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Entropy

Consider a microscopic system described by A where A is some set. The elements of A are called the states of the microscopic system.

Suppose that A is related to a macroscopic system B where B is some set. The elements of B are called the macroscopic states of the system.

Suppose we are given a mapping $f : A \to B$

where for every microscopic state there is a uniquely defined macrostate and that in general there are a finite number of microstates that correspond to a given macrostate

Let $\Omega_f : B \to \mathbb{N}$ be the number of microstates that correspond to a given macrostate.

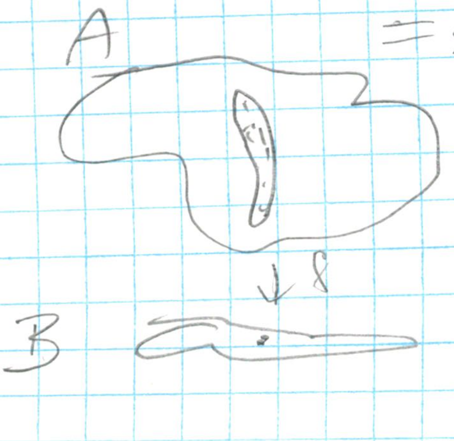
$$\forall\, b : B \bullet \Omega_f(b) = \#\{a : A \mid f(a) = b\}$$

i.e. $f^{\sim}(\{b\}) \in \mathbb{F}A$

The Boltzman entropy $S_f : B \to \mathbb{R}$

$$\forall\, b : B \bullet\ S_f(b) = k \ln N_f(b)$$

$$= k \ln(\#\{a \mid f(a) = b\})$$



Example 1. N identical particles.
Each particle can occupy some position in a discrete, finite phase space Φ of size d.

Let $\#\Phi = d$ $(\Phi \cong 1..d)$ $\Phi = \{\phi_1, \phi_2, \cdots, \phi_d\}$ be a finite phase space.

Then a microstate is given by a list of N positions in Φ

$$A = \{(a_1, \ldots, a_N) \mid a_i \in \Phi\} = 1..N \to \Phi = \Phi^n$$

$$A = \{a : 1..N \to \Phi\}$$

so $A = \Phi^N$ and $\#A = d^N$

Let the macrostates be the set of all counts of particles in each cell of Φ

$B = \Phi \to \mathbb{N}$ with the constraint

that $\sum_{i=1}^{d} n(\phi_i) = N$ $\quad n : \Phi \to \mathbb{N}$

i.e. $B \cong \{(n_1, n_2, \ldots, n_d) \mid n_1 + n_2 + \ldots + n_d = N\}$

n is the occupancy number of each phase space cell.

The map $f : A \to B$ forgets the microscopic details.

$$f : \Phi^N \to (\Phi \to \mathbb{N})$$

let $a \in A = \Phi^N$, $\phi \in \Phi$

$$f_a(\phi) = \sum_{i=1}^{N} \delta(a_i, \phi)$$

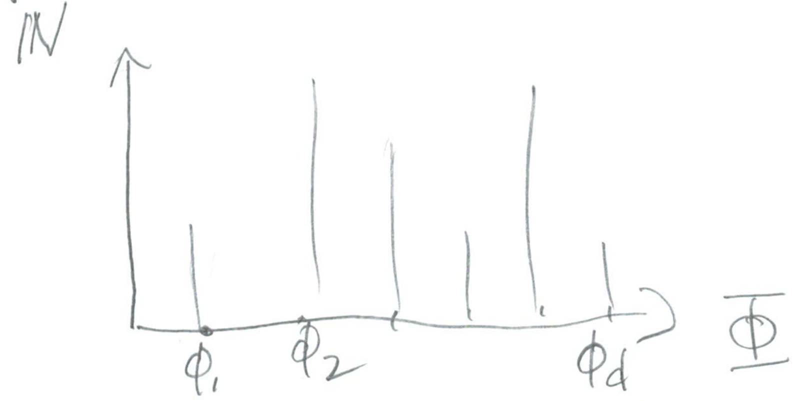
where $\delta : \Phi \times \Phi \to \mathbb{N}$ is defined by

$\forall\ \phi, \phi' \in \Phi$

$$\delta(\phi, \phi') = \begin{cases} 1 & \text{if } \phi = \phi' \\ 0 & \text{if } \phi \neq \phi' \end{cases}$$

This is the Kronecker delta function.

f_a is the histogram on Φ defined by the dataset a



Given a histogram $n : \Phi \to \mathbb{N} \in B$

Compute its Boltzman entropy S

Let's call the triple (A, B, f) a <u>statistical system</u>.

$$A \xrightarrow{f} B \qquad \forall b \in B \ f^{-1} b \text{ is finite.}$$

An arrow is a pair (r, s) such that the following diagram is commutative.

$$\begin{array}{ccc} A & \xrightarrow{r} & C \\ \downarrow f & & \downarrow g \\ B & \xrightarrow{s} & D \end{array}$$

Given the macroscopic state $(n_1, n_2, \ldots, n_d)$ where $\sum n_i = N$

Compute the entropy.

The number of microstates Ω is as follows.

One micro state is

$$(\underbrace{1, 1, \ldots, 1}_{n_1}, \underbrace{2, 2, \ldots, 2}_{n_2}, \ldots, \underbrace{d, d, \ldots, d}_{n_d})$$

we can permute this $N!$ ways but there is a lot of duplication. The number of unique states is

$$\Omega = \frac{N!}{n_1! \, n_2! \cdots n_d!}$$

which is the multinomial coefficient.

$$\ln \Omega = \ln N! - \sum_{i=1}^{d} \ln n_i!$$

Now consider the case where N is large and each of n_i is large. Use Stirling's approximation for $n!$.

$$n! \sim \sqrt{2\pi n} \cdot \left(\frac{n}{e}\right)^n$$

$$\ln n! \sim \frac{1}{2}\ln(2\pi n) + n\ln\left(\frac{n}{e}\right)$$

$$= \frac{1}{2}\ln(2\pi) + \frac{1}{2}\ln(n) + n\ln(n) - n\ln(e)$$

$$= n\ln(n) - n \underbrace{+\frac{1}{2}\ln(n) + \frac{1}{2}\ln(2\pi)}_{\text{neglect these.}}$$

Therefore

$$\ln(\Omega) = \ln(N!) - \sum_{i=1}^{d} \ln(n_i!)$$

$$= N\ln(N) - N - \sum_{i=1}^{d} (n_i \ln n_i - n_i)$$

$$= N\ln(N) - N - \sum_{i=1}^{d} n_i \ln(n_i) + \sum_{i=1}^{d} n_i$$

$$= N\ln(N) - \sum_{i=1}^{d} n_i \ln(n_i)$$

$$= \sum_{i=1}^{d} \left[n_i \ln(N) - n_i \ln(n_i) \right]$$

$$= -\sum_{i=1}^{d} n_i \left[\ln(n_i) - \ln(N) \right]$$

$$= -\sum_{i=1}^{d} n_i \ln\left(\frac{n_i}{N}\right)$$

$$= -N \sum_{i=1}^{d} p_i \ln(p_i)$$ where $p_i = \frac{n_i}{N}$ is the probability

The later expression is the Shannon entropy

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

so $S = k \ln \Omega = kNH$

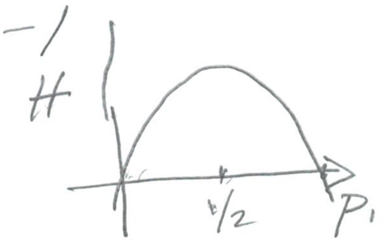
The second law of thermodynamics says that entropy increases for irreversible processes. Therefore a system in thermodynamic equalibrium is in a state of maximum entropy.

Given a discrete probability distribution, what values of p_i maximize Shannon entropy?

At a maximum $\frac{\partial H}{\partial p_i} = 0$ since $\sum p_i = 1$ only $d-1$ are independent.

$$p_1 + \sum_{i=2}^{d} p_i = 1$$

$$p_1 = 1 - \sum_{i=2}^{d} p_i \qquad \frac{\partial p_1}{\partial p_i} = -1$$



$$H = -\sum_{i=1}^{d} p_i \ln p_i$$

$$= -p_1 \ln p_1 - \sum_{i=2}^{d} p_i \ln p_i$$

$$\frac{\partial H}{\partial p_i} = -\left[\frac{\partial p_1}{\partial p_i} \cdot \ln p_1 + p_1 \cdot \frac{1}{p_1} \frac{\partial p_1}{\partial p_i}\right]$$

$$- \left[\ln p_i + 1\right]$$

$$= -\left[-1 \cdot \ln p_1 - 1\right] - \left[\ln p_i + 1\right]$$

$$= \ln p_1 + 1 - \ln p_i - 1$$

$$= \ln p_1 - \ln p_i$$

Therefore $\frac{\partial H}{\partial p_i} = 0 \Rightarrow p_1 = p_i$

Since this holds for all $i = 2, \ldots, d$ we have

$$p_1 = p_2 = \cdots = p_d = \frac{1}{d} \Rightarrow \text{Uniform distribution.}$$

$$H = -\sum p_i \ln p_i = -\frac{1}{d} \sum_i \ln \frac{1}{d} = \ln d$$

Summary For N identical particles in a phase space that has d cells

$$S = k \ln \Omega = k N H$$

where $$H = -\sum_{i=1}^{d} p_i \ln p_i$$

The entropy is maximized when the macroscopic state defines a uniform distribution on the single particle phase space and the maximum entropy is $H = \ln d$

so $$S = k N \ln d$$
$$= k \ln d^N$$
$$= k \ln \# \Phi^N$$

i.e. $\Omega = \#\Phi^N$ which is the whole space!

which says that every microstate defines the unique macrostate which is the state of maximum entropy. This doesn't make sense.

Unless using Stirling's formula is only valid for the case of large n_i and in that case virtually any state, i.e. a randomly chosen microstate results in a uniform distribution. This is probably just a consequence of the law of large numbers. To get a better result, keep more of Stirling's formula.

Do a more accurate calculation of

$$\ln \Omega = \ln(N!) - \sum_{i=1}^{d} \ln(n_i!)$$

$$= \ln N! - \sum_i \left[n_i \ln n_i - n_i + \tfrac{1}{2}\ln(2\pi n_i) \right]$$

$$= N\ln N - N + \tfrac{1}{2}\ln 2\pi N$$

$$- \sum n_i \ln n_i + \underbrace{\sum n_i}_{N} - \sum \tfrac{1}{2}\ln(2\pi n_i)$$

$$= N\ln N - \sum n_i \ln n_i + \underbrace{\tfrac{1}{2}\ln(2\pi N) - \sum \tfrac{1}{2}\ln(2\pi n_i)}_{\tfrac{1}{2}\left(\ln 2\pi N - \sum \ln 2\pi n_i\right)}$$

$$= \underbrace{N\ln N - \sum N p_i \ln N p_i}_{\sum\left[N p_i \ln N - N p_i \ln N p_i\right]}$$

$$\underbrace{\sum\left[N p_i \ln N - N p_i \ln N p_i\right]}_{-N\sum p_i \ln p_i}$$

$$\underbrace{-N\sum p_i \ln p_i}_{NH}$$

$$\ln 2\pi N - \sum \ln 2\pi n_i = \ln 2\pi N - \sum \ln 2\pi N p_i$$

$$= \ln 2\pi + \ln N - \sum\left(\ln 2\pi N + \ln p_i\right)$$

$$= \ln 2\pi N - d\ln 2\pi N - \sum \ln p_i$$

$$= \underbrace{(1-d)\ln 2\pi N - \sum \ln p_i}_{\text{correction term.}}$$

at maximum entropy $p_i = \frac{1}{d}$ so $\ln p_i = -\ln d$

$$\text{so } \ln\Omega = NH + (1-d)\ln 2\pi N + d\ln d$$

$$= N\ln d + (1-d)\ln(2\pi N) + d\ln d$$

$$= (N+d)\ln d + (1-d)\ln(2\pi N)$$

This quantity diverges as $N \to \infty$ & $d \to \infty$

Basically $\Omega \sim d^N$ at maximum entropy.

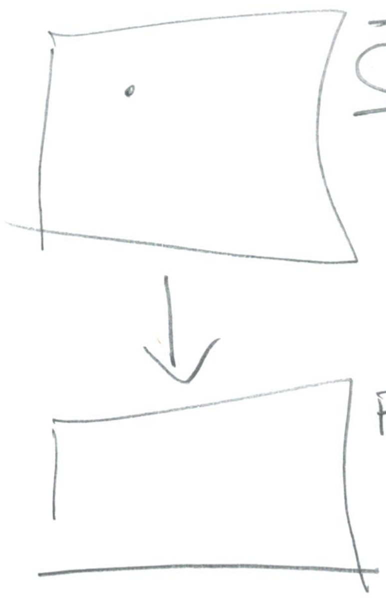
Clearly, we can't simply count states in the case of a continuous phase space.

However, there is a definite thermodynamic definition of entropy

$$dS \underset{rev}{=} \frac{\delta Q}{T}$$ What does this mean?

Instead of counting states, count phase space volume.

micro Φ^N — a finite (but large) dimensional manifold $\sim \mathbb{R}^{6 \times 6.022 \times 10^{23}}$



macro prob(Φ) — an infinite dimensional manifold.

What if a macrostate was a smooth probability distribution on the single particle phase space? Still infinite dimensional

There are two independent aspects of going from micro to macro:

1) permutation symmetry $\rightarrow$ does not reduce dimension
2) averaging over space & time $\rightarrow$ smoothing

Focus on averaging.
Suppose there was a length scale that defined the limit of spatial resolution, and a time scale.
Let $0 < \lambda$ be the length scale
and $0 < \tau$ be the time scale.
We can divide Φ into cells whose dimensions are defined by λ & τ

$\sim \lambda^3 \times \sim \rho^3$ $\quad \rho = \frac{m\lambda}{\tau}$?

?

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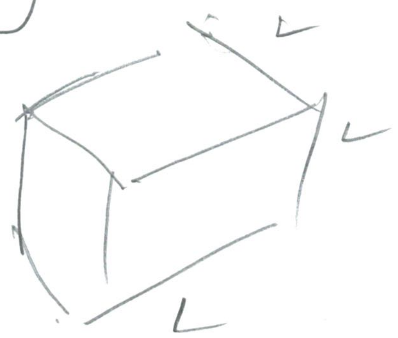
Rather than consider ALL smooth distributions on Φ, perform a Fourier decomposition and cut off the series at some wavelength. This makes $\text{prob}_\lambda(\Phi)$ a finite dimensional space. Define the volume fraction in Φ^N at some energy E.



space is bounded with spatial volume L^3

$$K.E. = \text{kinetic energy} = \sum_{i=1}^{N} \frac{m}{2} v_i^2 = \sum_{i=1}^{N} \frac{p^2}{2m}$$

define temperature $T = \frac{1}{N} K.E.$ = mean kinetic energy.

Given an energy E then the region of Φ^N is like $[0,L]^N \times S_E^{N-1}$

where the radius of the sphere is $R = \sqrt{2mE}$

so $V_E = L^N \cdot C_{N-1} R^{N-1}$ where C_n is the volume of the unit S^{N-1} sphere.

The volume element is $d^N x \wedge \underbrace{d^{N-1}\Omega}_{\text{sphere}} \wedge r^{N-1} dr$

where $r = \sqrt{2mE}$ and $E = \sum_{i=1}^{N} \frac{p_i^2}{2m}$

define $p^2 = \sum_{i=1}^{N} p_i^2 \qquad p = \sqrt{p^2}$