Shannon Entropy

Let:

x — variable can attain Ω discrete values x_i

P_i — probability that x acquires a value x_i

$$\sum_{i=1}^{\Omega} P_i = 1$$

Constraints:

$$\langle f(x) \rangle = \sum_{i=1}^{\Omega} P_i f(x_i)$$

Example: microcanonical ensemble

Only energy is conserved

$$P_i = \frac{1}{\Omega}$$

Shannon entropy

$$S = -\sum_{i=1}^{\Omega} P_i \ln P_i$$

comparison: Gibbs entropy $S = -k_B \sum P_i \ln P_i$

P_i — prob. of a microstate

Principle: maximize S subject to $\sum_i P_i = 1$

For microcanonical ensemble need to extremize (maximize):

$$S = -\sum_{i=1}^{\Omega} \left(P_i \ln P_i - \lambda P_i \right)$$

λ — Lagrange multiplier

$$\frac{\partial S}{\partial P_i} = -\left[1 + \ln P_i - \lambda\right]$$

$$\frac{\partial^2 S}{\partial P_i \partial P_j} = -\delta_{ij} \frac{1}{P_i}$$

Since $P_i > 0$ at extremum, S is a maximum:

$$1 + \ln P_i - \lambda = 0$$

$$\Rightarrow P_i = e^{\lambda - 1}$$

where λ is determined by requiring

$$\frac{\partial S}{\partial \lambda} = 0 \rightarrow \sum P_i = 1$$

Since P_i are independent of E

$$\sum P_i = \Omega e^{\lambda - 1} = 1$$

$$\Rightarrow e^{\lambda - 1} = \frac{1}{\Omega}$$

$$\Rightarrow P_i = \frac{1}{\Omega}$$

In fact, $S = -\sum_{i=1}^{\Omega} P_i \ln P_i$ (previous page)

$$\Rightarrow S = -\sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = + \ln \Omega$$

For Canonical Ensemble: let $\underset{f(x_i)}{A}$ - extensive variable

If there are other constraints, need to impose them as well

$$S' = -k_B \sum_{i=1}^{\Omega} \left(P_i \ln P_i - \lambda P_i + \beta P_i f(X_i)\right)$$

Maximizes S' with respect to P_i $\Big\}$ $\frac{\partial S'}{\partial P_i} = -k_B\left[\ln P_i + 1 - \lambda + \beta f(X_i)\right] \to 0$

$$P_i = \exp\left[\lambda - 1 - \beta f(x_i)\right]$$

$$\left.\begin{array}{l} \sum P_i = 1 \\ \Rightarrow e^{\lambda-1} \underbrace{\sum e^{-\beta f(x_i)}}_{Z(\beta)} = 1 \end{array}\right\} \quad P_i = \frac{1}{Z} e^{-\beta f(x_i)}$$

Thus, $Z(\beta) = \sum_i e^{-\beta f(x_i)} = e^{1-\lambda}$

$$\langle f \rangle = \sum_i P_i f(x_i)$$

$$\langle f \rangle = e^{\lambda-1} \sum f(x_i) e^{-\beta f(x_i)}$$

leads to $\langle f \rangle = -\frac{\partial \ln Z}{\partial \beta}$

where $f(x_i) \to$ energy $\beta = \frac{1}{T}$

and $1 - \lambda = -\beta A$

* In previous definitions

(i) Entropy depends on δE for small systems

(ii) Entropy is a fluctuating state variable — as in canonical ensemble

* In this definition

(i) Entropy f_n of P_i — no concept of fluctuation since nothing to do with state

(ii) Unambigous for any size

(iii) P_i can be time-dependent — no requirement of equilibrium

Grand Canonical Ensemble

Let $A = \underbrace{A_1 + A_2}_{\text{can exchange } E,\, N}$

$$\begin{cases} E_0 = E_1 + E_2 \\ N_0 = N_1 + N_2 \end{cases}$$

$$\Omega(E_0, N_0) = \sum_{N_1=0}^{N} \int_{E_0 < E < E_0 + \delta E} \frac{dE}{\delta E} \int \frac{dE_1}{\delta E} \Omega_1(E_1, N_1)\, \Omega_2(E - E_1; N_0 - N_1)$$

Each subsystem: Ω_i sharply peaked

$E_1 = \overline{E}_1; \quad N_1 = \overline{N}_1$

Here $S_1(E_1, N_1) + S_2(E_0 - E_1, N_0 - N_1)$ maximum

Extremum:

$\frac{\partial}{\partial E_1}: \Rightarrow \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)_{E_1 = \overline{E}_1} = 0$

$$\Rightarrow \boxed{\frac{1}{T_1} = \frac{1}{T_2}}$$

$\frac{\partial}{\partial N_1}: \Rightarrow \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right)_{N_1 = \overline{N}_1} = 0$

$$\Rightarrow \boxed{\frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}}$$

when $A_2 \gg A_1$, so that $E_1 \ll E_0$, $N_1 \ll N_0$

$\Downarrow$

expand around E_0, N_0