

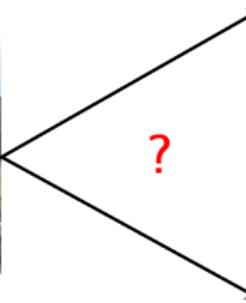
What is Entropy? Some Interesting Information

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What is entropy? Why should I care?



Entropy *is* a confusing concept!



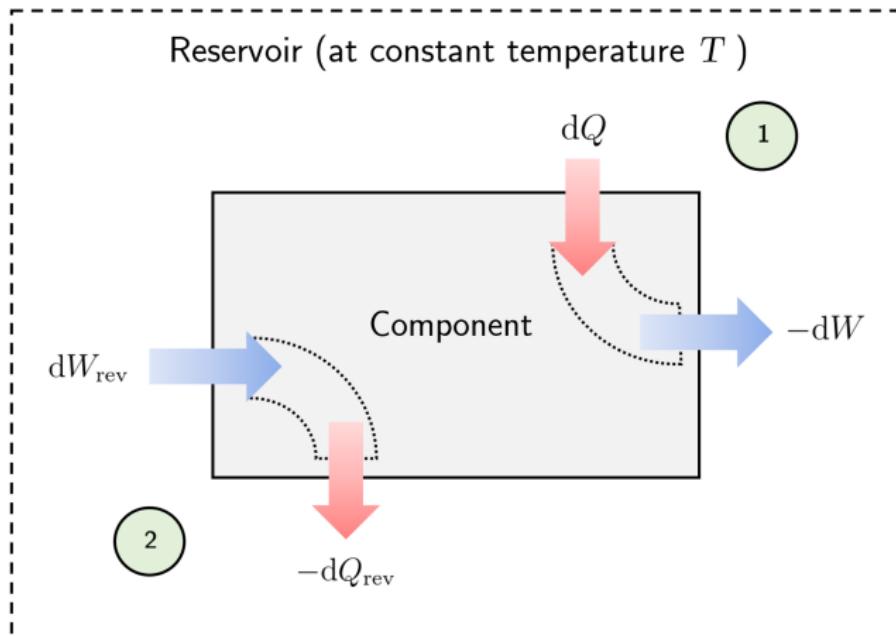
John von Neumann

“...no one knows what entropy *really* is...”

Entropy as “lost work”

System component undergoes a **cycle** consisting of two processes:

1. **Irreversible process:** $dU = dQ - dW$
2. **Reversible process:** $dU_{\text{rev}} = -dQ_{\text{rev}} + dW_{\text{rev}}$



Thermally isolated system

Entropy as “*lost work*” — deriving the idea

- By the first law of thermodynamics (as seen on the previous slide):
 - ▶ Irreversible process: $dU = dQ - dW$
 - ▶ Reversible process: $dU_{\text{rev}} = -dQ_{\text{rev}} + dW_{\text{rev}}$
- The component returns to its initial state upon completing the cycle:
 - ▶ $dU_{\text{net}} = dU + dU_{\text{rev}} = 0 \Rightarrow dQ_{\text{rev}} - dQ = dW_{\text{rev}} - dW$
 - ▶ $dS_{\text{component}} = 0 \Rightarrow dS_{\text{system}} = dS_{\text{reservoir}} = \frac{-dQ}{T} + \frac{dQ_{\text{rev}}}{T}$
- Thus:
$$dS_{\text{system}} = \frac{dQ_{\text{rev}} - dQ}{T} = \frac{dW_{\text{rev}} - dW}{T} \geq 0$$

Entropy as “*lost work*” — stated explicitly

For reference:

$$dS_{\text{system}} = \frac{dQ_{\text{rev}} - dQ}{T} = \frac{dW_{\text{rev}} - dW}{T} \geq 0$$

Entropy = “lost work”

The entropy of a thermally isolated system is a measure of the **thermal energy in the system that becomes unavailable for conversion into work**, due to irreversible thermodynamical interactions among the system's components.

Entropy as “*lost work*” — why the idea is **flawed**

For reference:

$$dS_{\text{system}} = \frac{dQ_{\text{rev}} - dQ}{T} = \frac{dW_{\text{rev}} - dW}{T} \geq 0$$

- Logical leap: entropy *change* (dS) $\not\equiv$ entropy (S)!
- Fundamental misconception: lost work $\equiv TdS \neq dS$!

“The Boltzmann constant k_B is just a dimensional conversion coefficient owing its existence to the fact that historically T is measured in Kelvins rather than in units of energy (as it should have been).”

— A. Schekochihin, *Lectures on Kinetic Theory of Gases and Statistical Physics* (2020)

Entropy as “*disorder*”: ‘macrostates’ and ‘microstates’

Analogy	The Real Thing
<p>System of two coins</p> <p>— Macrostate - - - Microstate</p> <p>Macrostate: State of the two coins in terms of number of heads/tails</p> <p>Microstate: Specific <u>arrangement</u> of heads and tails</p>	<p>System of n particles</p> <p>Macrostate: State of system in terms of its macroscopic properties (i.e., total energy, volume, number of particles)</p> <p>Microstate: Specific <u>configuration</u> of positions and momenta of the particles</p> $\{(x_1, p_1), (x_2, p_2), \dots, (x_n, p_n)\}$

Key Idea: Any particular macrostate corresponds to, or emerges from, one or more microstate(s).

Entropy as “*disorder*”: Boltzmann’s entropy

According to Boltzmann (or Planck, really):

$$S = k_B \ln \Omega$$



Boltzmann’s formulation of entropy (in words)

The entropy of a system in a *fixed macrostate* is directly proportional to the natural logarithm of the **number of possible microstates associated with the macrostate**.

Entropy as “*disorder*”: the association explained

For reference:

$$S = k_B \ln \Omega$$

Disorder \equiv lack of *structural restraint* on the *atomic level*

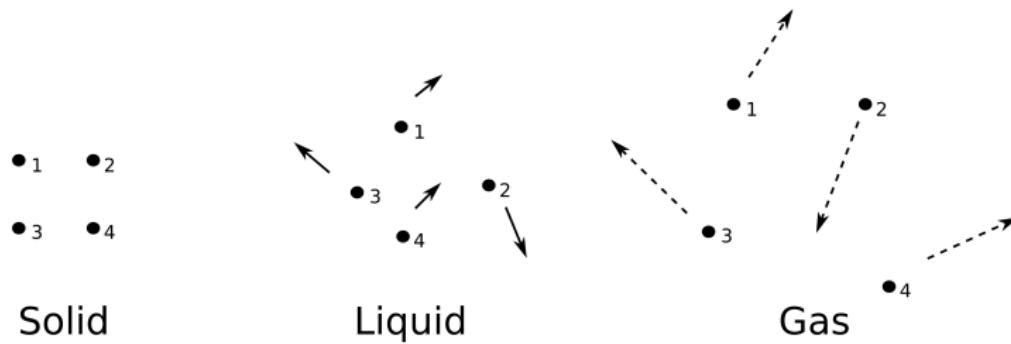


Image Source

Entropy as “*disorder*”: why the association is **not** ideal

- Entropy-driven *order* exists!
- Entropy \equiv disorder *only in a specific sense*.
- ‘Disorder’ is a *subjective* concept.
- Entropy is additive, disorder **isn’t**:

$$S = k_B \ln \Omega$$

$$S = k_B \ln \Omega$$

$$S_{\text{total}} = 2 \times k_B \ln \Omega = 2S \quad \checkmark \quad \cdot \quad \text{disorder}_{\text{combined system}} = 2 \times \text{disorder}_{\text{each system}} \quad ?$$

Entropy as “*missing information*”: Gibbs’ entropy

According to Gibbs, the entropy of a general system is:

$$S = -k_B \sum_{i=1}^m p_i \ln p_i$$

m : number of accessible microstates

p_i : probability that the system is in the i^{th} microstate

Gibbs’ formulation of entropy (in words)

The entropy of a system measures the size of the **missing information** required to specify the microstate of the system at any instant.

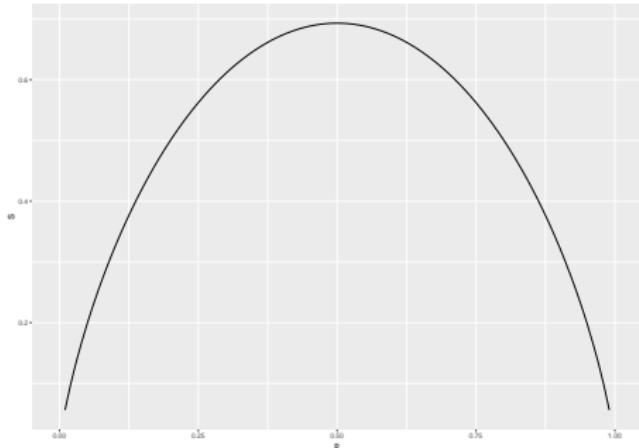
Entropy as “*missing information*”: capturing the intuition

- (For reference) Gibbs' entropy:

$$S = -k_B \sum_{i=1}^m p_i \ln p_i$$

- S is maximised when $p_1 = p_2 = \dots = p_m$.

- ▶ Read: if all microstates are equiprobable, the *uncertainty* about the actual microstate is maximised.



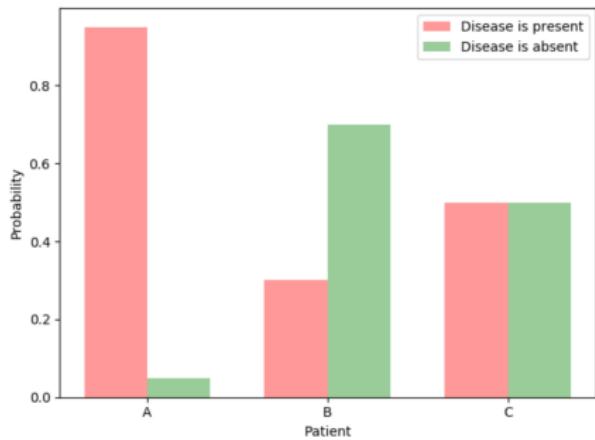
Plot of $S = -p \ln p - (1-p) \ln(1-p)$, i.e., Gibbs' entropy (divided by k_B) when $m = 2$. Notice that S reaches its maximum value at $p = p_1 = p_2 = 0.5$.

Entropy as “*missing information*”: grasping the intuition

- (For reference) Gibbs' entropy:

$$S = -k_B \sum_{i=1}^m p_i \ln p_i$$

- The more skewed the probability distribution is, the lower the value of S .
 - ▶ Read: the more likely some microstates are than others, the less information needed to specify the actual microstate of the system.



A simple illustration. Which of the three patients is confronted with the greatest degree of uncertainty? (Answer: **Patient C**)

Image Source

Entropy as “*missing information*”: *strengthening* the intuition

- (For reference) Gibbs' entropy:

$$S = -k_B \sum_{i=1}^m p_i \ln p_i$$

- If one of the p_i 's equals 1 (\therefore the other p_i 's equal 0), then $S = 0$.
 - ▶ Read: if the system is in one particular microstate with *absolute* certainty, then there is *no* missing information about the actual microstate of the system.

Entropy as “*missing information*”: mastering the intuition

- (For reference) Gibbs' entropy:

$$S = -k_B \sum_{i=1}^m p_i \ln p_i$$

- As m increases, so does S , *ceteris paribus*.

- ▶ Read: in general, the greater the number of accessible microstates, the greater the uncertainty about the actual microstate.

Entropy as “*missing information*”: the physical intuition

The *physical* intuition, explained beautifully:

“...the velocities of particles become correlated when they scatter, but over time the information of their correlations disperses over phase space and is lost. A solid has lower entropy than a gas because we have more information about the location of the atoms.”

— Matthew Schwartz, *Lecture notes for Statistical Mechanics* (Harvard, Spring 2019)

Entropy as “*missing information*”: why it works

- The concept of missing information is **precise** and **quantitative**, unlike ‘disorder’.
- The concept of missing information **refers to entropy itself**, not entropy *change*. This is unlike ‘lost work’.
- If history had been different, the mathematical expression for entropy would not contain k_B , and entropy would *be* the size of the missing information!

In conclusion...

- ♠ “Lost work” and “disorder” are *not* ideal interpretations of entropy.
- ♠ I have tried to convince you that

The **entropy** of a system measures the size of the **missing information** required to specify the microstate of the system at any instant.

♠ Thank you for listening! 😊

* Remember: Questions are optional!

Appendix: The origin of Clausius' entropy

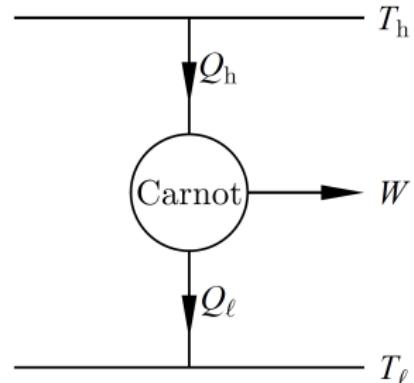
- For a Carnot cycle: $\frac{Q_h}{Q_\ell} = \frac{T_h}{T_\ell}$
- If we define ΔQ_{rev} as the heat *entering* the Carnot engine at each point, and T as the temperature of the point of thermal contact, we then obtain

$$\sum_{\text{cycle}} \frac{\Delta Q_{\text{rev}}}{T} = \frac{Q_h}{T_h} + \frac{(-Q_\ell)}{T_\ell} = 0$$

- Replacing the sum with an integral around the closed path described by the Carnot cycle, we obtain:

$$\oint \frac{dQ_{\text{rev}}}{T} = 0$$

← Important!



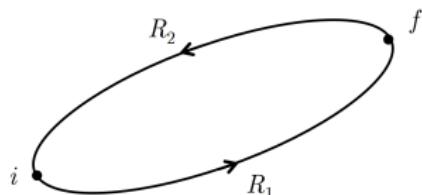
(Blundell & Blundell, 2009)

A cycle describes a *closed* path on the pV diagram. A *Carnot* cycle describes a closed *and reversible* path on the pV diagram.

Any system undergoing the Carnot cycle is in thermodynamic equilibrium throughout the cycle. The subscript 'rev' in ' ΔQ_{rev} ' serves as a reminder of the **reversibility** of the process.

Appendix: The origin of Clausius' entropy

- Consider the following reversible cycle (Bain, 2019):



- Start in initial state i .
- Take reversible path R_1 to final state f .
- Return to initial state via reversible path R_2 .

- We can write $\oint \frac{dQ_{\text{rev}}}{T} = \int_{R_1}^f \frac{dQ_{\text{rev}}}{T} + \int_{R_2}^i \frac{dQ_{\text{rev}}}{T} = 0$
- Thus: $\int_{R_1}^f \frac{dQ_{\text{rev}}}{T} = - \int_{R_2}^i \frac{dQ_{\text{rev}}}{T} = \int_{R_2}^f \frac{dQ_{\text{rev}}}{T}$
- So: $\int_i^f \frac{dQ_{\text{rev}}}{T}$ is *path-independent!*

Appendix: The origin of Clausius' entropy

- $\int_i^f \frac{dQ_{\text{rev}}}{T}$ is path-independent $\Rightarrow \frac{dQ_{\text{rev}}}{T}$ can be thought of as the differential of a *function of state* which Clausius denoted as ' S '.
- Therefore:
$$dS = \frac{dQ_{\text{rev}}}{T}$$

Clausius' Theorem (CT)

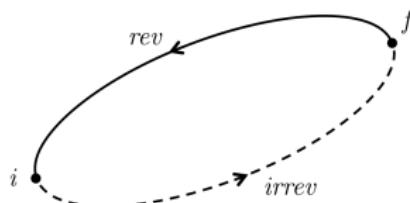
For **any** cycle, $\oint \frac{dQ}{T} \leq 0$. (Equality if cycle is reversible[†].)

$${}^{\dagger} \therefore \text{reverse cycle and CT} \Rightarrow \oint \frac{(-dQ_{\text{rev}})}{T} \leq 0 \Rightarrow \oint \frac{dQ_{\text{rev}}}{T} \geq 0 \stackrel{\text{CT}}{\Rightarrow} \oint \frac{dQ_{\text{rev}}}{T} = 0.$$

This is *exactly* what we obtained previously.

Appendix: How entropy *never* decreases

- Consider the following cycle (Bain, 2019):



- Irreversible cycle consisting of an irreversible process from i to f , followed by a reversible process from f back to i .

- Apply CT: $\oint \frac{dQ}{T} = \int_i^f \frac{dQ}{T} + \int_f^i \frac{dQ_{\text{rev}}}{T} \leq 0$
- Thus: $\int_i^f \frac{dQ}{T} \leq - \int_f^i \frac{dQ_{\text{rev}}}{T} = \int_i^f \frac{dQ_{\text{rev}}}{T} = \int_i^f dS = \Delta S$
- Now: For a thermally isolated system, $dQ = 0$, so: $\boxed{\Delta S \geq 0}$

Appendix: How ‘entropy’ came into existence

- In words: The S of a thermally isolated system either increases (irreversible process) or stays the same (reversible process).
 - ▶ If the *universe* is a thermally isolated system, then S_{universe} can *only* increase or stay the same! (Read: it **never** decreases!)
- Clearly — as Clausius realised — S is a *very* special quantity. (on the same level of significance as energy.)

*“I prefer going to the ancient languages for the names of important scientific quantities, so that they mean the same thing in all modern languages. I propose, accordingly, to call S the **entropy** of a body, after the Greek word for ‘transformation’. I have intentionally coined the word ‘entropy’ to be similar to ‘energy’, for these two quantities are so nearly allied in their physical meanings, that a certain similarity in designation seems to be desirable.”*

— Rudolf Clausius, *The Mechanical Theory of Heat* (1867)

Appendix: Why coining 'entropy' was a bad idea

- On Clausius branding S as 'entropy':

*"By doing this, rather than extracting a name from the body of the current language (say: lost heat), he succeeded in coining a word that meant the same thing to everybody: **nothing.**"*

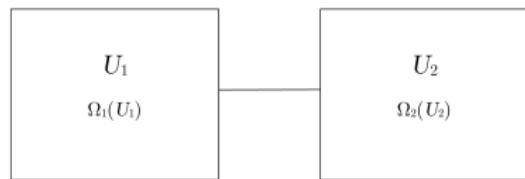
— Leon Cooper, *An Introduction to the Meaning and Structure of Physics* (1968)

Appendix: Defining temperature using statistical mechanics

- The *theoretical basis* of temperature lies in the concept of thermal equilibrium. Thus, for any two bodies:

having the **same temperature** \Leftrightarrow being in **thermal equilibrium**

- Consider two bodies in thermal contact with each other, but **thermally isolated** from their surroundings:



- The two bodies have internal energies U_1 and U_2 . Thermally isolated $\Rightarrow U = U_1 + U_2$ is conserved.
- Ω_i : The number of microstates corresponding to the macrostate of body i (characterised by U_i, V_i, N_i).
- V_i and N_i are constant $\Rightarrow \Omega_i(U_i, V_i, N_i) = \Omega_i(U_i)$.

- ★ When the bodies reach thermal equilibrium, the system settles into the *most likely* macrostate — the macrostate which corresponds to the maximum number of microstates![†]

[†]This is in fact a nontrivial statement; there are a few assumptions that need to be made. But given that it is somewhat intuitive, I have left it here as it is.

Appendix: Defining temperature using statistical mechanics

- Total number of possible microstates: $\Omega_{\text{total}} = \Omega_1(U_1) \cdot \Omega_2(U_2)$
- Maximise Ω_{total} : $\frac{d\Omega_{\text{total}}}{dU_1} = \frac{d[\Omega_1(U_1) \cdot \Omega_2(U_2)]}{dU_1} = 0$
- $U = U_1 + U_2$ is conserved $\Rightarrow dU_1 = -dU_2$
- We would eventually obtain:

$$\frac{1}{\Omega_1} \frac{d\Omega_1}{dU_1} - \frac{1}{\Omega_2} \frac{d\Omega_2}{dU_2} = 0 \Rightarrow \frac{d \ln \Omega_1}{dU_1} = \frac{d \ln \Omega_2}{dU_2}$$

- Hence: We define the temperature T by

$$\boxed{\frac{1}{k_B T} = \frac{d \ln \Omega}{dU}}$$

Appendix: Deriving Boltzmann's entropy

- First law of thermodynamics: $dU = TdS - pdV$
 - ▶ Derivation: Originally, $dU = dQ + dW$. For reversible processes, $dQ = TdS$ and $dW = -pdV$. Thus, $dU = TdS - pdV$ for reversible processes. However, dU , dS , dV are *path-independent*. Therefore, $dU = TdS - pdV$ for *irreversible* processes too!
- For a system in a **fixed macrostate**, $dV = 0 \Rightarrow \frac{1}{T} = \frac{dS}{dU}$
- Comparing with $\frac{1}{k_B T} = \frac{d \ln \Omega}{dU}$ yields: $S = k_B \ln \Omega$
- In words: The entropy of an **isolated system** (or, equivalently, a system in a **fixed macrostate**) is proportional to the natural logarithm of the **number of microstates corresponding to the macrostate**.

Appendix: Deriving Gibbs' entropy

- Previously: We derived Boltzmann's entropy (only works for *isolated systems*).
- Now: We seek the entropy of a *general system* with m possible microstates.
- Make \mathcal{N} mental copies of the system and join them together into one *isolated giant system*. Imagine, without loss of generality, that
 - \mathcal{N}_1 copies of the original system are in the 1st microstate,
 - \mathcal{N}_2 copies of the original system are in the 2nd microstate,
 - ...
 - \mathcal{N}_m copies of the original system are in the m^{th} microstate,

where $\mathcal{N} = \mathcal{N}_1 + \mathcal{N}_2 + \dots + \mathcal{N}_m$.

- The *giant system* is *isolated* \Rightarrow its entropy can be obtained via $S = k_B \ln W$, where W denotes the number of possible microstates *of the giant system*.

Appendix: Deriving Gibbs' entropy

- There are $\mathcal{N}!$ ways to arrange the \mathcal{N} system-copies in the **giant system**. However, we do not want to distinguish among system-copies in the same microstate.
- Hence: $W = \frac{\mathcal{N}!}{\mathcal{N}_1! \cdots \mathcal{N}_m!}$
- We then note *Stirling's approximation*: $\ln \mathcal{N}! \approx \mathcal{N} \ln \mathcal{N} - \mathcal{N}$
- Thus, the entropy of the **giant system** is:

$$\begin{aligned} S_{\text{giant}} &= k_B \ln \left(\frac{\mathcal{N}!}{\mathcal{N}_1! \cdots \mathcal{N}_m!} \right) \approx k_B \left[\mathcal{N} \ln \mathcal{N} - \mathcal{N} - \sum_{i=1}^m (\mathcal{N}_i \ln \mathcal{N}_i - \mathcal{N}_i) \right] \\ &= -k_B \mathcal{N} \sum_{i=1}^m \frac{\mathcal{N}_i}{\mathcal{N}} \ln \left(\frac{\mathcal{N}_i}{\mathcal{N}} \right) = -k_B \mathcal{N} \sum_{i=1}^m p_i \ln p_i \end{aligned}$$

- The entropy of the **original system** is then

$$S = \frac{S_{\text{giant}}}{\mathcal{N}} = -k_B \sum_{i=1}^m p_i \ln p_i$$

Appendix: Generality of Gibbs' entropy

- According to Gibbs, the entropy of a general system is:

$$S = -k_B \sum_{i=1}^m p_i \ln p_i$$

where m denotes the total number of possible microstates[†], and p_i denotes the probability that the system is in the i^{th} microstate.

- Boltzmann's entropy can be derived from Gibbs' entropy, as follows: put the system in a fixed macrostate corresponding to Ω microstates, so that $p_i = \Omega^{-1}$.

Substitute this and $\sum_{i=1}^{\Omega} p_i = 1$ into the expression for Gibbs' entropy. ■

- Clausius' entropy can be derived from Gibbs' entropy as well.[‡]

[†]Not just for a particular macrostate, but across *all* accessible macrostates.

[‡]I omit the derivation due to its involved nature and time constraints.