Entropy – From Physics, and Beyond

Eason Shao

Physics Problem Solving Society
St Paul's School

10.02.2025

What is Entropy?

Questions we aim to answer today …

- Does entropy belong to a state (like potential energy), or a process (like heat transferred)?
- What is the formulae(s) for entropy?
- What properties do entropy have?
- How can we intuitively understand entropy?
- What is the unit for entropy?

Famous Formulae about Entropy

These are only a few that I could think of:

- $S = k_{\mathrm{B}} \ln \Omega$,
- $S = -\sum p_i \log_2 p_i$
- $\mathrm{d}S = \dfrac{\delta Q_{\mathrm{rev}}}{T}$,
- $\Delta G = \Delta H - T\Delta S$,

Famous Quotes about Entropy

...We may express in the following manner the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat: the energy of the universe is constant; the entropy of the universe tends to a maximum.
— Rudolf Clausius (1865), Mechanical Theory of Heat

Nature never undertakes any change unless her interests are served by an increase in entropy.
— Max Planck (1903), Article

The increase of disorder or entropy is what distinguishes the past from the future, giving a direction to time.
— Stephen Hawking (1988), A Brief History of Time

Entropy as a mesurement of disorder

To describe 'order' quantitively ...

Definition (Macrostate and Microstate)

- A **macroscopic description** of a system is given by its observable quantities. This defines the **macrostate** of the system.
- A **microscopic description** of a system is given by the states of each individual particle that makes up the system. This defines the **microstate** of the system.
- The **multiplicity** of a **macrostate**, Ω, is the number of microstates corresponding to the given macrostate.

Macrostate and Microstate

Example (Balloon containing Helium)

- The **macrostate** of such balloon can be defined by quantities such as the **pressure** P, **volume** V, and the **temperature** T.

- The **microstate** of such balloon can be defined by the **position** $\vec{x}_i$ and **velocity** $\vec{v}_i$ of the individual molecules:

$$\{(\vec{x}_1, \vec{v}_1), (\vec{x}_2, \vec{v}_2), \ldots\}.$$

- For each (P, V, T), there can be multiple different microstates corresponding to such macrostate.

Remark

For a gas which is not mono-molecular, there is an extra component in each microstate, which is the orientation of the molecule.

Boltzmann's Entropy Formula

Given that all microstates are equally likely …

Definition (Boltzmann's Entropy Formula)

$$S = k_B \ln \Omega,$$

where k_B is the Boltzmann Constant, which is approximiately $1.380649 \times 10^{-23} \, \text{J K}^{-1}$.

Entropy is a property of a state.

This means that if we combine two system A and B together as one system, we will have

$$\begin{aligned}
S_{A+B} &= k_B \ln \Omega_{A+B} \\
&= k_B \ln(\Omega_A \Omega_B) \\
&= k_B \ln \Omega_A + k_B \ln \Omega_B \\
&= S_A + S_B,
\end{aligned}$$

and entropy is additive!

Boltzmann's Entropy Formula – Example

Example

Consider a box where it is split into two halves, and I have four different balls. I use the pair (x, y) where $x + y = 4$ to represent a macrostate observed, when there are x balls on the left half and y balls on the right half.

- What is the multiplicity of the macrostate $(0, 4)$? **1**.
- What about $(1, 3)$ and $(2, 2)$? **4**, **6**.
- How many ways are there to arrange in total? **16**.

The macrostate $(2, 2)$ has the highest entropy, since it has the hightest multiplicity.

It is the most disordered, and we can gain least information on the arrangement of the spheres give a macrostate.

Entropy is a measure of disorder.

Second Law of Thermodynamics

Theorem (Second Law of Thermodynamics)

The entropy of an isolated system alays increases.

It gives a necessary criteria for a **spontaneous process**.

Example

Consider a container with 2 compartments containing 2 different gases, hydrogen and oxygen. We denote this as macrostate A.

After the divider of the 2 compartments is removed, the gases will mix freely. We now denote this as macrostate B.

There are many more ways that the gas molecules can spread themselves over the container.

Therefore, $\Omega_B > \Omega A$, and $S_B > S_A$, entropy increases.

Third Law of Thermodynamics

Theorem (Third Law of Thermodynamics)

For all perfect crystalline substances:

$$\lim_{T \to 0K} S = 0.$$

Proof.

At absolute zero, the only possible configuration for a crystal is for all atoms to stay in place and have no vibration. Therefore, $\Omega = 1$, and $S = 0$. $\square$

Example - Third Law of Thermodynamics

Problem

Suppose a system consisting of a crystal lattice with N identical atoms at $T = 0\text{K}$. An incoming photon is absorbed by the lattice. What is the new entropy, S of the system?

Solution

Since all atoms are identical, there are N possible microstates after absorption (since there is a unique atom that interacts and absorbs the photon), determined by the only excited atom.
This means the new multiplicity of the system is $\Omega = N$, and therefore the new entropy is simply

$$S = k_B \ln \Omega.$$

Why are all microstates equally probable?

They are not. (But Boltzmann is not wrong either.)
In short – Boltzmann Entropy only applies to **isolated systems in global thermodynamical equilibrium**.
In most systems that we want to study, system microstates are not equal probable, since we would like to study **the interaction between the system and the surroundings**, but the system + surrounding microstates are still equally probable like before. (We can show that the system microstates follow a certain distribution.)

Definition (Gibbs Entropy)

$$S_G = -k_B \sum p_i \ln p_i,$$

where p_i is the probability of obtaining a certain microstate.

Gibbs Entropy

Problem

Show that when all p_is are equal, the definition of Gibbs Entropy reduces to the Boltzmann Entropy.

$$S_G = -k_B \sum p_i \ln p_i.$$

Solution

When all p_is are equal, we have $\sum p_i = 1$, therefore $p_i = \frac{1}{\Omega}$.
Plugging this in gives us

$$\begin{aligned}
S_G &= -k_B \sum p_i \ln p_i \\
&= -k_B \cdot \Omega \cdot \left(\frac{1}{\Omega} \cdot \ln \frac{1}{\Omega} \right) \\
&= -k_B(-\ln \Omega) \\
&= k_B \ln \Omega.
\end{aligned}$$

Information Theory

We mentioned that *most disordered state gives us the least information* –
so the higher the entropy, the less the information gained.
Imagine rolling two dice and summing the resuts. Mathematically, consider
independent random variables $X_1, X_2 \sim U(6)$, and let $Y = X_1 + X_2$.
The probability mass function (p.m.f) of Y is as follows:

y	2	3	4	5	6	7	8	9	10	11	12
$36 \cdot \mathbb{P}(Y = y)$	1	2	3	4	5	6	5	4	3	2	1

The less likely an event, the more **surprisal** it gives you, **the more
information you gain**.

Shannon Entropy

Definition (Surprisal of an Event)

For an event $X = i$ for some i, its surprisal is denoted as $\gamma(i)$:

$$\gamma(i) = -\log_2 p_i.$$

Definition (Shannon Entropy)

For a random variable X, its Shannon entropy $H(X)$ is defined as

$$H(X) = \mathbb{E}[\gamma(i)] = \sum p_i \gamma(i) = -\sum p_i \log_2 p_i.$$

Compare this to Gibbs Entropy: $S = -k_B \sum p_i \ln p_i$.

Significance of Shannon Entropy

Problem (Shannon's First Question)

*What is the limit to which information can be **reliably compressed**?*

Theorem (Shannon's Source Coding Theorem)

The limit of reliable compression of N i.i.d. random variables $X_1, X_2, \ldots, X_n \sim X$ each with entropy $H(X)$ is $N \cdot H(X)$ bits.

Data Compression – Example

Problem

There are four horses, A, B, C and D in a particular series of races for horses. The probabilities of individual horses winning, respectively, is as in the table below.

Horse	A	B	C	D
Probability	1/2	1/4	1/8	1/8

- *If we use the random variable X to denote the winner each race, find the Shannon Entropy $H(X)$.*
- *Naturally, we would like to use 2 bits to encode the winner for each race, but Shannon's First Theorem suggests a better encoding. Can you come up with one?*
- *Why is $H(X)$ a fraction number of bits, how does it make sense?*

Black Holes

Black hole seems to have not have an interior, so it probably has only one microstate, and has no entropy

Consider a system of a hot cup of water and a black hole. Now the hot cup of water falls into the black hole.

The entropy **disappeared**.

Entropy of Black Holes

Jacob Bekenstein in 1972 suggested that the entropy of a black hole $S_{\mathrm{BH}} \propto A$, the area of the event horizon.
Stephen Hawking set out to prove him wrong – but in 1974 not only did he found Bekenstein right, he also derived the constant of proportionality!

$$S_{\mathrm{BH}} = \frac{k_{\mathrm{B}} A}{4 \ell_{\mathrm{P}}^2}.$$

But don't we use GR to describe giant stellar objects ..., how is the Planck Length involved here?
How is this related to $S = k_{\mathrm{B}} \ln \Omega$?

Questions we aim to answer in the future ...

- Why is there a constant of k_B before the formula for entropy?
- Why is entropy also a measure of useable energy?
- How are the definitions of the two entropies equivalent?
- Why is the Maxwell-Boltzmann Distribution the one we see?

Just as the constant increase of entropy is the basic law of the universe, so it is the basic law of life to be ever more highly structured and to struggle against entropy.
— Vaclav Havel (1986), Czech playwright, Letter to Dr. Gustav Husak, Living in Truth

References I

[1]   ACuriousMind. *What is the conceptual difference between Gibbs and Boltzmann entropies?* URL: https://physics.stackexchange.com/questions/141321/what-is-the-conceptual-difference-between-gibbs-and-boltzmann-entropies.

[2]   Nilanjana Datta and UK Maths Trust. *Entropy – ubiquitous, enigmatic & unique, UKMT IMO Celebration Lecture 2024.* URL: https://youtu.be/VQ-RoiTU2ns.

[3]   Patch Thomas. *When are all microstates equally probable?* URL: https://physics.stackexchange.com/questions/317563/when-are-all-microstates-equally-probable.

[4]   Mozibur Ullah. *Why did people think that black holes have zero entropy before the works of Bekenstein and Hawking?* URL: https://physics.stackexchange.com/q/667962.

References II

[5] Wikipedia. *Black hole thermodynamics*. URL: https:
     //en.wikipedia.org/wiki/Black_hole_thermodynamics.

[6] Wikipedia. *Boltzmann's entropy formula*. URL: https:
     //en.wikipedia.org/wiki/Boltzmann%27s_entropy_formula.

[7] Wikipedia. *Entropy*. URL:
     https://en.wikipedia.org/wiki/Entropy.

[8] Wikipedia. *Entropy (Statistical Thermodynamics)*. URL:
     https://en.wikipedia.org/wiki/Entropy_(statistical_
     thermodynamics).

[9] Wikipedia. *Second law of thermodynamics*. URL: https:
     //en.wikipedia.org/wiki/Second_law_of_thermodynamics.

[10] Wikipedia. *Shannon's source coding theorem*. URL: https://en.
     wikipedia.org/wiki/Shannon%27s_source_coding_theorem.