partition fn for ideal gas.

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

$$\bar{P} = \frac{1}{\beta}\frac{\partial \ln Z'}{\partial V} = \frac{1}{\beta}\frac{N}{V} \longrightarrow \boxed{PV = NkT}$$

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

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

Remark on fluctuations

$$\overline{(\Delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} \longrightarrow \text{at const } V.$$

$$\overline{(\Delta E)^2} = -\left(\frac{\partial \bar{E}}{\partial T}\right)_V \frac{\partial T}{\partial \beta}$$

$$= kT^2 \left(\frac{\partial \bar{E}}{\partial T}\right)_V .$$

$$\boxed{\overline{(\Delta E)^2} = kT^2 C_V}$$

Monatomic ideal gas.

$$\overline{(\Delta E)^2} = kT^2 C_V$$

$$= \frac{3}{2} N k^2 T^2$$

$$\overset{*}{\Delta} E = \sqrt{\overline{(\Delta E)^2}}$$

$$\frac{\overset{*}{\Delta} E}{\overline{E}} = \frac{\sqrt{\frac{3}{2} N k^2 T^2}}{\frac{3}{2} N k T} = \sqrt{\frac{2}{3N}}.$$

$N \sim 10^{23}$

$$\frac{\overset{*}{\Delta} E}{\overline{E}} \ll 1$$

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

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

$$\boxed{\begin{aligned} S &= Nk\left[\ln V + \frac{3}{2}\ln T + \sigma\right] \\ \sigma &= \frac{3}{2}\ln\left(\frac{2\pi m}{h_0^2}\right) + \frac{3}{2} \end{aligned}}$$

$$S = Nk\left[\ln V + \frac{3}{2}\ln T + \sigma\right] \quad \text{—} \circledast$$

Observations

- Breaks down in limit $T \to 0$, ideal gas description not valid there.

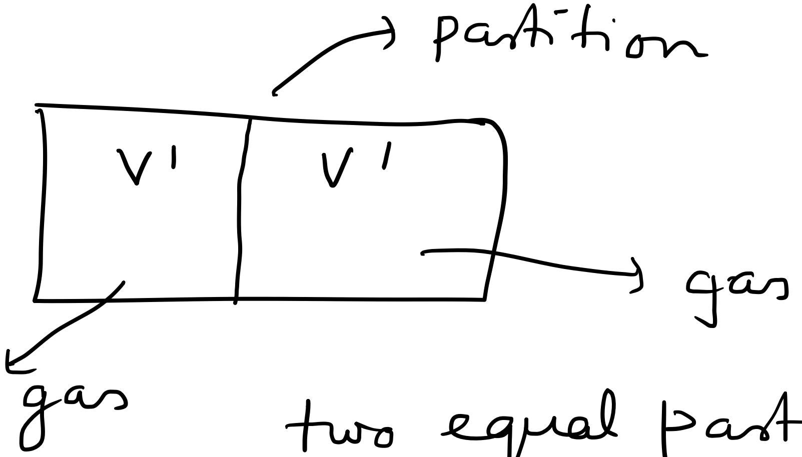
- clearly something wrong in $\circledast$ S does not behave as an extensive qty.

  scale system by a factor α, $N \to N\alpha$, $V \to \alpha V$

  $S \not\to \alpha S$ → culprit → $N \ln V$.

  $\bar{E} = \frac{3}{2}\frac{N}{\beta}$ $\quad \bar{E} \to \alpha \bar{E}$

Let us consider



$$\underbrace{S = S' + S''}_{\text{additivity}}.$$

two equal parts.

with partition

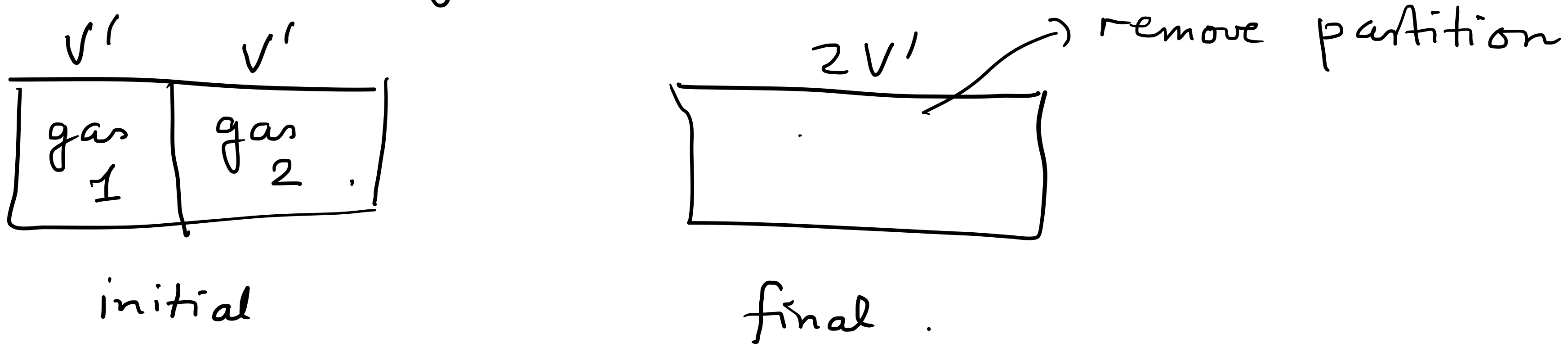
$$S' = S'' = N'k\left[\ln V' + \frac{3}{2}\ln T + \sigma\right]$$

without partition

$$= 2N'k\left[\ln V' + \frac{3}{2}\ln T + \sigma\right].$$

$$\left.\begin{aligned} S - 2S' &= 2N'k\ln(2V') - 2N'k\ln V' \\ &= 2N'k\ln 2 \neq 0 \quad !! \end{aligned}\right\} \text{Gibbs Paradox.}$$

Two different gases



we expect entropy increase → entropy of mixing

for same gas, there is a paradox

"Resolution"

particles of same gas as indistinguishable.

N! permutations do not lead to distinct states.

$$Z \longrightarrow \frac{Z}{N!}$$

$$Z = \frac{Z'}{N!} = \frac{\zeta^N}{N!}$$

$$\ln Z = N \ln \zeta - \ln N!$$

$$= N \ln \zeta - \underbrace{N \ln N + N}$$

Differs from original by this factor.

$\bar{P}$, $\bar{E}$ depend on derivatives of $\ln Z$, not affected.

S is affected

$$S = kN\left[\ln V + \frac{3}{2}\ln T + \sigma\right] + k\left(-N\ln N + N\right).$$

$$= kN\left[\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right] \Big\} \quad \sigma_0 = \sigma + 1$$

Now scales correctly.

$N \Rightarrow \alpha N$.

$V \Rightarrow \alpha V$.

$S \Rightarrow \alpha S$

for the same gas case $\Delta S = 0$

Equipartition Theorem

$$E = E(q_1, q_2 \cdots q_f, p_1 \cdots p_f).$$

a. $E = \epsilon_i(p_i) + E'(\underbrace{q_1, \ldots q_f, p_1 \ldots p_f}_{\text{no } p_i})$. → does not depend on p_i

b. $\epsilon_i(p_i) = b p_i^2$.

- p_i = momentum $\quad K.E = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$ $\quad$ ideal monatomic gas.

  $U(q_1, \ldots q_f) \longrightarrow$ does not depend on p_i

- a, b satisfied for q_i instead of p_i, e.g harmonic oscillator
  $U(q_1 \cdots q_f) = k \sum q_i^2$

$\longrightarrow$ $\boxed{\text{Average energy per "quadratic" degree of freedom } = \frac{1}{2} kT}$