Entropy for Mathematicians or …
The final Blaubeuren chapters

Who? Stephan Fackler
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Life, the Universe and Everything

“The general struggle for existence of animate beings is not a struggle for raw materials – these, for organisms, are air, water and soil, all abundantly available – nor for energy which exists in plenty in any body in the form of heat, but a struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth.”

– L. Boltzmann

Figure: Ludwig Boltzmann
The classical definition in physics

**Definition**

Given a reversible physical process, its infinitesimal change in entropy is

$$dS = \frac{\delta Q}{T}.$$  

- $T$: absolute heat of the system
- $\delta Q$: amount of reversible heat transfer

*Macroscopic definition of entropy*

By the way: this is still mysterious because one needs a good definition of temperature!
Well, you did not understand that?

At least you’re not alone …

*Every mathematician knows it is impossible to understand an elementary course in thermodynamics.*

– V.I. Arnold
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So let’s do it not too elementary!
The basic concepts

Consider a cup containing four identical (red) balls

- What we see: how many balls are on the left half? (macroscopic configuration)
- What we do not see: is our favorite ball on the left half? (microscopic configuration)
The microscopic definition

- $S$ set of all macroscopic states
- $\mathcal{M}_\psi$ set of microscopic states in the macroscopic state $\psi$

$(\mathcal{M}_\psi, \Sigma_\psi, P_\psi)$ discrete probability space

The entropy $S(\psi)$ of the state $\psi \in S$ is defined as

$$S(\psi) = -k_B \sum_{m \in \mathcal{M}_\psi} P_\psi(\{m\}) \log P_\psi(\{m\}).$$

Boltzmann showed that entropy changes in the microscopic and macroscopic definition are proportional: to get the same one introduces

$$k_B \quad \text{(Boltzmann constant)}$$
Suppose that $\mathcal{M}_\psi$ has $W \in \mathbb{N}$ elements and
\[ P_\psi(\{m\}) = \frac{1}{W} \]
for all $m \in \mathcal{M}_\psi$. Then
\[ S(\psi) = k_B \sum_{m \in \mathcal{M}_\psi} \frac{1}{W} \log W = k_B \log W, \]
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*Boltzmann’s equation (isolated & in thermal equilibrium)*

Figure: The equation as carved on Boltzmann’s gravestone
Equal a priori probability postulate

In physics one usually assumes that all microscopic states have the same probability.

Over long periods of time, the time spent by a system in some region of microstates is proportional to the volume of this region.

All microstates are equiprobable over a long time.
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For a density $f \in L^1(\mathcal{M}_\psi)$ and Koopman operators

$$
\lim_{T \to \infty} \frac{1}{T} \int_0^T T(s)f \, ds = \int_{\mathcal{M}_\psi} f \, d\mathbb{P}_\psi.
$$

*The birth of ergodic theory!*
Let’s go back to the red balls!

Example (4 balls left)

1 microscopic configuration: \( W = 1 \)

Example (2 balls left)

6 microscopic configurations: \( W = 6 \)
First conclusions

Essentially, you have to count!

We’re talking about the order of $10^{23}$ molecules, there’s a lot to count!

The entropy depends on the choice of macroscopic states, i.e. on the observer!
Theorem

Second law of thermodynamics

The entropy of an isolated system is non-decreasing.

This is a probabilistic consequence (10^{23} molecules).

This is not an absolute truth in a mathematical sense.

If you’re interested in “violations” of the second law at small scales, look up the fluctuation theorem (verified for RNA foldings).
“The law that entropy always increases holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations — then so much the worse for Maxwell’s equations. If it is found to be contradicted by observation — well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.”

– Sir Arthur Stanley Eddington
So gas has maximal entropy if it is homogeneously distributed throughout space, right?

We follow J. Baez and take a huge amount of gas in outer space …
Under the influence of gravity such gas is building structure …

So does gravity violate the second law?
As the cloud gets denser (decrease in entropy), it gets hotter (increase in entropy). However, for a cloud of radius $R$ we still have

$$\frac{dS}{dR} > 0.$$ \(\text{In fact, one has for the cloud}\)

$$\frac{dE}{dR} > 0, \quad \frac{dS}{dR} > 0, \quad \frac{dT}{dE} < 0$$

(the less energy the gas has, the higher its temperature).
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Dividing the second by the first equation and using the definition of temperature $\frac{1}{T} = \frac{dS}{dE}$

$$\frac{dS}{dR} \cdot \frac{dR}{dE} = \frac{dS}{dE} = \frac{1}{T} > 0.$$

Multiplying the first with the third equation

$$\frac{dE}{dR} \cdot \frac{dT}{dE} = \frac{dT}{dR} < 0.$$
So why is the second law of thermodynamics not violated? It is literally before your very eyes …
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The decrease in entropy of the gas is way than more compensated by the increase in entropy due to the emitted radiation!
Let’s get singular …

Gravitationally bound systems can never be in thermal equilibrium with their environment! They shrink and shrink until …

The entropy of the cloud decreases until the very end. So what is the entropy of a black hole?
The entropy of black holes

- Does a black hole have non-zero entropy?
  - Thought experiment: Throw some mass into the black hole
  - A zero entropy black hole would destroy the entropy of the particle
  - The holy second law forbids that
  - Consequence: a black hole has non-zero entropy

Hawking calculated the entropy of black holes using (thermal) Hawking radiation

\[ S_{\text{BH}} = k_B A^4 \ell^2_p \]

By the Bekenstein bound the entropy \( S(A) \) contained in a surface of area \( A \) satisfies

\[ S(A) \leq k_B A^4 \ell^2_p \]

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\[ S_{BH} = k_B \frac{A}{4\ell_p^2}, \quad \ell_p = \sqrt{\frac{G\hbar}{c^3}}. \]

- By the Bekenstein bound the entropy \( S(A) \) contained in a surface of area \( A \) satisfies

\[ S(A) \leq k_B \frac{A}{4\ell_p^2}. \]

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A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.

– Albert Einstein
Nothing in life is certain except death, taxes and the second law of thermodynamics. All three are processes in which useful or accessible forms of some quantity, such as energy or money, are transformed into useless, inaccessible forms of the same quantity. That is not to say that these three processes don’t have fringe benefits: taxes pay for roads and schools; the second law of thermodynamics drives cars, computers and metabolism; and death, at the very least, opens up tenured faculty positions.

– Seth Lloyd
Merry Christmas!