Entropy - From Physics, and Beyond

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Physics Problem Solving Society St Paul's School

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Questions we aim to answer today ...

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- How can we intuitively understand entropy?
- What is the unit for entropy?

These are only a few that I could think of:

• $S = k_B \ln \Omega$,

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$$S = -\sum p_i \log_2 p_i$$

$$\bullet \ \mathsf{d} S = \frac{\delta Q_{\mathsf{rev}}}{T},$$

$$\bullet \ \Delta G = \Delta H - T \Delta S,$$

...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.

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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

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- 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.

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Remark

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

Given that all microstates are equally likely ...

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Definition (Boltzmann's Entropy Formula)

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

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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

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$$= S_{A} + S_{B},$$

and entropy is additive!



Boltzmann's Entropy Formula - Example

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Entropy is a measure of disorder.

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The entropy of an isolated system alays increases.

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

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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.



Problem

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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

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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.)

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Definition (Gibbs Entropy)

$$S_{\mathsf{G}} = -k_{\mathsf{B}} \sum p_i \ln p_i,$$

where p_i is the probability of obtaining a certain microstate.

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

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Solution

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

$$S_G = -k_B \sum_i p_i \ln p_i$$

$$= -k_B \cdot \Omega \cdot \left(\frac{1}{\Omega} \cdot \ln \frac{1}{\Omega}\right)$$

$$= -k_B (-\ln \Omega)$$

$$= k_B \ln \Omega.$$

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The probability mass function (p.m.f) of Y is as follows:

У	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

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

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

Significance of Shannon Entropy

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Theorem (Shannon's Source Coding Theorem)

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

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.

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- 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?

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The entropy **disappeared**.

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How is this related to $S = k_B \ln \Omega$?

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- 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

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