~~To: Robin Nicholas~~ To: Michael Barnes

Statistical Mechanics 5 Ziyan Li

1. a)

$$\ln(15!) = 27.8993$$

$$15\ln 15 - 15 = 25.6208$$

$$\text{percent difference} = \left| \frac{25.6208 - 27.8993}{27.8993} \right| = 8\%$$

Calculator gives:

$$\frac{\ln(49!) - (49\ln(49) - 49)}{\ln(49!)} = 0.0198$$

$$\frac{\ln(48!) - (48\ln(48) - 48)}{\ln(48!)} = 0.0203$$

$\therefore$ $N \geq 49$ for percent difference $< 2\%$

b) Consider the integral $T(n) = \int_0^\infty x^n e^{-x}\,dx$

$$T(n) = \int_0^\infty x^n e^{-x}\,dx = \underbrace{-[e^{-x}x^n]_{-\infty}^{\infty}}_{0 \text{ (exponential decay faster than polynomial)}} - \int_0^\infty n x^{n-1}\,d(-e^{-x})$$

$$= n\int_0^\infty x^{n-1}e^{-x}\,dx = nT(n-1)$$

$$T(0) = \int_0^\infty e^{-x}\,dx = -e^{-x}\Big|_0^\infty = 1$$

$$\therefore \quad T(n) = n!$$

$$\therefore \quad n! = \int_0^\infty x^n e^{-x}\, dx$$

Define $f(x)$: $e^{f(x)} = x^n e^{-x} = e^{n \ln x - x}$ $\Rightarrow$ $f(x) = n \ln x - x$

set $\frac{df}{dx} = 0$ to find the the maximum of the integrand and thus $f(x)$

$$\Rightarrow \quad \frac{df}{dx} = \frac{n}{x} - 1 = 0 \quad \Rightarrow \quad x = n \quad \text{at maximum}$$

$$\frac{d^2f}{dx^2} = -\frac{n}{x^2} \quad (>0, \therefore \text{maximum})$$

~~Tah~~ Taylor expansion around maximum $(x=n)$

$$f(x) = f(n) + \left(\frac{df}{dx}\right)_{x=n}(x-n) + \frac{1}{2!}\left(\frac{d^2f}{dx^2}\right)_{x=n}(x-n)^2 + \ldots$$

$$= n\ln n - n + (0)(x-n) - \frac{1}{2}\frac{n}{n^2}(x-n)^2$$

$$= n \ln n - n - \frac{(x-n)^2}{2n} + \ldots$$

$$\therefore \quad n! = \int_0^\infty e^{f(x)}\, dx = \int_0^\infty e^{n\ln n - n} e^{-(x-n)^2/2n}\, dx$$

$$= e^{n\ln n - n}\int_0^\infty e^{-\frac{(x-n)^2}{2n}}\, dx$$

$$\simeq e^{n\ln n - n}\int_{-\infty}^\infty e^{-\frac{(x-n)^2}{2n}}\, dx$$

(from $-\infty$ to 0 the integral has negligible contribution)

$$= e^{n\ln n - n}\sqrt{2\pi n}$$

$\therefore \quad \ln n! \approx n\ln n - n + \cancel{\frac{1}{2}\sqrt{2\pi n}} \; \frac{1}{2}\ln 2\pi n$

When n is very large $\frac{1}{2}\sqrt{2\pi n}$ is ~~ne~~ negligible

$\therefore \quad \ln n! \approx n\ln n - n \quad (n \text{ large})$

Results in (a):

For ~~ln 11~~ $\ln 15!$:

percent difference $\cancel{\frac{\sqrt{2\pi \times 15}}{2\ln 15!}}$

$= \frac{\ln 2\pi \times 15}{2\ln 15!} = 8\%$

For the least N:

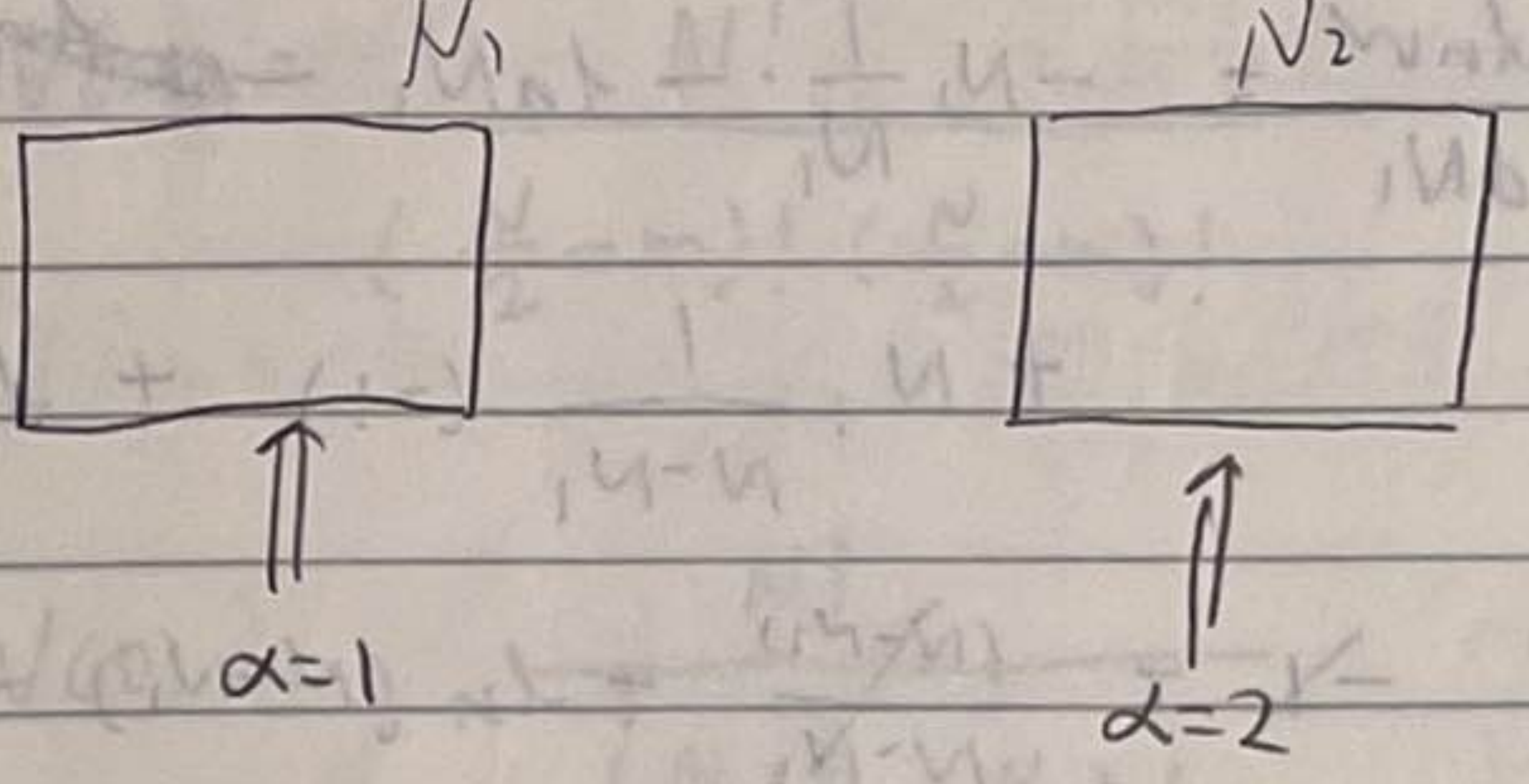
$\frac{\ln 2\pi N}{2\ln N!} \approx 2\% \Rightarrow$

$\frac{\ln 2\pi \times 48}{2\ln 48!} = 0.0202$

$\frac{\ln 2\pi \times 49}{2\ln 49!} = 0.0198$

$\Rightarrow \quad N \geq 49$ for percent difference $< 2\%$

2. (a)



$N!$ ways of ~~permuting~~ permutating each toss

First N_1 falls into $\alpha=1$, and the rest $N_2 = N - N_1$ falls into $\alpha=2$

Switching order of coins within $\alpha=1$ and $\alpha=2$ yields the same assignment of probabilities

Hence we divide by the permutations within $\alpha=1$ and $\alpha=2$ ($N_1!$ and $N_2!$ respectively)

$$\therefore \boxed{W = \frac{N!}{N_1!\,N_2!}}$$

$$\ln W = \ln\left(\frac{N!}{N_1!\,N_2!}\right) = \ln N! - \ln N_1! - \ln N_2!$$

$$\approx N\ln N - N - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2$$

$$= N\ln N - N_1 \ln N_1 - (N-N_1)\ln(N-N_1)$$

(use Stirling's formula and $N_1 + N_2 = N$)

maximise $W \Rightarrow$ maximise $\ln W$

$$0 = \frac{d\ln W}{dN_1} = -N_1 \frac{1}{N_1} - \ln N_1 \cancel{+1} - N\frac{1}{N-N_1}(-1)$$

$$+ N_1 \frac{1}{N-N_1}(-1) + \ln(N-N_1)$$

$$\Rightarrow 0 = \cancel{-1} + \underbrace{\frac{(N-N_1)}{N-N_1}}_{1} + \ln(N-N_1) - \ln N_1$$

$$= \ln\left(\frac{N-N_1}{N_1}\right) = \ln\left(\frac{N}{N_1} - 1\right)$$

$$\Rightarrow \frac{N}{N_1} - 1 = 1 \Rightarrow \frac{N}{N_1} = 2 \Rightarrow N_1 = \frac{N}{2}$$

$$\therefore \max \ln W \approx N\ln N - N_1 \ln N_1 - N_2 \ln N_2$$

$$= N\ln N - \frac{N}{2}\ln\left(\frac{N}{2}\right) - \frac{N}{2}\ln\frac{N}{2}$$

$$= N\ln(N) - N\ln\left(\frac{N}{2}\right) = N\ln\left(\frac{N}{N/2}\right) = N\ln 2$$

$$\therefore W = e^{N\ln 2} = \boxed{2^N}$$

$$P_1 = P_2 = \frac{N/2}{N} = \boxed{\frac{1}{2}}$$

Gibb's Entropy : $S_G = -P_1 \ln P_1 - P_2 \ln P_2$

$$= -\frac{1}{2}\ln\left(\frac{1}{2}\right) - \frac{1}{2}\ln\left(\frac{1}{2}\right) = -\ln\left(\frac{1}{2}\right)$$

$$= \boxed{\ln 2}$$

(b) $W(m) = \dfrac{N!}{(\frac{N}{2}-m)!\,(\frac{N}{2}+m)!}$

$$W(0) = \frac{N!}{(\frac{N}{2})!\,(\frac{N}{2})!}$$

$$\therefore \quad \frac{W(m)}{W(0)} = \frac{(\frac{N}{2})!\,(\frac{N}{2})!}{(\frac{N}{2}-m)!\,(\frac{N}{2}+m)!}$$

$$\ln\left(\frac{W(m)}{W(0)}\right) = \ln\left(\frac{N}{2}!\right) + \ln\left(\frac{N}{2}!\right) - \ln\left(\left(\frac{N}{2}-m\right)!\right)$$

Stirling's formula $\Rightarrow$

$$-\ln\left(\left(\frac{N}{2}+m\right)!\right) \approx \frac{N}{2}\ln\left(\frac{N}{2}\right) - \cancel{\frac{N}{2}} + \frac{N}{2}\ln\left(\frac{N}{2}\right) - \cancel{\frac{N}{2}}$$

$$- \left(\frac{N}{2}-m\right)\ln\left(\frac{N}{2}-m\right) + \left(\cancel{\frac{N}{2}} - \cancel{m}\right) - \left(\frac{N}{2}+m\right)\ln\left(\frac{N}{2}+m\right)$$

$$+ \left(\frac{N}{2}+m\right)\ln\left(\frac{N}{2}+m\right) + \left(\cancel{\frac{N}{2}} + \cancel{m}\right)$$

$$= N\ln\left(\frac{N}{2}\right) - \left(\frac{N}{2}-m\right)\left[\ln\left(\frac{N}{2}\left(1-\frac{2m}{N}\right)\right)\right] - \cancel{\frac{N}{2}+}$$

$$\left(\frac{N}{2}+m\right)\ln\left(\frac{N}{2}\left(1+\frac{2m}{N}\right)\right)$$

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

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

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

$\ln(1+x) = x - \frac{x^2}{2} + \ldots$

$$\approx -\left(\frac{N}{2}-m\right)\left[\cancel{\frac{2m}{N}} - \frac{2m}{N} - \left(\frac{2m}{N}\right)^2\frac{1}{2}\right] - \left(\frac{N}{2}+m\right)\left[\frac{2m}{N} - \left(\frac{2m}{N}\right)^2\frac{1}{2}\right].$$

$\frac{m}{N} \ll 1$

$$= -\left(\frac{N}{2}-m\right)\left[-\frac{2m}{N} - \frac{2m^2}{N^2}\right] - \left(\frac{N}{2}+m\right)\left[\frac{2m}{N} - \frac{2m^2}{N^2}\right]$$

$$= +\cancel{m} - \frac{2m^2}{N} + \frac{m^2}{N} - \cancel{\frac{2m^3}{N^2}} - \cancel{m} - \frac{2m^2}{N} + \frac{m^2}{N} + \cancel{\frac{2m^3}{N^2}}$$

$$= -\frac{2m^2}{N}$$

$$\Rightarrow \ln\left(\frac{W(m)}{W(0)}\right) = -\frac{2m^2}{N}$$

$$\Rightarrow \frac{W(m)}{W(0)} = \exp(-2m^2/N)$$

Relative widen is defined to be ~~when~~ the width is when m is such that $\frac{W(m)}{W(0)} = \frac{1}{2}$

$$\Rightarrow \frac{1}{2} = \exp(-2m^2/N)$$

$$\Rightarrow \frac{1}{2} \approx 1 - \frac{2m^2}{N} \Rightarrow \frac{1}{2} = \frac{2m^2}{N}$$

$$\Rightarrow \frac{1}{4N} = \frac{m^2}{N^2} = \left(\frac{m}{N}\right)^2$$

$$\Rightarrow \frac{m}{N} = \pm\frac{1}{2\sqrt{N}}$$

Hence $\delta p = \left(+\frac{1}{2\sqrt{N}}\right) - \left(-\frac{1}{2\sqrt{N}}\right) = \boxed{\frac{1}{\sqrt{N}}}$

3. (a) maximising Gibbs free entropy = ~~S_g~~

$S_G \to \max$ subject to the constraint

$\sum_\alpha P_\alpha = 1$

Use Lagrange multiplier :

$$S_G - \lambda\left(\sum_\alpha P_\alpha - 1\right) \to \max$$

$$dS_G - \lambda \sum_\alpha dP_\alpha - \left(\sum_\alpha P_\alpha - 1\right) d\lambda = 0$$

$\because$ $S_g = -\sum_\alpha P_\alpha \ln P_\alpha$

$$\therefore \quad dS_g = -\sum_\alpha dP_\alpha \ln P_\alpha - \sum_\alpha dP_\alpha \left(\frac{P_\alpha}{P_\alpha}\right)$$

$$= -\sum_\alpha (\ln P_\alpha + 1) dP_\alpha$$

Hence $-\sum_\alpha (\ln P_\alpha + 1) dP_\alpha - \lambda \sum_\alpha dP_\alpha - \left(\sum_\alpha P_\alpha - 1\right) d\lambda = 0$

$$\Rightarrow \quad -\sum_\alpha \underbrace{(\ln P_\alpha + 1 + \lambda)}_{0} dP_\alpha - (\underbrace{\sum_\alpha P_\alpha - 1}_{0}) d\lambda = 0$$

$$\Rightarrow \quad \ln P_\alpha + 1 + \lambda = 0 \Rightarrow P_\alpha = e^{-1-\lambda}$$

$\therefore$ all P_α's are the same

$\because$ $\sum_\alpha P_\alpha = 6P_\alpha = 1 \Rightarrow P_\alpha = \frac{1}{6}$

$$\therefore \boxed{P_1 = P_2 = \dots = P_6 = \frac{1}{6}}$$

$$\langle \alpha \rangle = \sum_\alpha P_\alpha \alpha = \frac{1}{6}(1+2+\cdots+6)$$

$$= \left(\frac{1}{6}\right)\frac{(6)(7)}{2} = \boxed{3.5}$$

(b) $S_G \to \max$ subject to the constraints

$$\sum_\alpha P_\alpha = 1 \quad \text{and} \quad \langle \alpha \rangle = \sum_\alpha P_\alpha \alpha = 3.667$$

$$\therefore \quad S_G - \lambda\left(\sum_\alpha P_\alpha - 1\right) - \beta\left(\sum_\alpha P_\alpha \alpha - 3.667\right) \to \max.$$

$$\cancel{dS_G = -\sum_\alpha (\ln P_\alpha + 1)\, dP_\alpha}$$

$$\therefore \quad 0 = -\sum_\alpha (\ln P_\alpha + 1)\, dP_\alpha - \lambda \sum_\alpha dP_\alpha - \left(\sum_\alpha P_\alpha - 1\right) d\lambda$$

$$- \beta \sum_\alpha \alpha\, dP_\alpha - \left(\sum_\alpha P_\alpha \alpha - 3.667\right) d\beta$$

$$= -\sum_\alpha (\underbrace{\ln P_\alpha + 1 + \lambda + \beta\alpha}_{0})\, dP_\alpha - (\underbrace{\sum_\alpha P_\alpha - 1}_{0})\, d\lambda$$

$$- (\underbrace{\sum_\alpha P_\alpha \alpha - 3.667}_{0})\, d\beta$$

$$\Rightarrow \quad \ln P_\alpha + 1 + \lambda + \beta\alpha = 0$$

$$\Rightarrow \quad \cancel{P_\alpha = e^{-1-\lambda-\beta\alpha}}$$

$$P_\alpha = e^{-1-\lambda-\beta\alpha}$$

$$\sum_\alpha P_\alpha = 1 \Rightarrow \sum_\alpha e^{-1-\lambda} e^{-\beta\alpha} = 1$$

define $Z(\beta) = \sum_\alpha e^{-\beta\alpha}$ then

$$e^{-1-\lambda} Z(\beta) = 1 \Rightarrow e^{-1-\lambda} = \frac{1}{Z(\beta)}$$

$$\therefore \; P_\alpha = \frac{e^{-\beta\alpha}}{Z(\beta)}$$

$$\cancel{\sum_\alpha P_\alpha 1} \quad \sum_\alpha P_\alpha \alpha - 3.667 = 0$$

$$3.667 = \frac{1}{Z(\beta)} \sum_\alpha \alpha e^{-\beta\alpha} = -\frac{1}{Z(\beta)} \frac{\partial Z(\beta)}{\partial \beta} = -\frac{\partial \ln Z(\beta)}{\partial \beta}$$

$$\therefore \; -\frac{\partial \ln Z}{\partial \beta} = 3.667$$

$$Z(\beta) = \sum_\alpha e^{-\beta\alpha} = e^{-\beta} + e^{-2\beta} + \cdots + e^{-6\beta} = \frac{1 - e^{-6\beta}}{e^{\beta} - 1}$$

$$\therefore \; P_\alpha = \frac{e^{\beta} - 1}{1 - e^{-6\beta}} e^{-\beta\alpha} = \boxed{\frac{1 - e^{-\beta}}{1 - e^{-6\beta}} e^{-(\alpha-1)\beta}}$$

To get β we solve the equation.

$$-\frac{1}{Z} \frac{dZ}{d\beta} = 3.667$$

$$\frac{dZ}{d\beta} = \frac{d}{d\beta}\left(\frac{1-e^{-6\beta}}{e^{\beta}-1}\right) = \frac{(e^{\beta}-1)(6)e^{-6\beta} - (1-e^{-6\beta})e^{\beta}}{(e^{\beta}-1)^2}$$

$$= \frac{6e^{-6\beta}(e^{\beta}-1) - (1-e^{-6\beta})e^{\beta}}{(e^{\beta}-1)^2}$$

$$-\frac{1}{Z}\frac{dZ}{d\beta} = -\left(\frac{\cancel{e^{\beta}-1}}{1-e^{-6\beta}}\right)\left(\frac{6e^{-6\beta}}{\cancel{e^{\beta}-1}}\right) + \left(\frac{\cancel{e^{\beta}-1}}{\cancel{1-e^{-6\beta}}}\right)\left(\frac{\cancel{(1-e^{-6\beta})}e^{\beta}}{(e^{\beta}-1)^2}\right)$$

$$= \cancel{-\frac{6e^{-6\beta}}{e^{\beta}-1}} - \frac{6e^{-6\beta}}{1-e^{-6\beta}} + \frac{e^{\beta}}{e^{\beta}-1}.$$

$$= -\frac{6}{e^{6\beta}-1} + \frac{e^{\beta}}{e^{\beta}-1}$$

$$= 1 - \frac{6}{e^{6\beta}-1} + \frac{1}{e^{\beta}-1}$$

$$\Rightarrow \quad 1 - \frac{6}{e^{6\beta}-1} + \frac{1}{e^{\beta}-1} = 3.667$$

$$\Rightarrow \quad \beta = -0.0574$$

$\therefore \quad P_1 = 0.144, \ P_2 = 0.152, \ P_3 = 0.161$

$P_4 = 0.171, \ P_5 = 0.181, \ P_6 = 0.191$

4. a) $U = -\frac{\partial \ln Z}{\partial \beta}$ $\quad Z = \sum_\alpha e^{-\beta E_\alpha} \quad \beta = \frac{1}{k_B T}$

$$C_V = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{} = \frac{dU}{d\beta}\frac{d\beta}{dT} = \left(-\frac{1}{k_B T^2}\right)\frac{dU}{d\beta}$$

all E_α's stay invariant under constant V

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

$$= -k_B\beta^2 \frac{d}{d\beta}\left(-\frac{1}{Z}\frac{dZ}{d\beta}\right)$$

$$= -k_B\beta^2\left[-\frac{1}{Z}\frac{d^2 Z}{d\beta^2} + \left(\frac{1}{Z}\frac{dZ}{d\beta}\right)^2\right]$$

$$\Rightarrow \boxed{C_V = k_B\beta^2\left[\frac{1}{Z}\frac{d^2 Z}{d\beta^2} - \left(\frac{1}{Z}\frac{dZ}{d\beta}\right)^2\right]}$$

b) For monatomic ideal gas the partition function is given by

$$Z = \frac{Z_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N \quad \text{where } \lambda_{th} = \hbar\sqrt{\frac{2\pi}{mk_B T}}$$

$$\therefore Z = \frac{1}{N!}\left(\frac{V}{\hbar^3\left(\frac{2\pi}{m}\beta\right)^{3/2}}\right)^N = \underbrace{\frac{1}{N!}\left(\frac{V}{\hbar^3\left(\frac{2\pi}{m}\right)^{3/2}}\right)^N}_{\equiv C}\beta^{-3N/2}$$

$$\Rightarrow \quad Z = c\beta^{-3N/2} \quad \text{where} \quad \frac{\partial c}{\partial \beta} = 0$$

$$C_V = k_B\beta^2\left[\frac{1}{Z}\frac{d^2Z}{d\beta^2} - \left(\frac{1}{Z}\frac{dZ}{d\beta}\right)^2\right]$$

$$\frac{dZ}{d\beta} = \frac{d}{d\beta}\left(c\beta^{-3N/2}\right) = \left(-\frac{3N}{2}\right)c\beta^{-\frac{3N}{2}-1}$$

$$= \underbrace{\left(-\frac{3N}{2}\right)\frac{1}{\beta}Z}$$

$$\frac{d^2Z}{d\beta^2} = \left(-\frac{3N}{2}\right)\left(-\frac{3N}{2}-1\right)c\beta^{-\frac{3N}{2}-2}$$

$$= \underbrace{\left(-\frac{3N}{2}\right)\left(-\frac{3N}{2}-1\right)\frac{1}{\beta^2}Z}$$

$$C_V = k_B\cancel{\beta^2}\left[\left(-\frac{3N}{2}\right)\left(-\frac{3N}{2}-1\right)\frac{1}{\cancel{\beta^2}} - \left(-\frac{3N}{2}\right)^2\frac{1}{\cancel{\beta^2}}\right].$$

$$= \left(\frac{3}{2}N\right)\left[\underbrace{\frac{3N}{2}+1-\frac{3N}{2}}_{1}\right]k_B = \boxed{\frac{3}{2}Nk_B}$$

(c) $$Z = \sum_\alpha e^{-\beta E_\alpha}, \quad \frac{dZ}{d\beta} = -\sum_\alpha E_\alpha e^{-\beta E_\alpha}$$

$$\frac{1}{Z}\frac{dZ}{d\beta} = -\sum_\alpha E_\alpha\left(\frac{e^{-\beta E_\alpha}}{Z}\right) = -\sum_\alpha P_\alpha E_\alpha = -U = -\langle E\rangle$$

$$\frac{1}{Z}\frac{d^2Z}{d\beta^2} = \frac{1}{Z}\sum_\alpha E_\alpha^2 e^{-\beta E_\alpha} = \sum_\alpha E_\alpha^2 P_\alpha = \langle E^2\rangle$$

$$\therefore \quad C_V = \frac{1}{k_B T^2}\left(\langle E^2\rangle - \langle E\rangle^2\right) = \boxed{\frac{\langle \Delta E^2\rangle}{k_B T^2}}$$

$T^2 > 0$, $k_B > 0$, Now I prove $\langle \Delta E^2\rangle \geq 0$

$$\langle \Delta E^2\rangle = \langle E^2\rangle - \langle E\rangle^2$$

$$\langle E^2\rangle = \sum_\alpha E_\alpha^2 P_\alpha \qquad \langle E\rangle^2 = \left(\sum_\alpha E_\alpha P_\alpha\right)^2$$

Use the Cauchy - Schwarz Inequality

$$\left(\sum_i x_i^2\right)\left(\sum_i y_i^2\right) \geq \left(\sum_i x_i y_i\right)^2$$

choose $x_i = \sqrt{P_i}$, $y_i = (\sqrt{P_i})E_i$

$$\therefore \quad \langle E^2\rangle = \sum_\alpha E_\alpha^2 P_\alpha = \Big(\underbrace{\sum_i (\sqrt{P_i})^2}_{1}\Big)\Big(\underbrace{\sum_i (E_i\sqrt{P_i})^2}_{\langle E^2\rangle}\Big) \geq$$

$$\left(\sum_i (\sqrt{P_i})[(\sqrt{P_i})E_i]\right)^2 = \left(\sum_\alpha E_\alpha P_\alpha\right)^2 = \langle E\rangle^2$$

$$\Rightarrow \langle E^2\rangle \geq \langle E\rangle^2 \quad \Rightarrow \langle \Delta E^2\rangle = \langle E^2\rangle - \langle E\rangle^2 \geq 0$$

Hence $C_V \geq 0$

(d) As the size of the system $\to \infty$,

the system becomes completely isolated.

Hence the system becomes a microcanonical ensemble and all states are equiprobable, $P_\alpha = \frac{1}{\Omega}$

$$\because \quad P_\alpha = \frac{e^{-\beta E_\alpha}}{Z} = \frac{1}{\Omega} \quad , \quad U = \sum_\alpha P_\alpha E_\alpha = E \; , \quad Z = \sum_\alpha e^{-\beta E_\alpha}$$

$\Rightarrow$ ~~P_α~~ $\Rightarrow$ $E_\alpha = E$, all states have the same energy

$$\therefore \quad \langle E^2 \rangle = \sum_\alpha P_\alpha E_\alpha^2 = E^2$$

$$\langle E \rangle^2 = \left(\sum_\alpha P_\alpha E_\alpha \right)^2 = (E)^2 = E^2$$

$$\frac{\langle \Delta E^2 \rangle}{U^2} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{\langle E \rangle^2} = \frac{\langle E^2 \rangle}{\langle E \rangle^2} - 1$$

$$\to \frac{E^2}{E^2} - 1 = 0$$

as size of system $\to \infty$

To: Michael Barnes

Statistical Mechanics 5

Corrected Question 5

Ziyan Li

5.

a) There are 2^N microseates, each corresponds to a ~~combination of permutation of possible~~ possible combination of vertical and horizontal ~~chains~~. segments. The chains are localised, thus distinguishable so we consider the ordering.

Single-segment partition function

$$Z_1 = \underbrace{e^{-\beta(0)}}_{\text{horizontal}} + \underbrace{e^{-\beta(\gamma a)}}_{\text{vertical}} = 1 + e^{-\beta\gamma a}$$

Partition function of entire chain:

$$Z = (1 + e^{-\beta\gamma a})^N$$

b) $U = \sum_\alpha P_\alpha E_\alpha$, $L = \sum_\alpha P_\alpha l_\alpha$

$$E_\alpha^{(1)} = \begin{cases} 0 & \text{horizontal,} \\ \gamma a & \text{vertical} \end{cases}$$

$$l_\alpha^{(1)} = \begin{cases} a & \text{horizontal} \\ 0 & \text{vertical} \end{cases}$$

for single-segment

$$\# \text{ of horizontal chain} = \frac{l_\alpha}{a}$$

$$\# \text{ of vertical chain} = N - \frac{l_\alpha}{a}$$

$$E_\alpha = \# \text{ of vertical chain} \times \gamma a$$

$$= \left(N - \frac{l_\alpha}{a}\right)\gamma a = N\gamma a - l_\alpha \gamma$$

$\therefore \quad E_\alpha = N\gamma a - l_\alpha \gamma$

$$\therefore \quad l_\alpha = Na - \frac{E_\alpha}{\gamma}$$

$$L = \sum_\alpha P_\alpha l_\alpha = \sum_\alpha P_\alpha \left(Na - \frac{E_\alpha}{\gamma} \right)$$

$$= \left(\sum_\alpha P_\alpha \right) Na - \frac{1}{\gamma} \underbrace{\sum_\alpha P_\alpha E_\alpha}_{U}$$

$$= Na - \frac{U}{\gamma}$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{d}{d\beta}\left(N \ln (1 + e^{-\beta\gamma a}) \right)$$

$$= -N(-\cancel{\beta}\gamma a) \frac{e^{-\beta\gamma a}}{1 + e^{-\beta\gamma a}}$$

$$= N\gamma a \frac{e^{-\beta\gamma a}}{1 + e^{-\beta\gamma a}}$$

$$= \frac{N\gamma a}{1 + e^{\beta\gamma a}}$$

$$L = Na - \frac{U}{\gamma} = \cancel{NA}\, Na \left(1 - \frac{1}{1 + e^{\beta\gamma a}} \right)$$

$$\Rightarrow \quad L = Na \frac{e^{\beta\gamma a}}{1 + e^{\beta\gamma a}}$$

$$\Rightarrow \quad \cancel{L = Na} \quad \boxed{L = \frac{Na}{1 + e^{-\beta\gamma a}}}$$

For $\beta \gamma a \ll 1 \Rightarrow \frac{\gamma a}{k_B T} \ll 1 \Rightarrow \boxed{T \gg \frac{\gamma a}{k_B}}$

$$e^{-\beta\gamma a} = e^{-\frac{\gamma a}{k_B T}} \simeq 1 - \frac{\gamma a}{k_B T}$$

$$L = \frac{Na}{1+e^{-\beta\gamma a}} \simeq \frac{Na}{2 - \frac{\gamma a}{k_B T}} = Na\left(2 - \frac{\gamma a}{k_B T}\right)^{-1}$$

$$= \frac{Na}{2}\left(1 - \frac{\gamma a}{2k_B T}\right)^{-1}$$

$$\simeq \frac{Na}{2}\left(1 + \frac{\gamma a}{2k_B T}\right)$$

$$= \boxed{\frac{Na}{2} + \left(\frac{Na^2}{4k_B}\right)\frac{\gamma}{T}}$$

$$\Rightarrow \quad L = L_0 + A\frac{\gamma}{T}$$

$$L_0 = \frac{Na}{2}, \quad A = \frac{Na^2}{4k_B}$$

c) $C_\gamma = \left(\frac{\partial U}{\partial T}\right)_\gamma = \frac{\partial}{\partial T}\left(\frac{N\gamma a}{1+e^{+\frac{\gamma a}{k_B T}}}\right)$

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

$$= \frac{N\gamma^2 a^2 e^{+\gamma a/k_B T}}{k_B(1+e^{+\gamma a/k_B T})^2 T^2}$$

$$\Rightarrow \boxed{C_\gamma = \frac{N\gamma^2 a^2 e^{\gamma a/k_B T}}{k_B(1+e^{\gamma a/k_B T})^2 T^2}}$$

When $T \to 0$:

$e^{\frac{\gamma a}{k_B T}} \to \infty \quad T^2 \to 0$, but exponentials grow faster than polynomials

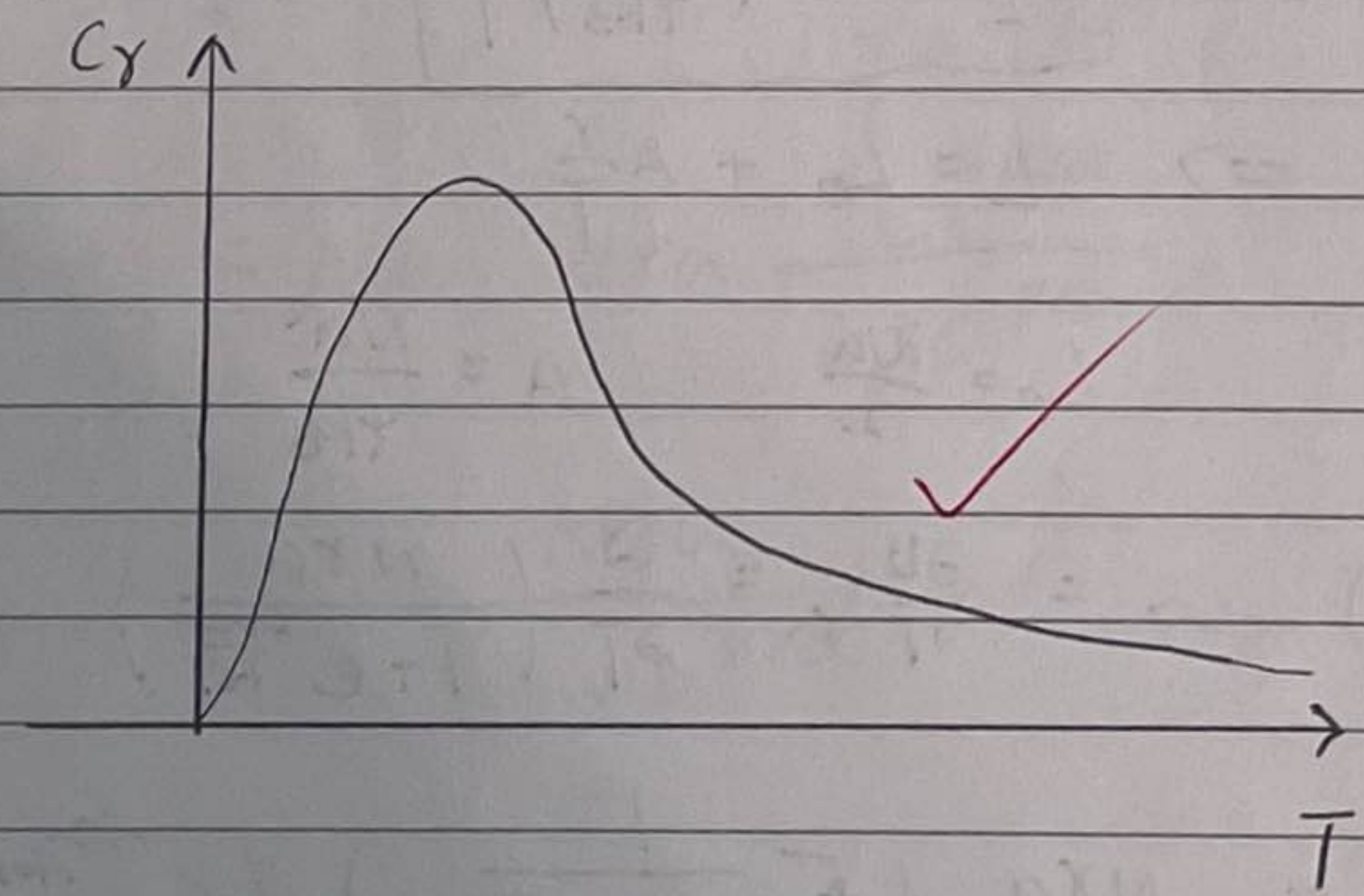
$$\Rightarrow \left(1 + e^{\frac{\gamma a}{k_B T}}\right)^2 T^2 \to \infty$$

$$\therefore \quad C_\gamma \to 0$$

When $T \to \infty$, $T^2 \to \infty$

$$\Rightarrow \quad C_\gamma \to 0$$

Plot: C_γ vs. T



As $T \to 0$, $U \to 0$, the chain stays in ground state with all segments horizontal. During the process of in-creasing T from 0 to something comparable to $\frac{\gamma a}{k_B}$, each segment can hardly jump to the vertical state so the ~~total~~ internal energy U remains constant throughout. Hence heat capacity $= 0$.

As $T \to \infty$, $U = \frac{Na\gamma}{2}$, ~~th~~ each segment of the chain has equal probability of being in the horizontal or vertical state.

Increasing T further does not change this probability distribution so does not change U

$\therefore$ Heat capacity $= 0$

d) $$U = \frac{Na\gamma}{1+e^{\beta\gamma a}}$$

$$\therefore \quad (1+e^{\beta\gamma a})U = Na\gamma$$

$$\therefore \quad e^{\beta\gamma a} = \frac{Na\gamma}{U} - 1$$

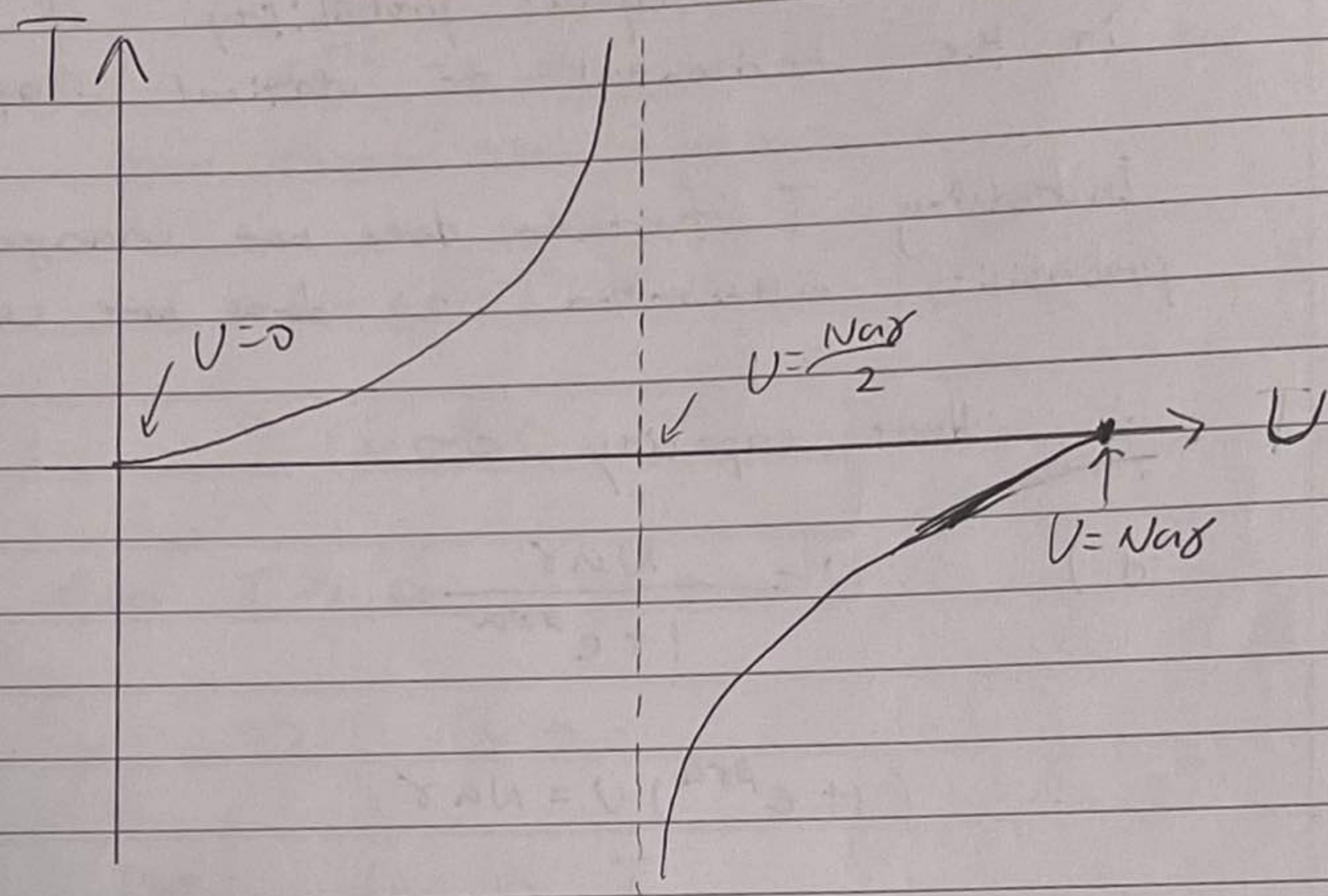
$$\therefore \quad \frac{\gamma a}{k_B T} = \ln\left(\frac{Na\gamma}{U} - 1\right)$$

$$\therefore \quad T = \frac{\gamma a}{k_B} \frac{1}{\ln\left(\frac{Na\gamma}{U} - 1\right)}$$

$T < 0$ when $0 < \frac{Na\gamma}{U} - 1 < 1$

$$\Rightarrow \quad 1 < \frac{Na\gamma}{U} < 2$$

$$\Rightarrow \quad \boxed{\tfrac{1}{2}Na\gamma < U < Na\gamma}$$



→ It is possible for this system to have negative temperature because the partition function allows T to be negative, ~~Unlike~~ unlike ideal gas, ~~in~~ for which the partition function has the term $\lambda_{th} = \hbar\sqrt{\frac{2\pi}{mk_BT}}$ where T cannot be negative

→ The stability argument from Notes §10.5.2 does not apply because each segment of the chain is localised. They do not have mean velocity $\vec{u}_i$. Since $\vec{u}_i$ is not a variable of the system, the condition $\frac{\partial^2 S}{\partial \vec{u}_i^{\,2}} < 0$ does not exist anymore. Therefore no condition will restrict T to be positive

e) We wish to maximise $S_G = -\sum_\alpha P_\alpha \ln P_\alpha$

subject to the constraints $\sum_\alpha P_\alpha - 1 = 0$, $\sum_\alpha P_\alpha E_\alpha - U = 0$,

and $\sum_\alpha P_\alpha l_\alpha - L = 0$, where $E_\alpha = \gamma(Na - l_\alpha)$

Use method of Lagrange multipliers, we

maximise unconditionally

$$S_G' = S_G - \lambda(\sum_\alpha P_\alpha - 1) - \beta(\sum_\alpha P_\alpha E_\alpha - U) - \sigma(\sum_\alpha P_\alpha l_\alpha - L)$$

where λ, β, σ are Lagrange multipliers

set $dS_G' = 0$, using $dS_G = -\sum_\alpha(\ln P_\alpha + 1)\, dP_\alpha$

We get:

$$-\sum_\alpha(\ln P_\alpha + 1)\, dP_\alpha - \lambda \sum_\alpha dP_\alpha - \left[\sum_\alpha (P_\alpha) - 1\right] d\lambda - \beta \sum_\alpha E_\alpha\, dP_\alpha$$

$$- (\sum_\alpha P_\alpha E_\alpha - U)\, d\beta - \sigma \sum_\alpha l_\alpha\, dP_\alpha - (\sum_\alpha P_\alpha l_\alpha - L)\, d\sigma$$

$$= 0$$

$$\Rightarrow \quad \ln P_\alpha + 1 + \lambda + \beta E_\alpha + \sigma l_\alpha = 0 \quad ①$$

$$\sum_\alpha P_\alpha - 1 = 0 \quad ②$$

$$\sum_\alpha P_\alpha E_\alpha - U = 0 \quad ③$$

$$\sum_\alpha P_\alpha l_\alpha - L = 0 \quad ④$$

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

② $\Rightarrow \quad \sum_\alpha e^{-1-\lambda} e^{-\beta E_\alpha - \sigma l_\alpha} = 1$

$$\Rightarrow \quad e^{-1-\lambda} = \frac{1}{\sum_\alpha e^{-\beta E_\alpha - \sigma l_\alpha}}$$

$$\Rightarrow \quad P_\alpha = \frac{e^{-\beta E_\alpha - \sigma l_\alpha}}{\sum_\alpha e^{-\beta E_\alpha - \sigma l_\alpha}}$$

③ $\Rightarrow \quad U = \sum_\alpha P_\alpha E_\alpha = \dfrac{\sum_\alpha E_\alpha e^{-\beta E_\alpha - \sigma l_\alpha}}{\sum_\alpha e^{-\beta E_\alpha - \sigma l_\alpha}}$

④ $\Rightarrow \quad L = \sum_\alpha P_\alpha l_\alpha = \dfrac{\sum_\alpha l_\alpha e^{-\beta E_\alpha - \sigma l_\alpha}}{\sum_\alpha e^{-\beta E_\alpha - \sigma l_\alpha}}$

Note that $E_\alpha = \gamma(Na - l_\alpha) \Rightarrow E_\alpha + \gamma l_\alpha = Na\gamma$

③ + γ * ④ $\Rightarrow$

$$U + \gamma L = \frac{\sum_\alpha \overbrace{(E_\alpha + \gamma l_\alpha)}^{Na\gamma} e^{-\beta E_\alpha - \sigma l_\alpha}}{\sum_\alpha e^{-\beta E_\alpha - \sigma l_\alpha}} = Na\gamma$$

$\Rightarrow \quad U + \gamma L - Na\gamma = 0$ ⑤

①, ②, ③, ④ only has solutions if ⑤ is satisfied, i.e. U and L has to have the relationship that

$$\boxed{U + \gamma L - Na\gamma = 0}$$

If this is satisfied, then ③ and ④ essentially becomes the same equation.

$$\cancel{\text{let } \beta'} \quad -\beta E_\alpha - \sigma \lambda_\alpha = -\beta E_\alpha - \sigma \left(N_a - \frac{E_\alpha}{\gamma}\right)$$

$$= -\left(\beta - \frac{\sigma}{\gamma}\right) E_\alpha - \sigma N_a$$

③ $\Rightarrow$ $$U = \frac{\sum_\alpha E_\alpha e^{-(\beta - \frac{\sigma}{\gamma}) E_\alpha} \cancel{e^{-\sigma N_a}}}{\sum_\alpha e^{-(\beta - \frac{\sigma}{\gamma}) E_\alpha} \cancel{e^{-\sigma N_a}}}$$

let $\beta' = \beta - \frac{\sigma}{\gamma}$ $\Rightarrow$ $$U = \frac{\sum_\alpha E_\alpha e^{-\beta' E_\alpha}}{\sum_\alpha e^{-\beta' E_\alpha}}$$

let $\sum_\alpha e^{-\beta' E_\alpha} = Z(\beta')$. ~~then~~

then $$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta'} = -\frac{\partial \ln Z(\beta')}{\partial \beta'} \quad ⑥$$

So equations ①, ②, ③, ④ reduces to

$$P_\alpha = \frac{e^{-\beta' E_\alpha}}{Z(\beta')} \quad ⑦$$

$e^{-1-\lambda'} Z(\beta') = 1$ $\Leftarrow$ $$e^{-1-\lambda-\sigma N_a} Z(\beta') = 1 \quad ⑧$$

$$U = -\frac{\partial \ln Z(\beta')}{Z(\beta')} \quad ⑥$$

⑦, ⑧, ⑥ gives solutions to $\{P_\alpha, \lambda', \beta'\}$

where $\beta' = \beta - \frac{\sigma}{\gamma}$ and $\lambda' = \lambda + \sigma N_a$

$\therefore$ ~~and γ β and σ such that~~

$\therefore$ we can choose σ ~~arbitrary~~ arbitrarily

and the set $\beta = \beta' + \frac{\sigma}{\gamma}$, then the
(and $\lambda = \lambda' - \sigma N a$)

set $\{ P_\alpha, \lambda, \beta, \sigma \}$ solves ⑦, ⑧, ⑨,

and thus solves ①, ②, ③, ④.

$\therefore$ the Lagrange multiplier σ can be arbitrary

$\therefore$ ~~th~~

Similar argument applies for making β or λ arbitrary.

$\therefore$ ~~The~~ One of β, λ, ~~and~~ and σ can be made arbitrary.

$\therefore$ The constraint is superfluous.

6. a)

For a single particle in a 3-D box:

the TISE gives $\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi$

and $V = \begin{cases} 0 & -\frac{L_x}{2} < x < \frac{L_x}{2},\ -\frac{L_y}{2} < y < \frac{L_y}{2},\ -\frac{L_z}{2} < z < \frac{L_z}{2} \\ \infty & \text{otherwise} \end{cases}$

$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = E\psi$

separation of variables, try $\psi(x,y,z) = X(x)Y(y)Z(z)$

$\Rightarrow -\frac{\hbar^2}{2m}(X''YZ + XY''Z + XYZ'')\psi = EXYZ$

$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z}\right) = E$

$\Rightarrow \frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} = -\frac{2mE}{\hbar^2} \equiv -k^2$

$\because$ $\frac{X''}{X}$ is a function only of x

$\frac{Y''}{Y}$ is a function only of y

$\frac{Z''}{Z}$ is a function only of z

$\therefore$ let $\frac{X''}{X} = -k_x^2$, $\frac{Y''}{Y} = -k_y^2$, $\frac{Z''}{Z} = -k_z^2$

for periodic solutions since we are looking for solutions that vanish at the boundary of the box

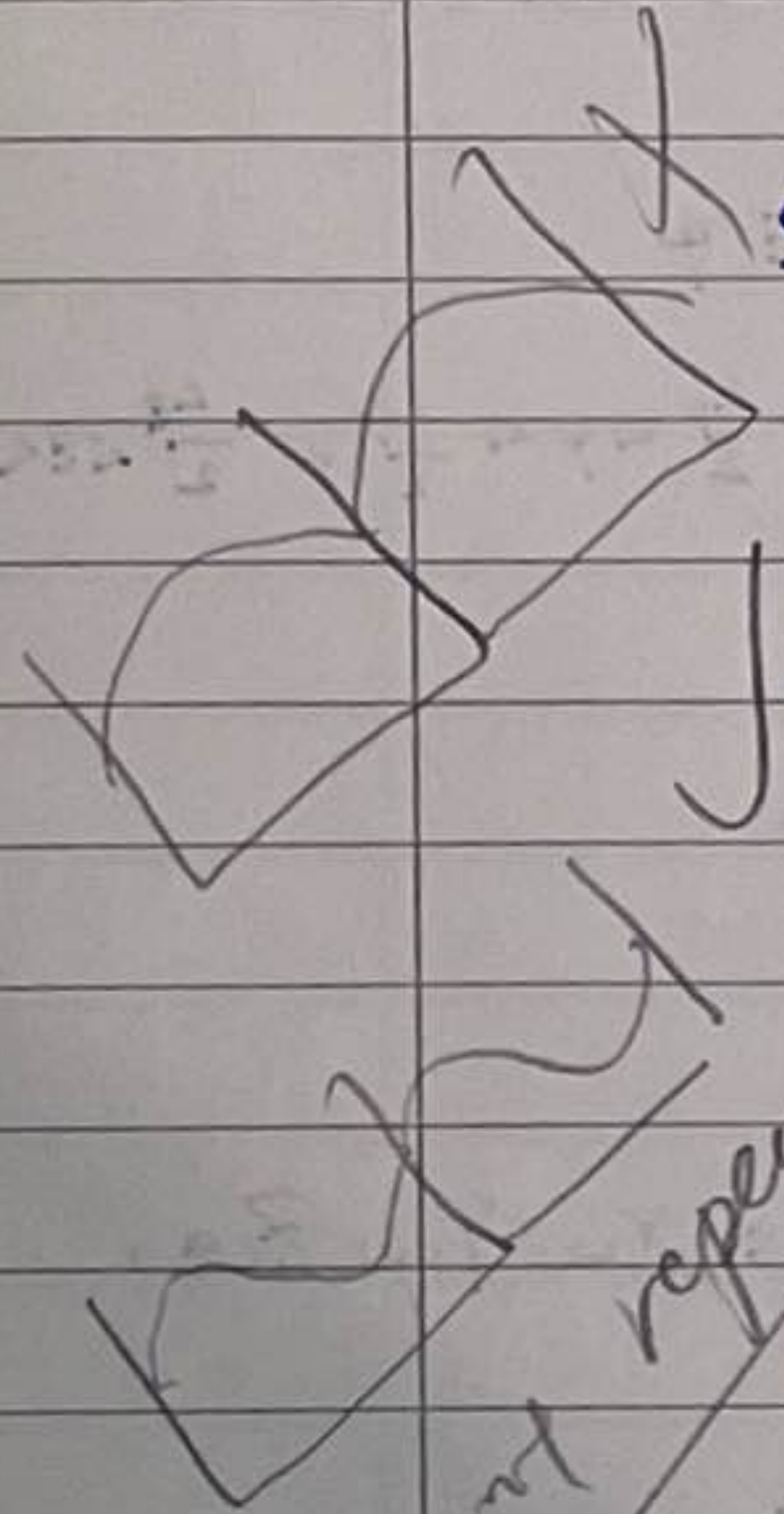
$(k_x, k_y, k_z, k \in \mathbb{R})$

$$\frac{X''}{X} = -k_x^2 \Rightarrow X'' + k_x^2 X = 0$$

$$\Rightarrow X(x) = C_x e^{ik_x x} + D_x e^{-ik_x x}$$

Similarly $Y(y) = C_y e^{ik_y y} + D_y e^{-ik_y y}$

$Z(z) = C_z e^{ik_z z} + D_z e^{-ik_z z}$



General Solution : (Apply principle of superpositions)

want repeatable

$$\psi(x,y,z) = XYZ = \sum_{k_x^2+k_y^2+k_z^2=k^2} A_{k_x,k_y,k_z} e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

Boundary Conditions :

$$\psi(-\tfrac{L_x}{2}, y, z) = \psi(\tfrac{L_x}{2}, y, z) = 0$$

$$\Rightarrow 0 = \sum A_{k_x,k_y,k_z} e^{ik_x L_x/2} e^{ik_y y} e^{ik_z z}$$

$$= \sum A_{k_x k_y k_z} e^{-ik_x L_x/2} e^{ik_y y} e^{ik_z z}$$

$$\Rightarrow \sum A_{k_x k_y k_z} \left(e^{ik_x L_x/2} - e^{-ik_x L_x/2}\right) e^{ik_y y} e^{ik_z z} = 0$$

This is true for any $-\frac{L_y}{2} < y < \frac{L_y}{2}$ and $-\frac{L_z}{2} < z < \frac{L_z}{2}$

Hence $e^{ik_x L_x/2} - e^{-ik_x L_x/2} = 0$

$\Rightarrow e^{ik_x L_x/2} = e^{-ik_x L_x/2}$ for any allowed values of k_x

$$\Rightarrow e^{ik_x L_x} = 1 \Rightarrow k_x L_x = 2\pi n_x$$

$$\Rightarrow k_x = \frac{2\pi}{L_x} n_x$$

~~(n_x is an integer~~ ($n_x \in \mathbb{Z}$)

Hence apply the same reasoning to k_y and k_z we get

$$k_x = \frac{2\pi}{L_x} n_x \quad , \quad k_y = \frac{2\pi}{L_y} n_y \, , \quad k_z = \frac{2\pi}{L_z} n_z$$

$$(n_x, n_y, n_z \in \mathbb{Z} \quad , \quad k_x^2 + k_y^2 + k_z^2 = k^2)$$

Define the wave number vector $\vec{k}$ to be

$$\vec{k} = \left(\frac{2\pi}{L_x} n_x \, , \; \frac{2\pi}{L_y} n_y \, , \; \frac{2\pi}{L_z} n_z \right) = (k_x, k_y, k_z)$$

where (n_x, n_y, n_z) define a countablly infinite number of single-particle states.

Corresponding energy $\varepsilon_{\vec{k}}$ is given by

$$-\frac{2m\varepsilon_{\vec{k}}}{\hbar^2} = -k^2 \Rightarrow \quad \varepsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$$

→ If particles are distinguishable :

Single-particle partition function is

$Z_1 = \sum_{\vec{k}} e^{-\beta \varepsilon_{\vec{k}}}$, and collective microstates ~~of~~

and energies of the gas is

$$\alpha = \{ \vec{k_1}, \cdots, \vec{k_n} \} \quad \text{and} \quad E_\alpha = \sum_{i=1}^{N} \varepsilon_{\vec{k_i}}$$

The partition function is

$$Z = \sum_{\{\vec{k_1}, \cdots, \vec{k_N}\}} e^{-\beta(\varepsilon_{\vec{k_1}} + \cdots + \varepsilon_{\vec{k_N}})}$$

$$= \left(\sum_{\vec{k}} e^{-\beta\varepsilon_{\vec{k}}}\right)^N = Z_1^N$$

And we have :

$$Z_1 = \sum_{\vec{k}} e^{-\beta\varepsilon_{\vec{k}}} = \sum_{k_x, k_y, k_z} \underbrace{\frac{L_x L_y L_z}{(2\pi)^3}}_{1} \overbrace{\left(\frac{2\pi}{L_x}\right)}^{\Delta k_x} \overbrace{\left(\frac{2\pi}{L_y}\right)}^{\Delta k_y} \overbrace{\left(\frac{2\pi}{L_z}\right)}^{\Delta k_z} e^{-\beta\varepsilon_{\vec{k}}}$$

$$\approx \int dk_x \int dk_y \int dk_z \frac{V}{(2\pi)^3} e^{-\beta\hbar^2 k^2/2m}$$

$$= \frac{V}{(2\pi)^3} \left(\int_{-\infty}^{\infty} dk_x\, e^{-\beta\hbar^2 k_x^2/2m}\right)\left(\int_{-\infty}^{\infty} dk_y\, e^{-\beta\hbar^2 k_y^2/2m}\right)\left(\int_{-\infty}^{\infty} dk_z\, e^{-\beta\hbar^2 k_z^2/2m}\right)$$

$$= \frac{V}{(2\pi)^3} \left(\frac{2m}{\beta\hbar^2}\pi\right)^{3/2} \underset{\beta = \frac{1}{k_B T}}{=} \boxed{\frac{V}{\hbar^3}\left(\frac{m k_B T}{2\pi}\right)^{3/2}}$$

Define $\boxed{\lambda_{th} \equiv \hbar\sqrt{\frac{2\pi}{m k_B T}}}$, then

$$\boxed{Z_1 = \frac{V}{\lambda_{th}^3}}, \quad Z = \left(\frac{V}{\lambda_{th}^3}\right)^N$$

$$F = -k_B T \ln Z = -k_B T N \ln\left(\frac{V}{\lambda_{th}^3}\right)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B N \ln\left(\frac{V}{\lambda_{th}^3}\right) + k_B T N \frac{\partial}{\partial T}\left(\ln\left(\frac{V}{\lambda_{th}^3}\right)\right)$$

$$= \cancel{k_B T}\ k_B N \ln\left(\frac{V}{\lambda_{th}^3}\right) + k_B T N \left(\frac{\lambda_{th}^3}{V}\right) V \frac{\partial}{\partial T}\left(\frac{1}{\lambda_{th}^3}\right)$$

$$\frac{d}{dT}\left(\frac{1}{\lambda_{th}^3}\right) = -3\frac{1}{\lambda_{th}^4}\frac{d\lambda_{th}}{dT}$$

$$= -\frac{3}{\lambda_{th}^4}\ \hbar\sqrt{\frac{2\pi}{mk_B}}\ \frac{d}{dT}\left(T^{-\frac{1}{2}}\right)$$

$$= -\frac{3}{\lambda_{th}^4}\ \hbar\sqrt{\frac{2\pi}{mk_B}}\left(-\frac{1}{2}\right)T^{-\frac{3}{2}}$$

$$= \frac{3}{2}\frac{1}{\lambda_{th}^4}\lambda_{th} T^{-1}$$

$$= \frac{3}{2}\frac{1}{\lambda_{th}^3}\frac{1}{T}$$

$$\Rightarrow \quad S = k_B N \ln\left(\frac{V}{\lambda_{th}^3}\right) + k_B \cancel{T} N \frac{\cancel{\lambda_{th}^3}}{\cancel{V}} \cancel{V} \frac{3}{2}\left(\frac{1}{\cancel{\lambda_{th}^3}}\right)\left(\frac{1}{\cancel{T}}\right)$$

$$= k_B N \ln\left(\frac{V}{\lambda_{th}^3}\right) + \frac{3}{2}k_B N$$

let $n = \frac{N}{V}$ = number density of particles

$$\Rightarrow \quad S = k_B N \left[\ln(V) - \ln(\lambda_{th}^3) + \frac{3}{2}\right]$$

$$= k_B N\left[\ln(N/n) - \ln(\lambda_{th}^3) + \frac{3}{2}\right]$$

$$\Rightarrow \quad \underline{S = k_B N\left[\ln N + \frac{3}{2} - \ln(n\lambda_{th}^3)\right]}$$

If entropy is additive, when we double the amount of gas, $N \to 2N$, $V \to 2V$ ($n = \frac{N}{V}$ = constant), we should get

$S \to 2S$ i.e. $S_{new} = 2S_{old}$

For this S we just got:

$$\cancel{S_{old}} \quad S_{new} = 2k_B N [\ln 2N + \frac{3}{2} + \ln(n\lambda_{th}^3)].$$

$$S_{new} - 2S_{old} = 2k_B N \ln 2 \neq 0$$

$\therefore$ Entropy is not additive

This is a problem because entropy ~~so~~ should be additive. Our entire theory was built on additivity of entropy. Gibbs-Shannon entropy is ~~Proof~~ additive by definition.

$\longrightarrow$ particles are indistinguishable:

If number of available single particle states $\gg$ number of particles N, then we can use the $1/N!$ factor to ~~$\neq$~~ correct the partition function Z

Because ~~是~~ in this case, microstates in a box is given by $\alpha = \{n_{\vec{k}_1}, \cancel{=}, n_{\vec{k}_2}, n_{\vec{k}_3}, \cdots\}$

$$\sum_{\vec{k}} n_{\vec{k}} = N \quad (n_{\vec{k}_i}\text{'s are occupation numbers})$$

$$Z = \sum_{\{n_{\vec{k}}\}} e^{-\beta \sum_{\vec{k}} n_{\vec{k}} \varepsilon_{\vec{k}}} \quad \left(E_\alpha = \sum_{\vec{k}} n_{\vec{k}} \varepsilon_{\vec{k}} \right)$$

if number of available single-particle states >> N, then

it is very unlikely that a ~~states~~ state can have more than one particle sitting in it.
(more than one particle can have the same single-particle state is unlikely)

$\therefore \quad n_{\vec{k}} = 0$ or 1

In this case ~~we can~~ we overcounted $N!$ times the same state in Z_1^N

Hence ~~Z_1~~ $Z = \dfrac{Z_1^N}{N!}$

~~Z_1~~ $\because Z_1 = \sum_{\vec{k}} e^{-\varepsilon_{\vec{k}}/k_B T}$

For likely states $e^{-\varepsilon_{\vec{k}}/k_B T} \sim 1$

For unlikely states $e^{-\varepsilon_{\vec{k}}/k_B T} \sim 0$

$\therefore Z_1 \sim$ # of available states

$\therefore$ The condition becomes $Z_1 >> N$

$$\Rightarrow \quad \frac{V}{\lambda_{th}^3} >> N \quad \Leftrightarrow \quad \boxed{n \lambda_{th}^3 << 1}$$

Now partition function $Z = \dfrac{1}{N!} \left(\dfrac{V}{\lambda_{th}^3} \right)^N$

$$F = -k_B T \ln Z = -k_B T \left[N \ln\left(\frac{V}{\lambda_{th}^3}\right) - \ln N! \right]$$

$$\underbrace{\simeq}_{\text{Stirling's formula}} k_B T \left[N \ln N - N \ln(n \lambda_{th}^3) - (N \ln N - N) \right]$$

$$= -k_B T N \left(1 - \ln(n \lambda_{th}^3)\right)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial F}{\partial T}\right)_n$$

$$= k_B N - \frac{\partial}{\partial T} T k_B N \ln(n \lambda_{th}^3)$$

$$= k_B N - T k_B N \frac{n}{n \lambda_{th}^3} \frac{d}{dT}(\lambda_{th}^3) - k_B N \ln(n \lambda_{th}^3)$$

$$= k_B N \left(1 - \ln(n \lambda_{th}^3)\right) - k_B T N \frac{1}{\lambda_{th}^3} (3 \lambda_{th}^2) \frac{d}{dT}(\lambda_{th})$$

$$\frac{d}{dT}(\lambda_{th}) = \hbar \sqrt{\frac{2\pi}{m k_B}} \frac{d}{dT}\left(T^{-1/2}\right) = \hbar \sqrt{\frac{2\pi}{m k_B}} \left(-\frac{1}{2}\right) T^{-\frac{3}{2}}$$

$$= -\frac{\lambda_{th}}{2T}$$

$$\Rightarrow \quad S = k_B N \left(1 - \ln(n \lambda_{th}^3)\right) \underbrace{- k_B T N \frac{1}{\lambda_{th}^3} (3 \lambda_{th}^2) \left(-\frac{\lambda_{th}}{2T}\right)}_{-\frac{3}{2} k_B N}$$

$$\Rightarrow \quad \boxed{S = k_B N \left(\frac{5}{2} - \ln(n \lambda_{th}^3)\right)}$$

When $N \to 2N$. $V \to 2V$, ~~n~~ (n is constant)

$$S_{new} - 2S_{old} = 2k_B N\left(\tfrac{5}{2} - \ln(n\lambda_{th}^3)\right) - 2k_B N\left(\tfrac{5}{2} - \ln(n\lambda_{th}^3)\right)$$

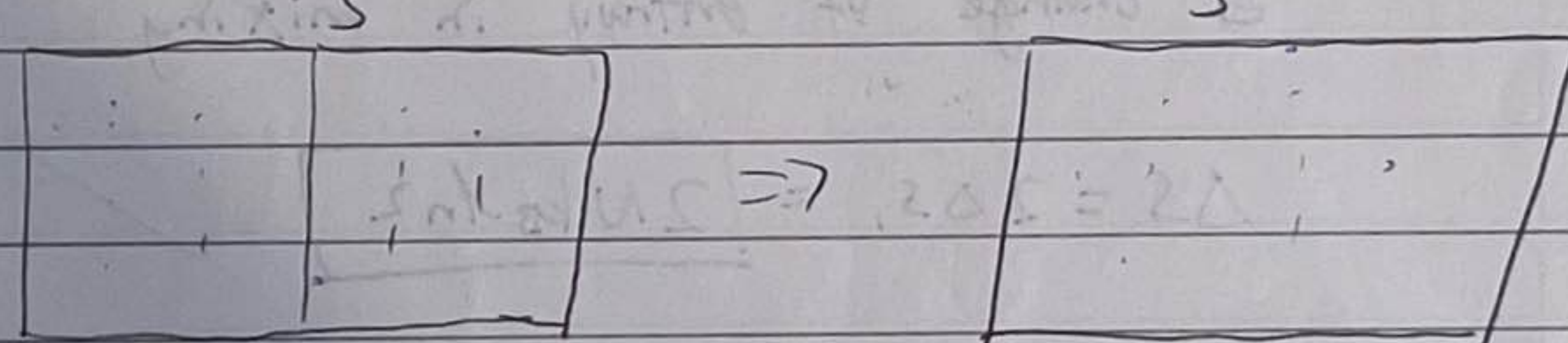
$$= 0$$

$\Rightarrow$ $S_{new} = 2S_{old}$, $S \to 2S$

$\Rightarrow$ Entropy is additive

b) (i) identical particles:

S $\qquad\qquad$ S'



N, n $\quad$ N, n $\qquad\qquad$ $2N, n$

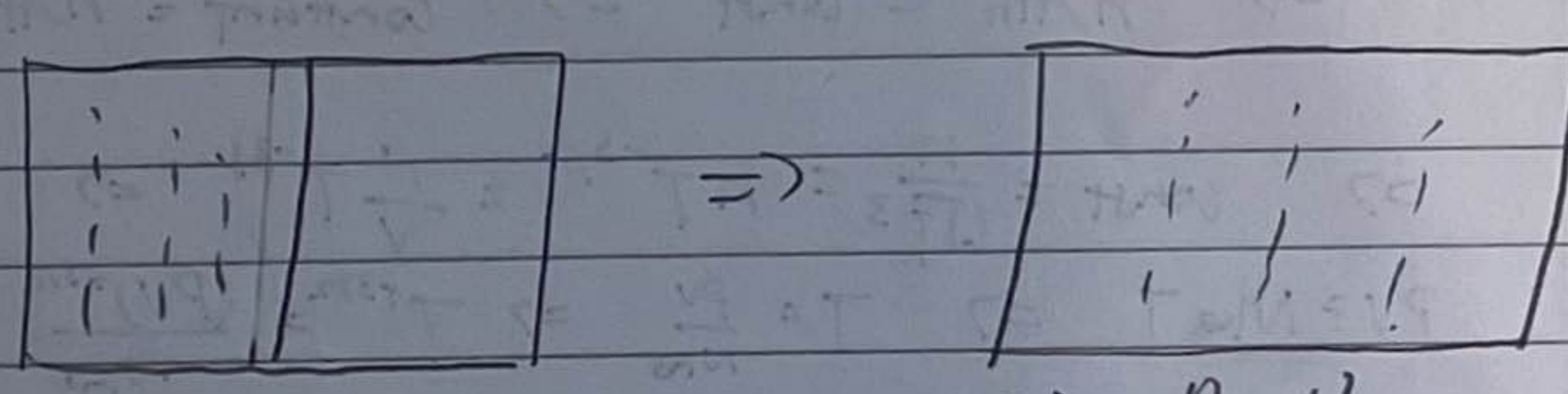
$$S = \cancel{2k_B} \; 2 \times k_B N\left(\tfrac{5}{2} - \ln(n\lambda_{th}^3)\right)$$

$$= 2k_B N\left(\tfrac{5}{2} - \ln(n\lambda_{th}^3)\right)$$

$$S' = k_B(2N)\left(\tfrac{5}{2} - \ln(n\lambda_{th}^3)\right) = 2k_B N\left(\tfrac{5}{2} - \ln(\lambda_{th}^3 n)\right)$$

$$\therefore \quad \Delta S = S' - S = \boxed{0}$$

(ii) Different particles:

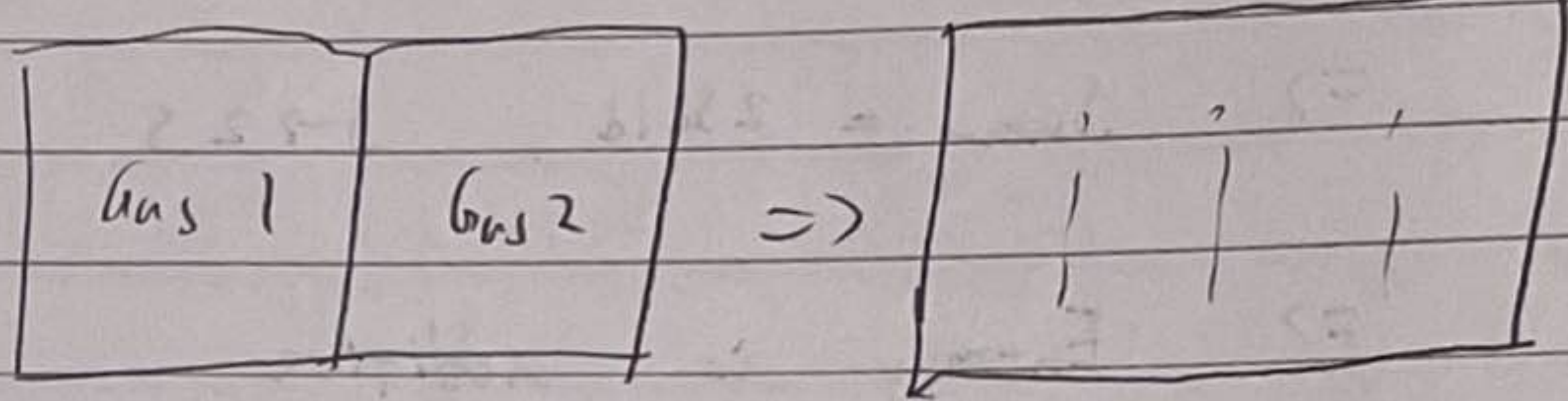


S_1 $\quad$ n, N $\qquad\qquad$ S_1' $\quad$ $\frac{n}{2}, N$

Joule Expansion of one kind of particle

$$\Rightarrow \Delta S_1 = S_1' - S_1 = Nk_B\left[\frac{5}{2} - \ln\left(\frac{n}{2}\lambda_{th}^3\right)\right] - Nk_B\left[\frac{5}{2} - \ln(n\lambda_{th}^3)\right]$$

$$= Nk_B \ln 2$$



$S = 2S_1$ $\quad\quad$ $S' = 2S_1'$

change of entropy in mixing

$$\Delta S = 2\Delta S_1 = \boxed{2Nk_B \ln 2}$$

Answers are different, this makes physical sense because mixing of 2-different gases is a irreversible process whereas mixing of ~~two~~ identical gases is a reversible process (simply putting the partition back in we get ~~back~~ back to the original state)

c) Adiabatic process $dS = 0 \Rightarrow S = \cancel{const}$ const

$$\Rightarrow \text{const} = S = \ln k_B N\left(\frac{5}{2} - \ln(n\lambda_{th}^3)\right)$$

# of particles $N = \text{const}$

$$\Rightarrow n\lambda_{th}^3 = \text{const} \Rightarrow \text{constant} = n\lambda_{th}^3 = n\hbar\left(\sqrt{\frac{2\pi}{mk_BT}}\right)^3$$

$$\Rightarrow \text{const} = \frac{n}{(\sqrt{T})^3} = nT^{-3/2} = \frac{N}{V}T^{-3/2} \Rightarrow VT^{+3/2} = \text{const}$$

$$PV = Nk_BT \Rightarrow T = \frac{PV}{Nk_B} \Rightarrow T^{+3/2} = \frac{(PV)^{+3/2}}{Nk_B}$$

$$\therefore \quad (PV)^{+3/2} V = \text{const.}$$

$$\Rightarrow \quad P^{+3/2} V^{3/2} V = \text{const}$$

$$\Rightarrow \quad P^{3/2} V^{5/2} = \text{const}$$

$$\Rightarrow \quad (P V^{5/3})^{3/2} = \text{const}$$

$$\Rightarrow \quad \boxed{PV^{5/3} = \text{const}}$$

7. The time-independent Klein-Gordon Equation:

$$-\hbar^2 c^2 \nabla^2 \psi + (mc^2)^2 \psi = E^2 \psi$$

let $\psi = \psi(x, y, z) = X(x)\, Y(y)\, Z(z)$

and $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

~~then~~

then $-\hbar^2 c^2 (X''YZ + XY''Z + XYZ'') + (mc^2)^2 XYZ = E^2 XYZ$

$$\Rightarrow \quad -\hbar^2 c^2 \Big(\underbrace{\frac{X''}{X}}_{-k_x^2} + \underbrace{\frac{Y''}{Y}}_{-k_y^2} + \underbrace{\frac{Z''}{Z}}_{-k_z^2} \Big) = \underbrace{E^2 - (mc^2)^2}_{+\hbar^2 c^2 k^2}$$

$\cancel{X'' + k_x^2 X, \ Y'' + k_y Y}$.

$$X'' + k_x^2 X = 0, \quad Y'' + k_y^2 Y = 0, \quad Z'' + k_z^2 Z = 0$$

leads to the same wave number vector $\vec{k}$ as question (6)

$$\Rightarrow \quad \vec{k} = \left(\frac{2\pi}{L_x} n_x, \frac{2\pi}{L_y} n_y, \frac{2\pi}{L_z} n_z \right)$$

$$(n_x, n_y, n_z \in \mathbb{Z}, \ k_x^2 + k_y^2 + k_z^2 = k^2)$$

$\therefore$ As in (6), the triplet (n_x, n_y, n_z) describes the microstates of a single particle

But in this relativistic case, the energy is different.

$$\varepsilon_{\vec{k}} = \sqrt{\hbar^2 c^2 k^2 + (mc^2)^2}$$

∴ Single - particle partition function :

$$Z_1 = \sum_{\vec{k}} e^{-\beta \varepsilon_{\vec{k}}} = \cancel{\int} \frac{V}{(2\pi)^3}\int d^3\vec{k}\, e^{-\beta\varepsilon_{\vec{k}}}$$

$$= \frac{V}{(2\pi)^3}\int d^3\vec{k}\, e^{-\beta\sqrt{\hbar^2c^2k^2+(mc^2)^2}}$$

For ultra-relativistic gases.

$$\hbar^2c^2k^2 \gg (mc^2)^2 \Rightarrow \varepsilon_k \simeq \hbar c|k| = \hbar c\sqrt{k_x^2+k_y^2+k_z^2}$$

$$\therefore \cancel{Z_1 = \frac{V}{(2\pi)^3}\int d^3k\, e^{-\beta\hbar c|k|}}$$

$$\cancel{= 8\frac{V}{(2\pi)^3}\left(\int_0^\infty dk_x\, e^{-\beta\hbar c k_x}\right)^3}$$

$$\cancel{= \frac{1}{-\beta\hbar c}e^{-\beta\hbar c k_x}\Big|_0^\infty = \frac{1}{\beta\hbar c} = \frac{k_B T}{\hbar c}}$$

$$\Rightarrow \cancel{8\beta}$$

$$Z_1 = \frac{V}{(2\pi)^3}\int d^3k\, e^{-\beta\hbar c\sqrt{k_x^2+k_y^2+k_z^2}}$$

$$= \frac{V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk\, e^{-\beta\hbar c k}$$

$$= \frac{V}{2\pi^2}\int_0^\infty dk\, k^2 e^{-\beta\hbar c k}$$

let $x = \beta \hbar c k$ $\quad$ $\cancel{d}$ $k^2 = \left(\frac{1}{\beta\hbar c}\right)^2 x^2$

$$dk = \frac{1}{\beta \hbar c} dx$$

$$\Rightarrow \quad z_1 = \frac{V}{2\pi^2}\left(\frac{1}{\beta\hbar c}\right) \int_0^\infty \underbrace{dx\, e^{-x} x^2}_{2!}$$

$$\Rightarrow \quad Z_1 = \frac{V}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^3 \qquad \left(\beta = \frac{1}{k_B T}\right)$$

$$\cancel{Z = \frac{Z_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\pi^2}\right)^N \left(\frac{k_B T}{\hbar c}\right)^{3N}}$$

let $\boxed{\lambda \equiv \frac{\hbar c \pi^{2/3}}{k_B T}}$

$\cancel{F = -k_B T \ln Z =}$

then $\quad z_1 = \frac{V}{\lambda^3}$

$$\Rightarrow \quad Z = \frac{Z_1^N}{N!} \quad \Rightarrow \quad Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

$$F = -k_B T \ln Z = \cancel{-k_B T N \ln}$$

$$= -k_B T N \left(1 - \ln(n\lambda^3)\right)$$

Pressure $\quad P = -\left(\frac{\partial F}{\partial V}\right)_T = \cancel{-\left(\frac{\partial F}{\partial n}\right)_T \frac{\partial F}{\partial}} \quad -\left(\frac{\partial F}{\partial n}\right)_T \underbrace{\left(\frac{\partial n}{\partial V}\right)_T}_{-\frac{N}{V^2}.}$

$$\left(\frac{\partial F}{\partial n}\right)_T = \cancel{-k_B T N \frac{1}{n \lambda^3}} \quad k_B T N \frac{1}{n\lambda^3} \lambda^3$$

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

$$\therefore \quad P = k_B T V \frac{N}{V^2} = k_B T \frac{N}{V} \Rightarrow \boxed{PV = N k_B T}$$

This equation of state is unchanged because for both non-relativistic and relativistic cases,

$$Z_1 \propto V \quad \therefore \quad Z_N \propto V^N$$

$$F = -k_B T \ln Z \propto -N k_B T \ln V + \text{terms independent of } V \quad \cancel{\text{constants.}}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\partial}{\partial V}(N k_B T \ln V) = \frac{N k_B T}{V}$$

$$\Rightarrow \quad \underline{PV = N k_B T.} \qquad \left(\text{As } \frac{\partial}{\partial V}\int d^3\vec{k}\, e^{-\beta\sqrt{\hbar^2 c^2 k^2 + (mc^2)^2}} = 0, \right.$$

in fact we do not need ultrarelativistic assumption to get $PV = N k_B T$)

(b) $$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\frac{\partial}{\partial T}\left(-N k_B T(1 - \ln(n\lambda^3))\right)$$

$$= N k_B - \cancel{\frac{1}{n\lambda^3}} N k_B \ln(n\lambda^3) - N k_B \frac{1}{n\lambda^3}(n)\, 3\lambda^2 \frac{d}{dT}(\lambda)$$

$$\lambda = \frac{\hbar c \pi^{2/3}}{k_B T} = \frac{C}{T} \qquad \left(C = \frac{\hbar c \pi^{2/3}}{k_B} \right)$$

$$\frac{d\lambda}{dT} = -\frac{C}{T^2} = -\frac{C}{T}\frac{1}{T} = -\frac{\lambda}{T}$$

$$\Rightarrow S = N k_B(1 - \ln(n\lambda^3)) - N k_B \underbrace{\frac{1}{n\lambda^3}\, n\, 3\lambda^2 \left(-\frac{\lambda}{T}\right)}_{+3Nk_B}$$

$$\Rightarrow \boxed{S = N k_B(4 - \ln(n\lambda^3))}$$

Adiabatic process $\Rightarrow dS = 0 \Rightarrow S = \text{const}$

$$\Rightarrow \quad n\lambda^3 = \text{const.} \Rightarrow \frac{N}{V}\frac{C}{T^3} = \text{const}$$

$$\Rightarrow \quad VT^3 = \text{const.}$$

$\because \; PV = Nk_BT \Rightarrow T = \frac{PV}{Nk_B}$

$$\Rightarrow \left(\frac{PV}{Nk_B}\right)^3 V^3 = \text{const}$$

$$\Rightarrow P^3V^4 = \text{const}$$

$$\Rightarrow (PV^{4/3})^3 = \text{const}$$

$$\Rightarrow \boxed{PV^{4/3} = \text{const}}$$

c) $\quad U = -\frac{\partial \ln Z}{\partial \beta}$

$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \qquad \ln N! \approx N\ln N - N$

$$\Rightarrow \ln Z = N(\ln V - \ln\lambda^3) - N\ln N + N$$
$$= N(1 - \ln(n\lambda^3))$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = \cancel{-\frac{\partial \ln Z}{\partial \beta}\frac{\partial \beta}{\partial T}} \quad \cancel{\frac{\partial \ln Z}{\partial \beta}}$$

$$= -\frac{\partial \ln Z}{\partial T}\frac{\partial T}{\partial \beta} = N\frac{n}{n\lambda^3}3\lambda^2\left(-\frac{\lambda}{T}\right)\frac{\partial T}{\partial \beta}.$$

$$\frac{\partial T}{\partial \beta} = \frac{1}{\left(\frac{\partial \beta}{\partial T}\right)} = \left(\frac{\partial}{\partial T}\left(\frac{1}{k_BT}\right)\right)^{-1} = \left(\frac{-1}{k_BT^2}\right)^{-1} = -k_BT^2$$

$$\therefore \; U = -3N\frac{1}{T}(-k_BT^2) = 3Nk_BT.$$

internal energy density $\varepsilon = \frac{U}{V} = \frac{3Nk_BT}{V}$

$\because \; P = \frac{Nk_BT}{V} \quad \therefore \; \boxed{P = \frac{\varepsilon}{3}}$

For non-relativistic gases

$$U = \frac{3}{2} N k_B T \ , \quad \Rightarrow \quad \mathcal{E} = \frac{3Nk_BT}{2V}$$

~~Use~~ $$p = \frac{Nk_BT}{V}$$

$$\Rightarrow \quad p = \frac{2}{3}\mathcal{E}$$

∴ They are different because energy is linearly ~~perpt~~ proportional to momentum in ~~relativ~~ the relativistic case rather than quadratic as in the non-relativistic case. ($E \propto p$, not $E \propto p^2$)

Hence equipartition theorem fails and we have different ~~values~~ result for the internal energy.

8. a)

For 2-D box

$$Z_1 = \frac{L_x}{2\pi}\frac{L_y}{2\pi}\int d^2\vec{k}\ e^{-\beta\varepsilon_k}$$

$$= \frac{A}{(2\pi)^2}\int d^2\vec{k}\ e^{-\beta\varepsilon_k} = \frac{A}{(2\pi)^2}\int_0^\infty dk \cdot k \cdot e^{-\beta\varepsilon_k}\underbrace{\int_0^{2\pi} d\theta}_{2\pi}$$

$$\cancel{= \frac{A}{2\pi}} = \int_0^\infty dk \left(\frac{A}{2\pi}\right) k\, e^{-\beta\varepsilon_k}$$

$$\equiv \int_0^\infty g(k)\, dk\ e^{-\beta\varepsilon_k}$$

$$\Rightarrow \quad g(k) = \boxed{\frac{Ak}{2\pi}}$$

For 1-D box

$$Z_1 = \frac{L_x}{2\pi}\int d\vec{k}\ e^{-\beta\varepsilon_k} = \int_{-\infty}^{\infty} dk \left(\frac{L}{2\pi}\right) e^{-\beta\varepsilon_k}$$

$$= \int_0^\infty dk \left(\frac{L}{\pi}\right) e^{-\beta\varepsilon_k}. \equiv \int_0^\infty dk\, g(k)\, e^{-\beta\varepsilon_k}$$

$$\Rightarrow \quad g(k) = \boxed{\frac{L}{\pi}}$$

b) For a d- dimensional box :

$$Z_1 = \frac{L_1 L_2 \cdots L_d}{(2\pi)^d} \int d^d\vec{k}\, e^{-\beta \varepsilon_k}$$

$$= \cancel{\frac{V_d}{(2\pi)^d} \int d^d}$$

$$= \frac{V_d}{(2\pi)^d} \int dk\, k^{d-1} S_d\, e^{-\beta \varepsilon_k}.$$

Where S_d is the full solid angle in d- dimensions.

~~Or~~ Consider the Gaussian integral in d- dimensions

$$I_d \equiv \left(\int_{-\infty}^{\infty} dx\, e^{-x^2} \right)^d = \pi^{d/2}$$

~~Id~~ Also $I_d = \int dx_1 \cdots dx_d \exp(-x_1^2 - \cdots - x_d^2)$

$$= \int_0^\infty dr\, S_d r^{d-1} e^{-r^2}$$

change of variable $y = r^2$ $dy = 2r\,dr$

$$\Rightarrow dr = \frac{dy}{2r}$$

$$I_d = \cancel{S_d \int_0^\infty} \frac{S_d}{2} \int_0^\infty dy \frac{1}{r} r^{d-1} e^{-r^2} = \frac{S_d}{2} \int_0^\infty dy\, r^{d-2} e^{-y}$$

$$= \frac{S_d}{2}\int_0^\infty \underbrace{dy\; y^{\frac{d}{2}-1} e^{-y}}_{\Gamma(\frac{d}{2})} = \frac{S_d}{2}\Gamma\left(\frac{d}{2}\right)$$

(Γ is the Gamma function. $\Gamma(t) = \int_0^\infty x^{t-1} e^{-x}\, dx$)

$$\Rightarrow \quad \pi^{d/2} = \frac{S_d\, \Gamma(\frac{d}{2})}{2}$$

$$\Rightarrow \quad S_d = \frac{2\pi^{d/2}}{\Gamma(\frac{d}{2})}$$

$$Z_1 = \frac{V_d}{(2\pi)^d}\int_0^\infty S_d\, dk\, k^{d-1} e^{-\beta\varepsilon_k}$$

$$\equiv \int_0^\infty dk\; g(k)\, e^{-\beta\varepsilon_k}$$

$$\Rightarrow \quad g(k) = \frac{S_d V_d}{(2\pi)^d} k^{d-1}$$

$$\Rightarrow \quad \boxed{g(k) = \frac{V_d k^{d-1}}{2^{d-1}\pi^{d/2}\,\Gamma(\frac{d}{2})}}$$

(V_d is the volume of ~~box~~ the d-dimensional box)