Entropy and Probability

probability distribution $P(s)$

$$P(s) \geq 0 \quad \text{for all } s$$

$$\sum_s P(s) = 1$$

entropy: $S \equiv -\sum_s P(s) \log P(s)$ (Gibbs 1878)

If a probability distribution $P(s,s')$ is the product of two independent probability distributions $P_A(s)$ and $P_B(s')$

then S is the sum of their entropies

verify: $S = -\sum_{ss'} P(s,s') \log P(s,s')$

$$= -\sum_{ss'} P_A(s)\, P_B(s') \log\left[P_A(s)\, P_B(s')\right]$$

$$= -\sum_{ss'} P_A(s)\, P_B(s')\left(\log P_A(s) + \log P_B(s')\right)$$

$$= -\sum_s P_A(s) \log P_A(s) \cdot \sum_{s'} P_B(s') - \sum_s P_A(s) \sum_{s'} P_B(s') \log P_B(s')$$

$$= S_A \cdot 1 + 1 \cdot S_B$$

$$= S_A + S_B$$

Microcanonical ensemble with energy U

$$P(s) = \frac{1}{\Omega(U)} \quad \text{if } U_s = U$$
$$= 0 \quad \text{if } U_s \neq U$$

$$S = -\sum_s P(s) \log P(s)$$

$$= -\sum_{s:U_s=U} \frac{1}{\Omega(U)} \log \frac{1}{\Omega(U)}$$

$$= -\frac{1}{\Omega(U)} \left[-\log \Omega(U)\right] \sum_{s:U_s=U} 1$$

$$= \frac{1}{\Omega(U)} \log \Omega(U) \cdot \Omega(U)$$

$$= \log \Omega(U)$$

Canonical ensemble with temperature T

$$P(s) = \frac{1}{Z} e^{-\beta U_s} \qquad \beta = \frac{1}{T}$$

$$Z = \sum_s e^{-\beta U_s}$$

$$S = -\sum_s P(s) \log P(s)$$

$$= -\sum_s \frac{1}{Z} e^{-\beta U_s} \log\left(\frac{1}{Z} e^{-\beta U_s}\right)$$

$$= -\frac{1}{Z} \sum_s e^{-\beta U_s} \left(-\log Z - \beta U_s\right)$$

$$= \frac{1}{Z} \log Z \sum_s e^{-\beta U_s} + \frac{\beta}{Z} \sum_s U_s e^{-\beta U_s}$$

$$= \frac{1}{Z} \log Z \cdot Z + \beta \cdot \bar{U}$$

$$= \log Z + \beta \bar{U}$$

$$= -\beta F + \beta \bar{U}$$

$$= -\beta (F - \bar{U})$$

$$\Longrightarrow \quad F = \bar{U} - ST$$