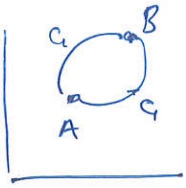
Finishing with TD

~~date~~

$$\boxed{\oint \frac{dQ}{T}\Big|_{rev} = 0 \qquad \oint \frac{dQ}{T}\Big)_{gen} \le 0}$$



$$\int_A^B \frac{dQ}{T}\Big)_{rev,\,C_1} = \int_A^B \frac{dQ}{T}\Big)_{rev,\,C_2}$$

$$\frac{dQ}{T}\Big)_{rev} = dS \qquad \int_A^B dS = S_B - S_A$$

$$\int_A^B \frac{dQ}{T}\Big)_{rev} + \int_B^A \frac{dQ}{T}\Big)_{gen} \le 0$$

$S(B) - S(A)$

$$\int_B^A \frac{dQ}{T}\Big)_{gen} \le S(A) - S(B)$$

$$\boxed{\frac{dQ}{T} \le dS}$$

$$dU = dQ - PdV$$

$$dQ = dU + PdV \le dS\,T$$

$$dU = TdS - PdV \quad (rev)$$

$$\frac{\partial U}{\partial S}\Big)_V = T \qquad \frac{\partial S}{\partial U}\Big)_V = \frac{1}{T} \qquad \frac{\partial U}{\partial V}\Big)_S = -P$$

TD. Potential Helmholtz Free Energy

(*) Derivatives give useful relations

(*) We will obtain A from statistical physics.

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

...

$$TdS = dU - dA - SdT \ge dQ$$

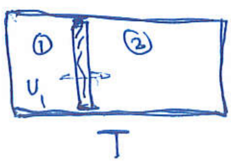
$$\cancel{dQ} - PdV - SdT \geq dA$$

Eqn. of state

$$\boxed{\frac{\partial A}{\partial V}\Big)_T = -P} \qquad \frac{\partial A}{\partial T}\Big)_V = -S$$

if $dV=0$, $dT=0$ then $dA \le 0$

A reaches a minimum at equilibrium



$$A = A_1(V_1, T) + A_2(V_2, T)$$

$$\frac{\partial A}{\partial V_1}\Big)_{V,T} = 0 \qquad \frac{\partial}{\partial V_1}\left[A(V_1, T) + A_2(V - V_1, T)\right] = 0$$

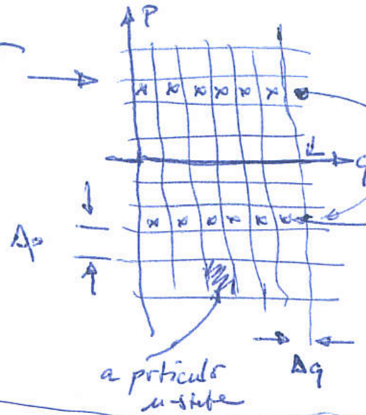
$$P_1 = P_2 \Longleftarrow \qquad \frac{\partial A_1}{\partial V_1}\Big)_T - \frac{\partial A_2}{\partial V_2}\Big)_T \qquad \frac{\partial A_2}{\partial V_2}\frac{\partial V_2}{\partial V_1}$$

μ-States of a system

Classical: position $\vec{q}$, momentum $\vec{p}$

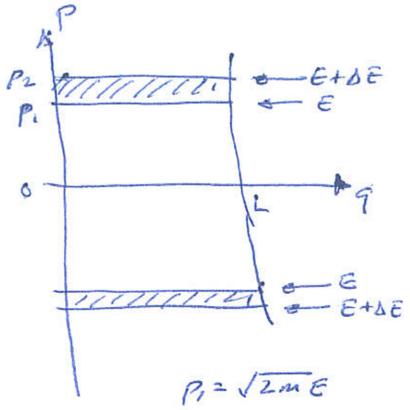
e.g. in one dimension, one particle

Phase space Γ →



constant energy E

divide into pieces such that $\Delta q \cdot \Delta p \sim h$



$p_1 = \sqrt{2mE}$

$p_2 = \sqrt{2m(E+\Delta E)} = \sqrt{2mE}\sqrt{1+\frac{\Delta E}{E}}$ $\quad (1+\frac{\Delta E}{2E})$

$p_2 - p_1 = \sqrt{2mE}\,\frac{\Delta E}{2E}$

# of states $\frac{\sqrt{2mE}}{2E}\frac{\Delta E \cdot L}{h} \times 2$

$\frac{\sqrt{2mE}\,\Delta E L}{E h}$

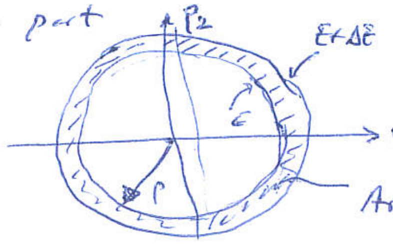
$\pm p$ states

$\Omega(E)\,\Delta E$ = # of states that satisfy $E < H < E+\Delta E$

2 particles in 1-D

position space simple $0<q_1<L$, $0<q_2<L$

momentum part



$E < \frac{p_1^2+p_2^2}{2m} < E+\Delta E$

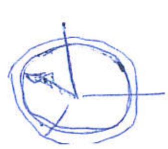
Area $\Delta(\pi p^2) = \underbrace{\pi \cdot 2m(E+\Delta E) - \pi \cdot 2mE}_{2m\pi\Delta E}$

$\frac{p^2}{2m} = E \Rightarrow p = \sqrt{2mE}$

← Too much algebra - just motivate

~~Volume~~ ~~Area~~ Number of all possible μ states for this system $\frac{(\pi\, 2m\cancel{E})\cdot L^2}{h^2}\,\cancel{\Delta E}$

3 particles in 1D



$\frac{4}{3}\pi(2m(E+\Delta E))^{3/2} - \frac{4}{3}\pi(2mE)^{3/2}$

$4\pi(2mE)$

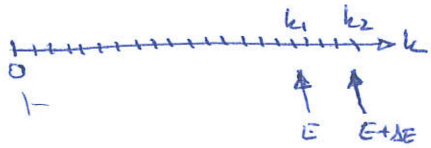
$\frac{4}{2}\pi(2mE)^{1/2}\Delta E\, 2m$

$\frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3$

$= 4\pi r^2 dr$ ✓

QM case

$k = \frac{2\pi}{\lambda} = \frac{\pi}{\lambda/2} = \frac{\pi}{L/n} = \frac{n\pi}{L}$



$E+\Delta E = \frac{\hbar^2 k_2^2}{2m}$ $\qquad k_2^2 = \frac{2m(E+\Delta E)}{\hbar^2}$

$E = \frac{\hbar^2 k_1^2}{2m}$ $\qquad k_1^2 = \frac{2mE}{\hbar^2}$

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

$= \frac{\sqrt{2mE}\,L}{E h}\Delta E$

$k_2 - k_1 = \sqrt{\frac{2m}{\hbar^2}}\left(\sqrt{E+\Delta E} - \sqrt{E}\right)$

$= \sqrt{\frac{2m}{\hbar^2}}\left(\sqrt{E}\sqrt{1+\frac{\Delta E}{E}} - \sqrt{E}\right)$

$= \sqrt{\frac{2m}{\hbar^2}}\sqrt{E}\left(+\frac{\Delta E}{2E}\right) = \frac{\sqrt{2mE}}{\hbar}\frac{\Delta E}{2E}$

of μstates: $\frac{k_2-k_1}{\pi/L} = \frac{\sqrt{2mE}}{2E\hbar}\frac{L}{\pi}\Delta E$

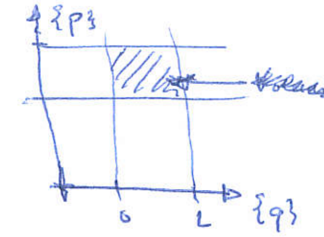
A system with N particles

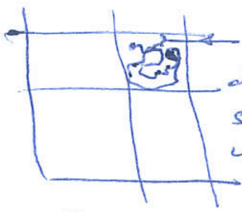
Classical: $\underbrace{q_{1x}, q_{1y}, q_{1z}, \dots q_{Nz}}_{\substack{3N \\ \text{coordinates}}}$, $\underbrace{p_{1x}, p_{1y}, p_{1z}, \dots p_{Nz}}_{\substack{3N \\ \text{momenta}}}$

Quantum mechanical: E.g. $k_x = \frac{n_x \pi}{L}$, $k_y = \frac{n_y \pi}{L}$, $k_z = \frac{n_z \pi}{L}$

μ-state Specify k_x, k_y, k_z for all N particles.

Specifically

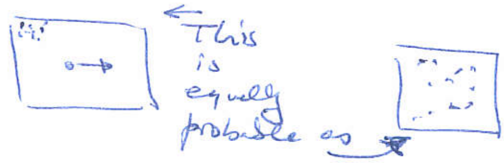




Discuss ergodicity

Postulate of equal a-priori probability:

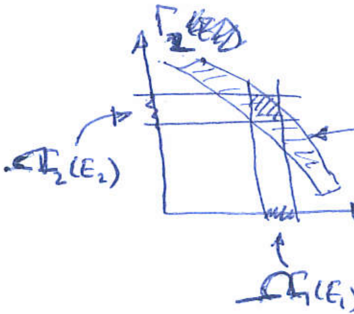
All μ-states that satisfy the macroscopic constraints are equally probable



But there are a lot more "random looking" configurations

Let's see what happens when we put two systems in contact with one another

So, the total energy constraint is now $E < E_1 + E_2 < E + \Delta$



Change notation
$\Gamma(E) \to \Omega(E)$
to avoid confusion between Γ and $\Gamma(E)$

$$\Omega(E) = \sum_{i=0}^{E/\Delta E} \Omega_1(E_i)\,\Omega_2(E - E_i)$$

One of them will contribute the most: max term $= \Omega_1(\bar{E}_1)\,\Omega_2(E_1 - \bar{E}_1)$

$$\frac{\partial}{\partial E_1}\left(\Omega_1(E_1)\,\Omega_2(\overset{E_2}{E - E_1})\right) = 0$$

$$\frac{\partial \Omega_1}{\partial E}\Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial E_2} = 0 \;\to\; \frac{\frac{\partial \Omega_1}{\partial E_1}}{\Omega_1} = \frac{\frac{\partial \Omega_2}{\partial E_2}}{\Omega_2}$$

$$\frac{\partial}{\partial E_1}\ln \Omega_1 = \frac{\partial}{\partial E_2}\ln \Omega_2$$

We can show that the maximum term $\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)$ dominates the summation

$$\Omega(E) = \sum_{i=0}^{E/\Delta E} \Omega_1(E_i)\Omega_2(E-E_i)$$

$$\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2) \leq \Omega(E) \leq \frac{E}{\Delta}\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)$$

$\Omega(E)$ contains additional terms

This would be the case if all terms were equal to this

$$\ln\left[\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)\right] \leq \ln\Omega(E) \leq \underbrace{\ln\frac{E}{\Delta}}_{\text{order } \ln N} + \ln\left[\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_2)\right]$$

Again, all energy distributions are equally probable but the one for $\max(\Omega_1(E_1)\Omega_2(E_2))$ dominates!

What is the significance of $\underbrace{\frac{\partial}{\partial E_1}\ln\Omega_1(E_1)}_{\sim T_1 \to \sim \frac{1}{T_1}} = \underbrace{\frac{\partial}{\partial E_2}\ln\Omega_2(E_2)}_{\sim T_2 \to \sim \frac{1}{T_2}}$?

Remember

$$dU = dQ - P\,dV$$
$$= T\,dS - P\,dV$$
$$dS = \frac{dU}{T} + \frac{P}{T}dV$$
$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

$\ln\Omega(E) \propto S(E)$

"Logarithm of the number of possibilities"

What does this signify?

If I have two possible states

(1)
(2) $S \sim \ln 2$

. All logarithms are proportional to one another!

$$y = \ln x \Rightarrow x = e^y = 2^{(\log_2 e)y}$$
$$(\log_2 e)\,y = \log_2 x$$
$$(\log_2 e)\ln x = \log_2 x$$

Let us use base 2 for this problem

(1)
(2) $S = \log_2 2 = 1$ bit ← convention for $\log_2$ 1 bit sufficient

(1)(2)(3)(4) → $S = \log_2 4 = 2$ bits ← 2 bits necessary to specify

3,5

$y = \log_2 x \qquad 2^y = x \qquad e^{y \ln 2} = x$

$= \frac{\ln x}{\ln 2}$

Information in a message

passed?	Failed?
90%	10%

missing info = ~~[illegible]~~

$= -0.9 \log_2 0.9 - 0.1 \log_2 0.1$

$= 0.47$ bits

Info;

Student	Passed/failed?
A	1
B	1
C	1
D	0
E	1
⋮	1
	0
Z	1

Message

$\underbrace{1\,1\,1\,0\,1\,1\,0\,1 \ldots}$

can I reduce the number of bits in the message?

Use patterns:

~~1~~ 0 means 11

pattern

end of pattern

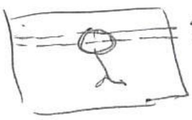
~~1~~10 – means 10

110 – means 01

1110 – means 00

Data compression

eg. pictures



← one line very similar to next

jpeg, png, etc.

Opposite – Use redundancy

Information content in a probabilistic event

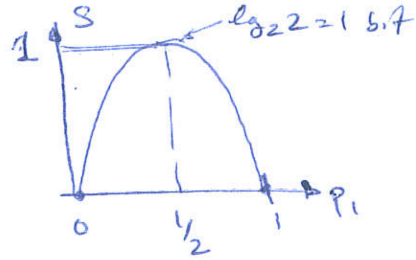
Missing information, entropy

$$S = -\sum_i p_i \log_2 p_i \quad \text{bits}$$

Give examples — Info in messages
— Noise
— Compression

Two possibility case

$$S = -p_1 \log_2 p_1 - (1-p_1)\log_2(1-p_1)$$



General case, maximum entropy

Consider $F = -\sum_i p_i \log p_i + \lambda \underbrace{\left(\sum_i p_i - 1\right)}_{\text{constraint}}$

λ — Lagrange multiplier

$\frac{\partial F}{\partial \lambda} = 0 \Rightarrow$ constraint

$\frac{\partial F}{\partial p_i} = 0 \Rightarrow$ maximize

$$\frac{\partial F}{\partial p_i} = 0 \Rightarrow -\log \bar{p}_i - 1 + \lambda = 0 = \log \bar{p}_i = \lambda - 1$$

$\Rightarrow$ all $\bar{p}_i$'s equal

constraint $\Rightarrow$ $\bar{p}_i = 1/N$

$$\text{Max } S = -\sum_i \frac{1}{N} \log_2 \frac{1}{N} = \log_2 N$$

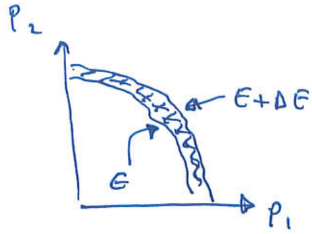
Equal probability $\leftrightarrow$ Max Entropy $= \log(\#\text{ of states})$

Discuss Boltzmann transport Eqn.

- An equation for $p(v, q; t)$ Non linear, Integro-differential
- Boltzmann showed that $-\int p(v,q,t) \ln p(v,q,t)\, d^3v\, d^3q$ is an increasing function of time.

  $\Rightarrow$ Equilibrium for the maximum of this function
- Non-linear phenomena such as hydrodynamics, etc. may be derived from it.

Entropy of the classical ideal gas.



We want to calculate how many states there are for

$$E < \frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{1z}^2}{2m} + \dots + \frac{p_{Nz}^2}{2} < E + \Delta E$$

Note that $\sum_{i=1}^{6N} \frac{p_i^2}{2m} = E$ corresponds to ~~the~~ a sphere with radius $p = \sqrt{2mE} = R$

What is the volume of an $\underbrace{3N}_{n}$ dimensional sphere?

$d=2$	$\int_0^R 2\pi r\, dr = \pi R^2$
$d=3$	$\int_0^R 4\pi r^2 dr = \frac{4}{3}\pi R^3$

A trick to determine it:

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} e^{-p_1^2 - p_2^2 - \dots - p_n^2}\, dp_1\, dp_2 \cdots dp_n = \left(\sqrt{\pi}\right)^n$$

set $p_1^2 + p_2^2 \cdots p_N^2 = P^2$

$$= \int_0^\infty e^{-P^2} \big[\underbrace{S_n P^{n-1}}_{\text{surface area of n-dim sphere}}\big]\, dP$$

$$= S_n \int_0^\infty e^{-P^2} P^{n-1}\, dP$$

$$\cancel{\int e^{-\alpha p^2} p^{n-1} dP = \left(\frac{-\partial}{\partial\alpha}\right)^{\frac{n-1}{2}} \int_0^\infty e^{-\alpha p^2} dP = \left(\frac{-\partial}{\partial\alpha}\right)^{\frac{n-1}{2}} \left(\frac{\pi}{\alpha}\right)^{1/2}}$$

$\left(-\frac{\partial}{\partial\alpha}\right)^m$	m
$\frac{1}{\alpha}$	0
$\frac{1}{\alpha^2}$	1
$2\frac{1}{\alpha^3}$	2
$3\frac{1}{\alpha^4}$	3
$\vdots$	

	m
$\cancel{\left(\frac{\pi}{\alpha}\right)^{1/2}}$	0
$\cancel{\frac{1}{2}\frac{\sqrt{\pi}}{\alpha^{3/2}}}$	1
$\cancel{\frac{3}{4}\frac{\sqrt{\pi}}{\alpha^{5/2}}}$	2
$\cancel{\frac{3\cdot 5}{8}\frac{\sqrt{\pi}}{\alpha^{7/2}}}$	3
$\frac{(2m-1)!!}{2^m}\frac{\sqrt{\pi}}{\alpha^{(2m+1)/2}}$	

$u = P^2$
$du = 2P\,dP$

$$= S_n \int_0^\infty e^{-u}\, u^{\frac{n-1}{2}} \frac{du}{2u^{1/2}}$$

$$= \frac{S_n}{2} \int_0^\infty e^{-u}\, u^{\frac{n}{2}-1}\, du = \frac{S_n}{2}\left(\frac{n}{2}-1\right)!$$

$$\int_0^\infty u^m e^{-\alpha u} du = \left(-\frac{\partial}{\partial\alpha}\right)^m \int_0^\infty e^{-\alpha u} du = \left(-\frac{\partial}{\partial\alpha}\right)^m \frac{1}{\alpha} = \frac{m!}{\alpha^{m+1}}$$

$$S_n = \frac{2}{\left(\frac{n}{2}-1\right)!}\left(\sqrt{\pi}\right)^n \quad \times R^{n-1} \text{ for surface area}$$

Surface area of sphere with radius $\sqrt{2mE}$ in 3N dim:

$$R^{n-1}\cdot S_E = \frac{2}{\left(\frac{3N}{2}-1\right)!}\, \pi^{\frac{3N}{2}} \cdot (2mE)^{\frac{3N-1}{2}}$$

$$\Delta p \times \text{Surface} = \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}(2mE)^{\frac{3N-1}{2}} \cdot \frac{\sqrt{2mE}}{E}\,\Delta E$$

$p = \sqrt{2mE}$

$\Delta p = \frac{\sqrt{2mE}}{2E}\Delta E = m\frac{\Delta E}{\sqrt{2mE}}$

$\frac{p^2}{2m} = E$

$\frac{2p\Delta p}{2m} = \Delta E$

$$\Omega(E) = \frac{2\pi^{3N/2}}{(3\frac{N}{2}-1)!}(2mE)^{\frac{3N-1}{2}}\frac{\sqrt{2mE}}{2mE}\cdot \cancel{2m}\ \cancel{\delta E}\ V^N$$ (8)

$$= \frac{2\pi^{3N/2}}{(3\frac{N}{2}-1)!}(2mE)^{\frac{3N-3/2}{2}}\cdot \cancel{2m}\cdot\cancel{\delta E}\ \frac{V^N}{h^{3N}}$$

$\ln n! \sim n\ln n - n$

$$\frac{1}{N}\ln\Omega(E) = \left[\frac{\ln(4m)}{N} + \frac{3N}{2N}\ln\pi + \frac{3\frac{N}{2}-\frac{3}{2}}{N}\ln(2mE) + \ln\frac{V}{h^3} - \frac{(3\frac{N}{2}-1)\ln(\frac{3N}{2}-1)}{N} + \frac{3\frac{N}{2}-1}{N}\right]$$

$$= \ln\frac{\pi^{3/2}(2mE)^{\frac{3}{2}}V}{(\frac{3}{2})^{3/2}N^{\frac{3}{2}}h^3} + \frac{3}{2}$$

$$= \ln\left[\left(\frac{2\pi\cdot 2mE}{3Nh^2}\right)^{3/2}V\right] + \frac{3}{2}$$

$$\frac{\partial}{\partial E}\ln\Omega(E) = N\frac{3}{2}\frac{\frac{4\pi m}{Nh^2}}{\frac{4\pi mE}{Nh^2}} = N\frac{3}{2}\cdot\frac{1}{E}$$

$$= \frac{1}{k_BT}$$

Putting in $E = \frac{3}{2}k_BTN$

So, take $S = k_B\,\Omega(E)$

So that $\frac{\partial S}{\partial E} = \frac{1}{T}$

Free expansion

$V_1 \to V_2$

$$\Delta S = k_B\left[\ln[\cdots V_2] - \ln[\cdots V_1]\right]$$

$$= k_B\ln\frac{V_2}{V_1}\ \checkmark$$

$k_B\ln 2$ if $V_2 = 2V_1$

$\log_2 2 = 1$ bit

info lost/particle

(which volume info)

Expansion of two different gases into each other

equal volumes

equal U

equal T

$S_1 + S_2$

Constant E

Important feature

$$\Omega(E) \sim \frac{V^N}{(\frac{3}{2}N-1)!}\times\cdots$$

$$\frac{1}{N}\ln\Omega \sim \ln\frac{V}{N^{3/2}} + \cdots$$

$$\Omega = \Omega(2E, 2N, 2V)$$

$$\frac{1}{2N}\ln\Omega = \frac{1}{2N}\ln\frac{(2V)^{2N}}{(\frac{3}{2}2N-1)!}$$

$$- \frac{1}{2N}\frac{3}{2}2N\ln\frac{3}{2}2N$$

$$= \ln\frac{2V}{(3N)^{3/2}}$$

$$\Omega = \Omega_1(E,N,V)\,\Omega_2(E,N,V)$$

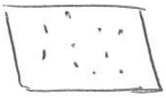
$$\frac{1}{2N}\ln\Omega = \frac{N}{2N}\frac{1}{N}\ln\Omega_1 + \frac{N}{2N}\frac{1}{N}\ln\Omega_2$$

$$= \frac{1}{2}(S_1 + S_2)$$

$$= \ln\frac{V}{N^{3/2}}$$

(7)

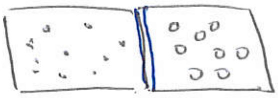
$\ln \Omega \sim \ln \left(\cdots \left(\frac{E}{N}\right)^{3/2 N} V^N \right)$



V, N, E

$S = \frac{k_B}{N} \ln \Omega \sim \ln \left(\cdots \left(\frac{E}{N}\right)^{3/2} V \right)$
$= S_0$

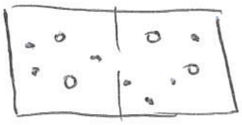
$\ln \Omega = \ln \Omega_1 (V,N,E)\, \Omega_1 (V,N,E)$



V, N, E   V, N, E

$S = \frac{N}{2N}\left(\frac{k_B}{N} \ln \Omega_1 (V,N,E) + \frac{k_B}{N} \ln \Omega_2 (V,N,E) \right)$
$= \frac{1}{2}(S_1 + S_2)$ ✓
$= S_0$

$\ln \Omega = \ln \left(\cdots \left(\frac{2E}{2N} \right)^{\frac{3}{2}\cdot 2N} (2V)^{2N} \right)$



2E, 2V, 2N

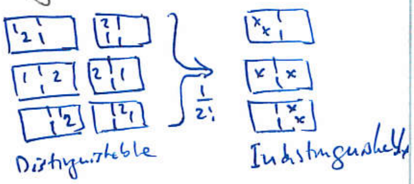
$S = \frac{k_B}{2N} \ln \left(\cdots \left(\frac{E}{N}\right)^{\frac{3}{2}\cdot 2N} (2V)^{2N} \right)$
$= k_B \ln \left(\cdots \left(\frac{E}{N}\right)^{3/2} 2V \right)$
$= S_0 + k_B \ln 2$

$\log_2 2 = 1$ bit
lost info to locate particle → $\Delta S = k_B \ln 2$ per particle.

But what if atoms are the same?
then we should get $\Delta S = 0$ (gas "diffuses" into itself.)

Corrected Boltzmann counting: ~~Partic~~ Identical particles are indistinguishable.

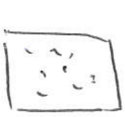
$\Omega(N,E,V) \to \frac{1}{N!} \Omega(N,E,V)$



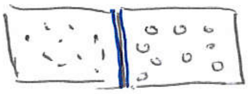
$\ln \Omega \to \ln \Omega - \ln N! = \ln \Omega - N \ln N + N$

$\ln \Omega \to \ln \left(\cdots \left(\frac{E}{N}\right)^{3/2 N} \left(\frac{V}{N}\right)^N \right) + N$

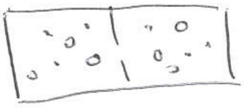
Sackur–Tetrode eqn



$S = \frac{1}{N} \ln \Omega = \ln \left(\left(\frac{4m}{3h^2}\frac{E}{N}\right)^{3/2} \frac{V}{N} \right) + \frac{5}{2}$



$S = \frac{1}{2N}\left(\ln \Omega_1 \Omega_2\right) = \frac{N}{2N}\left(\frac{1}{N} \ln \left[\left(\frac{E}{N}\right)^{3/2 N} \frac{V}{N} \right] + \frac{1}{N} \ln \left[\left(\frac{E}{N}\right)^{3/2} \frac{V}{N} \right] \right)$
$= S_1 + S_2$



$S = \frac{1}{2N} \ln \left(\cdots \left(\frac{2E}{2N} \right)^{\frac{3}{2}\cdot 2N} \frac{(2V)^{N\cdot 2}}{N!\,N!} \right)$ two types of particles $\ln \left(\cdots \left(\frac{E}{N}\right)^{3/2} \frac{2V}{N} \right)$
(increased)

$= \frac{1}{2N} \ln \left(\cdots \left(\frac{2E}{2N} \right)^{3/2\, 2N} \frac{(2V)^{N\cdot 2}}{(2N!)} \right)$ same type of particles $\ln \left(\cdots \left(\frac{E}{N}\right)^{3/2} \left(\frac{V}{N}\right) \right)$
(unchanged)

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

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