3 Counting Microstates (microcanonical ensemble)

Book: p13-17.

Which distribution of particles is the most likely?

From thermodynamics, equilibrium is when entropy is maximised.

Therefore the macrostate is an entropy maximum.

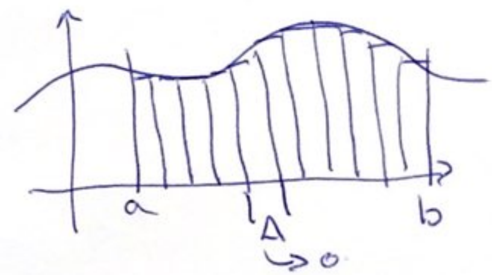
Boltzmann that entropy S is some function of the number of microstates Ω, i.e. $S(\Omega)$.

What form? We know that for independent events Ω is multiplicative, i.e. $\Omega_{AB} = \Omega_A \Omega_B$, ~~not $\Omega_{AB} = \Omega_A + \Omega_B$~~

Boltzmann thought that

$$S = k_B \ln \Omega$$

k_B: Boltzmann constant.



Stirling's Approx

For $N \to \infty$ we have $\ln N! \simeq N \ln N - N \left\{ + O(\ln N) \right\}$

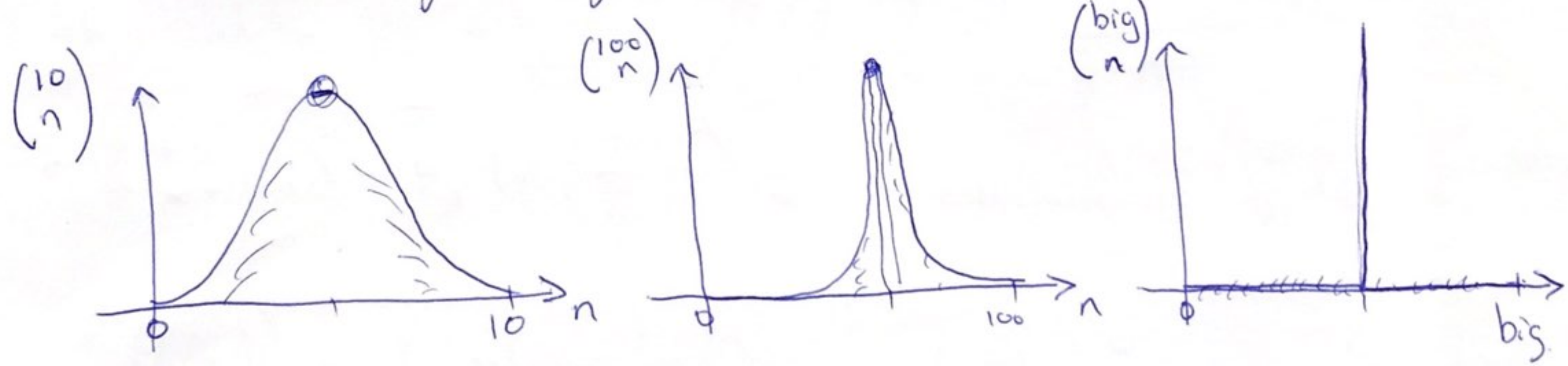
Proof $\underline{\ln N!} = \sum_{k=1}^{N} \ln k \cdot 1 \simeq \int_1^N \ln k \, dk = \left[k \ln k - k \right]_1^N = \underline{N \ln N - N.}$

Sometimes written $N! \simeq \left(N/e\right)^N$

With large numbers, is it a good enough approximation to say that $\Omega \simeq \underline{\Omega(\max\{n_i\})}$?

so $S \simeq S(\max\{n_i\})$.

Not intuitive at first sight.



Let's have states i with energy ε_i and occupation n_i

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \varepsilon_i = U.$$

We want the distribution $\{n_1, n_2, \ldots,\}$

First calculate the entropy: $\Omega(\{n_i\}) = \dfrac{N!}{\prod_i n_i!}$

$$S(\{n_i\}) = k_B \ln\left(\frac{N!}{\prod_i n_i!}\right) \leftarrow \text{a maximum of equilibrium.}$$

$$\frac{S(\{n_i\})}{k_B} = \ln N! - \ln\left(\prod_i n_i!\right) = \ln N! - \sum_i \ln n_i! \quad (\text{log rules}).$$

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

$$\frac{S(\{n_i\})}{k_B} = \sum_i n_i \ln N - \sum_i n_i \ln n_i$$

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

$$\frac{1}{N} \frac{S(\{n_i\})}{k_B} = -\sum_i \frac{n_i}{N} \ln \frac{n_i}{N}$$

Let's define $p_i = n_i/N$ probability particle is in state i (with energy ε_i)

$$\Rightarrow \quad S(\{p_i\}) = -N k_B \sum_i p_i \ln p_i$$

Gibbs expression for entropy

Statistical entropy (Boltzmann)

$$S = k_B \ln \Omega \geq 0$$

Gibbs entropy

$$S(\{p_i\}) = -N k_B \sum_i p_i \ln p_i \geq 0$$

Bridges thermodynamic and probabilistic concepts of entropy.

N being large means $N!$ is huge (really huge!!) - fluctuations are extremely rare - essentially the 2nd law of thermodynamics.

Find the most probable distribution.

[look at video on Lagrangian multipliers]

$$\frac{S(\{n_i\})}{k_B} = N \ln N - \sum_i n_i \ln n_i \quad \leftarrow \text{maximize}$$

with constraints $\underline{\sum_i n_i = N}$ and $\underline{\sum_i n_i \varepsilon_i = U}$.

For these two constraints we introduce 2 Lagrange multipliers (α, β).

and maximise:

$$N \ln N - \sum_i n_i \ln n_i - \alpha \sum_i n_i - \beta \sum_i n_i \varepsilon_i$$

with respect to the occupation numbers of the states, i.e. n_i

We have to take the derivatives $\partial/\partial n_i$ for each i.

$$\frac{\partial}{\partial n_i}\left[N\ln N - \sum_i n_i \ln n_i - \alpha \sum_i n_i - \beta \sum_i n_i \varepsilon_i \right] = 0$$

$$\Rightarrow \quad 0 + \underbrace{(-\ln n_i - 1)}_{\substack{\{\text{only the } i^{th} \\ \text{term survives}\}}} - \alpha\, 1 - \beta\, \varepsilon_i\, 1 = 0$$

$$\Rightarrow \ln n_i = \overbrace{-1-\alpha}^{A} - \beta \varepsilon_i$$

$$\Rightarrow n_i = e^A e^{-\beta \varepsilon_i}$$