# Chapter 3.3: The Ideal Gas in the Canonical Ensemble

**Independent particles** $\{\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \vec{r}_3, \vec{p}_3, ...., \vec{r}_N, \vec{p}_N\}$

$$\varepsilon_j = \frac{p_j^2}{2m}$$

$$\int_{-\infty}^{\infty} dx\, e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$$

$$\varepsilon(\{\vec{r}_j, \vec{p}_j\}) = \sum_j \frac{\vec{p}_j^{\,2}}{2m} = \sum_j \varepsilon_j$$

$$Z_1 = \int d\vec{r}_1\, d\vec{p}_1\, e^{-\beta\varepsilon_1} = V \int d^3\vec{p}\, e^{-\beta\frac{p^2}{2m}}$$

$$= V \int dp_x\, e^{-\beta\frac{p_x^2}{2m}} \int dp_y\, e^{-\beta\frac{p_y^2}{2m}} \int dp_z\, e^{-\frac{p_z^2}{2m}}$$

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

$$Z = (Z_1)^N$$

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

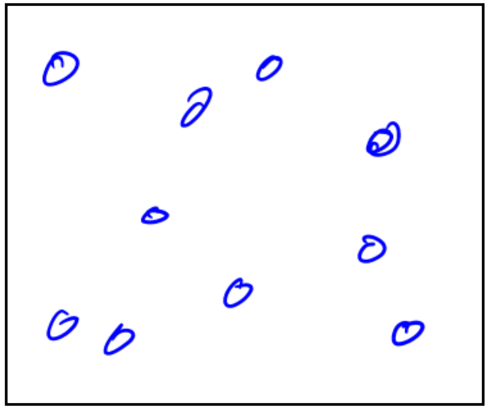
$$\ln Z = N\left(\ln V - \frac{3}{2}\ln\beta + \text{const}\right)$$

$$E = -\frac{\partial \ln Z}{\partial\beta} = +N\frac{3}{2}\frac{1}{\beta} = \frac{3}{2}Nk_BT \quad \checkmark \qquad \frac{E}{T} = \frac{3}{2}Nk_B$$

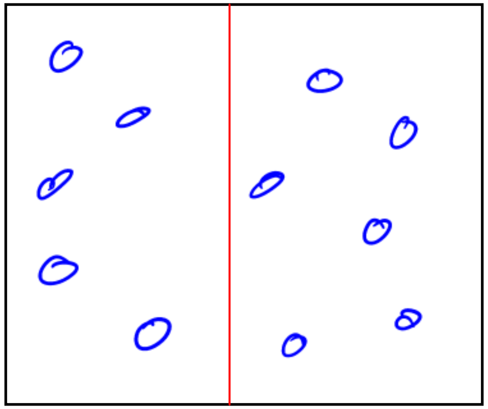
$$p = -\left(\frac{\partial F}{\partial V}\right)_T = k_BT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{Nk_BT}{V} \quad \checkmark$$

$$S = -\frac{F}{T} + \frac{E}{T} = k_B \ln Z + \frac{E}{T} = Nk_B\left(\ln V - \frac{3}{2}\ln\beta + \text{const}\right)$$

## Entropy



$N/2, V/2$ $\quad$ $N/2, V/2$



$S_{1/2}$ $\quad$ $S_{1/2}$

$$S_{before} = N k_B \left( \ln \frac{V}{\bar N} - \frac{3}{2} \ln \beta + const \right)$$

$$S_{after} = S_{1/2} + S_{1/2} = 2 \times S_{1/2}$$

$$= 2 \times \frac{N}{2} k_B \left( \ln \frac{V}{2}\frac{2}{N} - \frac{3}{2} \ln \beta + const \right)$$

$$= N k_B \left( \ln \frac{V}{\bar N} - \frac{3}{2} \ln \beta + const \right) \cancel{- N k_B \ln 2}$$

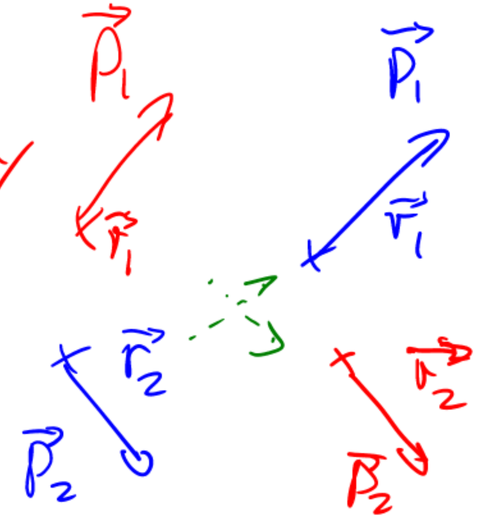
$$S_{after} = S_{before} \cancel{- N k_B \ln 2}$$

↯ reversible!

## Gibbs paradox and Gibbs factor

$\frac{1}{N!}$

Same state




For indistinguishable particles avoid overcounting by exchanging indices:

integration over all $\{\vec{p}_j, \vec{r}_j\}$ there are too many microstate

$$\int \prod_j d^3\vec{r}_j d^3\vec{p}_j \;\rightarrow\; \frac{1}{N!}\int \prod_j d^3\vec{r}_j d^3\vec{p}_j$$

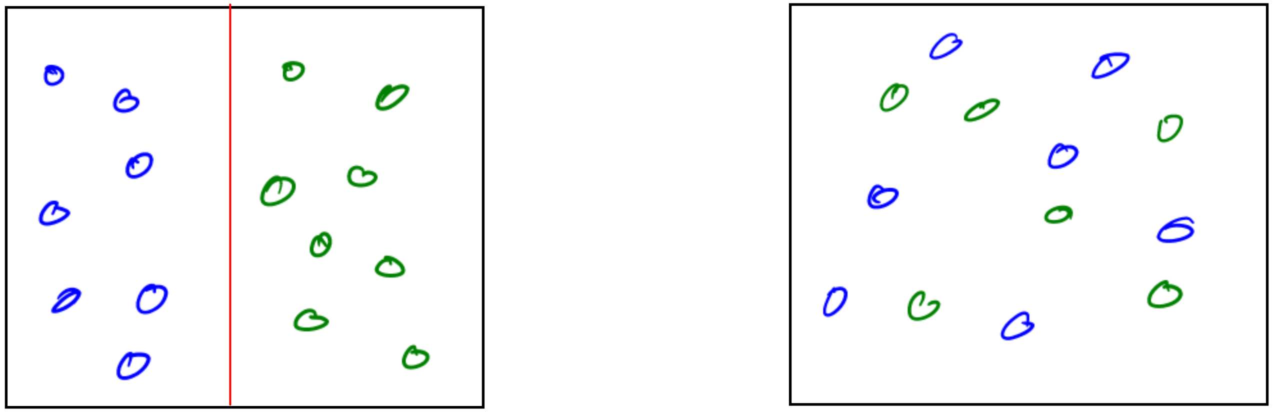
$$Z = \frac{(Z_1)^N}{N!} = \frac{1}{N!}\int d\Gamma\, e^{-\beta \sum_j \varepsilon_j}$$

$$\ln Z = N \ln Z_1 - \ln N! = N \ln Z_1 - N \ln N + N$$

$$S = k_B \ln Z + \frac{E}{T} = k_B N\left(\ln V - \frac{3}{2}\ln\beta + \text{const}\right) - k_B N \ln N$$

$$= k_B N\left(\ln \frac{V}{N} - \frac{3}{2}\ln\beta + \text{const}\right)$$

## Entropy of mixing



$N/2, V/2$ $\quad$ $N/2, V/2$

$$S_{before} = 2 \times \frac{N}{2} k_B \left( \ln \frac{V \cdot 2}{2 \cdot N} - \frac{3}{2} \ln \beta + \text{const} \right)$$

$$S_{after} = 2 \times \frac{N}{2} k_B \left( \ln \frac{2 \cdot V}{N} - \frac{3}{2} \ln \beta + \text{const} \right) = S_{before} + k_B N \ln 2$$

"Entropy of mixing" non-reversible