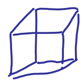
Entropy maximization (Maximum Entropy principle)



6 faces

$\boxed{p_i = 1/6}$ $i \in (1, 6)$ → Unbiased probability.

when only constraint is $\sum_{i=1}^{6} p_i = 1$.

Case of non-uniform (biased) Probability :

function : $f(\{p_i\}) = S/Nk_B = -\sum_{i=1}^{t} p_i \ln p_i$

Constraints : $g(\{p_i\}) = \sum_{i=1}^{t} p_i - 1 = 0$

$h(\{p_i\}) = \sum_{i=1}^{t} \epsilon_i p_i - \epsilon = 0$ ... $\epsilon = \sum_{i=1}^{t} \epsilon_i p_i$

Maximize $f(\{p_i\}) = S/Nk_B$

keeping g & h intact.

$$\mathcal{L} = f - \lambda g - \beta h$$ ..... A new multiplier for each constraint

$$= -\sum_{i=1}^{t} p_i \ln p_i - \lambda\left(\sum_{i=1}^{t} p_i - 1\right) - \beta\left(\sum_{i=1}^{t} \epsilon_i p_i - \epsilon\right)$$

$$\frac{\partial \mathcal{L}}{\partial p_j} = 0 = -(1 + \ln p_j) - \lambda - \beta \epsilon_j$$

$$\Rightarrow \ln p_j = -1 - \lambda - \beta \epsilon_j$$

$$\Rightarrow p_j = e^{-1-\lambda} \cdot e^{-\beta \epsilon_j}$$

p_j: Probability of j^{th} face

$e^{-\beta \epsilon_j}$ → depends of j

p_j turns out to be non-uniform

Normalize p_j: $\mathcal{N} = \sum_{j=1}^{t} p_j$

$$= e^{-1-\lambda} \sum_{j=1}^{t} e^{-\beta \epsilon_j}$$

Normalized $p_j = \dfrac{e^{-1-\lambda} \cdot e^{-\beta \epsilon_j}}{e^{-1-\lambda} \sum_{j=1}^{t} e^{-\beta \epsilon_j}}$

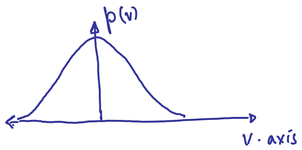
$$p_j = \frac{e^{-\beta \epsilon_j}}{\sum_{j=1}^{t} e^{-\beta \epsilon_j}}$$ "Maxwell-Boltzmann distribution"

$$\mathcal{N} = \sum_{j=1}^{t} e^{-\beta \epsilon_j} = Z(\beta)$$

$p_j = \frac{1}{t}$ "Uniform probability" $\sum_{i}^{t} p_i = 1$ $\rightarrow$ One Constraint	$p_j = \frac{e^{-\beta \epsilon_j}}{\sum_{i=1}^{t} e^{-\beta \epsilon_j}}$ "Non-uniform probability" $\left. \begin{array}{l} \sum_{i}^{t} p_i = 1 \\ \sum_{i}^{t} \epsilon_i p_i = \epsilon \end{array} \right\}$ two constraints

Case of continuos probabilities: One dimensional ideal gas

At temperature T



$\langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}k_B T$ "Equipartition theorem"

$p(v) = ?$ " Unknown "

(i) function to maximize : $\underline{\underline{S}} = -\int_{v=-\infty}^{+\infty} p(v) \ln p(v)\, dv$

(ii) $p(v)$ is normalized : $\underline{\underline{g}} = \int_{v=-\infty}^{+\infty} p(v)\, dv - 1 = 0$

(iii) Equipartition theorem: $\langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}k_B T$

we get.. $\underline{\underline{h}} = \underbrace{\int_{v=-\infty}^{+\infty} \left(\frac{1}{2}mv^2\right) p(v)\, dv}_{\langle \frac{1}{2}mv^2 \rangle} - \frac{1}{2}k_B T = 0$

$$\mathcal{L} = f - \lambda g - \beta h$$

$$= -\int_{v=-\infty}^{+\infty} p(v) \ln p(v)\, dv - \lambda\left(\int_{v=-\infty}^{+\infty} p(v)\, dv - 1\right) - \beta\left(\int_{-\infty}^{+\infty} p(v) \frac{1}{2}mv^2\, dv - \frac{k_B T}{2}\right)$$

$$\frac{\partial L}{\partial p(v)} = -\int_{v=-\infty}^{+\infty} \left[1 + \ln p(v) + \lambda + \beta \frac{mv^2}{2}\right] dv = 0$$

... integral is zero for any arbitrary integrand.

$$1 + \ln p(v) + \lambda + \beta \frac{mv^2}{2} = 0$$

$$p(v) = e^{-1-\lambda} \cdot e^{-\beta mv^2/2}$$

"Non uniform PDF".

Normalizing: $N = \int_{-\infty}^{+\infty} p(v)\, dv = e^{-1-\lambda} \sqrt{\frac{2\pi}{\beta m}}$

Velocity distribution: $p(v) = e^{-\beta mv^2/2} \cdot \sqrt{\frac{m}{2\pi k_B T}}$

"Maxwell-Boltzmann distribution of velocities"