frac{1}{k_B T} (\epsilon_\alpha - \mu N_\alpha)\right)$$

$$= \sum_{\alpha} e^{-\beta(\epsilon_\alpha - \mu N_\alpha)}$$

Grand Canonical Distribution is recovered.

12. a) Gibbs entropy $S_G = - \sum_{\alpha} P_{\alpha} \ln P_{\alpha}$ subject to

Constraints $\sum_{\alpha} P_{\alpha} - 1 = 0$, $\sum_{\alpha} P_{\alpha} E_{\alpha} - U = 0$

$$\sum_{\alpha} P_{\alpha} V_{\alpha} - \bar{V} = 0$$

\Rightarrow maximising unconditionally

$$S_G' = S_G - \lambda (\sum_{\alpha} P_{\alpha} - 1) - \beta (\sum_{\alpha} P_{\alpha} E_{\alpha} - U) - \sigma (\sum_{\alpha} P_{\alpha} V_{\alpha} - \bar{V})$$

$$\begin{aligned} \therefore 0 = dS_G' &= - \sum_{\alpha} (\ln P_{\alpha} + 1) dP_{\alpha} - \sum_{\alpha} \lambda dP_{\alpha} - \sum_{\alpha} \beta E_{\alpha} dP_{\alpha} - \sum_{\alpha} \sigma V_{\alpha} dP_{\alpha} \\ &- (\sum_{\alpha} P_{\alpha} - 1) d\lambda - (\sum_{\alpha} P_{\alpha} E_{\alpha} - U) d\beta - (\sum_{\alpha} P_{\alpha} V_{\alpha} - \bar{V}) d\sigma \end{aligned}$$

$$0 = - \sum_{\alpha} (\ln P_{\alpha} + 1 + \lambda + \beta E_{\alpha} + \sigma V_{\alpha}) dP_{\alpha}$$

$$\Rightarrow \ln P_{\alpha} + 1 + \lambda + \beta E_{\alpha} + \sigma V_{\alpha} = 0$$

$$\Rightarrow P_{\alpha} = e^{-1 - \lambda - \beta E_{\alpha} - \sigma V_{\alpha}}$$

sub into $\sum_{\alpha} P_{\alpha} = 1 \Rightarrow e^{-1 - \lambda} \sum_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}} = 1$

$$\therefore e^{-1 - \lambda} = \frac{1}{\sum_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}}}$$

$$\therefore P_{\alpha} = \frac{e^{-\beta E_{\alpha} - \sigma V_{\alpha}}}{\sum_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}}}$$

\rightarrow Grand Partition function $Z = \sum_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}}$

$$\sum_{\alpha} p_{\alpha} E_{\alpha} - U = 0$$

$$\Rightarrow U = \frac{1}{Z} \sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\sum_{\alpha} p_{\alpha} V_{\alpha} - \bar{V} = 0$$

$$\Rightarrow \bar{V} = \frac{1}{Z} \sum_{\alpha} V_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \sigma} = -\frac{\partial \ln Z}{\partial \sigma}$$

$\therefore Z = Z(\beta, \sigma)$, U and \bar{V} are ~~constants~~ ^{known}

$$\therefore U = -\frac{\partial \ln Z}{\partial \beta} \quad \text{①} \quad \text{and} \quad \bar{V} = -\frac{\partial \ln Z}{\partial \sigma} \quad \text{②}$$

are a ~~set~~ ^{system} of implicit equations for β and σ .

$\therefore \beta$ and σ can be determined from ① and ②

b) $\therefore S_G = S/k_B$

$$\therefore S = k_B S_G = -k_B \sum_{\alpha} P_{\alpha} \ln P_{\alpha}$$

$$= -k_B \sum_{\alpha} \frac{1}{Z} - k_B \sum_{\alpha} P_{\alpha} \ln \left[\frac{e^{-\beta E_{\alpha} - \sigma V_{\alpha}}}{Z} \right]$$

$$= -k_B \sum_{\alpha} \left(P_{\alpha} (-\beta E_{\alpha}) + P_{\alpha} (-\sigma V_{\alpha}) \right) + k_B \ln Z \sum_{\alpha} P_{\alpha}$$

$$= -k_B \beta \sum_{\alpha} P_{\alpha} E_{\alpha} + k_B \sigma \sum_{\alpha} P_{\alpha} V_{\alpha} + k_B \ln Z$$

$$\Rightarrow S = k_B (\beta U + \sigma \bar{V} + \ln Z)$$

$$\begin{aligned} \frac{dS}{k_B} &= \beta dU + U d\beta + \sigma d\bar{V} + \bar{V} d\sigma + \frac{dZ}{Z} \\ &= \beta dU + \cancel{U d\beta} + \sigma d\bar{V} + \cancel{\bar{V} d\sigma} + \sum_{\alpha} \frac{e^{-\beta E_{\alpha} - \sigma V_{\alpha}}}{Z} (-\beta dE_{\alpha} - E_{\alpha} d\beta - \sigma dV_{\alpha} - V_{\alpha} d\sigma) \end{aligned}$$

$$= \cancel{\beta dU + \sigma d\bar{V}} + \cancel{\sum_{\alpha} \beta P_{\alpha} dE_{\alpha} + \sigma \sum_{\alpha} P_{\alpha} dV_{\alpha}}$$

$$= \beta dU + \sigma d\bar{V} - \sum_{\alpha} P_{\alpha} (\beta dE_{\alpha} + \sigma dV_{\alpha})$$

$$\rightarrow \frac{dS}{k_B} = \beta dU + \sigma d\bar{V} - \sum_{\alpha} P_{\alpha} \left(\beta \frac{\partial E_{\alpha}}{\partial N} dN + \sigma \frac{\partial V_{\alpha}}{\partial N} dN \right)$$

But E_{α} and V_{α} are not dependent on N because adding a particle to the system essentially changes all the states of the system.

$$\Rightarrow \frac{\partial E_{\alpha}}{\partial N} = 0 \rightarrow dE_{\alpha} = 0$$

$$\frac{\partial V_{\alpha}}{\partial N} = 0 \rightarrow dV_{\alpha} = 0$$

$$\therefore \frac{dS}{k_B} = \beta dU + \sigma d\bar{V} = \beta \left(dU + \frac{\sigma}{\beta} d\bar{V} \right)$$

$$= \frac{dQ_{rev}}{k_B T}$$

$$\Rightarrow \beta = \frac{1}{k_B T}$$

In adiabatic process $dU = -P d\bar{V}$

$$\therefore P = - \left(\frac{\partial U}{\partial \bar{V}} \right)_S$$

$$\therefore dU = T dS - \frac{\sigma}{\beta} d\bar{V}$$

$$\therefore - \left(\frac{\partial U}{\partial \bar{V}} \right)_S = \frac{\sigma}{\beta}$$

$$\therefore \frac{\sigma}{\beta} = P \quad \therefore \sigma = \beta P = \boxed{\frac{P}{k_B T}}$$

$$(c) \quad \therefore \frac{\sigma}{\beta} = P$$

~~$$\therefore dU = T dS - P d\bar{V}$$~~

$$\Rightarrow \boxed{dU = T dS - P d\bar{V}}$$

$$dS = \frac{1}{T} dU + \frac{P}{T} d\bar{V} \Rightarrow \left(\frac{\partial S}{\partial U} \right)_{\bar{V}, N} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial \bar{V}} \right)_{U, N} = \frac{P}{T}$$

Consider 2 systems in equilibrium

$$U = U_1 + U_2 \rightarrow \text{const}$$

$$\bar{V} = \bar{V}_1 + \bar{V}_2 \rightarrow \text{const}$$

$$S = S_1 + S_2 \rightarrow \text{max}$$

$$dS = \left(\frac{\partial S_1}{\partial U_1} \right)_{\bar{V}_1, N_1} dU_1 + \left(\frac{\partial S_1}{\partial \bar{V}_1} \right)_{U_1, N_1} d\bar{V}_1$$

$$+ \left(\frac{\partial S_2}{\partial U_2} \right)_{\bar{V}_2, N_2} dU_2 + \left(\frac{\partial S_2}{\partial \bar{V}_2} \right)_{U_2, N_2} d\bar{V}_2$$

$\underbrace{\hspace{10em}}_{-dU_1} \qquad \qquad \qquad \underbrace{\hspace{10em}}_{-d\bar{V}_1}$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) d\bar{V}_1 = 0$$

$$\frac{1}{T_1} = \frac{1}{T_2} \Rightarrow T_1 = T_2$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\therefore T_1 = T_2$$

$$\therefore P_1 = P_2$$

($dU_1, d\bar{V}_1$ can be arbitrarily chosen)

Hence pressure equalise in equilibrium

c) Consider 2 systems in equilibrium

From (b), it is obvious that

$$\underline{dU = TdS - PdV}$$

$$\text{max} \rightarrow Z_1 + Z_2 = Z$$

$$\bar{U}_1 \left(\frac{26}{N_1} \right) + \bar{U}_2 \left(\frac{26}{N_2} \right) = 26$$

$$\bar{U}_1 \left(\frac{26}{N_1} \right) + \bar{U}_2 \left(\frac{26}{N_2} \right) +$$

$$0 = \bar{U}_1 \left(\frac{26}{N_1} - \frac{26}{N_2} \right) + 26 \left(\frac{1}{N_1} - \frac{1}{N_2} \right) =$$

$$\frac{1}{N_1} = \frac{1}{N_2} \Rightarrow T_1 = T_2$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$T_1 = T_2$$

$$P_1 = P_2 = P$$

Hence

$$dU = TdS - PdV$$

(d)

$$S = k_B (\beta \bar{U} + \sigma \bar{V} + \ln Z)$$

$$= k_B \left(\frac{1}{k_B T} \bar{U} + \frac{P}{k_B T} \bar{V} + \ln Z \right)$$

$$\therefore TS = \bar{U} + P\bar{V} + k_B T \ln Z$$

$$\therefore -k_B T \ln Z = \bar{U} - TS + P\bar{V} = G$$

$$e) \quad dG = d\bar{U} - Tds - sdT + Pd\bar{V} + \bar{V}dp$$

$$= Tds - Pd\bar{V} - Tds - sdT + Pd\bar{V} + \bar{V}dp$$

$$= -sdT + \bar{V}dp$$

Equations of state:

$$S = - \left(\frac{\partial G}{\partial T} \right)_P \quad \bar{V} = \left(\frac{\partial G}{\partial P} \right)_T$$

e)

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}}$$

The microstates $\alpha = \{\alpha_V, V\}$

$$\therefore Z = \sum_{\alpha} e^{-\beta E_{\alpha}} e^{-\sigma V_{\alpha}} = \sum_V e^{-\sigma V} \underbrace{\sum_{\alpha_V} e^{-\beta E_{\alpha_V}}}_{Z_N}$$

$$= \sum_V e^{-\sigma V} Z_N = \sum_V e^{-\sigma V} \frac{Z_1^N}{N!}$$

$$= \sum_V e^{-\sigma V} V^N \left(\frac{Z_{int}}{\lambda_{th}^3} \right)^N \frac{1}{N!}$$

$$= \frac{1}{\Delta V} \frac{1}{N!} \left(\frac{Z_{int}}{\lambda_{th}^3} \right)^N \int_0^{\infty} e^{-\sigma V} V^N dV$$

$$= \frac{1}{\Delta V N!} \left(\frac{Z_{int}}{\lambda_{th}^3} \right)^N \underbrace{\left(\int_0^{\infty} e^{-x} x^N dx \right)}_{N!} \frac{1}{\sigma^{N+1}} \quad (x = \sigma V)$$

$$= \left(\frac{Z_{int}}{\lambda_{th}^3} \right)^N \frac{1}{\sigma^N} \frac{1}{\sigma \Delta V} = \left(\frac{Z_{int} k_B T}{\lambda_{th}^3 P} \right)^N \frac{1}{\sigma \Delta V}$$

$$= \boxed{\left(\frac{Z_{int} k_B T}{\lambda_{th}^3 P} \right)^N \frac{k_B T}{P \Delta V}}$$

f)

$$G = -k_B T \ln Z$$

$$= N k_B T \ln \left(\frac{\lambda_{th}^3}{Z_{int}} \frac{P}{k_B T} \right) + k_B T \ln \left(\frac{P \Delta V}{k_B T} \right)$$

(standard formula for ideal gas ~~is~~ is
of \hat{G}

$$G = N k_B T \ln \left(\frac{\lambda_{th}^3}{Z_{int}} \frac{P}{k_B T} \right)$$

For G to be independent of ΔV ,

$$\frac{P \Delta V}{k_B T} = 1$$

\rightarrow

$$\Delta V = \frac{k_B T}{P}$$

g) $\bar{V} = \left(\frac{\partial G}{\partial P} \right)_T = N k_B T \frac{\partial}{\partial P} \left(\ln P + \ln \frac{\lambda_{th}^3}{Z_{int} k_B T} \right)$

$$= N k_B T \frac{\partial}{\partial P} \ln P = \frac{N k_B T}{P}$$

\Rightarrow

$$P \bar{V} = N k_B T$$

let

$$n = \frac{N}{\bar{V}}$$

\Rightarrow

$$P = n k_B T$$

$\Delta U/V$ is an unphysical quantity so it

should not affect any physically testable results.

if our theory is sensible

so the term $\left| \ln \frac{P\Delta U}{k_B T} \right|$ must be ~~negligible~~

negligibly small compare to $\left| N \ln \left(\frac{\lambda_{th}^3 P}{Z_{int} k_B T} \right) \right|$

$$\therefore \left| \ln \frac{P\Delta U}{k_B T} \right| \ll \left| N \ln \left(\frac{\lambda_{th}^3 P}{Z_{int} k_B T} \right) \right|$$

g) $G = N k_B T \ln \left(\frac{\lambda_{th}^3 P}{Z_{int} k_B T} \right)$ (ignoring the ΔU term)

$$\bar{V} = \left(\frac{\partial G}{\partial P} \right)_T = N k_B T \frac{\partial}{\partial P} \left(\ln P + \ln \frac{\lambda_{th}^3}{Z_{int} k_B T} \right)$$

$$= N k_B T \frac{\partial}{\partial P} \ln P = \frac{N k_B T}{P}$$

$$\therefore P \bar{V} = N k_B T \quad \text{let } n = \frac{N}{V}$$

$$\Rightarrow \boxed{P = n k_B T}$$

Ideal gas law is recovered

Now we go back and check ΔV

$$\therefore P = n k_B T \quad \therefore \frac{P}{k_B T} = n$$

$\frac{1}{n}$ is the volume per particle so

for ΔV to be small enough for the sum to be approximated to an integral.

$$\Delta V \ll \frac{1}{n} \rightarrow \Delta V \ll \frac{P}{k_B T}$$

~~Also~~ But ΔV isⁿ an unphysical quantity and it should not affect physically testable results.

$$\rightarrow \left| \ln \frac{P \Delta V}{k_B T} \right| \ll \left| \ln \frac{\lambda_{th}^3 P}{Z_{int} k_B T} \right|$$

$$\therefore \Delta V \ll \frac{1}{n} = \frac{P}{k_B T} \quad \therefore \frac{P \Delta V}{k_B T} < 1$$

For ideal gas $n \lambda_{th}^3 \ll 1$, $Z_{int} > 1$ $\therefore \frac{\lambda_{th}^3 P}{Z_{int} k_B T} < 1$.

\therefore both log functions ~~have negative~~ are negative

$$\therefore \frac{P \Delta V}{k_B T} \gg \left(\frac{\lambda_{th}^3 P}{Z_{int} k_B T} \right)^N$$

$$\therefore \frac{k_B T}{P} \left(\frac{\lambda_{th}^3 P}{Z_{int} k_B T} \right)^N \frac{k_B T}{P} \ll \Delta V \ll \frac{k_B T}{P}$$

is the condition that ΔV must satisfy.