

Facets of Entropy

Elliott Lieb
Princeton University

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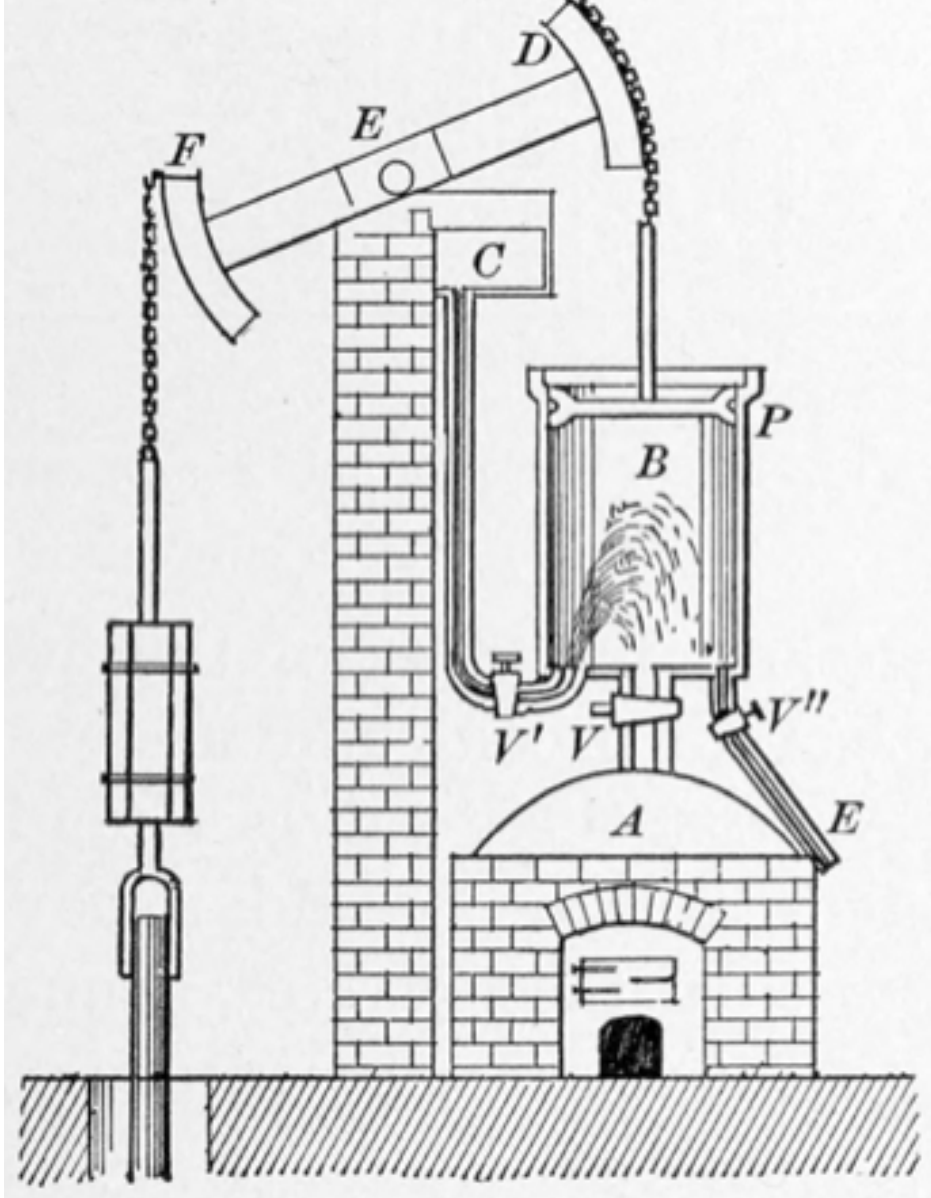
Sadi Carnot

In 1824 (age 28!) Carnot was trying to perfect heat engines and figured out that the *efficiency of an engine depended not on the working substance but only on the high temperature and the low temperature of the engine's cycle*. He wrote this up in

Reflections on the Motive Power of Fire

and perfected an imaginary cycle for his engine, which he proved to be the most efficient one possible.





Newcomen engine
(1712)

A question for today: What is temperature? Why does the mark on a thermometer determine the efficiency of an engine? Could we say that a high efficiency heat engine is a thermometer?

Sadi Carnot

Caloric (later called heat) always flows like a waterfall downhill from a hot body to a cold body, and in the process useful work could be extracted. Carnot and others understood that caloric, unaided, could not flow back from cold to hot and that *Motive power in a steam engine is due not to a consumption of caloric but to its passage from a hot body to a cold one*

Not quite right. Some of the caloric is consumed and turned into **Work**.

Second Question for today: What is heat?

No one has seen, touched or tasted **heat**. The same is true of **caloric**.
Are they really needed to define entropy?

The Origin of ENTROPY



In 1850 **Rudolf Clausius** used Carnot's observations and the idea of breaking up a simply connected region in the pressure-temperature plane into tiny Carnot cycles, to conclude that the integral $\int dQ/T$ (with $Q =$ heat and $T =$ temperature) around a closed curve for an actual engine cycle was either zero (best case) or negative (inefficient case). This is the **'Second Law' of thermodynamics**. Clausius published this theory in 1850 with the title *On the Moving Force of Heat and the Laws of Heat which may be Deduced Therefrom*

The Origin of ENTROPY

In 1856 Clausius coined the word entropy for the quantity whose change from state 1 to a state 2 is $S(2) - S(1) = \int_1^2 dQ/T$.

The new term made it possible to state the second law in the brief but alarming form: “The entropy of the universe tends toward a maximum.”

Thus, entropy is originally related to possible **changes** – **NOT to Chaos or to Information Theory**. The **important point** is that $S(2) - S(1) \geq 0$ is necessary for changing from 1 to 2 without changing the rest of the universe.

Third Question for today: What is the entropy of the universe? Is it possible to define it?

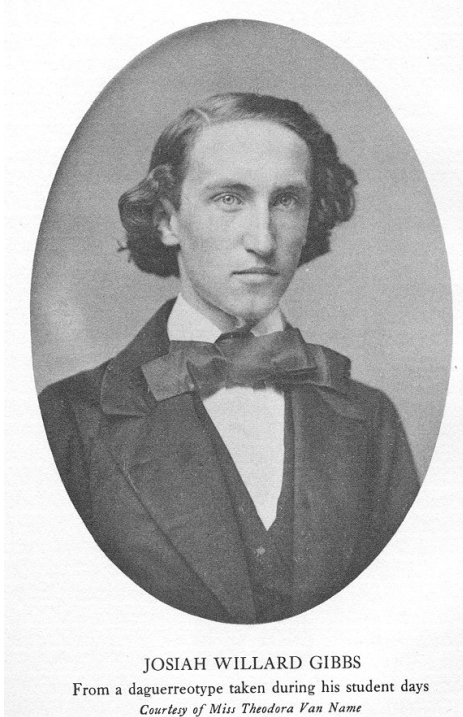
Interlude: Confusion and Chaos Appears

Shannon asked von Neumann what name to give to his information-theoretic uncertainty function:

“You should call it entropy [...]. Nobody knows what entropy really is, so in a debate you will always have the advantage.”



Boltzmann, Gibbs, Maxwell & Stat. Mech.



Boltzmann, Gibbs, Maxwell & Stat. Mech.

Boltzmann had the wonderful insight that he could explain entropy and, at the same time, **prove the existence of atoms**, which was by no means universally accepted at the time.

Idea: Any humanly visible macrostate (defined by a few observables like temperature, pressure, etc.) is realized by very many different microstates, defined by the positions of atoms and what not (coarse-graining on a microscopic scale). Boltzmann called the number of them W , interpreted W as a relative probability, and said the entropy S of the macrostate is

$$S = k \log W$$

A question for the future and the day after as well: *What is an exact definition of a microstate?* Changing the scale and type of coarse graining only changes S by additive/multiplicative constants. But how does one calibrate all possible systems so that S is **additive** for **totally unrelated systems**?

Boltzmann, Gibbs, Maxwell & Stat. Mech.

Since the last question remains unanswered, Boltzmann's formula does not specify an absolute entropy. As Einstein put it,

It is dubious whether the Boltzmann principle has any meaning without a complete molecular-mechanical theory [...] The formula $S = k \log W$ seems without content, from a phenomenological point of view, without giving, in addition, such an Elementartheorie."

A. Einstein (1910) (transl. A. Pais 1982)

Boltzmann, Gibbs, Maxwell & Stat. Mech.

There were other criticisms. For example:

“Boltzmann was right about atoms but utterly wrong in believing that atoms provided a necessary basis for thermodynamics. The second law does not require atoms. Thermodynamics would be equally correct if the basic constituents of the world were atoms, or quantum fields, or even strings.”

Leo Kadanoff in a 2001 review of Lindley’s book about Boltzmann

Another example comes from economics theory (von Neumann-Morgenstern) where atoms \rightarrow money.

Boltzmann, Gibbs, Maxwell & Stat. Mech.

Statistical mechanics predicts entropy well in many equilibrium situations. For example:

1. **Residual entropy of ice (Pauling)**. Awesome agreement with experiment
2. **Measurement of Planck's constant \hbar** (believe it or not)
3. **Resolution of Gibbs' paradox** using quantum mechanics.

Sometimes it does *not* work well. Most writers pretend there is no difference between entropies defined by integrals, as in $Z = \int \exp(-H/kT)$, and sums, as in $Z = \sum \exp(-H/kT)$. Sums give $S \rightarrow 0$ as $T \rightarrow 0$, while integrals usually give $S \rightarrow -\infty$ as $T \rightarrow 0$. **Quantum Mechanics is Essential to get $S = 0$ when $T = 0$** (called the **Third Law of Thermodynamics**).

Back to Basics

Let's leave now the brave attempts to calculate entropy from 'first principles' and ask **What is Entropy?** Before we can decide whether we have a good explanation for it, we must first be absolutely clear about what it is we are trying to explain.

Recall our questions for today:

What is *heat*?

What is *temperature*?

What is the *entropy of the (visible) universe*? (or just gravitational systems?)

To which we add: What is *work*?, and what is the **second law of thermodynamics**?, which we will henceforth call the **“entropy principle”**.


“[The Second Law of thermodynamics] 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. [...] 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.”

A. Eddington (1915)

The Goal

Recall Clausius: *Entropy is related to possible changes.*

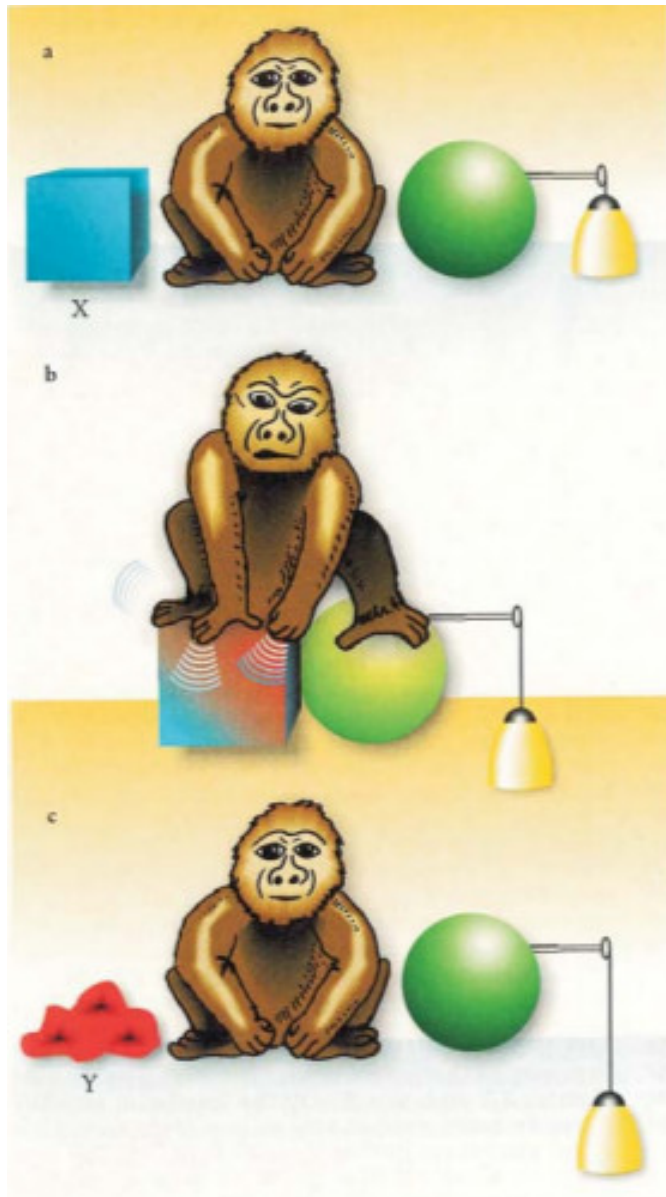
Let us imagine our laboratory full of containers with all sorts of substances in all possible *Equilibrium* states. We also imagine all possible machinery, intelligent and infinitely powerful — and a weight.

A weight?  What does that have to do with entropy? Well, we must make contact with energy and work, and lifting a weight is the gold-standard for this quantity (just as a meter bar is a standard for length).

All this apparatus can be utilized to try to change an equilibrium state of some system into an equilibrium states of the same or different system.

The only ground rule is

Adiabatic Accessibility



Artwork: Steinunn Jakobsdóttir

Adiabatic Accessibility: At the end of the day, nothing else in the universe has changed (including all the machinery) *except that the weight has possibly moved up or down.* This is Carnot speaking to us.

The process need not be smooth or slow. It can be arbitrarily violent. If entropy is eventually going to be a *state function* then *it must not depend on the way in which one state is derived from another.*

Adiabatic Accessibility

If we can go from one equilibrium state X to another equilibrium state Y by an adiabatic process, we write

$$X \prec Y$$

We then imagine a **huge** list containing all possible pairs of processes $X \prec Y$. Our goal is to **quantify this list** succinctly and *uniquely* by one function S .



Entropy and the entropy principle achieve this for us.

(Jakob Yngvason and E.L. 1998)

The Entropy Principle

For every equilibrium state X of every system there is a number $S(X)$, called Entropy, which has the following properties:

$$X \prec Y \text{ if and only if } S(X) \leq S(Y) \quad \text{monotonicity}$$

This function S is unique, up to multiplication by a universal constant.

Every (non-interacting) pair of systems can be regarded as a single system with states (X, Y) , and for any pair the entropy satisfies

$$S_{1,2}(X, Y) = S_1(X) + S_2(Y). \quad \text{additivity}$$

Thus, the ‘increase of entropy’ (the second law) is built into the definition of entropy – if it exists.

There is no mention of temperature or heat.

The Miracle of Additivity

Additivity, $S_{1,2}(X, Y) = S_1(X) + S_2(Y)$, comes almost for free with the Boltzmann-Gibbs ensembles in statistical mechanics. Nevertheless, it is amazing in what it predicts.

It says that while the entropy of individual systems appear to have indeterminate, unrelated **multiplicative constants** all the systems in creation can be adjusted to one another so that additivity holds. This, together with monotonicity, tells us *exactly* how much entropy increase is required of one system in order that a second system can *decrease* its entropy – even though the two systems are totally dissimilar and don't talk to each other.

Additivity lies behind the formula for the maximum possible efficiency of a heat engine: $\eta = 1 - T_0/T_1$.

A challenge for the construction of dynamical models: Try to get additivity of entropy for independent pairs of models.

The founder of axiomatic thermodynamics was C. Caratheodory (1909), with many followers, such as P.T. Landsberg, G. Falk & H. Jung, H.A. Buchdahl, J.J. Duistermaat, and particularly Robin Giles who wrote one of the unsung classics of mathematical physics

Mathematical Foundations of Thermodynamics (1964).

Here he eliminated the need of coordinates to define entropy and constructed it with almost nothing except a little common sense. Many properties of entropy, such as existence of thermal equilibria and *zeroth law* and the existence of temperature will need coordinates, however.

The following construction of the entropy function and the relation of additivity and ‘comparison’ was provided by Jakob Yngvason & E.L. in 1998.

Axioms needed to construct Entropy

A1. Reflexivity: $X \prec X$.

A2. Transitivity: If $X \prec Y$ and $Y \prec Z$, then $X \prec Z$.

A3. Consistency: If $X \prec X'$ and $Y \prec Y'$, then $(X, Y) \prec (X', Y')$.

A4. Scaling Invariance: If $\lambda > 0$ and $X \prec Y$, then $\lambda X \prec \lambda Y$.

A5. Splitting and Recombination: $X \prec ((1 - \lambda)X, \lambda X) \prec X$.

Comparison Property

The following property turns out to be *essential* for deriving an entropy function. It appears to be an additional axiom but it can actually be deduced when coordinates are introduced. We list it separately. The symbol Γ denotes the space of equilibrium states of some given system of a given size, $\lambda\Gamma$ is a scaled copy, and $\Gamma \times \Gamma'$ denotes the space of *pairs of states* in Γ and Γ' .

Comparability of two states X and Y means that either $X \prec Y$ or $Y \prec X$ (or both). The **Comparison Property** of a state space Γ is the following:

Any two states in $(1 - \lambda)\Gamma \times \lambda\Gamma$ are comparable, for all $0 \leq \lambda \leq 1$.

We require this property of *all* state spaces. It is this property that calibrates everything together to yield **a consistent entropy function.**

Comparison Property

If you did not catch the details of the previous slide, **don't worry.**

The important point is that the comparison hypothesis is the essential property that gives additivity of entropy – which comes for free in statistical mechanics via the partition function. As we shall see, the 6 axioms suffice to fix the entropy function for each system, but we need something else to calibrate all systems with one another and thereby have a universal entropy that is additive – even for mixing and for chemical reactions.

Uniqueness of the Entropy Function S

THEOREM:

The existence and uniqueness of entropy on Γ , up to a multiplicative and additive scale transformation, is equivalent to axioms A1-A5 about adiabatic accessibility, plus the comparison property.

The uniqueness is very important! It means that all methods to define entropy lead to the same result, provided the basic requirements (that the entropy characterizes adiabatic accessibility and is additive and extensive) are fulfilled.

Construction of the Entropy Function S

We shall now construct Entropy on a state space Γ *with our bare hands*. The way to *calibrate all state spaces* using comparison is a long story, for another day.

Pick two points X_0 and X_1 in Γ such that $X_0 \prec X_1$ but $X_1 \not\prec X_0$. Define $S(X_0) := 1$ and $S(X_1) := 2$.

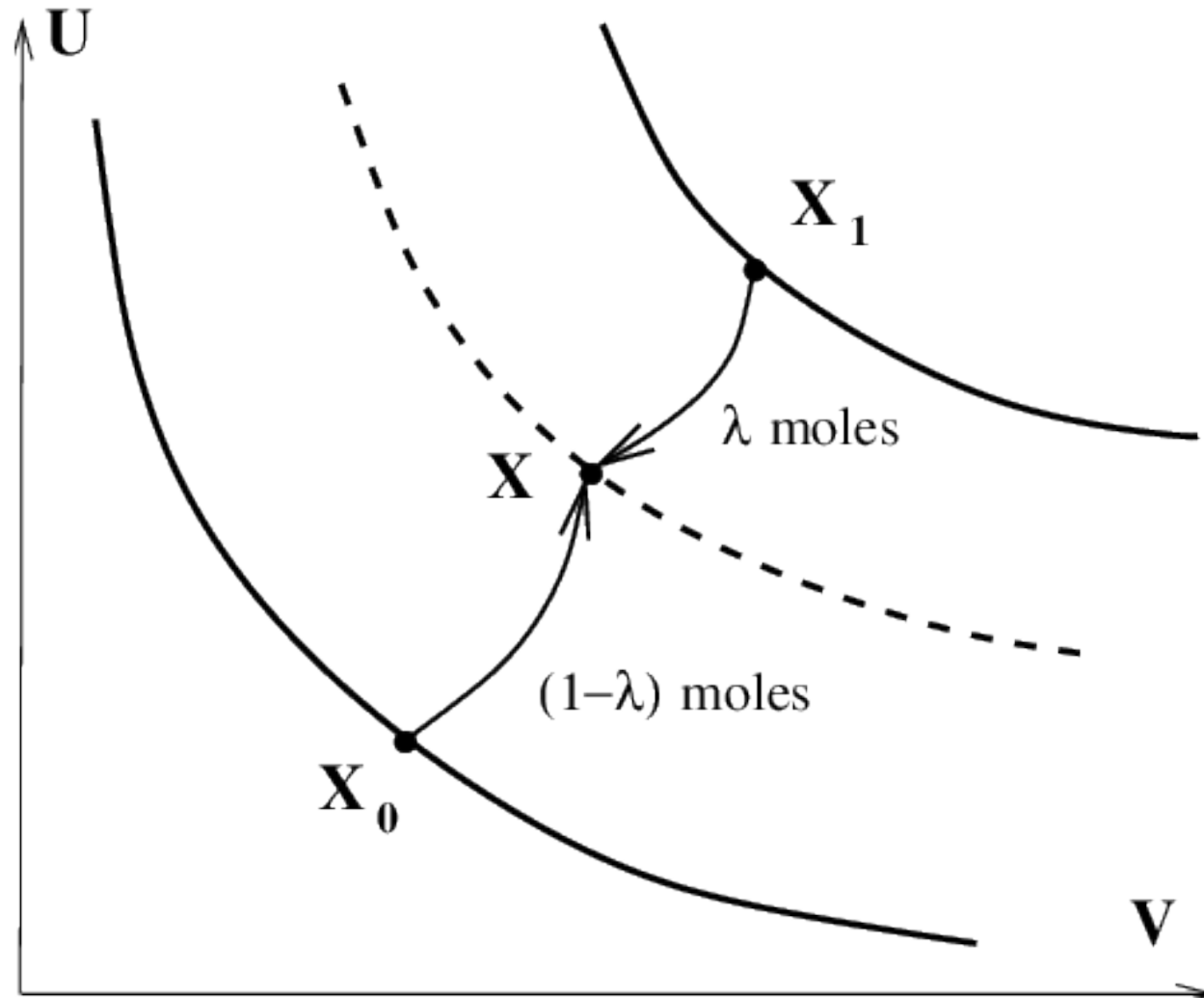
Now pick any other point X . For simplicity here assume $X_0 \prec X \prec X_1$.

Then

$$S(X) := S(X_0) + \sup \left\{ \lambda : ((1 - \lambda)X_0, \lambda X_1) \prec X \right\}$$

In other words, $S(X)$ is determined by the maximum amount of X_1 that (together with help from X_0) can be pulled backwards to produce X . The following diagram will make this clearer.

Construction of the Entropy Function S



Construction of the Entropy Function

Thus, entropy is determined by the enormous table of adiabatic processes $X \prec Y$, if the table satisfies certain non-controversial axioms. No mention need be made about engines, or heat, or temperature or atoms, or chaos, or dynamical models or “ideal” gases. It is essential, of course, that the ‘table’ is based on reproducible experiments.

Once again, *adiabatic* does not mean ‘slow’ or reversible or anything similar. It means here that an experiment carried out by an arbitrarily crafty experimenter leaves the rest of the universe unchanged except for the possible movement of a weight. **The existence of one label S that suffices to tell what can happen, and what cannot, is enormously useful and predictive in many unforeseen ways.**

Energy, Heat, Temperature

Another conceptual step is needed. **Cartesian Coordinates.**

To compute anything concretely, we need to specify a state space as a subset of some \mathbb{R}^n . For clear reasons it will be convex. An example is \mathbb{R}^2 where energy U and volume V are used. Energy is a *good coordinate*, i.e., its value, like S , does not depend on how we get from one state to another, however violently, and this fact is the **First Law of Thermodynamics**.

A few more axioms are needed here and the analysis is not as easy as before. For example, any two systems can be brought into **equilibrium** by passing a copper thread between them and thereby **maximizing the total entropy** by exchanging energy without changing other (i.e., 'work') coordinates, like volume. This maximization defines a new equilibrium system to which the axioms can be applied.

Energy, Heat, Temperature

Given two systems with entropies $S_1(U, V)$ and $S_2(U, V)$, the maximum entropy at given fixed volumes V_1, V_2 is

$$S_{1,2}(U, V_1, V_2) = \max_W [S_1(U - W, V_1) + S_2(W, V_2)] \quad (*)$$

Given an entropy function $S(U, V)$ we can define Temperature as

$$\frac{1}{T(U, V)} := \frac{\partial S(U, V)}{\partial U}$$

Thus, by elementary calculus and (*), the equality of temperatures $T_1 = T_2$ merely states the achievement of maximum entropy S_{12} , which is the condition for equilibrium.

Two systems in equilibrium have the same T , and conversely (zeroth law).

Uniqueness of S implies uniqueness of T (absolute Temperature scale)

Non-Equilibrium Entropy

Most physicists believe in the possibility of an entropy that increases in time, but it has not been possible to define this totally rigorously – apart from some simplified models, perhaps. **One can make an accurate theory for systems close to equilibrium**, but no one can really calculate the entropy of an exploding bomb. E.L. & J.Y. have, however, defined upper and lower entropies S_+ , S_- (even for a bomb), which delimit the range of adiabatic processes that can occur between non-equilibrium states.

Since the universe is certainly not in equilibrium, this is an indication that it will not be possible to define a precise *entropy of the universe*, or part of it, Clausius's heat death notwithstanding.

Entropy of Gravitating Systems

Gravitating systems, such as a nebula, can be in ‘equilibrium’ in the sense that they change very little over a billion years. Nevertheless, any attempt to define an entropy will run into several problems, such as:

1.) Since no thermodynamic limit is possible, entropy will *not be extensive or additive*. This will make it difficult to decide if equilibrium *between* such systems is possible.

2.) In Boltzmann–Gibbs classical statistical mechanics temperature is identified solely with kinetic energy. (Quantum mechanics is different, but not totally.) Gravitating systems, however, have the property that **kinetic energy goes up when the total energy goes down!** This is in direct confrontation with the second law!!

The *heat death of the universe* will be a lively one.

The Limits of Entropy

Just as ordinary thermodynamics *and statistical mechanics* break down at cosmic distances, they also have problems on the ultra-small scale. The **Scale invariance** and **Splitting** axioms, for example, do not obviously hold when only a few atoms are involved.

This is currently a lively topic of research for several groups. There are interesting suggestions (**Oppenheim, et al.**) that *several* entropies might be needed to characterize what is going on. There is, in fact, a theorem of **Shapley & Baucells (1989)** that says that under some assumptions, a relation $X \prec Y$ can be characterized by **several entropy functions**, but not necessarily only one function, as we have in thermodynamics.

Some Open Problems

1. If two systems are in a constrained equilibrium (e.g., two gases separated by a barrier) and if the constraint (e.g., barrier) is released, the entropy $S_1 + S_2$ goes up. What assumption will guarantee that each of the *individual* entropies, S_1 and S_2 , goes up? One can argue that before equilibrium is restored, each system is worked upon by the other, which would imply that each entropy must increase.
2. There is some similarity between the *decrease of entanglement* in quantum mechanics and the *increase of entropy* – as emphasized by several quantum information theorists. Try to clarify this – particularly *additivity*.
3. Identify *where the second law breaks down*. Is it at the *microscopic level* or is it at the *mesoscopic* level? (A few atoms or many thousands?) Is this question merely academic or is there some genuinely new physics involved– as in the origin of life, for example?

Some Take-Home Messages

Entropy is not like a thief that robs us when we are not paying attention, but rather can be viewed as a guide that constrains what can and cannot be done to change from one equilibrium state to another.

However one defines entropy, to be really useful it is important to show and to appreciate the fact that it is unique and **Additive** over unrelated systems.

THANKS FOR LISTENING !

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