$$Z = \sum_r e^{-\beta E_r}$$

$$S = k(\ln Z + \beta \bar{E})$$

We saw the definition

$S = k \ln \Omega \longrightarrow$ microcanonical ensemble

are equivalent upto a very small correction

Let us examine the partition fn in the low temp limit

$T \to 0$ or $\beta \to \infty$

$$Z = \sum_r e^{-\beta E_r}$$

$\downarrow$ only terms that contribute are those for the lowest possible energy $E_r \to \Omega_0$ states corresponding to ground state energy E_0.

as $T \to 0$

$$Z \to \Omega_0 e^{-\beta E_0}.$$

mean energy $T \to 0$, $\bar{E} \to E_0$

$$S \to (k \ln Z + \beta \bar{E}) \to k[\ln \Omega_0 - \cancel{\beta E_0} + \cancel{\beta E_0}]$$

As $T \to 0$

$$S \to k \ln \Omega_0$$

Third Law

Entropy approaches a value (equal to zero in the absence of randomness of nuclear spin orientations) independent of all parameters of ~~of~~ the system.

Detour into Thermo $\to$ consequences of 3rd Law

Heat Capacity.

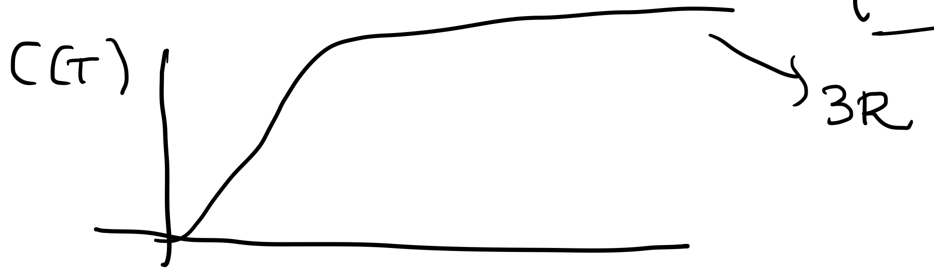
Consider a solid body heated at const pressure until its temp increases from $T_i = 0$ to $T_f = T$

$$S = \int_0^T \frac{C(T)\,dT}{T}$$

↓

Consequence of 3rd Law $S \longrightarrow 0$ as $T \longrightarrow 0$

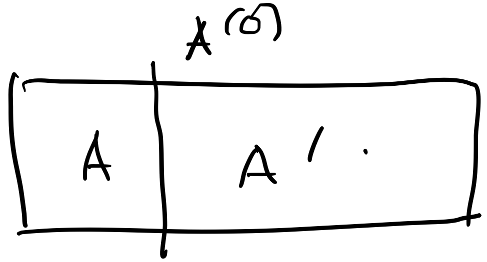
we must have $\boxed{C(T) = 0 \quad \text{as } T \longrightarrow 0}$ → agrees with experiment



Partition fn:s & properties

Composite system

$A^{(0)} \longrightarrow A$ & A' weakly interacting



$$E^{(0)}_{rs} = E_r + E'_s .$$

$$Z^{(0)} = \sum_{r,s} e^{-\beta E^{(0)}_{rs}} .$$

$$= \sum_{r,s} e^{-\beta\left(E_r + E'_s\right)} .$$

$$= \sum_r \sum_s e^{-\beta E_r} e^{-\beta E'_s} = \left(\sum_r e^{-\beta E_r}\right)\left(\sum_s e^{-\beta E'_s}\right)$$

$$= Z Z'$$

$$\boxed{Z^{(0)} = Z Z'}$$

$$\ln Z^{(0)} = \ln Z + \ln Z'.$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta}.$$

$$\bar{E}^{(0)} = \bar{E} + \bar{E}'$$

$\hookrightarrow$ $S^{(0)} = S + S'$ $\qquad S = k(\ln Z + \beta \bar{E}).$

Now consider
Two systems A, A' each separately in internal equilibrium with specific temp parameters β and β'.

P_r : prob of finding A in state r

P'_s : " " " A' in state s.

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad , \quad P'_s = \frac{e^{-\beta' E'_s}}{\sum_s e^{-\beta E'_s}} .$$

Now put the two A & A' in thermal contact.

They interact weakly with each other

P_{rs} of finding A in state r, and A' in state s.

$$P_{rs} = P_r P_s.$$

$$= \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \frac{e^{-\beta' E_s'}}{\sum_s e^{-\beta' E_s'}}.$$

Now if $\beta = \beta'$

$$P_{rs} = \frac{e^{-\beta(E_r + E_s')}}{\sum_{r,s} e^{-\beta(E_r + E_s')}} \longrightarrow$$

canonical dist corresponding to β of a system whose energies are $E_r + E_s' = E_{rs}$.

- A & A' <u>remain</u> in equilibrium after being joined.
- will not happen if $\beta \not\equiv \beta'$

Ideal Monatomic Gas in a container of volume V.

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(\vec{r_1}, \vec{r_2} \cdots \vec{r_N}).$$

Ideal gas $U \longrightarrow 0$.

Let us calculate partition fn.

$$Z' = \int \exp\left\{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right\} \frac{d^3\vec{r_1} \cdots d\vec{r_N}\; d^3\vec{p_1} \cdots d^3\vec{p_N}}{h_0^{3N}}$$

$$Z' = \frac{1}{h_0^{3N}} \int d^3\vec{r_1} \cdots d^3\vec{r_N} \int e^{-\beta/2m\, p_1^2} d^3 p_1 \cdots \int e^{-\beta/2m\, p_N^2} d^3\vec{p_N}$$

$$\int d^3\vec{r}_1 \cdots d^3\vec{r}_N = V^N .$$

$$Z' = \zeta^N$$

$$\ln Z' = N \ln \zeta .$$

$$\boxed{\zeta = \frac{V}{h_0^3} \int_{-\infty}^{+\infty} e^{-\frac{\beta p^2}{2m}} \, d^3\vec{p}}$$

$$\int_{-\infty}^{+\infty} e^{-\frac{\beta p^2}{2m}} \, d^3\vec{p} = \iiint_{-\infty}^{+\infty} e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} \, dp_x \, dp_y \, dp_z$$

$$= \int_{-\infty}^{+\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x \int_{-\infty}^{+\infty} e^{-\frac{\beta p_y^2}{2m}} dp_y \int_{-\infty}^{+\infty} e^{-\frac{\beta p_z^2}{2m}} dp_z .$$

$$= \left(\sqrt{\frac{2m\pi}{\beta}} \right)^3 .$$

$$\zeta = \frac{V}{h_0^3} \int_{-\infty}^{+\infty} e^{-\beta/2m \, p^2} d^3\vec{p}$$

$$\boxed{\zeta = V \left(\frac{2\pi m}{h_0^2 \beta} \right)^{3/2}}$$

$$\zeta = V\left(\frac{2\pi m}{h_0^2 \beta}\right)^{3/2}.$$

$$\ln Z' = N \ln \zeta .$$

$$\boxed{\ln Z' = N\left[\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h_0^2}\right)\right]}$$

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z'}{\partial V} = \frac{1}{\beta}\frac{N}{V}.$$

$$\boxed{\bar{p}V = NkT} \longrightarrow \text{Equation of state.}$$

$$\overline{E} = -\frac{\partial}{\partial \beta} \ln Z' = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2} NkT = N\overline{\epsilon}$$

$$\boxed{\overline{\epsilon} = \frac{3}{2} kT}$$

mean energy/molecule.

$$C_v = \frac{\partial \overline{E}}{\partial T} = \frac{3}{2} Nk = \frac{3}{2} \nu N_0 k$$

$[R = N_0 k]$

ν: # of moles

N_0: Avogadro.

$$= \frac{3}{2} \nu R.$$

$$\boxed{c_v = \frac{3}{2} R}$$