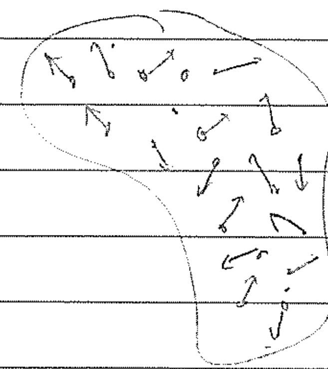
Classical Ideal Gas

N atoms (with volume v_0) confined in volume V

$$\log N \gg 1, \quad \log \frac{V}{v_0} \gg 1$$



total energy E

macrostate: (N, V, E)

microstate: $(\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \ldots, \vec{r}_N, \vec{p}_N)$

each $\vec{r}_n$ is inside volume V

$$H = \sum_{n=1}^{N} \frac{1}{2m} \vec{p}_n^{\,2}$$

Microcanonical Ensemble

number of microstates ~~with energy~~ E
with energy within $\frac{\Delta}{2}$ of E, where $\log \frac{E}{\Delta} \ll N$

$$\Omega(E, V, N) = \frac{1}{\omega_0} \times \left(\text{volume of phasespace with } E - \tfrac{\Delta}{2} < H < E + \tfrac{\Delta}{2}\right)$$

$$= \frac{1}{\omega_0} \int d\omega \; \delta\left(H(p,r) - E\right) \Delta$$

ω_0 = normalizing factor with dimensions of phase space $\qquad d\omega = d^3r_1 d^3p_1 \cdots d^3r_N d^3p_N$

entropy: $S(E,V,N) = \log \Omega(E,V,N)$

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

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

Hamiltonian: $H(p) = \sum_{n=1}^{N} \frac{1}{2m} \vec{p}_n^{\,2}$ if each $\vec{r}_n$ is inside volume V

$$\Omega(E,V,N) = \frac{1}{\omega_0} \int d^3r_1 d^3p_1 \cdots \int d^3r_N d^3p_N \ \delta(H(p) - E)\Delta$$

$$= \frac{1}{\omega_0} \underbrace{\int d^3r_1 \cdots \int d^3r_N}_{V^N} \int d^3p_1 \cdots \int d^3p_N \ \delta(H(p) - E)\Delta$$

$$\Omega(E,V,N) = V^N \times (\text{function of } E, N)$$

$$S(E,V,N) = N \log V + (\text{function of } E, N)$$

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

$$\frac{P}{T} = \frac{N}{V} \implies \boxed{PV = NT}$$

ideal gas law: $PV = N k_B T$ if temperature is measured in K and not energy units

$$\Omega(E,V,N) = \frac{1}{\omega_0} V^N \underbrace{\int d^3p_1 \cdots \int d^3p_N}_{\text{dimensions } p^{3N}} \underbrace{\delta\left(H(p) - E\right)\Delta}_{\text{dimensionless}}$$

deduce dependence on E using dimensional analysis

$$\sum_{n=1}^{N} \frac{1}{2m}\vec{p}_n^{\,2} = E \implies 2mE \text{ has dimensions } p^2$$

$$(2mE)^{3N/2} \quad \text{"} \quad p^{3N}$$

$$\Omega(E,V,N) = \frac{1}{\omega_0} V^N (2mE)^{3N/2} \times (\text{function of } N)$$

$$S(E,V,N) = N \log V + \frac{3N}{2} \log(2mE) + (\text{function of } N)$$

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{3N}{2E}$$

$$\frac{1}{T} = \frac{3N}{2E} \implies \boxed{E = \tfrac{3}{2}NT}$$

energy of monatomic ideal gas : $E = \frac{3}{2} N k_B T$

To complete calculation of $\Omega(E,V,N)$, calculate momentum integral

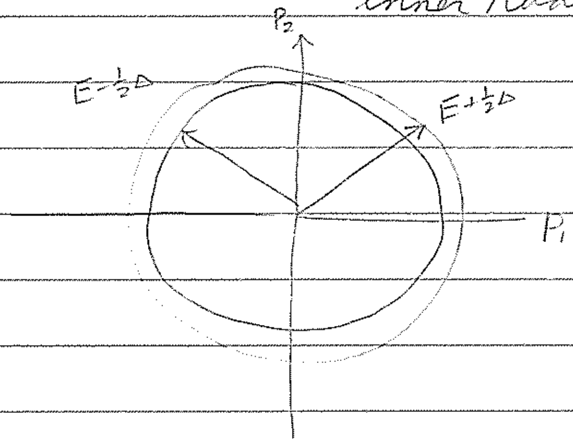
$$\int d^3p_1 \cdots \int d^3p_n \; \delta(H(p) - E)\Delta$$

$\simeq$ volume of 3N-dimensional momentum space satisfying $E - \frac{1}{2}\Delta < \sum_{n=1}^{N} \frac{1}{2m}\vec{p}_n^{\,2} < E + \frac{1}{2}\Delta$

= volume of shell in 3N-dimensional momentum space

with outer radius $2m(E+\frac{1}{2}\Delta)$

inner radius $2m(E-\frac{1}{2}\Delta)$



hyperhvolume of ball of radius R in n dimensions

$$\mathcal{V}_n = \frac{\pi^{n/2}}{(n/2)!} R^n \qquad \text{P+B, Appendix C}$$

where $z! \equiv \Gamma(z+1) = z\,\Gamma(z)$, $\quad \Gamma(1) = 1$, $\Gamma(\frac{1}{2}) = \sqrt{\pi}$

<u>checks</u> $\quad \mathcal{V}_1 = \frac{\pi^{1/2}}{\frac{1}{2}!} R = \frac{\sqrt{\pi}}{\Gamma(3/2)} R = \frac{\sqrt{\pi}}{\frac{1}{2}\sqrt{\pi}} R = 2$

$$\mathcal{V}_2 = \frac{\pi}{1!} R^2 = \pi R^2$$

$$\mathcal{V}_3 = \frac{\pi^{3/2}}{(3/2)!} R^3 = \frac{\pi\sqrt{\pi}}{\Gamma(5/2)} R^3 = \frac{\pi\sqrt{\pi}}{\frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi}} R^3 = \frac{4}{3}\pi R^3$$

$$\int d^3p_1 \cdots \int d^3p_N \, \delta(H(p)-E)\,\Delta$$

$$\simeq \frac{\pi^{3N/2}}{(3N/2)!}\left[2m(E+\tfrac{1}{2}\Delta)\right]^{3N/2} - \frac{\pi^{3N/2}}{(3N/2)!}\left[2m(E-\tfrac{1}{2}\Delta)\right]^{3N/2}$$

$$\simeq \frac{\pi^{3N/2}}{(3N/2)!}\,\frac{d}{dE}\left[2mE\right]^{3N/2}\cdot\Delta = \frac{\pi^{3N/2}}{(\frac{3N}{2}-1)!}\,(2mE)^{3N/2-1}\cdot 2m\Delta$$

$$\Omega(E,V,N) = \frac{1}{\omega_0} V^N \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{\frac{3}{2}N} \frac{3N\Delta}{2E}$$

$$S(E,V,N) = N \log V + \frac{3N}{2} \log(2mE) - \log\left(\left(\tfrac{3}{2}N\right)!\right)$$

$$- \log \omega_0 + \log N + \log \frac{3}{2} + \log \frac{\Delta}{E}$$

Stirlings formula for $n!$

$$\log n! = n \log n - n + \frac{1}{2} \log n + \frac{1}{2} \log(2\pi) + O\left(\frac{1}{n}\right)$$

$$\simeq n \log n - n$$

Keep only terms in S with explicit factor of N

$$S(E,V,N) \simeq N \log V + \frac{3N}{2} \log(2mE)$$

$$- \left[\tfrac{3}{2} N \log\left(\tfrac{3}{2}N\right) - \tfrac{3}{2}N\right] - \log \omega_0$$

$$= N\left[\log V + \tfrac{3}{2} \log(2mE) - \tfrac{3}{2} \log\left(\tfrac{3}{2}N\right) + \tfrac{3}{2}\right] - \log \omega_0$$

$$= N\left[\log V + \frac{3}{2} \log \frac{4mE}{3N} + \frac{3}{2}\right] - \log \omega_0$$

Note: S is not exactly extensive because of $\log V$ term

$$S(\lambda E, \lambda V, \lambda N) = \lambda N\left[\log(\lambda V) + \frac{3}{2} \log \frac{4mE}{3N} + \frac{3}{2}\right] - \log \omega_0$$

$$= \lambda S(E,V,N) + \lambda N \log \lambda$$

Gibbs paradox

two systems consisting of same atom
at same temperature T, pressure P
separated by barrier

E_1, V_1, N_1	E_2, V_2, N_2
T, P	T, P

if barrier is removed, macrostate is the same

$E_1+E_2,\ N_1+N_2,\ V_1+V_2$
$P \quad T$

entropy before: $S(E_1, V_1, N_1) + S(E_2, V_2, N_2)$

entropy after: $S(E_1+E_2, V_1+V_2, N_1+N_2)$

change in entropy:

$$\Delta S = (N_1+N_2)\log(V_1+V_2) - N_1 \log V_1 - N_2 \log V_2$$

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

removal of barrier: same microstate, different entropy

Gibbs fudge factor: divide Ω by $N!$

$$\Omega \longrightarrow \frac{1}{N!}\Omega$$

$$S \longrightarrow S - \log N!$$

$$\simeq S - (N \log N - N)$$

$$S(E,V,N) = N\left[\log\frac{V}{N} + \frac{3}{2}\log\frac{4mE}{3N} + \frac{5}{2}\right]$$

exactly extensive $\Longrightarrow$ no Gibbs paradox

<u>Quantum solution</u>

atoms of same isotope are <u>identical</u> <u>indistinguishable</u> particles

interchange of any 2 atoms gives same quantum state
permutation of N atoms "

integral over phase space of N atom
overcounts quantum states by factor of $N!$

correct counting of quantum states

$$\Omega(E,V,N) = \frac{1}{N!}\frac{1}{\omega_0}\int d\omega\ \delta(H(p,q) - E)\Delta$$