CHAPTER 5 – ENTROPY

$S = k \ell n W, \quad k = 1.38 x 10^{-23} J/K$

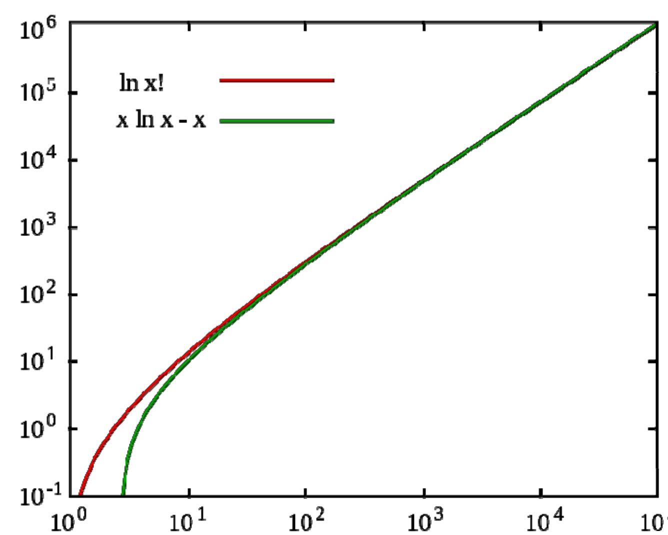
Why this functional form?

$$\Gamma(n) = (n-1)! = \int_0^\infty x^{n-1} e^{-x} dx$$

Recall $W = \dfrac{N!}{n_1! n_2! \ldots n_t!}$

The gamma function

Stirling's approximation $x! \approx \left(\dfrac{x}{e}\right)^x$ for large *x*



Then
$$W \approx \frac{(N/e)^N}{(n_1/e)^{n_1}(n_2/e)^{n_2}\ldots(n_t/e)^{n_t}}$$

$$= \frac{N^N}{(n_1)^{n_1}(n_2)^{n_2}\ldots(n_t)^{n_t}} = \frac{1}{\left(\frac{n_1}{N}\right)^{n_1}\left(\frac{n_2}{N}\right)^{n_2}\ldots\left(\frac{n_t}{N}\right)^{n_t}}$$

$$= \frac{1}{(p_1)^{n_1}(p_2)^{n_2}\ldots(p_t)^{n_t}}$$

$$\ell n W \approx -\ell n (p_i)^{n_1} - \ell n (p_2)^{n_2} - \ldots \ell n (p_t)^{n_t}$$

$$= -n_1 \ell n p_1 - n_2 \ell n p_2 - \bullet\bullet\bullet n_t \ell n p_t = -\sum_{i=1}^{t} n_i \ell n p_i$$

$$\frac{1}{N} \ell n W = -\sum_{i=1}^{t} p_i \ell n p_i = \frac{S_N}{Nk} = -\sum_{i=1}^{t} n_i \ell n p_i$$

$$\boxed{S = k \ell n W = -k \Sigma p_i \ell n p_i}$$

k = entropy per particle

$$S = R \ell n W, \qquad R = \eta k$$

R: entropy per mole

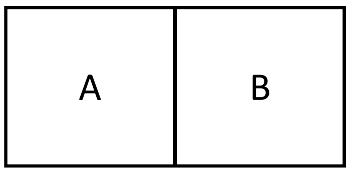
η: Avogadro's constant

$S_N =$ total entropy,

$S = \frac{S_N}{N} =$ entropy per trial

perfectly ordered state: *S = 0*
most random state: highest entropy

Consider a system that we divide into two parts, A and B



Whatever definition we use for Entropy, it has to obey $S_{tot} = S_A + S_B$

We already know that $W_{tot} = W_A W_B$

If we define $S = k\ell nW$

$$\ell nW_{tot} = \ell nW_A W_B = \ell nW_A + \ell nW_B$$

$$\Rightarrow S_{tot} = S_A + S_A$$

Biased *vs*. nonbiased (flat) distributions

many rolls of die expect avg to be $\frac{1+2+3+4+5+6}{6} = 3.5$

If you measure 3.5, the distribution could be flat (but it is not necessarily so)

If you get an average $\neq$ 3.5, it is **not** flat

If there are no constraints other than normalization, max entropy $\Rightarrow$ flat distribution

$$\sum_{i=1}^{t} p_i = 1 \rightarrow \sum dp_i = 0 \quad \longleftarrow$$ Normalization

$$S = -k \sum p_i \ell n p_i$$

for simplicity, set *k = 1*

$$\Lambda = -\sum p_i \ell n p_i - \alpha \left(\sum p_i - 1 \right)$$

α is the Lagrange multiplier

$$\frac{d\Lambda}{dp_i} = 0 = -\ell n p_i - 1 - \alpha \qquad \forall\, i$$

$$\ell n p_i{*} = -1 - \alpha \qquad p_i{*} = e^{(-1-\alpha)}$$

$$\sum p_i{*} = t e^{(-1-\alpha)} \Rightarrow \frac{p_i{*}}{\sum p_i{*}} = \frac{1}{t}$$

all p_i* equally probable $\Rightarrow$ flat distribution

Now consider introducing a bias

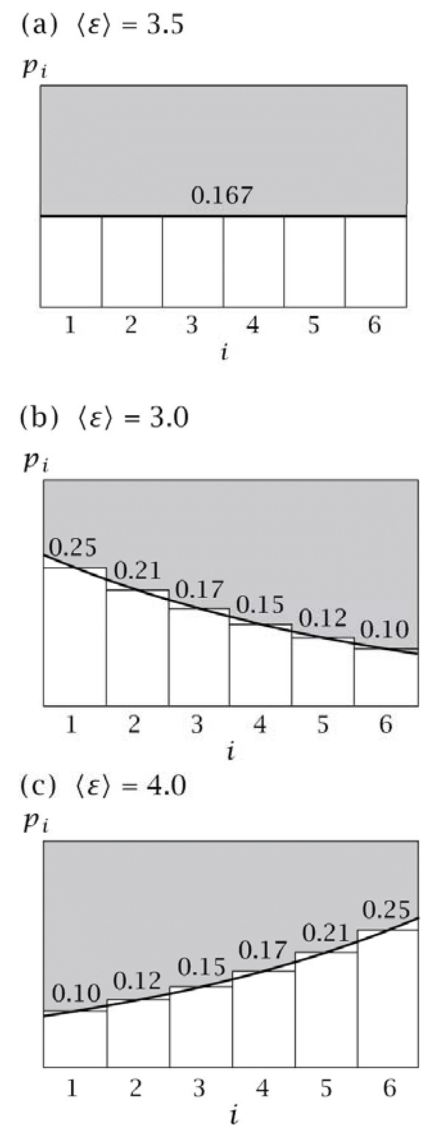
suppose the six sides of the die have numbers
$\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6$

$$E = \sum_{i=1}^{t} \varepsilon_i n_i = \text{ total \#}$$

$$p_i = \frac{n_i}{N}$$

$$\frac{E}{N} = \sum \varepsilon_i p_i = \langle \varepsilon \rangle$$

Also $\sum p_i = 1$



$$\Lambda = -\sum p_i \ell n p_i - \alpha\left[\sum p_i - 1\right] - \beta\left[\sum \varepsilon_i p_i - \langle \varepsilon \rangle\right]$$

Now have two constraints

$$\frac{d\Lambda}{dp_i} = -\ell n p_i - 1 - \alpha[1] - \beta[\varepsilon_i] = 0$$

$$\ell n p_i{}^* = -1 - \alpha - \beta\varepsilon_i$$

$$p_i{}^* = e^{-1-\alpha-\beta\varepsilon_i}$$

$$\sum p_i{}^* = \sum e^{-1-\alpha-\beta\varepsilon_i}$$

$$\frac{p_i{}^*}{\sum p_i{}^*} = \frac{e^{-1-\alpha-\beta\varepsilon_i}}{\sum e^{-1-\alpha-\beta\varepsilon_i}}$$

$$\boxed{p_i{}^* = \frac{e^{-\beta\varepsilon_i}}{\sum e^{-\beta\varepsilon_i}}}$$

define $$q = \sum e^{-\beta\varepsilon_i}$$

$$p_i{}^* = e^{-\beta\varepsilon_i} / q$$

Note: β must have units that are the inverse of the units of ε_l. If ε_l has units of energy, $\beta = 1/kT$

$$p_i{}^* = \frac{e^{-\varepsilon_i/kT}}{q}$$

$$\langle \varepsilon \rangle = \sum \varepsilon_i p_i * = \frac{1}{q} \sum \varepsilon_i e^{-\beta \varepsilon_i}$$

Now consider some examples

suppose $\varepsilon_i = i$ (standard die)

$$p_i * = \frac{e^{-\beta \varepsilon_i}}{\sum e^{-\beta \varepsilon_i}} = \frac{e^{-i\beta}}{e^{-1\beta} + e^{-2\beta} + e^{-3\beta} + e^{-4\beta} + e^{-5\beta} + e^{-6\beta}}$$

Let $x = e^{-\beta}$

$$p_i * = \frac{x^i}{x + x^2 + x^3 + x^4 + x^5 + x^6}$$

$$\varepsilon \left(x + x^2 + x^3 + x^4 + x^5 + x^6 \right) = \left(x + 2x^2 + 3x^3 + 4x^4 + 5x^5 + 6x^6 \right)$$

$$\langle \varepsilon \rangle = \frac{x + 2x^2 + 3x^3 + 4x^4 + 5x^5 + 6x^6}{x + x^2 + x^3 + x^4 + x^5 + x^6}$$

if $\langle \varepsilon \rangle = 3.5 \Rightarrow x = 1$

$\Rightarrow p_1 = p_2 = p_3 = p_4 = p_5 = p_6 = 1/6,$ result for unbiased die

Two ways of getting a flat distribution

(1) $\langle e \rangle =$ value expected from uniform distribution

(2) you have no information at all

if $\varepsilon = 3, \quad x = 0.84$

if $\varepsilon = 4. \quad x = 1.19$