Maxwell-Boltzmann distribution.

$$\ln(\Xi)_{cl} = \sum_j \exp(-\beta(\epsilon_j - \mu))$$

$$\langle n_j \rangle_{cl} = \exp(-\beta(\epsilon_j - \mu))$$

$$\ln(\Xi)_{cl} = z \sum_j \exp(-\beta \epsilon_j)$$

$$N = z \frac{\partial}{\partial z} \ln(\Xi_{cl}(\beta z V)) = z \sum_j \exp(-\beta \epsilon_j)$$

$$\langle n_j \rangle_{cl} = z \exp(-\beta \epsilon_j) = \frac{N \exp(-\beta \epsilon_j)}{\sum_j \exp(-\beta \epsilon_j)}$$

So,

$$\frac{\langle n_j \rangle_{cl}}{N} = \frac{\exp(-\beta \epsilon_j)}{\sum_j \exp(-\beta \epsilon_j)}$$

Discrete Maxwell-Boltzmann Distribution.

In the thermodynamical limit

$$\frac{\langle n_j \rangle_{cl}}{N} \longrightarrow p_o(v)\,dv = \frac{\frac{V}{(2\pi)^3} \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) d^3\vec{k}}{\frac{V}{(2\pi)^3} \int \exp\left(-\frac{\beta \hbar^2 k^2}{2m}\right) d^3\vec{k}}$$

Helmholtz

$$F = \phi + \mu N \qquad \text{and} \qquad N = -\left(\frac{\partial \phi}{\partial \mu}\right)_{T,V}$$

Taking ϕ_{cl}, we get

$$F = -K_B T N \left\{ 1 + \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(T) - \ln\left(\frac{1}{\gamma}\left(\frac{h^2}{2\pi m K_B}\right)^{3/2}\right) \right\}$$

$$\frac{\partial \phi}{\partial \mu} = -\gamma V \left(\frac{2\pi m}{h^2}\right)^{3/2} (K_B T)^{5/2} \frac{1}{K_B T} \exp\left(\frac{\mu}{K_B T}\right)$$

$$\longrightarrow N = \gamma V \left(\frac{2\pi m}{h^2}\right)^{3/2} (K_B T)^{3/2} \exp\left(\frac{\mu}{K_B T}\right)$$

$$\longrightarrow \mu = -K_BT \ln\left(\gamma \frac{V}{N} \left(\frac{2\pi m}{h^2}\right)^{3/2} (K_BT)^{3/2} \right)$$

$$\longrightarrow F = -K_BTN + (-K_BT) \ln\left(\gamma \frac{V}{N} \left(\frac{2\pi m}{h^2}\right)^{3/2} (K_BT)^{3/2} \right) N$$

we had already obtained it!!

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = N K_B \ln\left(\frac{V}{N}\right) + \frac{3}{2} K_B N \ln(T) + N s_0$$

$$s_0 = \frac{5}{2} K_B + K_B \ln\left(\frac{1}{\gamma} \left(\frac{h^2}{2\pi m K_B} \right)^{3/2} \right)$$

Using

$$pV = NK_BT \longrightarrow S = S(T, p, N)$$

Spectroscopic entropy $\longrightarrow$ Thermodynamical entropy