A Fresh Look at Entropy and the Second Law of Thermodynamics

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Abstract

The existence of entropy and its increase can be understood without reference to either statistical mechanics or heat engines.

In days long gone, the second law of thermodynamics (which predated the first law) was regarded as perhaps the most perfect and unassailable law in physics. It was even supposed to have philosophical import: It has been hailed for providing a proof of the existence of God (who started the universe off in a state of low entropy, from which it is constantly degenerating); conversely, it has been rejected as being incompatible with dialectical materialism and the perfectability of the human condition.

Alas, physicists themselves eventually demoted it to a lesser position in the pantheon—because (or so it was declared) it is "merely" statistics applied to the mechanics of large numbers of atoms. Willard Gibbs wrote: "The laws of thermodynamics may easily be obtained from the principles of statistical mechanics, of which they are the incomplete expression" [1]—and Ludwig Boltzmann expressed similar sentiments.

Is this really so? Is it really true that the second law is merely an "expression" of microscopic models or could it exist in a world that was featureless at the 10^{-8} cm level? We know that statistical mechanics is a powerful tool

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for understanding physical phenomena and calculating many quantities, especially in systems at or near equilibrium. We use it to calculate entropy, specific and latent heats, phase transition properties, transport coefficients and so on, often with good accuracy. Important examples abound, such as Max Planck's realization that by staring into a furnace he could find Avogadro's number or Linus Pauling's highly accurate back-of-the-envelope calculation of the residual entropy of ice. But is statistical mechanics essential for the second law?

In any event, it is still beyond anyone's computational ability (except in idealized situations) to account for a very precise, essentially infinitely accurate law of physics from statistical mechanical principles. No exception has ever been found to the second law of thermodynamics—not even a tiny one. Like conservation of energy (the "first" law) the existence of a law so precise and so independent of details of models must have a logical foundation that is independent of the fact that matter is composed of interacting particles. Our aim here is to explore that foundation. The full details can be found in [2].

As Albert Einstein put it, "A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown" [3].

In an attempt to reaffirm the Second Law as a pillar of physics in its own right, we have returned to a little noticed movement that began in the 1950's with the work of Peter Landsberg [4], Hans Buchdahl [5], Gottfried Falk, Herbert Jung [6], and others (see [2] for references) and culminated in the book of Robin Giles [7], which must be counted one of the truly great, but unsung works in theoretical physics. It is in these works that the concept of "comparison" (explained below) emerges as one of the key underpinnings of the second law. The approach of these authors is quite different from lines of thought in the tradition of Sadi Carnot that base thermodynamics on the efficiency of heat engines. (See [8], for example, for a modern exposition of the latter.)

The basic question

The paradigmatic event that the second law deals with can be described as follows. Take a macroscopic system in an equilibrium state X and place it in a room, together with a gorilla equipped with arbitrarily complicated machinery (a metaphor for the rest of the universe), and a weight—and close the door. As in the old advertisement for indestructible luggage, the gorilla can do anything to the system—including tearing it apart. At the end of the day, however, the door is opened and the system is found in some other equilibrium state, Y, the gorilla and machinery are found in their original state, and the only other thing that has possibly changed is that the weight has been raised or lowered. Let us emphasize that although our focus is on equilibrium states, the processes that take one such state into another can be arbitrarily violent. The gorilla knows no limits. (See figure 1.)

The question that the second law answers is this: What distinguishes those states Y that can be reached from X in this manner from those that cannot? The answer: There is a function of the equilibrium states, called entropy and denoted by S, that characterizes the possible pairs of equilibrium states X and Y by the inequality $S(X) \leq S(Y)$. The function can be chosen to be additive (in a sense explained below), and with this requirement it is unique, up to a change of scale. Our main point is that the existence of entropy relies only on a few basic principles, independent of any statistical model—or even of atoms.

What is exciting about this apparently innocuous statement is the uniqueness of entropy, for it means that all the different methods for measuring or computing entropy must give the same answer. The usual textbook derivation of entropy as a state function, starting with some version of "the second law", proceeds by considering certain slow, almost reversible processes (along adiabats and isotherms). It is not at all evident that a function obtained in this way can contain any information about processes that are far from being slow or reversible. The clever physicist might think that with the aid of modern computers, sophisticated feedback mechanisms, unlimited amounts of mechanical energy (represented by the weight) and lots of plain common sense and funding, the system could be made to go from an equilibrium state X to Y that could not be achieved by the primitive quasistatic processes used to define entropy in the first place. This cannot happen, however, no matter how clever the experimentalist or how far from equilibrium one travels!

What logic lies behind this law? Why can't one gorilla undo what another one has wrought? The atomistic foundation of this logic is not as simple as is often suggested. It not only concerns things like the enormous number of atoms involved (10^{23}), but also other aspects of statistical mechanics that are beyond our present mathematical abilities. In particular, the interaction of a system with the external world (represented by the gorilla and machinery) cannot be described in any obvious way by Hamiltonian mechanics. Although irreversibility is an important open problem in statistical mechanics, it is fortunate that the logic of thermodynamics itself is independent of atoms and can be understood without knowing its source.

The founders of thermodynamics—Rudolf Clausius, Lord Kelvin, Max Planck, Constantin Carathéodory, and so on—clearly had transitions between equilibrium states in mind when they stated the law in sentences such as "No process is possible, the sole result of which is that a body is cooled and work is done" (Kelvin). Later it became tacitly understood that the law implies a continuous increase in some property called entropy, which was supposedly defined for systems out of equilibrium. The ongoing, unsatisfactory debates (see refernce [9, for example) about the definition of this nonequilibrium entropy and whether it increases shows, in fact, that what is supposedly "easily" understood needs clarification. Once again, it is a good idea to try to understand first the meaning of entropy for equilibrium states—the quantity that our textbooks talk about when they draw Carnot cycles. In this article we restrict our attention to just those states; by "state" we always mean "equilibrium state". Entropy, as the founders of thermodynamics understood the quantity is subtle enough, and it is worthwhile to understand the "second law" in this restricted context. To do so it is not necessary to decide whether Boltzmann or Gibbs had the right view on irreversibility. (Their views are described in Joel L. Lebowitz's article "Boltzmann's Entropy and Time's Arrow", Physics Today, September 1993, page 32.)

The basic concepts

To begin at the beginning, we suppose we know what is meant by a thermodynamic system and equilibrium states of such a system. Admittedly these are not always easy to define, and there are certainly systems, such as a mixture of hydrogen and oxygen or an interstellar ionized gas, that can behave as if they are in equilibrium even if it is not truly so. The prototypical system is a "simple system", consisting of a substance in a container with a piston.

But a simple system can be much more complicated than that. Besides its volume it can have have other coordinates, which can be changed by mechanical or electrical means—shear in a solid, or magnetization, for example. In any event, a state of a simple system is described by a special coordinate U, which is its energy, and one or more other coordinates (such as the volume V) called work coordinates. An essential point is that the concept of energy, which we know about from the moving weight and Newtonian mechanics, can be defined for thermodynamic systems. This fact is the content of the first law of thermodynamics.

Another type of system is a "compound system", which consists of several different or identical independent, simple systems. By means of mixing or chemical reactions, systems can be created or destroyed.

Let us briefly discuss some concepts that are relevant for systems and their states, which are denoted by capital letters such as $X, X', Y, \ldots$. Operationally, the composition, denoted (X, X'), of two states X and X' is obtained simply by putting one system in a state X and one in a state X' side by side on the experimental table and regarding them jointly as a state of a new, compound system. For instance, X could be a glass containing 100 g of whiskey at standard pressure and 20° C, and X' a glass containing 50 g of ice at standard pressure and 0° C. To picture (X, X') one should think the two glasses standing on a table without touching each other. (See figure 2.)

Another operation is the "scaling" of a state X by a factor $\lambda > 0$, leading to a state denoted λX. Extensive properties like mass, energy and volume are multiplied by λ, while intensive properties such as pressure stay intact. For the states X and X' as in the example above the example above $\frac{1}{2}X$ is 50 g of whiskey at standard pressure and 20° C, and $\frac{1}{5}X'$ is 10 g of ice at standard pressure and 0° C. Compound systems scale in the same way: $\frac{1}{5}(X, X')$ is 20 g of whiskey and 10 g of ice in separate glasses with pressure and temperatures as before.

A central notion is adiabatic accessibility. If our gorilla can take a system from X to Y, as described above—that is, if the only net effect of the action, besides the state change of the system, is that a weight has possibly been raised or lowered, we say that Y is adiabatically accessible from X and write $X \prec Y$ (the symbol $\prec$ is pronounced "precedes"). It has to be emphasized that for macroscopic systems this relation is an absolute one: If a transition from X to Y is possible at one time, then it is *always* possible (that is, it is reproducible), and if it is impossible at one time it *never* happens. This absolutism is guaranteed by the large powers of 10 involved—the impossibility of a chair's spontaneous jumping up from the floor is an example.

The role of entropy

Now imagine that we are given a list of all possible pairs of states X, Y such that $X \prec Y$. The foundation on which thermodynamics rests, and the essence of the second law, is that this list can be simply encoded in an entropy function S on the set of all states of all systems (including compound systems) so that when X and Y are related at all, then

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

Moreover, the entropy function can be chosen in such a way that if X and X' are states of two (different or identical) systems, then the entropy of the compound system in this pair of states is given by

$$S(X, X') = S(X) + S(X').$$

This additivity of entropy is a highly nontrivial assertion. Indeed, it is one of the most far reaching properties of the second law. In compound systems such as the whiskey/ice example above, all states (Y, Y') such that $X \prec Y$ and $X' \prec Y'$ are adiabatically accessible from (X, X'). For instance, by letting a falling weight run an electric generator one can stir the whiskey and also melt some ice. But it is important to note that (Y, Y') can be adiabatically accessible from (X, X') without Y being adiabatically accessible from X. Bringing the two glasses into contact and separating them again is adiabatic for the compound system but the resulting cooling of the whiskey is not adiabatic for the whiskey alone. The fact that the inequality $S(X)+S(X') \leq S(Y) + S(Y')$ *exactly* characterizes the possible adiabatic transitions for the compound system, even when $S(X) \geq S(Y)$, is quite remarkable. It means that it is sufficient to know the entropy of each part of a compound system in order to decide which transitions due to interactions between these parts (brought about by the gorilla) are possible.

Closely related to additivity is extensivity, or scaling of entropy,

$$S(\lambda X) = \lambda S(X),$$

which means that the entropy of an arbitrary mass of a substance is determined by the entropy of some standard reference mass, such as 1 kg of the substance. Without this property engineers would have to use different steam tables each time they designed a new engine.

In traditional presentations of thermodynamics, based for example on Kelvin's principle given above, entropy is arrived at in a rather roundabout way which tends to obscure its connection with the relation $\prec$. The basic message we wish to convey is that existence and uniqueness of entropy are equivalent to certain simple properties of the relation $\prec$. This equivalence is the concern of [2].

An analogy leaps to mind: When can a vector-field, $\mathbf{E}(x)$, be encoded in an ordinary function (potential), $\phi(x)$, whose gradient is $\mathbf{E}$? The well-known answer is that a necessary and sufficient condition is that $\operatorname{curl} \mathbf{E} = 0$. The importance of this encoding does not have to be emphasized to physicists; entropy's role is similar to the potential's role and the existence and meaning of entropy are not based on any formula such as $S = -\Sigma_i p_i \ln p_i$, involving probabilities p_i of "microstates". Entropy is derived (uniquely, we hope) from the list of pairs $X \prec Y$; our aim is to figure out what properties of this list (analogous to the curl-free condition) will allow it to be described by an entropy. That entropy will then be endowed with an unambiguous physical meaning independent of anyone's assumptions about "the arrow of time", "coarse graining" and so on. Only the list, which is given by physics, is important for us now.

The required properties of $\prec$ do *not* involve concepts like "heat" or "reversible engines", not even "hot" and "cold" are needed. Besides the "obvious" conditions "$X \prec X$ for all X" (reflexivity) and "$X \prec Y$ and $Y \prec Z$ implies $X \prec Z$" (transitivity) one needs to know that the relation behaves reasonably with respect to the composition and scaling of states. By this we mean the following:

- Adiabatic accessibility is consistent with the composition of states: $X \prec Y$ and $Z \prec W$ implies $(X, Z) \prec (Y, W)$.
- Scaling of states does not affect adiabatic accessibility: If $X \prec Y$, then $\lambda X \prec \lambda Y$.
- Systems can be cut adiabatically into two parts: If $0 < \lambda < 1$, then $X \prec ((1-\lambda)X, \lambda X)$, and the recombination of the parts is also adiabatic: $((1-\lambda)X, \lambda X) \prec X$.
- Adiabatic accessibility is stable with respect to small perturbations: If $(X, \varepsilon Z) \prec (Y, \varepsilon W)$ for arbitrarily small $\varepsilon > 0$, then $X \prec Y$.

These requirements are all very natural. In fact, in traditional approaches they are usually taken for granted, without mention. They are not quite sufficient, however, to define entropy. A crucial additional ingredient is the comparison hypothesis for the relation $\prec$. In essence, this is the hypothesis that all equilibrium states, simple or compound, can be grouped into classes, such that if X and Y are in the same class, then either $X \prec Y$ or $Y \prec X$. In nature, a class consists of all states with the same mass and chemical composition—that is, with the same amount of each of the chemical elements. If chemical reactions and mixing processes are excluded, the classes are smaller and may be identified with the "systems" in the usual parlance. But it should be noted that systems can be compound, or consist of two or more vessels of different substances. In any case, the role of the comparison hypothesis is to insure that the list of pairs $X \prec Y$ is sufficiently long. Indeed, we shall give an example later where the list of pairs satisfies all the other axioms, but which is *not* describable by an entropy function.

The construction of entropy

Our main conclusion (which we do not claim isobvious, but whose proof can be found in reference [2]) is that the existence and uniqueness of entropy is a consequence of the comparison hypothesis and the assumptions about adiabatic accessibility stated above. In fact, if X_0, X and X_1 are three states of a system and λ is any scaling factor between 0 and 1, then either $X \prec ((1-\lambda)X_0, \lambda X_1)$ or $((1-\lambda)X_0, \lambda X_1) \prec X$ must be true, by the comparison hypothesis. If *both* alternatives hold, then the properties of entropy demand that

$$S(X) = (1-\lambda)S(X_0) + \lambda S(X_1).$$

If $S(X_0) \neq S(X_1)$ this equality can hold for at most one λ. With X_0 and X_1 as reference states, the entropy is therefore *fixed*, apart from two free constants, namely the values $S(X_0)$ and $S(X_1)$.

From the properties of the relation $\prec$ listed above, one can show that there is, indeed, always a $0 \leq \lambda \leq 1$ with the required properties, provided that $X_0 \prec X \prec X_1$. It is the *largest* λ, denoted $\lambda_{\rm max}$, such that $((1-\lambda)X_0, \lambda X_1) \prec X$. Defining the entropies of the reference states arbitrarily as $S(X_0) = 0$ and $S(X_1) = 1$ unit, we obtain the following simple *formula for entropy*:

$$S(X) = \lambda_{\rm max} \text{ units.}$$

The scaling factors $(1-\lambda)$ and λ measure the amount of substance in the states X_0 and X_1 respectively. The formula for entropy can therefore be stated in the following words: $S(X)$ is the maximal fraction of substance in the state X_1 that can be transformed adiabatically (that is, in the sense of $\prec$) into the state X with the aid of a complementary fraction of substance in the state X_0. This way of measuring S in terms of substance is reminiscent of an old idea, suggested by Pierre Laplace and Antoine Lavoisier, that heat be measured in terms of the amount of ice melted in a process. As a concrete example, let us assume that X is a state of liquid water, X_0 of ice and X_1 of vapor. Then $S(X)$ for a kilogram of liquid, measured with the entropy of a kilogram of water vapor as a unit, is the maximal fraction of a kilogram of vapor that can be transformed adiabatically into liquid in state X with the aid of a complementary fraction of a kilogram of ice. (See figure 3.)

In this example the maximal fraction $\lambda_{\max}$ cannot be achieved by simply exposing the ice to the vapor, causing the former to melt and the latter to condense. This would be an irreversible process—that is, it would not be possible to reproduce the initial amounts of vapor of ice adiabatically (in the sense of the definition given earlier) from the liquid. By contrast, $\lambda_{\max}$ is uniquely determined by the requirement that one can pass adiabatically from X to $((1-\lambda_{\max})X_0, \lambda_{\max}X_1)$ *and* vice versa. For this transformation it is necessary to extract or add energy in the form of work—for example by running a little reversible Carnot machine that transfers energy between the high-temperature and low-temperature parts of the system (see figure 3). We stress, however, that neither the concept of a "reversible Carnot machine" nor that of "temperature" is needed for the logic behind the formula for entropy given above. We mention these concepts only to relate our definition of entropy to concepts for which the reader may have an intuitive feeling.

By interchanging the roles of the three states, the definition of entropy is easily extended to situations where $X \prec X_0$ or $X_1 \prec X$. Moreover, the reference points X_0 and X_1, where the entropy is defined to be 0 and 1 unit respectively, can be picked consistently for different systems such that the entropy will satisfy the crucial additivity and extensivity conditions

$$S(X, X') = S(X) + S(X') \qquad \text{and} \qquad S(\lambda X) = \lambda S(X).$$

It is important to understand that once the existence and uniqueness of entropy has been established one need not rely on the $\lambda_{\max}$ formula displayed above to determine it in practice. There are various experimental means to determine entropy that are usually much more practical. The standard method consists of measuring pressures, volumes and temperatures (on some empirical scale), as well as specific and latent heats. The empirical temperatures are converted into absolute temperatures T (by means of formulas that follow from the mere existence of entropy but do not involve S directly), and the entropy is computed by means of formulas like $\Delta S = \int (dU + PdV)/T$, with P the pressure. The existence and uniqueness of entropy implies that this formula is independent of the path of integration.

Comparability of states

The possibility of defining entropy entirely in terms of the relation $\prec$ was first clearly stated by Giles [7]. (Giles's definition is different from ours, albeit similar in spirit.) The importance of the comparison hypothesis had been realized earlier, however [4, 5, 6]. All these authors take the comparison hypothesis as a postulate—that is, they do not attempt to justify it from other simpler premises. However, it is in fact possible to *derive* comparability for any pair of states of the same system from some natural and directly accessible properties of the relation $\prec$ [2]. In this derivation of comparison the customary parametrization of states in terms of energy and work coordinates is used, but it has to be stressed that such parametrizations are irrelevant, and therefore not used, for our definition of entropy—once the comparison hypothesis is established.

To appreciate the significance of the comparison hypothesis it may be helpful to consider the following example. Imagine a world whose thermodynamical sytems consist exclusively of incompressible solid bodies. Moreover, all adiabatic state changes in this world are supposed to be obtained by means of the following elementary operations:

- Mechanical rubbing of the individual systems, increasing their energy.
- Thermal equilibration in the conventional sense (by bringing the systems into contact.)

The state space of the compound system consisting of two identical bodies, 1 and 2, can be paramertized by their energies, U_1 and U_2. Figure 4 shows two states, X and Y of this compound system, and the states that are adiabatically accessible from eachof these states. It is evident from the picture that neither $X \prec Y$ nor $Y \prec X$ holds. The comparison hypothesis is therefore violated in this hypothetical example, and it is not possible to characterize adiabatic accessibility by means of an additive entropy function. A major part of our work consists of understanding why such situations do not happen—why the comparison hypothesis appears to be true in the real world.

The derivation of the comparison hypothesis is based on an analysis of simple systems, which are the building blocks of thermodynamics. As already mentioned the states of such systems are described by one energy coordinate U and at least one work coordinate, like the volume V. The following concepts play a key role in this analysis:

- The possibility of forming "convex combinations" of states of simple systems with respect to the energy U and volume V (or other work coordinates). This means that given any two states X and Z of one kilogram of our system one can pick any state Y on the line between them in U, V space and, by taking appropriate fractions λ and $1 - \lambda$ in states X and Z, respectively, there will be an adiabatic process taking this pair of states into the state Y. This process is usually quite elementary. For example, for gases and liquids one need only remove the barrier that separates the two fractions of the system. The fundamental property of entropy increase will then tell us that $S(Y) \geq \lambda S(X) + (1 - \lambda)S(Z)$. As Gibbs emphasized, this "concavity" is the basis for thermodynamical stability—namely positivity of specific heats and compressibilities.

- The existence of at least one irreversible adiabatic state change, starting from any given state. In conjuction with concavity of S this seemingly weak requirement excludes the possibility that the entropy is constant in a whole neighborhood of some state. The classical formulations of the second law follow from this.

- The concept of thermal equilibrium between simple systems, which means, operationally, that no state changes takes place when the systems are allowed to exchange energy with each other at fixed work coordinates. The zeroth law of thermodynamic says that if two systems are in thermal equilibrium with a third, then they are in thermal equilibrium with one another. This property is essential for the additivity of entropy, because it allows a consistent adjustment of the entropy unit for different systems. It leads to a definition of temperature by the usual formula $1/T = (\partial S/\partial U)_V$.

Using these notions (and a few others of a more technical nature) the comparison hypothesis can be established for all simple systems and their compounds.

It is more difficult to justify the comparability of states if mixing processes or chemical reactions are taken into account. In fact, although a mixture of whiskey and water at $0°$ C is obviously adiabatically accessible from separate whiskey and ice by pouring whiskey from one glass onto the rocks in the other glass, it is not possible to reverse this process adiabatically. Hence it is not clear that a block of a frozen whiskey/water mixture at $-10°$ C, say, is at all related in the sense of $\prec$ to a state in which whiskey and water are in separate glasses. Textbooks usually appeal here to *gedanken* experiments with "semipermeable membrane" that let only water molecules through and withhold the whiskey molecules, but such membranes really exist only in the mind [10]. However, without invoking any such device, it turns out to be possible to shift the entropy scales of the various substances in such a way that $X \prec Y$ always implies $S(X) \leq S(Y)$. The converse assertion, namely, $S(X) \leq S(Y)$ implies $X \prec Y$ provided X and Y have the same chemical composition, cannot be guaranteed *a priori* for mixing and chemical reactions, but it is empirically testable and appears to be true in the real world. This aspect of the second law, comparability, is not usually stressed, but it is important; it is challenging to figure out how to turn the frozen whiskey/water block into a glass of whiskey and a glass of water without otherwise changing the universe, except for moving a weight, but such an adiabatic process is possible.

What has been gained?

The line of thought that started more than forty years ago has led to an axiomatic foundation for thermodynamics. It is appropriate to ask what if anything has been gained compared to the usual approaches involving quasi-static processes and Carnot machines on the one hand and statistical mechanics on the other hand. There are several points. One is the elimination of intuitive, but hard-to-define concepts like "hot", "cold" and "heat". Another is the recognition of entropy as a codification of possible state changes,

$X \prec Y$, that can be accomplished without changing the rest of the universe in any way except for moving a weight. Temperature is eliminated as an *a priori* concept and appears in its natural place as a quantity derived from entropy and whose consistent definition really depends on the existence of entropy, rather than the other way around. To define enetropy, there is no need for special machines and processes on the empirical side, and there is no need for assumptions about models on the statistical mechanical side. Just as energy conservation was eventually seen to be a consequence of time translation invariance, in like manner entropy can be seen to be a consequence of some simple properties of the list of state pairs related by adiabatic accessibility.

If the second law can be demystified, so much the better. If it can be seen to be a consequence of simple, plausible notions then, as Einstein said, it cannot be overthrown.

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