Boltzmann distribution

$$p_i = \frac{\exp(-\beta\varepsilon_i)}{Z}$$

where

$$Z = \sum_{i=0}^{\text{all states}} \exp(-\beta\varepsilon_i) = \sum_{i=0}^{\text{all energy levels}} g_i \exp(-\beta\varepsilon_i)$$

with $\beta = \dfrac{1}{k_B T}$

Z is the "partition function".

a) Ensures that the p_i's are normalized i.e. $\sum_{i=0}^{\text{all states}} p_i = 1$

b) Describes how energy is "partitioned" over the ensemble i.e. states making a large contribution to Z have a high p_i hence a large share of the energy

c) Links microscopic description of an ensemble to its macroscopic variables/ functions of state.

e.g. ensemble of N identical systems:

$$U = N\bar{\varepsilon} = N\sum_{i=0}^{\infty} \varepsilon_i p_i$$

in equilibrium at temp T.

$$U = N\sum_{i=0}^{\infty} \varepsilon_i \frac{\exp(-\beta\varepsilon_i)}{Z} = \frac{N}{Z}\sum_{i=0}^{\infty} \varepsilon_i \exp(-\beta\varepsilon_i)$$

$$= -\frac{N}{Z}\sum_{i=0}^{\infty} \frac{\partial(\exp(-\beta\varepsilon_i))}{\partial\beta} = -\frac{N}{Z}\frac{\partial}{\partial\beta}\sum_{i=0}^{\infty} \exp(-\beta\varepsilon_i) = -\frac{N}{Z}\frac{\partial Z}{\partial\beta} = -N\frac{\partial \ln Z}{\partial\beta}$$

$$= -N\frac{\partial \ln Z}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}\beta}$$

$$\boxed{U = Nk_{\mathrm{B}}T^2 \frac{\partial \ln Z}{\partial T}}$$

(in equilibrium)

In general:

$$S = k_{\mathrm{B}} \ln \Omega$$

with

$$\Omega = \frac{N!}{\prod_{i=0}^{\infty} n_i!}$$

Hence

$$\ln \Omega = \ln N! - \sum_{i=0}^{\infty} \ln n_i!$$

Stirling's approx.:- for large x $\ln x! \approx x \ln x - x$

$$\therefore \ln \Omega = N \ln N - N - \sum_{i=0}^{\infty} (n_i \ln n_i - n_i)$$

$$= N \ln N - N - \sum_{i=0}^{\infty} n_i \ln n_i + \sum_{i=0}^{\infty} n_i$$

$$= N \ln N - \sum_{i=0}^{\infty} n_i \ln n_i \qquad \left(\text{as } \sum_{i=0}^{\infty} n_i = N\right)$$

$$= N \ln N - \sum_{i=0}^{\infty} Np_i \ln(Np_i) = N \ln N - \sum_{i=0}^{\infty} Np_i (\ln N + \ln p_i)$$

$$= N \ln N - N \ln N \sum_{i=0}^{\infty} p_i - N \sum_{i=0}^{\infty} p_i \ln p_i$$

$$= -N \sum_{i=0}^{\infty} p_i \ln p_i \qquad \left(\text{as } \sum_{i=0}^{\infty} p_i = 1\right)$$

$$\boxed{S = -Nk_{\mathrm{B}} \sum_{i=0}^{\infty} p_i \ln p_i}$$

(in general, for N and all n_i's large)

In equilibrium :-

$$S = -Nk_{\mathrm{B}} \sum_{i=0}^{\infty} p_i \ln\left(\frac{\exp(-\beta\varepsilon_i)}{Z}\right)$$

$$= -Nk_{\mathrm{B}} \sum_{i=0}^{\infty} p_i \left(-\beta\varepsilon_i - \ln Z\right) = Nk_{\mathrm{B}}\beta \sum_{i=0}^{\infty} p_i \varepsilon_i + Nk_{\mathrm{B}} \ln Z \sum_{i=0}^{\infty} p_i$$

$$= k_{\mathrm{B}}\beta U + Nk_{\mathrm{B}} \ln Z = \frac{U}{T} + Nk_{\mathrm{B}} \ln Z$$

$$\therefore U - TS = -Nk_{\mathrm{B}} T \ln Z$$

$U - TS$ is the Helmholtz Free Energy F, hence

$$\boxed{F = -Nk_{\mathrm{B}} T \ln Z}$$

valid in equilibirium

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk_{\mathrm{B}} \left(\frac{\partial (T \ln Z)}{\partial T}\right)_V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = Nk_{\mathrm{B}} T \left(\frac{\partial \ln Z}{\partial V}\right)_T$$