$$\Omega = \frac{N!}{\prod_i (n_i!)} \Longrightarrow \ln(\Omega) = \ln(N!) - \sum_i \ln(n_i!)$$

Stirling's Approximation

$$\ln(\Omega) \simeq N\ln(N) - N - \sum_i \left[n_i \ln(n_i) - n_i \right]$$

$$= N\ln(N) - \cancel{N} - \sum_i n_i \ln(n_i) + \underbrace{\sum_i n_i}_{\cancel{N}}$$

$$= N\ln(N) - \sum_i n_i \ln(n_i)$$

Replace $n_i = p_i N$

$$= N\ln(N) - N\sum_i p_i \ln(p_i N)$$

$$= \cancel{N\ln(N)} - N\sum_i p_i \ln(p_i) - \cancel{N\underbrace{\sum_i p_i}_{1}\ln(N)}$$

$$= -N\sum_i p_i \ln(p_i)$$

$p_i \leq 1$ so $\ln(p_i) < 0$

$$\ln(\Omega) \simeq -N\sum_i p_i \ln(p_i)$$

$$\frac{S}{k_B} = -\cancel{N}^{\,1} \sum_i p_i \ln(p_i) - \lambda\left(\sum_i p_i - 1\right) - \beta\left(\sum_i p_i E_i - U\right)$$

maximize with respect to p_i (or n_i)

$$0 \stackrel{!}{=} \frac{\partial\left(\frac{S}{k_B}\right)}{\partial p_\alpha} = -\sum_i \frac{\partial p_i}{\partial p_\alpha} \ln(p_i) - \sum_i p_i \frac{d \ln(p_i)}{d p_\alpha}$$

$$= \frac{1}{p_i}\frac{dp_i}{dp_\alpha}$$

$$- \lambda\Big(\sum_i \underbrace{\frac{dp_i}{dp_\alpha}}_{\delta_{i\alpha}}\Big) - \beta\Big(\sum_i \frac{dp_i}{dp_\alpha} E_i\Big)$$

$\delta_{i\alpha}$ – Kronecker delta $= \begin{cases} 1 & \text{same} \\ 0 & \text{diff} \end{cases}$

$$0 = -\ln(p_\alpha) - 1 - \lambda - \beta E_\alpha$$

$$\ln(p_\alpha) = -(1+\lambda) - \beta E_\alpha$$

$$p_\alpha = \underbrace{e^{-(1+\lambda)}}_{} \cdot e^{-\beta E_\alpha}$$

choose λ to satisfy unitarity constraint

$$\sum_{\alpha=1}^{\infty} p_\alpha = 1 \Rightarrow e^{-(1+\lambda)} = \frac{1}{Z} = \frac{1}{\sum_i e^{-\beta E_i}}$$

Z is the partition function.

$$P_\alpha = \frac{e^{-\beta E_\alpha}}{\sum_i e^{-\beta E_i}} \Rightarrow \sum_\alpha p_\alpha = \frac{\sum_\alpha e^{-\beta E_\alpha}}{\sum_i e^{-\beta E_i}} \equiv 1$$

$$P_\alpha = \frac{e^{-\beta E_\alpha}}{Z}$$

$$\frac{S}{k_B} = -\sum_i p_i \ln(p_i) - \lambda\left(\sum_i p_i - 1\right) - \beta\left(\sum_i p_i E_i - U\right)$$

$$\frac{\partial S/k_B}{\partial U} = \frac{1}{k_B T} = \beta$$

$$P_\alpha = \frac{e^{-\frac{E_\alpha}{k_B T}}}{Z}$$ Boltzmann's Law

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Average energy U

$$U = \sum_\alpha P_\alpha E_\alpha = \frac{\sum_\alpha E_\alpha e^{-\frac{E_\alpha}{k_B T}}}{Z} = \frac{\sum_\alpha E_\alpha e^{-\beta E_\alpha}}{Z}$$

$$= \frac{\sum_\alpha \left(-\frac{\partial}{\partial \beta} e^{-\beta E_\alpha}\right)}{Z} = \frac{-\frac{\partial}{\partial \beta} \boxed{\sum_\alpha e^{-\beta E_\alpha}}}{Z}$$

$$U = \frac{-\frac{\partial}{\partial\beta} Z}{Z} = -\frac{\partial}{\partial\beta} \ln(Z)$$

Next time

$$\frac{-\ln(Z)}{\beta} = F = A$$

Helmholtz free energy.