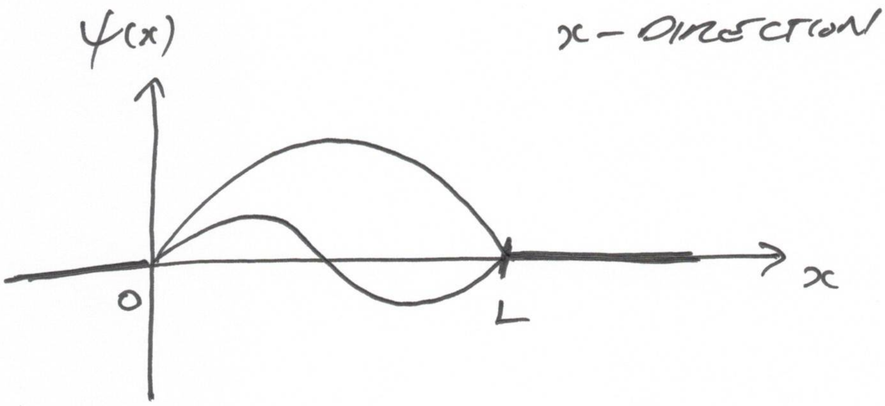
DERIVING MOMENTUM QUANTISATION

- THE DE BROGLIE WAVELENGTH λ OF A PARTICLE WITH MOMENTUM OF MAGNITUDE p IS

$$\boxed{\lambda = \frac{h}{p}}$$



STANDING WAVES : INTEGER NUMBER OF $\frac{1}{2}$ DE BROGLIE WAVELENGTHS MUST FIT INTO THE BOX

$$\lambda_x = \frac{h}{p_x}$$

SO $$\boxed{n_x \frac{\lambda_x}{2} = L}$$ $n_x = 1, 2, 3, \ldots$

$$\Rightarrow \quad n_x \frac{h}{2p_x} = L$$

$$\Rightarrow \quad \boxed{p_x = \frac{n_x h}{2L} = n_x \frac{\pi\hbar}{L}}$$

$$\hbar = \frac{h}{2\pi}$$

SIMILARLY FOR y & z DIRECTIONS

$$\Rightarrow \quad (p_x, p_y, p_z) = \frac{\pi\hbar}{L}(n_x, n_y, n_z)$$

$$n_x, n_y, n_z = 1, 2, 3, \ldots$$

IDEAL GAS IN CONTACT WITH A HEAT RESERVOIR

- THE THERMODYNAMICS IS DETERMINED BY THE CANONICAL PARTITION FUNCTION

$$Z(T, V, N) = \sum_{\substack{\text{energy of} \\ \text{e'states} \\ \text{of system}}} e^{-E_{STATE}/k_B T}$$

HERE WE ASSUME JUST ONE SPECIES OF PARTICLE

VIA $$F(T, V, N) = -k_B T \ln Z(T, V, N)$$

- FOR A MONATOMIC IDEAL GAS OF N ATOMS IN A CUBIC CONTAINER OF SIDE L, THE ENERGY E' STATES ARE LABELLED BY A "3N-VECTOR"

$$\vec{n} = (\underbrace{n_x^{(1)}, n_y^{(1)}, n_z^{(1)}}_{\text{QUANTUM No}^{\circ}\text{S FOR PARTICLE 1}}, \underbrace{n_x^{(2)}, n_y^{(2)}, n_z^{(2)}}_{\text{QUANTUM No}^{\circ}\text{S FOR PARTICLE 2}}, \ldots, \underbrace{n_x^{(N)}, n_y^{(N)}, n_z^{(N)}}_{\text{QUANTUM No}^{\circ}\text{S FOR PARTICLE } N})$$

[i.e. TO SPECIFY THE ENERGY OF EACH PARTICLE WE NEED 3 No°S, AND SO WE NEED A TOTAL OF 3N No°S TO SPECIFY THE STATE OF THE ENTIRE SYSTEM.]

THE ENERGY OF THE SYSTEM IS

$$E_{STATE} = E_{\vec{n}} = \frac{1}{2m}\left(\frac{\pi\hbar}{L}\right)^2 \Big(n_x^{(1)\,2} + n_y^{(1)\,2} + n_z^{(1)\,2}$$

$$+ \ldots + n_x^{(N)\,2} + n_y^{(N)\,2} + n_z^{(N)\,2} \Big)$$

$$Z = \sum_{\vec{n}} e^{-E_{\vec{n}}/k_B T}$$

$$= \sum_{(n_x^{(1)}, n_y^{(1)}, \ldots, n_z^{(N)})} e^{-E_{\vec{n}}/k_B T}$$

$$= \sum_{(\ldots\ldots)} e^{-\frac{\pi^2\hbar^2}{2mL^2 k_B T}\left(n_x^{(1)\,2} + \ldots + n_z^{(N)\,2}\right)}$$

$$= \left(\sum_{n_x^{(1)}=1}^{\infty} e^{-\frac{\pi^2\hbar^2}{2mL^2 k_B T} n_x^{(1)\,2}} \right) \left(\sum_{n_y^{(1)}=1}^{\infty} e^{-\frac{\pi^2\hbar^2}{2mL^2 k_B T} n_y^{(1)\,2}} \right)$$

$$\times \ldots \times \left(\sum_{n_z^{(N)}=1}^{\infty} e^{-\frac{\pi^2\hbar^2}{2mL^2 k_B T} n_z^{(N)\,2}} \right)$$

EACH FACTOR IN THIS PRODUCT IS EXACTLY THE SAME

SO

$$\boxed{Z = \left(\sum_{n=0}^{\infty} e^{-\frac{\pi^2 \hbar^2}{2mL^2 k_B T} n^2} \right)^{3N}} \quad -(1)$$

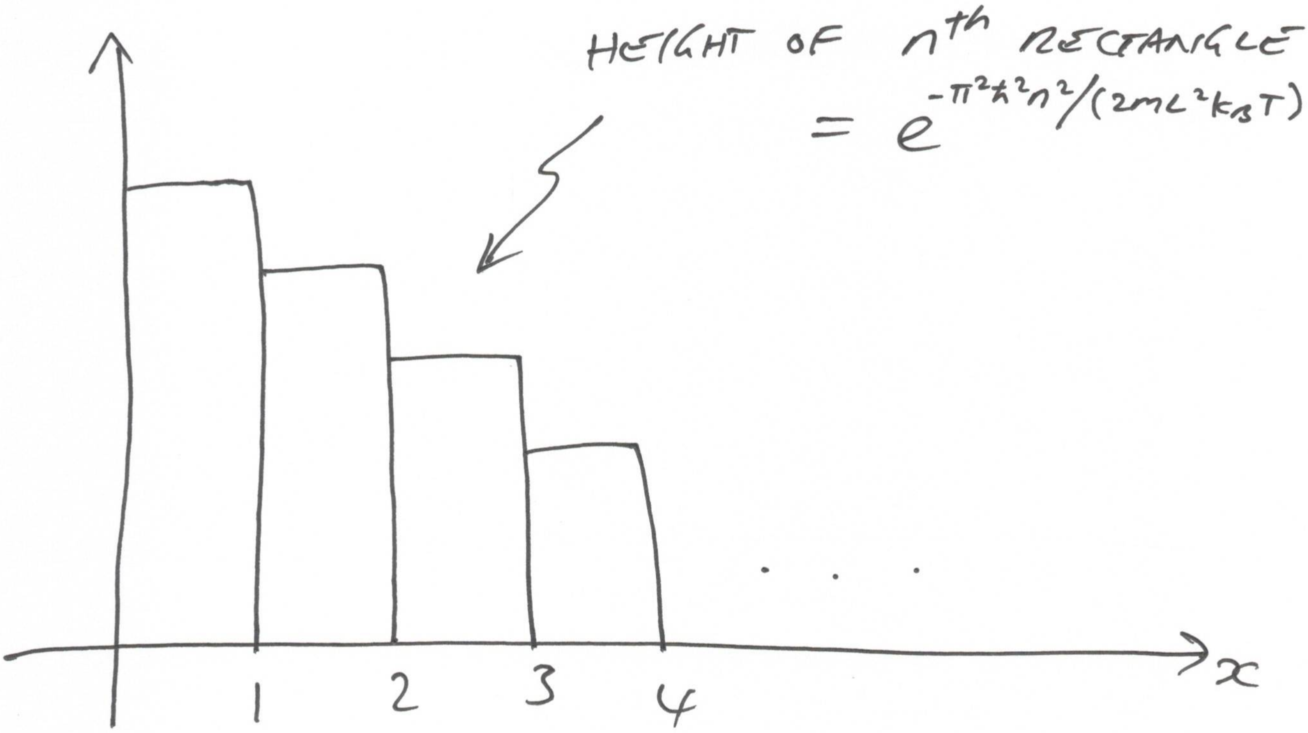
NOTICE THAT $\quad Z = Z(T, V, N)$

$V = L^3$

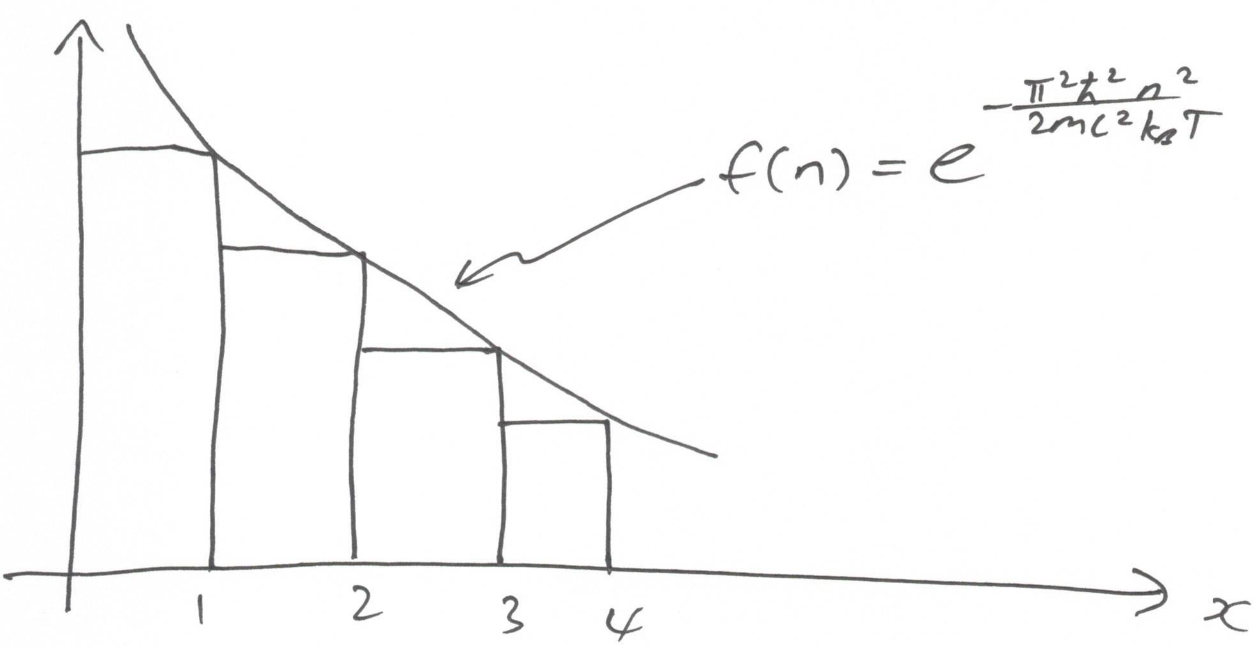
$\Rightarrow V^{\frac{2}{3}} = L^2$

THIS IS CONSISTENT WITH $\quad F = F(T, V, N) = -k_B T \ln Z$

- THE SUM IN (1) CANNOT BE COMPUTED EXACTLY & SO WE RESORT TO AN APPROXIMATION
- THE SUM CAN BE REPRESENTED AS THE AREA UNDER THE FOLLOWING GRAPH



WE CAN APPROXIMATE THE AREA OF THE RECTANGLES BY THE AREA UNDER THE SMOOTH CURVE (ie $\Sigma \rightarrow \int$)



NOW n IS CONSIDERED A CONTINUOUS VARIABLE HERE

SUM = AREA OF RECTANGLES

$$\approx \int_0^\infty e^{-\frac{\pi^2\hbar^2}{2mL^2k_BT}n^2}\,dn$$

GAUSSIAN INTEGRAL

$$= \frac{1}{2}\left(\frac{2mL^2k_BT}{\pi^2\hbar^2}\right)^{\frac{1}{2}}\sqrt{\pi}$$

$$\left[\int_0^\infty e^{-\alpha u^2}\,du = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \qquad \alpha = \text{CONSTANT}\right]$$

SO

$$\boxed{Z(T,V,N) \approx \left[\frac{\sqrt{\pi}}{2}\left(\frac{2mL^2k_BT}{\pi^2\hbar^2}\right)^{\frac{1}{2}}\right]^{3N}}$$

HOWEVER: WE HAVE OVERCOUNTED THE No° OF QUANTUM STATES OF THE SYSTEM. WE HAVE TREATED THE PARTICLES OF GAS AS DISTINGUISHABLE (WE LABELLED THEM 1 TO N).

ASIDE: WE CANNOT LABEL

IDENTICAL INDISTINGUISHABLE PARTICLES

IN QUANTUM MECHANICS. EXACTLY WHICH PARTICLE IS IN WHICH STATE CANNOT BE KNOWN.

ROUGHLY: THE UNCERTAINTY PRINCIPLE TELLS US THAT WE CANNOT KEEP TRACK OF EACH PARTICLE.

EXAMPLE: CONSIDER A TWO-PARTICLE SYSTEM WITH EACH HAVING TWO ENERGY LEVELS $n=1$ & $n=2$ AVAILABLE TO IT.

FOR DISTINGUISHABLE PARTICLES WE CAN LABEL THEM A & B

ALL POSSIBLE STATES OF SYSTEM

	$n=1$	$n=2$
STATE 1	A	B
STATE 2	B	A
STATE 3	AB	–
STATE 4	–	AB

FOR IDENTICAL INDISTINGUISHABLE PARTICLES

$A=B$

	$n=1$	$n=2$
STATE 1	A	A
STATE 2	AA	–
STATE 3	–	AA

TO TRY TO FIX THIS OVERCOUNTING WE DIVIDE BY $N! =$ No OF PERMUTATIONS.

SO

$$Z(T,V,N) \simeq \frac{1}{N!}\left(\frac{mk_BTL^2}{2\pi\hbar^2}\right)^{\frac{3N}{2}}$$

THE FREE ENERGY IS

$$F(T,V,N) = -k_BT\ln Z(T,V,N)$$

$$\simeq -k_BT\left(-\ln N! + \frac{3N}{2}\ln\left(\frac{mk_BTL^2}{2\pi\hbar^2}\right)\right)$$

USING $\quad L^2 = V^{2/3}$

WE FIND

$$\boxed{\begin{aligned} F(T,V,N) \approx\ & k_B T \ln N! - \frac{3}{2} N k_B T \ln T \\ & - N k_B T \ln V \\ & - \frac{3N}{2} k_B T \ln\left(\frac{m k_B}{2\pi\hbar^2}\right) \end{aligned}} \quad (2)$$

EQUATIONS OF STATE

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

$$\Longrightarrow \quad \boxed{pV = N k_B T}$$

IDEAL GAS LAW!

ENTROPY: $$S = -\frac{\partial F(T,V,N)}{\partial T}$$

$$\Rightarrow \boxed{S = -k_B \ln N! + \frac{3}{2} N k_B \ln T + \frac{3}{2} N k_B + N k_B \ln V + \frac{3}{2} N k_B \ln\left(\frac{m k_B}{2\pi\hbar^2}\right)} \quad (3)$$

RECALL $$F = \bar{E} - TS$$

$$\Rightarrow \bar{E} = F + TS$$

INSERT (2) INSERT (3)

$$\Rightarrow \boxed{\bar{E} = \frac{3}{2} N k_B T}$$

CONSISTENT WITH THE EQUIPARTITION THEOREM ($\frac{1}{2} k_B T$ PER PARTICLE PER DoF)

$$\mu = \frac{\partial F}{\partial N} = \text{CHEMICAL POTENTIAL}$$

[TO COMPUTE μ WE USE A "TRICK"

WRITE $\ln N! \approx N \ln N$, STIRLING'S

APPROXIMATION.]