A Simple Proof of the Second Law of Thermodynamics

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By expressing the Boltzmann statistical weight function \( W \) in terms of the Boltzmann thermodynamic probabilities \( p_r \), i.e. \( W = W(p_1, p_2, \ldots, p_{r-1}, p_r, p_{r+1}, \ldots, p_m) \), and thereafter evoking the here set-forth Thermodynamic Probability Evolution Hypothesis – namely that, at the very least, a microstate can only evolve from a state of low thermodynamic probability to one of a higher thermodynamic probability, we demonstrate a simple and veritable proof of the Second Law of Thermodynamics (SLT), namely that the entropy of an isolated thermodynamic system always increases. Effectively and resultantly, this proof requires or points to the idea that the SLT holds not only statistically for an isolated system as currently understood, but must hold exactly for each of the microstates making up the system, hence, the restriction that the SLT holds only for an isolated thermodynamic system, may have to fall by the wayside.

\[ W = W(p_1, p_2, \ldots, p_{r-1}, p_r, p_{r+1}, \ldots, p_m) , \quad (1) \]

we humbly make an attempt at a proof that may shed some light on the very foundations and meaning of the SLT.

2 The four manifestations of entropy

Entropy manifests itself in four different forms. The first form is via Clausius’ entropy, second is via Boltzmann’s entropy, third is via Gibb’s entropy and lastly is via the information theoretic entropy through Shannon’s entropy. The main thrust of the present section is to try and link these four manifestations of entropy so that a proof of just one of them is sufficient proof for the rest of the entropies. Herein, we prove for the case of Boltzmann’s entropy.

2.1 Clausius entropy

The great German physicist and mathematician – Rudolf Julius Emanuel Clausius (1822-1888), is – by and large – generally regarded as one of the central figures and founders of the science of thermodynamics. In his most important paper [5] entitled “On the Moving Force of Heat”, Clausius first stated the basic ideas of the SLT and later, he introduced the concept of entropy (Clausius [6]). Further, in 1870, Clausius introduced the Virial Theorem which applies to heat [7]. Clausius’ most famous statement of the SLT was published in both the German [8] and the English language [9]:

Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

Further, in this famous paper [5], Clausius showed that there was a contradiction between Carnot’s principle and the concept of conservation of energy and realising this, he restated
the two laws of thermodynamics to overcome this contradiction. For a system initially at temperature $T_i$ and final temperature $T_f$ and in-between these two temperature changes a net heat $dQ$ takes place, for such a system, Clausius defined the entropy change, as:

$$\text{d}S = \int_{T_i}^{T_f} \frac{dQ}{T}.$$  \hspace{1cm} (2)

For an isolated thermodynamics system, the entropy always increases [6], and this is stated in the famous Clausius Law as:

$$\text{d}S = \int \frac{dQ}{T} \geq 0.$$  \hspace{1cm} (3)

The landmark 1865 paper [6] in which he introduced the concept of entropy ends with the following summary of the First and Second Laws of Thermodynamics:

The energy of the Universe is constant.

The entropy of the Universe tends to a maximum.

### 2.2 Boltzmann entropy

Boltzmann’s goal in his work [10] was to explain the behaviour of macroscopic systems in terms of the most fundamental dynamical laws governing their microscopic constituents. For example, consider clear and clean water in a container. In this container pour a drop of say potassium permanganate. If left to itself, the potassium permanganate will gradually spread in the water until the water is color blue i.e. the potassium permanganate is evenly spread throughout the water. Why does the water and potassium permanganate mixture prefer to be in the equilibrium macrostate where the potassium permanganate is evenly spread? Why?

To the mundane, the answer is that this is the way things are and to expect anything different is nothing short of asking for a miracle. The pedestrian mind will insatiably absorb this as an effect and consequence of the natural order of the world – not to Boltzmann. According to Boltzmann, this requires an answer that penetrates deep into the microscopic nature of reality at its most elementary and most fundamental level. That is, this has something to do with the evolution of the entropy of the system.

Boltzmann (1877) published his statistical interpretation of the SLT in response to objections from Loschmidt who had said that the $H$-theorem singled out the direction in time in which his $H$-function decreases, whereas the underlying mechanics was the same whether time flowed forward or backward. It is this paper that Boltzmann published his famous equation – where accordingly, at any give time – the Boltzmann entropy $S_B$ of this system is given by:

$$S_B = k_B \ln \mathcal{W},$$  \hspace{1cm} (4)

where $k_B$ is the Boltzmann constant. Later, the reluctant German physicist [11], Max Karl Ernst Ludwig Planck (1858-1947), based the derivation of his black body radiation formula [12–14] on (4). Boltzmann’s Eq. (4) has been successful in describing systems with minimal-most interactions in Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein statistics. For later instructive purposes, in the subsequent sections, we shall write down the corresponding thermodynamic weights ($\mathcal{W}$).

#### 2.2.1 Maxwell-Boltzmann statistics

Maxwell–Boltzmann statistics (hereafter MB-statistics) describe the average distribution of non-interacting material particles over various energy states (microstates) in thermal equilibrium, and this kind of statistics is applicable in conditions where the temperature is high enough or where the particle density is low enough to render quantum effects negligible.

Suppose we have a gas of $\mathcal{N}$ identical point particles in a box of volume $V$. By “gas”, we here-and-after mean that the particles are non-interacting with one another, or more realistically, the effects of the interactions are negligibly small. Suppose we know the single particle states in this gas. In MB-statistics, what we would like to know is what are the possible macrostates of the system as a whole. That is, how many ways are there of arranging the microstates? If $n_r$ is the number of particles occupying the energy state $\epsilon_r$, then, an appeal to statistics will tell us that the multiplicity $\mathcal{W}$ of different ways of arranging such a system is:

$$\mathcal{W}_{MB} = \prod_{r=1}^{m} \frac{\mathcal{N}!}{n_r !}.$$  \hspace{1cm} (5)

It was pointed out by Gibbs, that the above expression for $\mathcal{W}$ does not yield an extensive entropy, and as such – it must be faulty somehow. This problem is known as the Gibbs paradox. The problem is that the particles considered by the above equation are not indistinguishable. In other words, for two particles (A and B) in two energy sublevels the population represented by [A,B] is considered distinct from the population [B,A] while for indistinguishable particles, they are not.

#### 2.2.2 Bose-Einstein statistics

If we carry out the same argument presented above in the MB-statistics – albeit, this time for indistinguishable particles, we are led to the Bose-Einstein (BE) multiplicity expression $\mathcal{W}_{BE}$ i.e.:

$$\mathcal{W}_{BE} = \prod_{r=1}^{m} \frac{(n_r + g_r - 1)!}{n_r !(g_r - 1)!}.$$  \hspace{1cm} (6)

The MB-distribution follows from this BE-distribution for temperatures well above absolute zero, implying that $g_r \gg 1$. The MB-distribution also requires low density, implying that $g_r \gg n_r$. The BE-theory of was developed in 1924-5 by the Indian theoretical physicist Satyendra Nath Bose (1894-1974) and in full collaboration with Bose [15], the idea
was later adopted and extended by the great Albert Einstein (1879-1955). Due to Dirac [16, 17], particles that follow the BE-theory are called \textit{bosons}.

2.2.3 Fermi-Dirac statistics

First derived in 1926 by the great Italian physicist – Enrico Fermi (1901-1954) [18, 19] and later in the same year by the finest and greatest English theoretical physicist of the modern age, Paul Adrian Maurice Dirac (1902-1984) [20], Fermi-Dirac statistics (here-and-after FD-statistics) describe a distribution of particles over energy states in systems consisting of many identical particles that obey the \textit{Pauli Exclusion Principle}, where according no two particle can occupy the same quantum state and this has a considerable effect on the properties of the system. Further, FD-statistics apply to identical particles with half-integer spin (fermions) in a system in thermodynamic equilibrium. Additionally, the particles in this system are assumed to have negligible mutual interaction (gas) and this allows the many-particle system to be described in terms of single-particle energy states.

As is the case in the derivation of \( W_{\text{BE}} \): suppose we have a number of energy levels, labelled by index \( i \) with each level having energy \( e_i \) and containing a total of \( n_r \) particles. Further, suppose each level contains \( g_r \) (degeneracy) distinct sub-levels, all of which have the same energy, and which are distinguishable. The Pauli exclusion principle allows that only one fermion can occupy any such sub-level. The number \( w_r \) of ways of distributing \( n_r \) indistinguishable particles among the \( g_r \) sub-levels of an energy level, with a maximum of one particle per sub-level, is given by the binomial coefficient, using its combinatorial interpretation:

\[
w_r = \frac{g_r!}{n_r!(g_r - n_r)!}.
\]

The number of ways that a set of occupation numbers \( n_r \) can be realized is the product of the ways that each individual energy level can be populated, i.e.:

\[
W_{\text{FD}} = \prod_{r=1}^{m} \frac{g_r!}{n_r!(g_r - n_r)!}.
\]

2.3 Gibbs entropy

The great theoretician – Josiah Willard Gibbs (1839-1903), after whom the Gibbs entropy is named, was an American mathematician, chemist and physicist who made important and fundamental theoretical contributions to mathematics, chemistry and physics. Gibbs argued that for a thermodynamic system with \( W \) macrostates, if \( P_r \) is the thermodynamic probability of occurrence of the \( r \)-th macrostate, then the entropy \( S_G \) of this system measured over all the macrostate \( r = 1, 2, \ldots, m-1 \), \( W' \) is defined [21, 22]:

\[
S_G = -k_B \sum_{r=1}^{w'} P_r \ln P_r ,
\]

where \( P_r \) is the probability of occurrence of the \( r \)-th macrostate. This definition, like Boltzmann’s entropy, is a fundamental postulate whose ultimate justification is its ability to explain experimental facts, especially for systems of interacting particles.

The work of Gibbs on the applications of thermodynamics was instrumental in transforming physical chemistry into a rigorous inductive science. In \textit{Statistical Mechanics} (a term coined by Gibbs himself), he combined the work of James Clerk Maxwell and Ludwig Boltzmann on the kinetic theory of gases, thus explaining the macroscopic laws of thermodynamics as a consequence of the underlying fundamental statistical properties of ensembles of the possible states of a physical system composed of many particles.

Gibbs’ approach is very useful in the study of “equilibrium” statistical mechanics and solid state physics [22], whereas Boltzmann’s approach is very useful in the study of gas-like systems such as electrons, photons, etc. However, Gibbs’ approach in the treatment of nonequilibrium systems presents contentious problems [22, 23].

The American – Wayman Crow Distinguished Professor of Physics at Washington University in St. Louis – Edwin Thompson Jaynes (1922-1998), demonstrated [24] in 1965 that the Gibbs entropy is equal to the classical “heat engine” entropy of Clausius (\( dS = \int_{f}^{T} dQ/T \)). Therefore, the Gibbs entropy is the same as the Clausius entropy, i.e.:

\[
S_G = S_C ,
\]

hence, a proof that \( dS_G \geq 0 \) is as well a proof that \( dS_C \geq 0 \). Later in the paper, we will prove that \( dS_G \geq 0 \) thus, accordingly, this proof is a proof of the Clausius entropy as well.

2.4 Shannon entropy

The concept of entropy in \textit{Information Theory} describes how much information there is in a signal or event. The \textit{Entropy Information Theory} was advanced by the American mathematician, electrical engineer, and cryptographer – Claude Elwood Shannon (1916 – 2001) in his now famous 1948 paper [25, 26] entitled “A Mathematical Theory of Communication”. The Shannon entropy is a carefully constructed function of a set of probabilities that satisfies a number of constraints. These constraints are chosen such that entropy measures the uncertainty associated with a probability distribution.

An intuitive understanding of information entropy relates to the amount of uncertainty about an event associated with a given probability distribution. As an example, consider a box of
containing many coloured balls. If the balls are all of different colours and no colour predominates, then our uncertainty about the colour of a randomly drawn ball is maximal. On the other hand, if the box contains more red balls than any other colour, then there is slightly less uncertainty about the result: the ball drawn from the box has more chances of being red (if we were forced to place a bet, we would bet on a red ball). Telling someone the colour of every new drawn ball provides them with more information in the first case than it does in the second case, because there is more uncertainty about what might happen in the first case than there is in the second. Intuitively, if we know the number of balls remaining, and they are all of one color, then there is no uncertainty about what the next ball drawn will be, and therefore there is no information content from drawing the ball. As a result, the entropy of the “signal” (the sequence of balls drawn, as calculated from the probability distribution) is higher in the first case than in the second.

Shannon, in fact, defined entropy as a measure of the average information content associated with a random outcome. Shannon’s definition of information entropy makes this intuitive distinction mathematically precise. His definition satisfies these desiderata:

1. The measure should be continuous – i.e. changing the value of one of the probabilities by a very small amount should only change the entropy by a small amount.
2. If all the outcomes (ball colours in the example above) are equally likely, then entropy should be maximal. In this case, the entropy increases with the number of outcomes.
3. If the outcome is a certainty, then the entropy should be zero.
4. The amount of entropy should be the same independently of how the process is regarded as being divided into parts.

In his paper [25, 26], Shannon makes the claim that the only function satisfying the above requirement will be of the form:

$$ S_t = -k_s \sum_{r=1}^{m} p_r \log_2 p_r $$

(11)

where $k_s$ is the Shannon constant. If the Shannon constant were to be set such that: $k_s = k_B \ln 2$, then, the Shannon entropy will equal the Gibbs entropy, i.e.:

$$ S_t = S_G. $$

(12)

Now, having discussed the four different manifestations of entropy, we shall proceed to describe our thermodynamic system.

3 Description of thermodynamic system

Key to our proof here is the clarity in the definition of what we here term the:

2. Thermodynamic Probability (TP).

As depicted in Table 1, we envisage a thermodynamic system to constitute discrete, finite and countable cells (microstates). These cells can each be numbered 1, 2, 3, ..., $r-1$, $r$, $r+1$, ..., $m-2$, $m-1$, $m$ and in these cells we are to fit a total of $\mathcal{N}$ particles. The number of particles in each of these cells at a given material time is $n_1$, $n_2$, $n_3$, ..., $n_{r-1}$, $n_r$, $n_{r+1}$, ..., $n_{m-2}$, $n_{m-1}$, $n_m$, respectively.

Now, the OFTM, $f_r$, of each of these microstates is such that:

$$ f_r = \frac{n_r}{\mathcal{N}}, $$

(13)

where $f_r$ is the total fraction of particles in the $r^{th}$ cell at a given material time. We must note that:

$$ \sum_{r=1}^{m} f_r = 1. $$

(14)

Now, to define the thermodynamic probability $p_r$, we need to introduce some new idea. This is the idea of the potential holding capacity of a given microstate. That is, take say the $r^{th}$ microstate. This microstate has $n_r$ particles occupying it, whereas the maximum possible number of particles that can occupy this microstate is $q_r$. What this means is that the microstate is not completely filled, but partially so. The tendency is to fill this microstate rather than empty it. The most probable state is that when this microstate is completely filled and the most unlikely is – likewise, when this microstate is empty.

Under such a setting, it follows that the ratio:

$$ p_r = \frac{n_r}{q_r}, $$

(15)

must give the probability that the $r^{th}$ microstate is occupied and $f_r$ is simply the fraction of the number of particles occupying this microstate at a given material time relative to the total number of particles making up the entire system. Clearly:

$$ 0 \leq n_r \leq q_r, $$

(16)

hence:

$$ 0 \leq p_r \leq 1, $$

(17)

thus:

$$ \left[ \sum_{r=1}^{m} 0 \leq \sum_{r=1}^{m} p_r \leq \sum_{r=1}^{m} 1 \right] \rightarrow \left[ 0 \leq \sum_{r=1}^{m} p_r \leq m \right]. $$

(18)

Writing (18) in a more succinct manner, we will have:

$$ 0 \leq \frac{1}{m} \left( \sum_{r=1}^{m} p_r \right) \leq 1. $$

(19)

Now, having defined the occupational frequency of a thermodynamic microstate ($f_r$) and the thermodynamic probability ($p_r$), we shall proceed to lay bare the assumption or working hypothesis that will lead us to our desired proof of the SLT.
**4 Hypothesis (assumption)**

We shall put forward our working hypothesis which we shall coin the name – Thermodynamic Probability Evolution Hypothesis (TPE-hypothesis), and this hypothesis states that:

Thermodynamic probability changes are always positive, i.e. $dP_r \geq 0$. That is to say, at time $t_i$, if the $r^{th}$ state has energy $e_i(t_i)$, and if this energy were to change to its next state $e_i(t_j)$, at a later time $t_j$ ($i > j$), then the accompanying thermodynamic probability changes $dP_r$, from the state $e_i(t_i)$, to the state $e_i(t_j)$, are always such that: $dP_r \geq 0$.

Given the above hypothesis (assumption), we shall now proceed to our most simple proof of the SLT from a Boltzmann entropy standpoint. But before that, we shall argue in the next section that a proof that the Boltzmann entropy always increases is sufficient proof that all the other three forms of entropy are bound by the same law, hence, a proof that the Boltzmann entropy always increases is a general proof of the SLT.

**5 Boltzmann and Gibbs entropies**

Our proof of the SLT to be presented in the next section makes use of the Boltzmann entropy. If we wanted a general proof that entropy always increases, this would mean we must prove the SLT for the four different manifestations of entropy. But, we do not need to do this because the Clausius and Shannon entropies are – one way or the other – equivalent to the Gibbs entropy, the meaning of which is that we would only need to prove for the two cases of the Gibbs and Boltzmann entropy. Again, because the Gibbs and Boltzmann entropy can be linked, it is sufficient to prove only for one of the two cases and in this paper, we prove for the case of the Boltzmann entropy.

To that end – i.e. in order to demonstrate this link between the Gibbs and Boltzmann entropy, we know that in the event that the probability of occurrence of all the $W$ macrostates, the Gibbs entropy reduces to the Boltzmann entropy. To see this, we know that in this event where all the $W$ macrostates are equally likely, we will have $P_r = 1/W$, so that:

$$S_G = -k_B \sum_{r=1}^W \frac{1}{W} \ln \left( \frac{1}{W} \right) = k_B \ln W = S_B .$$

(20)

In all other cases:

$$S_B < S_G ,$$

(21)

hence, in general, we have that:

$$[S_B \leq S_G ] \Rightarrow [ \text{if } (dS_B \geq 0), \text{ then } (dS_G \geq 0)] ,$$

(22)

hence, a proof that: $dS_B \geq 0$, is also a proof that: $dS_G \geq 0$. Consequently and according to the foregoing, a proof that: $dS_B \geq 0$, is indeed a general proof of the SLT for all the four different manifestations of entropy.

**6 Proof**

As a starting point, we shall as has been done in (1), assume that the Boltzmann statistical weight function $W_r$ of an arbitrary thermodynamic system is a function of the thermodynamic probabilities ($p_r$). With this assumption safely in place, we note that if we are to have:

$$W = \mathcal{W}_0 \exp \left( \sum_{r=1}^m p_r - \sum_{r=1}^m p_r \ln p_r \right) ,$$

(23)

where $\mathcal{W}_0$ is a constant for the given isolated thermodynamic system in question, then, we can very easily proffer a proof of the SLT on the basis of the TPE-hypothesis, because, from the Boltzmann Eq. (4), it follows from (1) that:

$$S_B = k_B \ln \mathcal{W}_0 + k_B \sum_{r=1}^m p_r - k_B \sum_{r=1}^m p_r \ln p_r ,$$

(24)

hence, taking a differential of (24), one obtains that:

$$dS_B = -k_B \sum_{r=1}^m dp_r \ln p_r .$$

(25)
Now, since $0 < p_r \leq 1$, it follows from this – that $\ln p_r \leq 0$, and from the TPE-hypothesis where one is given that $dp_r > 0$, it further follows that $dp_r \ln p_r \leq 0$, hence:

$$\sum_{j=i}^{m} dp_r \ln p_r \leq 0,$$

thus, inserting all these conditions into (25), we will have that:

$$dS = \sum_{i=0}^{m} p_r \ln p_r \geq 0,$$  \hspace{1cm} (26)

hence result. Clearly, the SLT follows directly from a simple definition of $W$ in terms of the thermodynamic probabilities of all the different microstates and as well as from the TPE-hypothesis.

7 General discussion

On the basis of the seemingly self-evident and reasonable Thermodynamic Probability Evolution Hypothesis here put forward, we have just “proved” (demonstrated) the SLT. If anything, the “proof” appears to us (and perhaps to the reader as well), to not only be very simple, but quite straightforward. Be that as it may – given the amount of effort that has gone into seeking a proof of the SLT, one can not help but wonder if this proof is really correct – are we not missing something here? How does it come about that such a very simple pedestrian proof has escaped the reach of those that have vigorously sought it? We do not know! All we can say is that, what we have before our eyes appears very strongly to be not only a veritable proof but a perdurable proof as well. We leave it up to the esteemed reader to be the judge on the validity or lack thereof the proof.

In addition, we do not know whether to call this a proof or a demonstration. The reason for this self-doubt is that, for a proof, the basis on which it stands must be firm – yet, in what we have presented, the basis is a mere hypothesis which we only evoked after we noted after a meticulous examination that if one were to express $S_B$, as function of $p_r$, i.e. $S_B = S_B(p_1, p_2, \ldots, p_r, \ldots, p_m)$; the experimental result, $dS \geq 0$ can be deduced from a number-theoretic viewpoint provided that $dp_r > 0$. Realising this, we evoked this as our working hypothesis wherefrom the proof flowed smoothly. In this way, it would not appear – but strongly so that, what we have is a reverse engineered proof. In this way, it, ultimately, would mean that the SLT directly implies the TPE-hypothesis. Even if this were the case, it is still a great leap forward in our understanding of the SLT as this would mean the source of this law is the manner in which the thermodynamic probabilities evolve from one value-state to the next.

That is to say, the SLT holds because the dynamic thermodynamic probabilities $p_r(t)$, of the different microstates only change to attain at least higher values than their previous, that is, the given energy state only evolves (i.e. changes its state) to allow at least a greater thermodynamic probability. Thus, whether one decides that this is not a genuine proof because it has worked backwards from an experimental result ($dS \geq 0$) in which process the TPE-hypothesis is implied, one thing is pristine clear:

It must be acknowledged that at the very least, the present demonstration (proof) has surely peered deeper into the nature of the SLT to unearth the TPE-hypothesis as a driver of this fundamental, paramount and sacrosanct law of Nature.

Hence, this paper may very well be a great – if not a giant leap forward, in humankind’s endeavour to understand the mysterious and arcane foundations of the Second Law of Thermodynamics.

Entropy is (and has always been) one of those physics concepts that are difficult to define, let alone understand. Through his entropy function [Eq. (4)], Boltzmann defined it as a measure of the multiplicity of a thermodynamic system. Of the three definitions i.e. Boltzmann, Gibbs and Clausius entropy), the Clausius energy has been and is – the most difficult to define and understand. According to what we have presented herein, one can safely define entropy as:

a measure of the probability of evolution of a thermodynamic system.

With entropy having been given this definition, it becomes much easier to understand the SLT as a simple statement about the dynamical evolution of the thermodynamic probability of the system.

References


