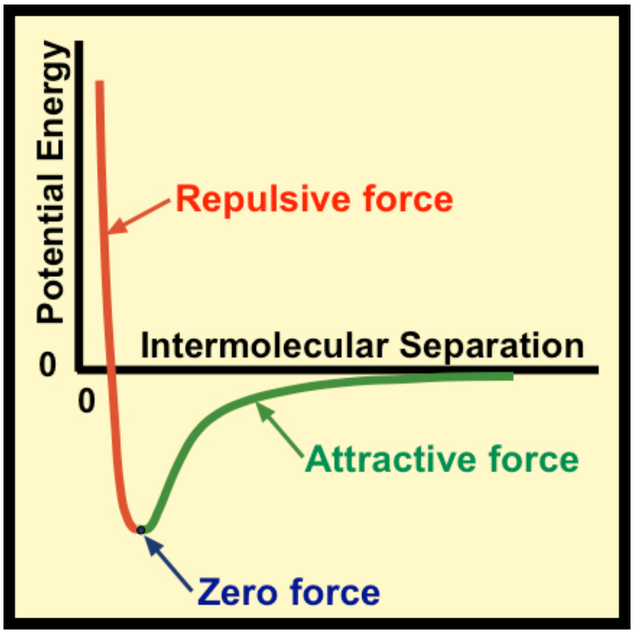
Classical gas

$$\mathcal{H} = \sum_{i=1}^{N} \frac{1}{2m} \vec{p}_i^{\,2} + \sum_{i<j} V(|\vec{r}_i - \vec{r}_j|)$$

where V stands for the potential by pairs.

$$r := |\vec{r}_i - \vec{r}_j|$$



$$Z_c = \underbrace{\int \cdots \int}_{V} d^3\vec{r}_1 \cdots d^3\vec{r}_N \int \cdots \int d^3\vec{p}_1 \cdots d^3\vec{p}_N \exp(-\beta \mathcal{H})$$

$$\int_{-\infty}^{\infty} dp \exp\left(\frac{-\beta p^2}{2m}\right) = \left(\frac{2\pi m}{\beta}\right)^{1/2}$$ 3N integrals

therefore,

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

where

$$Q_N := \underbrace{\int \cdots \int}_{V} d^3\vec{r}_1 \cdots d^3\vec{r}_N \exp\left[-\beta \sum_{i<j} V(|\vec{r}_i - \vec{r}_j|)\right]$$

for an ideal gas $Q_N = V^N$

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

then

$$\frac{1}{N}\ln(Z_c) = \frac{3}{2}\ln\left(\frac{2\pi m}{\beta}\right) + \ln(V)$$

Thermodynamical limit?

$$Z = \frac{1}{N!}\frac{1}{h^{3N}} Z_c = \frac{1}{N!}\left(\frac{2\pi m}{\beta \hbar^2}\right)^{3N/2} Q_N$$

$h \to$ plank constant

$N! \to$ correct counting

For an ideal gas

$$\frac{1}{N}\ln(Z) = -\frac{\ln(N!)}{N} + \frac{3N}{2N}\ln\left(\frac{2\pi m}{\beta h^2}\right) + \frac{N}{N}\ln(V)$$

$$\approx \frac{-N}{N}\ln(N) + 1 + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) + \ln(V)$$

$$= \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) + \ln\left(\frac{V}{N}\right) + 1 + \frac{\ln(N)}{N}$$

$$f = f(T,v) = -\frac{1}{\beta}\lim_{V,N\to\infty}\frac{1}{N}\ln(Z) \qquad ; \ \frac{V}{N} = v$$

$$= -\frac{3}{2}K_B T\ln(T) - K_B T\ln(v) - K_B T c$$

with $c = \frac{3}{2}\ln\left(\frac{2\pi m K_B}{h^2}\right) + 1$

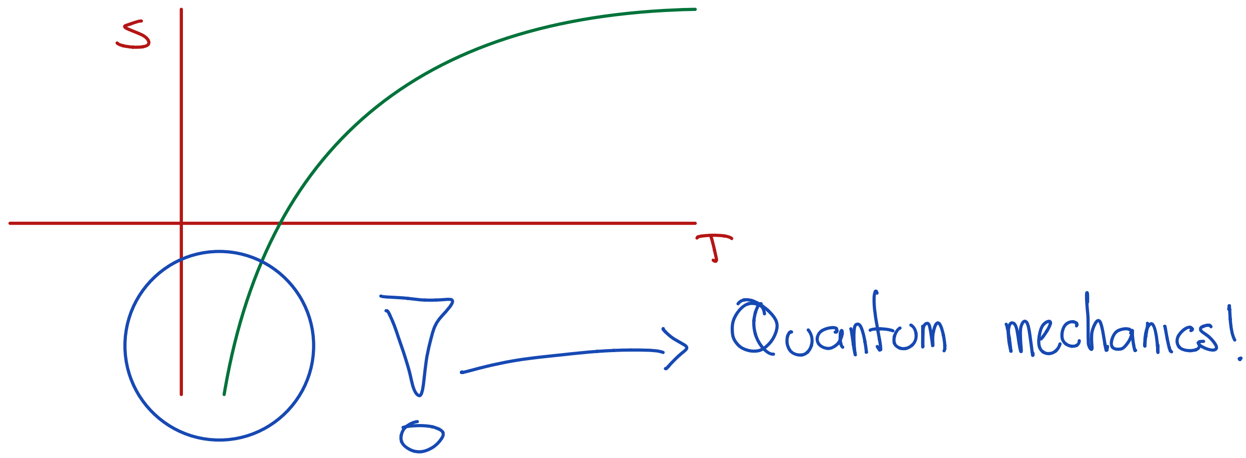
$$s = -\left(\frac{\partial f}{\partial T}\right)_v = \frac{3}{2}K_B\ln(T) + K_B\ln(v) - K_B c - \frac{3}{2}K_B$$

therefore

$$C_v = T\left(\frac{\partial s}{\partial T}\right)_v = \frac{3}{2}K_B$$

and

$$p = -\left(\frac{\partial f}{\partial v}\right)_T = \frac{K_B T}{v}$$ Boyle law



$$\langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln(Z) = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2} N k_B T$$

then,

$$u = \frac{3}{2} k_B T$$

Intern energy per particle

from $s(T, v)$, we get

$$\exp\left(\frac{s}{k_B} + C_1\right) = T^{3/2} v \qquad C_1 = C + \frac{3}{2}$$

$$T = v^{-2/3} \exp\left[\frac{2}{3}\left(\frac{s}{k_B} + C_1\right)\right]$$

$$u = \frac{3}{2} k_B v^{-2/3} \exp\left[\frac{2}{3}\left(\frac{s}{k_B} + C_1\right)\right]$$

finally,

$$s(u, v) = \frac{3}{2} k_B \ln(u) + k_B \ln(v) + \text{constant}$$

↳ As same as the microcanonical!