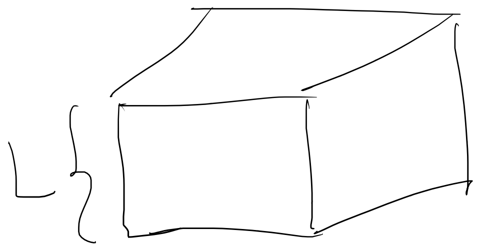
Ω

$S = k \ln \Omega$

Example Ideal Gas



$$\varepsilon_1 = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} \left(n_x^2 + n_y^2 + n_z^2\right)$$

$$E = \sum \frac{\hbar^2}{2m} \frac{\pi^2}{V^{2/3}} \left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right)$$

$$\Omega(N, EV^{2/3}) \Rightarrow \frac{3}{2} PV = E \Leftarrow$$

$$S = k \ln \Omega \Rightarrow S(N, EV^{2/3})$$

adiabatic process $\Rightarrow S = \text{const} \Rightarrow EV^{2/3} = \text{const.}$

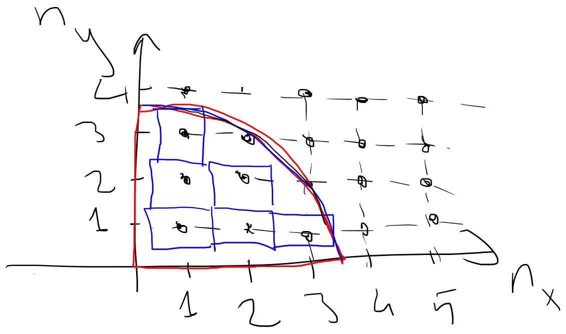
$$PV^{5/3} = \text{const}$$

$$E = \sum \frac{\hbar^2}{2m} \frac{\pi^2}{V^{2/3}} \left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right)$$

$$\Rightarrow \sum_i \left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right) = EV^{2/3} \frac{2m}{\hbar^2 \pi^2} \equiv \varepsilon$$

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

$$\boxed{n_x^2 + n_y^2 \le \varepsilon} \qquad n_x, n_y = 1, 2, 3, \ldots$$



$$\left(E - \frac{\Delta}{2}, E + \frac{\Delta}{2}\right)$$

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

$\Sigma(E)$: # of microstates having energy less then E

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

# of unit squares along the circumference $\sim \left(EV^{2/3}\right)^{3N-1}$

# of units squares inside the disc $\sim \left(EV^{2/3}\right)^{3N}$

ration $\sim \frac{1}{EV^{2/3}} \sim \frac{1}{N}$

$$\Sigma(E) = \frac{\pi \varepsilon^2}{4}$$

Back to original problem:

$$\sum_i \left(n_x^{i2} + n_y^{i2} + n_z^{i2}\right) \le EV^{2/3} \qquad \frac{2m}{\hbar^2 \pi^2} \equiv \varepsilon$$

$\Sigma(E)$ = volume of the 3N dimensional sphere of radius $\sqrt{E} \equiv R$

$$d^{3N}n = dn_x^1 dn_y^1 dn_z^2 \cdots$$

$$|n|^2 = n_x^{1\,2} + n_y^{1\,2} + n_z^{1\,2} + n_x^{2\,2} + \cdots$$

$$= \int_{|n|\leq R} d^{3N}n = \int_0^R dn\, n^{3N-1} d\Omega_{3N}$$

$$\Sigma(E) = \frac{R^{3N}}{3N} \int d\Omega_{3N} \frac{1}{2^N}$$

$$\underline{\int d\Omega_{3N} = ?}$$

$$\int d^{3N}n\, e^{-n^2} = (\sqrt{\pi})^{3N}$$

$$= \int_0^\infty dn\, n^{3N-1} d\Omega_{3N} e^{-n^2} = \left(\int d\Omega_{3N}\right) \int_0^\infty dn\, n^{3N-1} e^{-n^2}$$

$$= (\sqrt{\pi})^{3N}$$

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

$$n = \sqrt{x} \Rightarrow dn = \frac{dx}{2\sqrt{x}}$$

$$\int_0^\infty dn\, n^{3N-1} e^{-n^2} = \int_0^\infty \frac{dx}{2\sqrt{x}}\, x^{\frac{3N-1}{2}} e^{-x}$$

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

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

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

$$R^2 = E V^{2/3} \frac{2m}{\hbar^2 \pi^2}$$

$$\Sigma(E) = \left(E V^{2/3} \frac{2m}{\hbar^2 \pi^{\cancel{2}}} \right)^{3N/2} \frac{\cancel{\pi^{3N/2}}}{2^N \Gamma\left(\frac{3N}{2}+1\right)}$$

$$\boxed{\Sigma(E) = E^{\frac{3N}{2}} \left(V^{2/3} \frac{2m}{\hbar^2 \pi} \right)^{3N/2} \frac{1}{2^N \Gamma\left(\frac{3N}{2}+1\right)}}$$

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

$$= E^{\frac{3N}{2}-1} \left(V^{2/3} \frac{2m}{\hbar^2 \pi} \right)^{\frac{3N}{2}} \frac{1}{2^N \Gamma\left(\frac{3N}{2}\right)} \Delta$$

$$S = k \ln \Omega = \overbrace{\left(\frac{3N}{2} - \cancel{1}\right)} \ln E$$

$$+ \frac{3N}{2} \ln\left(V^{2/3} \frac{2m}{\hbar^2 \pi} \right) - N \ln 2$$

$$- \underbrace{\ln \Gamma\left(\frac{3N}{2}\right)} + \underbrace{\ln \Delta}_{\sim -10}$$

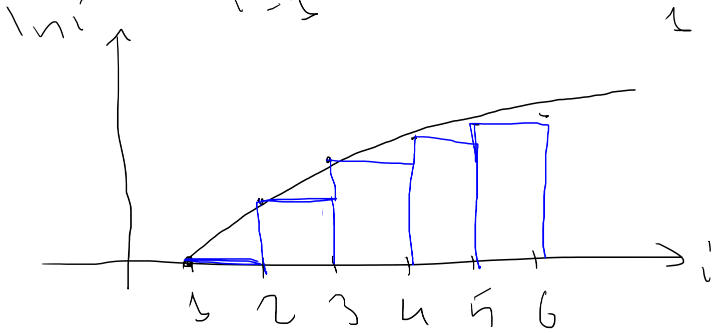
$$N \sim 10^{23}$$

$$\Delta \sim \frac{1}{\sqrt{N}} \sim 10^{-11} \Rightarrow \ln \Delta \sim -11$$

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

<u>Stirling approximation:</u>

$$\ln n! = \sum_{i=1}^{n} \ln i \simeq \int_1^n \ln x \, dx = n \ln n - n$$



$$S = k \ln \Omega = \left(\frac{3N}{2} - \cancel{1} \right) \ln E$$

$$+ \frac{3N}{2} \ln \left(\frac{V^{2/3}\, 2m}{\hbar^2 \pi} \right) - N \ln 2$$

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

$$S = \frac{3N}{2} \ln E + \frac{3N}{2} \ln \frac{V^{2/3}\, 2m}{\hbar^2 \pi} - N \ln 2$$

$$- \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2}$$

$$\boxed{S = k \frac{3N}{2} \ln \left(\frac{E\, 2m}{\hbar^2 \pi} \frac{e}{\frac{3N}{2}} \frac{1}{2^{2/3}} \right) + Nk \ln V}$$

$\Rightarrow S(EV^{2/3}, N) \Rightarrow$ in an adiabatic process $EV^{2/3} = \text{const}$

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

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

$$\Rightarrow \frac{1}{T} = k \frac{3N}{2E} \Rightarrow \boxed{E = \frac{3N}{2} kT}$$

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

$$\rightarrow \boxed{PV = NkT}$$

Gibbs Paradox

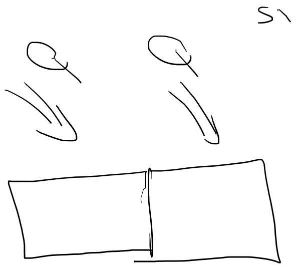
$$S = \frac{3N}{2}k\ln\left(\frac{E}{N}\right) + N\ln V + NC$$

C : is a constant independent of E, N, V

S should be extensive.
E should be extensive.

E, S, N : are extensive, i.e. proportional to the system size

T, P, μ : are intensive, i.e. independent of the size of the system.

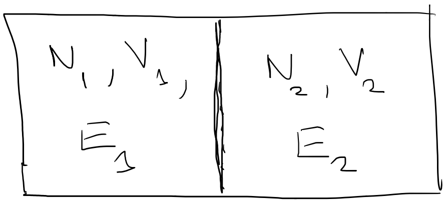


$$\Delta S = \frac{Q}{T}$$

$$(\Delta S)_{\text{combined system}} = \frac{2Q}{T} = \frac{Q}{T} + \frac{Q}{T}$$

$$= (\Delta S)_{\text{first}} + (\Delta S)_{\text{second}}$$

Example $S = \frac{3N}{2} k \ln\left(\frac{E}{N}\right) + N \ln V + N C$



$$S_T^i = \frac{3N_1}{2} k \ln\left(\frac{E_1}{N_1}\right) + N_1 \ln V_1 + N_1 C_1$$

$$+ \frac{3N_2}{2} k \ln\left(\frac{E_2}{N_2}\right) + N_2 \ln V_2 + N_2 C_2$$

$$S_T^f = \frac{3N_1}{2} k \ln\left(\frac{E_1}{N_1}\right) + N_1 \ln(V_1 + V_2) + N_1 C_1$$
$$+ \frac{3N_2}{2} k \ln\left(\frac{E_2}{N_2}\right) + N_2 \ln(V_1 + V_2) + N_2 C_1$$

$$\Delta S = S_T^f - S_T^i = N_1 \ln(V_1 + V_2) + N_2 \ln(V_1 + V_2)$$
$$- N_1 \ln(V_1) - N_2 \ln(V_2)$$

= entropy of mixing

$\Delta S = 0$ if both volumes contain the same gas!

$$\Delta S = N_1 \cancel{\ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right)} + N_1 \ln(N_1 + N_2)$$
$$+ N_2 \cancel{\ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right)} + N_2 \ln(N_1 + N_2)$$
$$- \cancel{N_1 \ln\left(\frac{V_1}{N_1}\right)} - N_1 \ln(N_1)$$

$$- N_2 \cancel{\ln\left(\frac{V_2}{N_2}\right)} - N_2 \ln(N_2)$$

$$\frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{V_1 + V_2}{N_1 + N_2}$$

$$\Delta S = (N_1 + N_2)\ln(N_1 + N_2) - N_1 \ln(N_1) - N_2 \ln(N_2)$$

$$= \underbrace{\left[(N_1 + N_2)\ln(N_1 + N_2) - \underline{(N_1 + N_2)}\right]}_{\ln (N_1+N_2)!}$$

$$- \underbrace{\left[N_1 \ln N_1 - \underline{N_1}\right]}_{\ln N_1!}$$

$$- \underbrace{\left[N_2 \ln N_2 - \underline{N_2}\right]}_{\ln N_2!}$$

$$\Delta S = S(N_1 + N_2) - S(N_1) - S(N_2)$$

$$= \ln(N_1 + N_2)! - \ln N_1! - \ln N_2!$$

$$\Rightarrow \left[S(N_1 + N_2) - \ln(N_1 + N_2)!\right]$$

$$- \left[S(N_1) - \ln N_1!\right]$$

$$- \left[S(N_2) - \ln N_2!\right] = 0$$

$$S(N) \longrightarrow S(N) - \ln(N!)$$

$$\Rightarrow \Omega^{(0)} \longrightarrow \Omega^{corr} = \frac{\Omega^{(0)}}{N!}$$

indistinguishable particles!

$(n_x^{(1)}, n_y^{(1)}, n_z^{(1)})$ $(n_x^{(2)}, n_y^{(2)}, n_z^{(2)})$; one state

$\quad$ 1 $\qquad\qquad\qquad$ 2

$(n_x^{(2)}, n_y^{(2)}, n_z^{(2)})$ $(n_x^{(1)}, n_y^{(1)}, n_z^{(1)})$: another state

$\quad$ 1 $\qquad\qquad\qquad$ 2

N identical particles,
we can assign the quantum numbers to these
N particles in $\dfrac{N!}{n_1!\, n_2! \cdots n_m!}$ different ways.

$n_1 + n_2 + \cdots + n_m = N$

There are n_1 identicle triplet (n_x, n_y, n_z) in the
the given microstate.

There are n_2 identicle " " " "
" " "

$p^{T,n}$	$p^{T,n}$