

I. FREE ENERGY

The Boltzmann weight of a configuration is

$$P(S_c) = \frac{e^{-\beta E_c}}{Z} \quad (1)$$

where Z is the partition function

$$Z = \sum_c e^{-\beta E_c} \quad (2)$$

and $\beta = 1/T$.

The internal energy is

$$U = \sum_c E_c P(S_c) = \frac{1}{Z} \sum_c E_c e^{-\beta E_c} \quad (3)$$

The entropy is

$$S = - \sum_c P(S_c) \log P(S_c) \quad (4)$$

$$= - \sum_c \frac{e^{-\beta E_c}}{Z} \log \left(\frac{e^{-\beta E_c}}{Z} \right) \quad (5)$$

$$= - \sum_c \frac{e^{-\beta E_c}}{Z} (-\beta E_c - \log Z) \quad (6)$$

$$= \log Z \left(\sum_c \frac{e^{-\beta E_c}}{Z} \right) + \beta \left(\sum_c \frac{E_c e^{-\beta E_c}}{Z} \right) \quad (7)$$

$$= \log Z + \beta U \quad (8)$$

The free energy is

$$F = U - TS \quad (9)$$

$$= U - T(\log Z + \beta U) \quad (10)$$

$$= -T \log Z \quad (11)$$