$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

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

Macroscopic (V, T, N)

Microscopic state

classical physics $\{q_i, p_i\}$

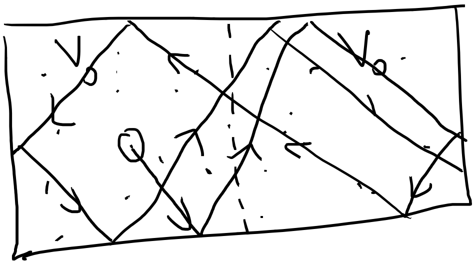
quantum physics $\left\{\begin{array}{l}\text{relevant} \\ \text{quantum} \\ \text{numbers}\end{array}\right\}$

(V, T, N) microscopic states

probability that the system is in microstate given the macrostate (V, T, N)

<u>Simple example</u>

$PV = NkT$



probability that I observe the particle on the left is $\equiv p = \frac{1}{2}$

Consider two particles:

1	2	prob
L	L	1/4
L	R	1/4
R	L	1/4
R	R	1/4

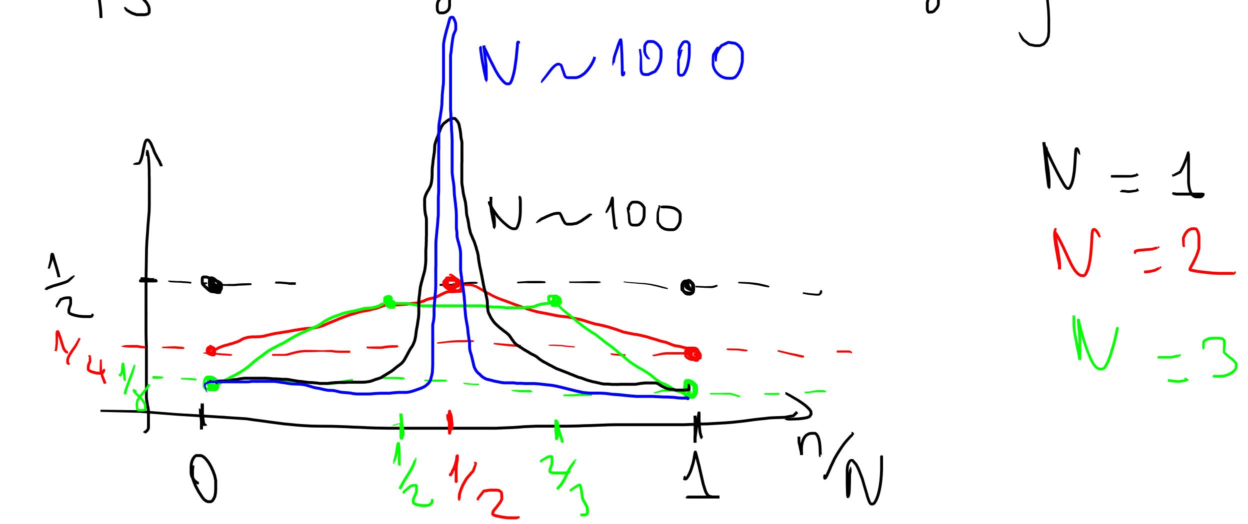
$4 = 2^2$

$P_2(n)$ = is the probability that n of the 2 particles is on the left

$P_2(0) = 1/4 \qquad P_2(1) = 1/2 \qquad P_2(2) = \frac{1}{4}$

consider $n=3$ $\quad 2^3 = 8$ configurations

$$\left.\begin{array}{ll} P_3(0) = \frac{1}{8} & P_3(1) = \frac{3}{8} \\ P_3(2) = \frac{3}{8} & P_3(3) = \frac{1}{8} \end{array}\right\}$$



$$\frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}}$$

<u>HW</u> Calculate $P_N(n)$ for an arbitrary N & n.

a) Plot

$$R_N(n) = \frac{P_N(n)}{P_N(N/2)}$$ as a function on n/N for $N=5$, $N=100$ and $N=10^4$

(hand in both your plot & code)

b) calculate

$\langle n \rangle$, $\langle (n - \langle n \rangle)^2 \rangle \equiv (\Delta n)^2$

and show that

$$\frac{\Delta n}{\langle n \rangle} \propto \frac{1}{\sqrt{N}}$$

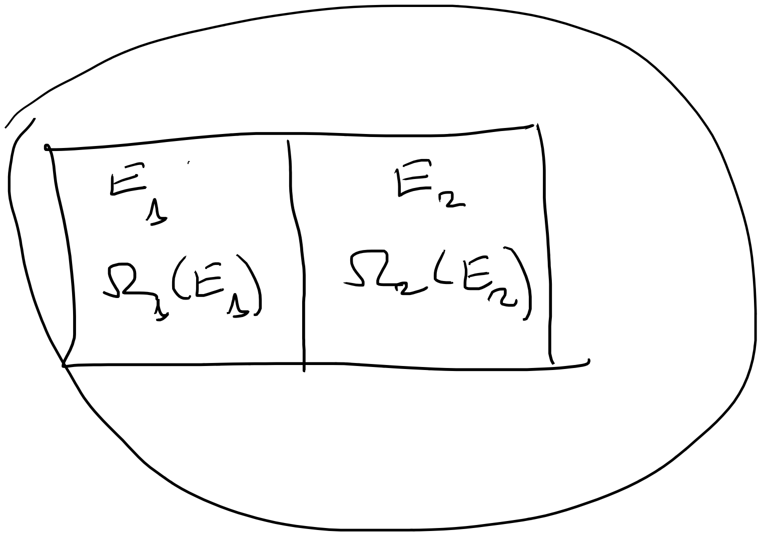
$N \sim 10^{22}$

$$\langle n \rangle = \sum_{n=0}^{N} P_N(n)\, n$$

$$P_3(1) = \frac{3}{8}$$

3 = # of microstates consistent with the given macrostate.

$$\Omega(E, V, N) = \#$$ of microstates consistent with the macrostate (E, V, N)



$$E^{(0)} = E_1 + E_2$$

$$\Omega(E_1, E_2) = \Omega_1(E_1)\,\Omega_2(E_2)$$

$$P(E_1) = \frac{\Omega(E_1, E^{(0)} - E_1)}{\sum_{E_1} \Omega(E_1, E^{(0)} - E_1)}$$

$$\frac{\partial \ln P(E_1)}{\partial E_1} = 0$$ in equilibrium.

$$\frac{\partial}{\partial E_1}\left(\ln\Omega_1(E_1)+\ln\Omega_2(\underbrace{E^{(0)}-E_1}_{E_2})\right)$$

$$\frac{\partial}{\partial E_1}\left(\ln\Omega_1(E_1)\right)+\frac{\partial\ln\Omega_2(E_2)}{\partial E_2}\overbrace{\frac{\partial E_2}{\partial E_1}}^{-1}=0$$

$$\frac{\partial\ln\Omega_1(E_1)}{\partial E_1}=\frac{\partial\ln\Omega_2(E_2)}{\partial E_2}\equiv\beta$$

$$\frac{\partial S(E_1)}{\partial E_1}=\frac{1}{T}$$

$$\frac{\partial\ln\Omega}{\partial S}=\frac{1}{\beta T}=\text{constant}$$

$$\boxed{S=k\ln\Omega}$$

Ideal Gas

$$\Omega(E,V,N)=V^N f(E,N)$$

$$S=k\ln\Omega=Nk\ln V+k\ln f(E,N)$$

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

$$\boxed{PV=NkT}$$

$$dE=TdS-PdV$$

$$dS=\frac{1}{T}dE+\frac{P}{T}dV$$

HW

$$\Omega \not\propto V^N$$

$$V(V-v_0)(V-2v_0)\cdots(V-(N-1)v_0)$$

$$\Omega \propto \prod_{n=0}^{N-1}(V-nv_0)\; f(E,N)$$

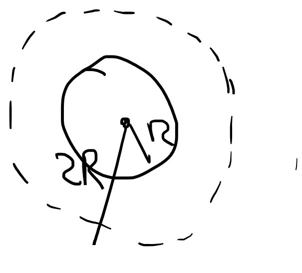
$$S = k\ln\Omega = k\sum_{n=0}^{N-1}\ln(V-nv_0) + (E,N)$$

$$\simeq k\int_0^{N-1} dn\, \ln(V-nv_0)$$

Fill in the gaps

$$P(V-b) = NkT \qquad b = 4N\left(\frac{4\pi}{3}R^3\right)$$

in the approximation $\frac{b}{V} \ll 1$



$$\Omega \longrightarrow S = k\ln\Omega(E)$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

$$E = \sum_{i=1}^{N} \varepsilon_i$$

$$\varepsilon_i = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right)$$

$$E = \frac{\hbar^2\pi^2}{2mL^2} \sum_{i=1}^{N} \left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right) \Longleftarrow$$

$$\Omega(V, N, E) = \# \text{ of } \{(n_x^i, n_y^i, n_z^i)\}$$

s.t

$$E = \frac{\hbar^2\pi^2}{2mL^2} \sum_{i=1}^{N} \left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right)$$

$$\sum_{i=1}^{N} \left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right) = \frac{2m}{\hbar^2\pi^2} L^2 E = g\left(E\,\underset{L^2}{\overset{\shortparallel}{V^{2/3}}}\right)$$

$$\Omega = \Omega(EV^{2/3}, N) = \left(V^{2/3}E\right)^{3/2 N} h(N)$$

$$\Omega = V^N E^{3/2 N} h(N)$$

$$\Downarrow$$

$$\ln\Omega = N\ln V + \frac{3}{2}N\ln E + \ln h(N)$$

$$\frac{P}{T} = \frac{\partial(k\ln\Omega)}{\partial V} = \frac{Nk}{V} \Rightarrow PV = NkT$$

$$\frac{1}{T} = \left(\frac{\partial(k\ln\Omega)}{\partial E}\right)_{V,N} = \frac{3}{2}\frac{Nk}{E}$$

$$\boxed{E = \frac{3}{2}NkT}$$

$$\Omega = V^N E^{3/2 N} h(N)$$

$$S = k \ln \Omega = kN \ln V E^{3/2} + k \ln h(N)$$

adiabatic process $\Rightarrow S$ is constant

$$\Rightarrow V E^{3/2} = \text{const}$$

$$V T^{3/2} = \text{const} \qquad T V^{2/3} = \text{const}$$

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

$$\Omega = \sum_{\substack{\text{suitably} \\ \text{chosen} \\ \text{microstates}}} 1$$

$S(E,V,N) = ?$ for the ideal gas

$n^i_{x,y,z} =$

$n_{x,y,z} = 1, 2, \ldots$

$\Rightarrow \psi = \mathcal{N} \sin \frac{n_x \pi}{L} x \sin \frac{n_y \pi}{L} y \sin \frac{n_z \pi}{L} z$

if $\psi = 0$ on the boundary

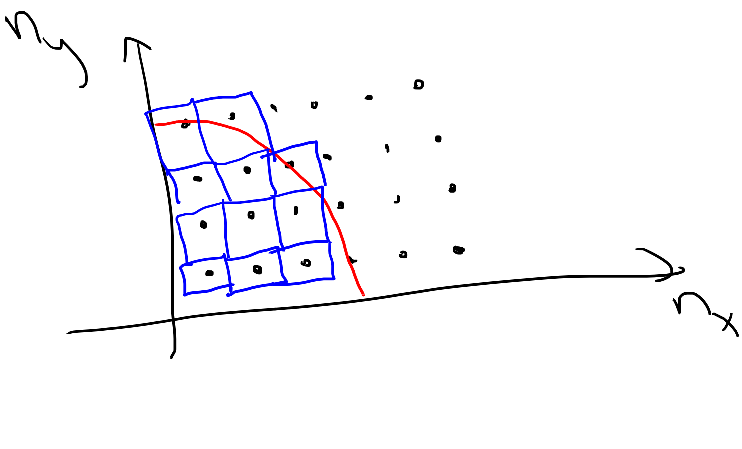
$$\psi = \mathcal{N}' e^{i\left(\frac{n_x}{2L}\pi x + \frac{n_y}{2L}\pi y + \frac{n_z}{2L}\pi z\right)}$$

if ψ is periodic $(n_{x,y,z} = 0, \mp 1, \mp 2, \ldots)$

$\Rightarrow \psi = \mathcal{N}' \cos\left(\frac{n_x \pi}{L} x\right) \cos\left(\frac{n_y \pi}{L} y\right) \cos\left(\frac{n_z \pi}{L} z\right)$

if $\partial\psi = 0$ on the boundary

$n_{x,y,z} = 0, 1, 2, \ldots$



(n_x, n_y)

st

$$\frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2) = E$$

circle $\left\{ n_x^2 + n_y^2 = \frac{2mL^2 E}{\hbar^2 \pi^2} \right.$

$n_{x,y} = 1, 2, 3$

$\Sigma(E) = \#$ of microstates that have energy less than E

$\Sigma(E) =$ Volume of the sphere in $\{(n_x^i, n_y^i, n_z^i)\}$ space having radius

$$R = \sqrt{\frac{2mL^2E}{\hbar^2\pi^2}}$$

$$= \int_{\text{sphere}} d^{3N} n = \underbrace{\int_0^R n^{3N-1}\, dn\, d\Omega_{3N}}$$

$N = 1$

$$\int d^3 n = \int n^2\, dn \underbrace{d\Omega_3}_{4\pi} = \int_0^R 4\pi n^2\, dn$$

$3N = 2$

$$\int d^2 n = \int n\, dn \underbrace{d\Omega_2}_{2\pi} = \int \underbrace{2\pi n}\, \underbrace{dn}$$

$$\Sigma(E) = \frac{R^{3N}}{3N} \int d\Omega_{3N}$$

$$\left(\int_{-\infty}^{\infty} dx\, e^{-x^2} \right)^{3N} = (\sqrt{\pi})^{3N}$$

$$\int \prod_{i=1}^{3N} dx_i\, e^{\underbrace{-\sum_{i=1}^{3N} x_i^2}} = \pi^{3N/2}$$

$$\int r^{3N-1} dr e^{-r^2} d\Omega_{3N} = \pi^{3N/2}$$

$$\int d\Omega_{3N} = \frac{\pi^{3N/2}}{\int_0^\infty r^{3N-1} dr e^{-r^2}}$$

$$\int_0^\infty u^{n-1} e^{-u} du \equiv \Gamma(n)$$

$$\int_0^\infty r^{3N-1} dr e^{-r^2} \underset{r=\sqrt{u}}{=\!=} \int_0^\infty \frac{du}{2\sqrt{u}} u^{\frac{3N}{2}-\frac{1}{2}} e^{-u}$$

$$= \frac{1}{2}\Gamma\left(\frac{3N}{2}\right)$$

$$\int d\Omega_{3N} = \frac{\pi^{3N/2}}{\frac{1}{2}\Gamma\left(\frac{3N}{2}\right)} = \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}$$

$$\Sigma(E) = \frac{R^{3N}}{3N} \int d\Omega_{3N}$$

$$\Sigma(E) = \left(\frac{2mV^{2/3}E}{h^2\pi^2}\right)^{3N/2} \frac{1}{3N} \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}$$

$$\Omega(E) = \Sigma\left(E+\frac{\Delta}{2}\right) - \Sigma\left(E-\frac{\Delta}{2}\right)$$

$$\boxed{\Omega(E) = \frac{\partial \Sigma}{\partial E}\Delta}$$

$$\Omega(E) = \frac{\partial \Sigma}{\partial E} E \left(\frac{\Delta}{E}\right)$$

$$\ln \Omega(E) = \ln \frac{3N}{2E} \left(\frac{2mV^{2/3} E}{\hbar^2 \pi^2}\right)^{3N/2} \frac{1}{3N} \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \Delta$$

$$= \ln \left(\frac{2mV^{2/3} E}{\hbar^2 \pi^2}\right)^{3N/2} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)} + \ln\left(N \frac{\Delta}{E} \frac{3}{2}\right)$$

$$\Gamma\left(\frac{3N}{2}+1\right) = \frac{3N}{2} \Gamma\left(\frac{3N}{2}\right)$$

$$\ln \Omega(E) = \overbrace{\ln \Sigma(E)}^{10^{24}} + \overbrace{\ln\left(N \frac{\Delta}{E} \frac{3}{2}\right)}^{O(10^3)}$$

$$\ln \Sigma(E) \propto N \sim 10^{24}$$

$$\ln\left(N \frac{\Delta}{E} \frac{3}{2}\right) \sim 24 + (-6) \sim O(10)$$

$$S = k \ln \left(\frac{2mV^{2/3} E}{\hbar^2 \pi^4}\right)^{3N/2} \frac{\cancel{\pi^{3N/2}}}{\Gamma\left(\frac{3N}{2}+1\right)}$$

$$= \frac{3N}{2} k \ln\left(\frac{2mV^{2/3} E}{\hbar^2 \pi}\right) - k \ln \Gamma\left(\frac{3N}{2}+1\right)$$

$$\ln \Gamma\left(\frac{3N}{2}+1\right) = \ln\left(\frac{3N}{2}\right)! \simeq \frac{3N}{2} \ln\left(\frac{3N}{2}\right) - \left(\frac{3N}{2}\right)$$

Stirling's approximation

$$\ln(n!) = \sum_{m=1}^{n} \ln m \underset{n \gg 1}{\simeq} \int_1^n (\ln m)\, dm = m \ln m - m \Big|_{m=1}^{n} \underset{n \gg 1}{\simeq} n \ln n - n$$

$$= \frac{3N}{2} k \ln\left(\frac{2mV^{2/3}E}{\hbar^2 \Omega}\right) - k\left[\frac{3N}{2}\ln\left(\frac{3N}{2}\right) - \frac{3N}{2}\right]$$

$$\boxed{S = \frac{3Nk}{2}\ln\left(\frac{2mV^{2/3}E}{\hbar^2 \Omega}\,\frac{2}{3N}\right) + \frac{3Nk}{2}}$$

$$S = k \ln \Omega$$

$$E = \frac{3}{2}NkT \Rightarrow S \xrightarrow[T\to 0]{} \frac{3Nk}{2}\ln T \neq 0$$