Does the Clausius statement of the second law, or its violation, have any meaning during a time-reversed heat energy transfer process?

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Abstract

We might assume that if time ran backwards, heat energy would be transferred spontaneously from colder to hotter. However, if heat energy actually did *flow* spontaneously from colder to hotter, then equilibrium states and temperatures required for thermodynamics would not be established. As a simple example, consider if heat energy flow were to flow from colder-to-hotter, such as in a metal rod heated at one end. Any distribution of temperatures in the metal rod causes further colder-to-hotter flow between adjacent layers of the metal. This results in hot regions of undetermined thickness – and an equilibrium temperature is not established for the rod. So, if time were reversed, we argue that *during* a heat energy transfer process, the Clausius statement of the second law is not merely violated but is *meaningless*. Yet, based on the initial and final states of a time-reversed process, the Clausius statement does appear to hold *overall*. We consider the implication that the Clausius statement is not continuously reversible in time - and wonder if the other equivalent forms of the second law have meaning for time reversal.

1. INTRODUCTION

In this paper, we consider the Clausius statement of the second law of thermodynamics with regards to both a forwards and backwards direction of time. We might consider that if time were reversed then heat energy could flow spontaneously from colder to hotter. At first, this may seem to "only" violate the Clausius statement of the second law of thermodynamics.

However, in a fairly recent paper by Kaufman and Leff[1], "What if Energy Flowed from Cold to Hot? Counterfactual Thought Experiments", they considered a world where energy flowed from colder-to-hotter. They abbreviate this as a C2H world and showed that a spontaneous flow of heat energy from colder to hotter would not result in equilibrium states or temperatures. A key point from their paper was, "The C2H world is not simply a time-reversed hot-to-cold-world." In this paper, we go a little further by asking if cold-to-hot energy flow - and the Clausius statement of the second law or its violation - has any meaning during a time-reversed heat energy transfer process.

In the next section, we provide some background into the laws of thermodynamics, the equivalence of the statements of the second law of thermodynamics, and some related observations. The subsequent section discusses an association between the arrow of time and the second law that is found in the literature. Then the Clausius statement, its violation, and whether it has any meaning during a time-reversed heat energy transfer process is discussed.

2. BRIEF BACKGROUND OF THE LAW OF THERMODYNAMICS

Historically, the second law was developed before the first law. However, we will describe the laws in their sequential order. A quote from Kaufman and Leff[1] about the first law states:

> **First law of thermodynamics:** The first law of thermodynamics is a generalized form of conservation of energy that is adopted for thermodynamic processes and is based on the existence of equilibrium states. The first law applies to processes that connect initial and final equilibrium states *i* and *f*, and conserves energy.

They state that it is important to understand that the first law says more than just conservation of energy. It requires the existence of *equilibrium states* for thermodynamics. The attainment of equilibrium states in thermodynamics will be critical to the discussion in the present paper. The mathematical form of the first law is:

$$\Delta \boldsymbol{U} = \boldsymbol{Q} + \boldsymbol{W} \tag{1}$$

where the left side is the difference $\Delta \boldsymbol{U} \equiv \boldsymbol{U_f} - \boldsymbol{U_i}$ between the internal energy values in the final and initial equilibrium states, and $\boldsymbol{Q}$ and $\boldsymbol{W}$ are the heat energy and work energy transfers to a system during the process that induces the energy change.

The second law of thermodynamics and entropy were based on investigations into steam engines during the nineteenth century.[2] Carnot[3] and Clausius were interested in maximizing work and efficiency for heat engines that operated with idealized hot and cold temperature reservoirs. A maximally efficient heat engine, such as the Carnot cycle, is reversible. During the Carnot cycle, the maximum possible net-work output W is obtained for the cycle operating between a hot temperature reservoir at temperature T_h and a cold temperature reservoir at temperature T_c. The maximal thermal efficiency is given by the Carnot efficiency, $1 - \frac{T_c}{T_H}$. Specifically, the Carnot cycle extracts heat energy Q_h isothermally from the hot temperature reservoir at temperature T_h and rejects heat energy Q_c isothermally to the cold temperature reservoir at temperature T_c. For the adiabatic processes between the temperature reservoirs, no heat energy is exchanged (there is no heat energy transfer through a finite temperature difference). It is well-known that the relation $Q_h\ /T_h\ = Q_C/T_C$ was established by this cycle, which motivated Clausius to define the state variable entropy, $dS = \frac{\partial Q}{T}$.

Some heat energy must always be transferred from the heat source to the heat sink in order to generate this maximum amount of work. Yet, since a reversible cycle generates the maximum possible amount of work when transferring heat energy from the hot temperature reservoir to the cold temperature reservoir, then no entropy is generated.

When entropy generation has occurred for a heat engine, then energy, which could have otherwise been transferred to work by a maximally efficient cycle, has been transferred to a cold temperature reservoir that is closer to absolute 0. Since heat energy transfer only occurs spontaneously from hotter-to-colder, then the amount of work that can be generated in the universe has decreased. This is captured in a statement found in the literature:

Entropy is a measure of the unavailability of energy for doing work.[4]

For all reversible processes, the change in entropy of the universe, $\Delta S_{universe}$ does not change:

$$\Delta \boldsymbol{S}_{\boldsymbol{universe}} = \mathbf{0} \quad \textbf{For reversible processes only}^{5} \tag{2}$$

When two finite objects at different temperatures are allowed to interact thermally, heat energy transfer occurs spontaneously from the hotter object to the colder object until thermal equilibrium exists between the objects; they obtain the same temperature. In this case, heat energy transfer occurs without generating any work. This process involves the maximum generation of entropy.

For all irreversible processes, the change in entropy of the universe, $\Delta S_{universe}$ increases:

$$\Delta \boldsymbol{S}_{\boldsymbol{universe}} > \mathbf{0} \quad \textbf{For all natural (that is, irreversible) processes}^{5} \tag{3}$$

Combining equations 1 and 2, we have the Principle of Entropy Increase (PEI), which is a form of the Second Law of Thermodynamics:

$$\Delta \boldsymbol{S}_{\boldsymbol{universe}} \geq \mathbf{0} \tag{4}$$

Entropy generation only occurs when there is heat energy transfer from hotter-to -colder without the accompanying maximal work output possible. This loss in the potential of energy to do work, or "lost work", is prevalent in the literature,[6,7,8,9] as are discussions of "exergy".

It is important to note that this lost work capability must refer to the amount of work that can be generated in the entire universe. The essence of this point is captured by the words of Sir William Thomson (Lord Kelvin) himself:[10]

> The second great law of thermodynamics involves a certain principle of *irreversible action in Nature.* It is thus shown that, although mechanical energy is *indestructible,* there is a universal tendency to its dissipation, which produces gradual augmentation and diffusion of heat, cessation of motion, and exhaustion of potential energy through the material universe. The result would inevitably be a

state of universal rest and death, if the universe were finite and left to obey existing laws...

Observation 1:

Entropy generation reduces the amount of work that can be generated in the universe.

When entropy increases for a system undergoing a process, irreversibilities are associated with the process. In this context, a process cannot be reversed which results in the initial states for the system and the universe. For an extensive discussion of reversibility and irreversibility, see Norton's paper[11], "The impossible process: Thermodynamic reversibility."

It is also important to note that idealized temperature reservoirs were used during the development of the Carnot cycle and entropy. The hot source temperature reservoir remained at temperature T_h during energy extraction, and the cold sink temperature reservoir remained at T_c during energy absorption. This allowed Carnot and Clausius to perform much simpler calculations then if the source or sink temperatures changed as energy was extracted or absorbed, respectively.

That is, it becomes mathematically simpler (*i.e.*, less specific to the circumstances and more general) to use idealized temperature reservoirs that do not change temperature when heat energy is added or removed. Of course, we do not see these idealized temperature reservoirs in our observable universe.

The use of idealized temperature reservoirs might only be thought of as a useful approximation, especially when the energy requirements of the cycle are much less than the energy available in a source or sink. If so, then any energy extracted or absorbed by a temperature reservoir does not significantly impact the reservoir's temperature. However, this means that the thermodynamics becomes decoupled from the size requirements of a cycle. In other words, *any* cycle which operates between the temperature reservoirs, no matter how large, would have no impact on the reservoir temperatures. Moreover, a cycle which is repeated again and again would have no impact on a reservoir's temperatures. We do not see this in our universe.

For the sake of argument, let us assume that the arguments put forth by Clausius and Carnot hold for idealized temperature reservoirs and their constant temperatures. With idealized temperature reservoirs, entropy generation could not reduce the amount of work that can be generated in the universe because temperature reservoirs can always supply an infinite amount of heat energy from which work could be generated. Therefore, the use of temperature reservoirs indicate that the amount of work generated in the universe could *never* be reduced. This is at odds with Key Point 1: *Entropy generation reduces the amount of work that can be generated in the universe*.

Observation 2:

There is an irony that Clausius developed the Principle of Entropy Increase, which points to a limited amount of work that can be generated in the universe, from a cycle that utilized

temperature reservoirs with a seemingly inexhaustible supply of energy capable of producing work.

This irony for the Principle of Entropy Increase may not have been previously recognized from the underlying theory on which it is based. While Clausius may have been motivated to come up with the Principle of Entropy Increase from idealized temperature reservoirs, it is clear that he also recognized that they were impossible, because he predicted the heat death of the universe (as quoted earlier). Clausius's use of idealized temperature reservoirs might be considered as an ironic guide to the Principle of Entropy Increase.

Here we note a comment made by Mella and Rodriquez.[12] The *PEI* can be applied to a thermally isolated system, where there is no heat energy exchange through the system boundary. Yet, the *PEI* will still hold if work is done on or by the system with the surroundings. They demonstrate this using the entropy for a process with initial and final states A and B, respectively:

$$S_B - S_A \geq \int_A^b \frac{\bar{d}Q}{T}$$

where Q is the heat exchanged with a reservoir at temperature T. There is no work term in the change in entropy. This observation is completely consistent with the statement shown earlier that, "Entropy is a measure of the unavailability of energy for doing work." That is, any work done on or by a system does not change its ability to do work. It is only when there is spontaneous heat energy transfer that entropy will change, *i.e.*, increase.

Other forms of the second law include the Clausius statement and the Kelvin Planck statement:

> **Clausius original statement (CS) of the second law:** "Heat cannot, of itself, pass from a colder to a hotter body."[13] This has been interpreted to mean that a spontaneous (workless) heat energy transfer cannot occur from a colder to a hotter body.

> **Kelvin-Planck statement (*KPS*) of the second law**: "It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat [energy] from a reservoir and the performance of an equivalent amount of work."[14]

The *PEI*, *CS*, and *KPS* statements of the second law are all equivalent. This can be shown by establishing a two-way implication for equivalence. An equivalence means that when one statement is true, then so is the other. Likewise, when one statement is false, then so is the other. Equivalence does not mean that the statements are the same (for otherwise they would be the same statement).

Specifically, the literature and textbooks show a well-known demonstration that the *KPS* and *CS* are equivalent: $KPS \Longleftrightarrow CS$.[15,16] The literature also shows text[17] that states that the *PEI* is "entirely equivalent to" these other forms of the second law. However, a more rigorous proof is shown in some recent papers.[18,19,20] So, we have that $KPS \Longleftrightarrow CS \Longleftrightarrow PEI$.

In the next section, we consider the direction of time and what has been referred to as the thermodynamic arrow of time.

3. BACKGROUND OF THE ARROW OF TIME AND ITS ASSOCIATION TO THE SECOND LAW

Most readers of this paper are probably aware of an association that is made between the arrow of time and the principle of entropy increase from the Second Law of Thermodynamics.[21,22,23] There are many references for this thermodynamic arrow of time. In essence, these references take the point of view that an arrow of time emerges from our macroscopic perspective of the principle of entropy increase. That is, the increasing entropy of our universe defines a thermodynamic arrow of time which is somehow reflected in our sense of the flow of time.[24] Sometimes this is formulated as: time flows into the future, but not the past, because entropy is exceedingly likely to increase into the future.

For the sake of completeness, we point out, in the Appendix, that there are objections to the point of view that there is a thermodynamic arrow of time. However, in the interest of avoiding controversy, the present paper will remain agnostic about whether there is a thermodynamic arrow of time. Instead, we consider if the implications of time flowing backwards in our universe and what this says about the meaning of the second law of thermodynamics.

Feng and Crooks[25] begin the abstract of their paper with the statement, "*An unresolved problem in physics is how the thermodynamic arrow of time arises from an underlying time reversible dynamics.*" They state:

> … almost all of the fundamental theories of physics—classical mechanics, electrodynamics, quantum mechanics, general relativity, and so on—are symmetric with respect to time reversal. The only fundamental theory that picks out a preferred direction of time is the second law of thermodynamics, which asserts that the entropy of the Universe increases as time flows towards the future.[26]

This statement is reflected by many references. Aside from the Second Law of Thermodynamics, the laws of physics are said to be time-invariant; these laws are valid if time ran backwards or forwards. This can be visualized by watching a film of an elastic collision of two balls where the associated laws (conservation of momentum, conservation of energy, and conservation of mass) hold whether the film is played forward or backwards. For example, Cengal and Boles[27] state, "*The first law places no restriction on the direction of a process*..."

The Second Law has been associated with a forward arrow of time due to the principle of entropy increase, *i.e.*, such as the spontaneous transfer of heat energy from a hotter temperature to a colder temperature. Conversely, a reversed arrow of time is associated with an entropy decrease, *i.e.*, such as the spontaneous flow of heat energy from colder temperature to a hotter temperature. Penrose[28] has stated, "*Since the entropy increases in the future direction of time, it must decrease in the past direction of time*." The idea that entropy would decrease with time reversal is not new. In a situation analogous to a reversed film, Gold[29] considered a stack of subsequent snapshots, or pictures, taken over a period of time from which the laws of physics could be ascertained. These snapshots are considered in the reverse direction, as if thumbing through a flipbook in the wrong direction. He states, "*Heat would tend to flow from cold bodies to hot bodies. Entropy of isolated systems would tend to decrease*." Later, Gold states, "*All thermodynamic processes would go in reverse.*" In this paper, we will challenge this last statement.

The thermodynamic arrow of time due to increasing entropy has also been associated with the "past hypothesis." This postulates that the universe must have started in a low entropy state, which is presumed to be minimal for the Big Bang. But Josef Loschmidt brought up an apparent paradox that must be mentioned here. He considered the argument put forth by Ludwig Boltzmann that entropy increases due to the statistical nature of molecules to spread out over time due to their interactions and collisions. In response to Boltzmann, Loschmidt argued that if the velocities of all the molecules were reversed, then entropy should be just as likely to decrease. In fact, this argument shows that entropy could reach a minimum and then increase again with time reversal, so that entropy might even increase before the Big Bang. Although opinions vary about the paradox, Hurley[30] does take a position about it while still providing a lot of background for the interested reader.

4. THE GAP IN MEANING FOR A VIOLATION OF THE CLAUSIUS STATEMENT DURING REVERSED TIME HEAT TRANSFER PROCESSES

The Clausius statement was given in section 2 as: "a spontaneous (workless) heat energy transfer *cannot* occur from a colder to a hotter body." This statement holds for transfers of energy that occur during our forward direction of time. The negation, or violation, of the Clausius statement says that a spontaneous heat energy transfer *can* occur from a colder to a hotter body. Juxtaposed with the forward direction of time, the reversed time direction appears to show a spontaneous heat energy transfer from a colder body to a hotter body that violates that Clausius statement.

However, fairly recently Kaufman and Leff[1] showed that a universe with colder-to-hotter (C2H) energy flow does not result in thermal equilibrium. The paper shows that if heat energy flowed spontaneously from colder-to-hotter in a universe, then equilibrium would not result. In such a universe, temperature variations within an object would not smooth out and would not lead to a uniform temperature necessary for the equilibrium conditions of thermodynamics.

They provide a key point, "The C2H world is not simply a time-reversed hot-to-cold world." They also state that in C2H, energy flows are "…not all in one direction."

We illustrate this in a way similar here. Figure 1 shows a thin metal rod in between a hot plate and an ice cube. Let us consider the film of the ice cube melting on the hot plate. If the film were reversed, we would see water form an ice cube as heat energy flowed from the water towards the hot plate. We never see this happen; the reversed film is a clear violation of the Second Law, *i.e.*, it violates the principle of entropy increase and Clausius's statement that heat energy only flows from hotter-to-colder. Initially, we might view this reversed film to show a universe where colder-to-hotter energy flow results in a frozen ice cube.

However, if heat energy flow were to actually occur from colder-to-hotter, then any distribution of temperatures in the metal rod causes further colder-to-hotter flow between adjacent layers of the metal. The resulting white and dark bands symbolize cold and hot regions and are of undetermined thickness. No uniform temperature is reached for the rod, and in fact, the hot plate and ice cube would also form these indeterminate bands.

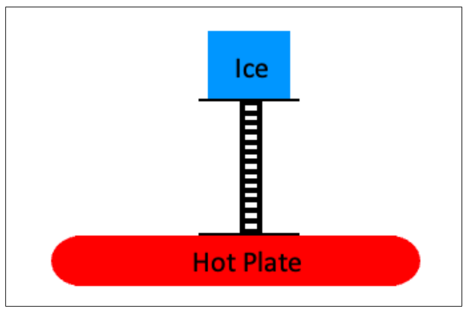

Figure 1: Depiction of colder-to-hotter energy through a metal rod. The white and dark bands are symbolic regions of cold and hot regions of ambiguous thickness, etc…

It must be noted that if time ran backwards and heat energy were to flow spontaneously from colder-to-hotter, then there is no reason why it should stop doing so in order to establish the initial temperatures for the forward direction of time.

Roberts[31] has noted how Brown and Uffink[32] have previously concluded that time-reversal does not result in equilibrium: "*Their argument is that when a system approaching equilibrium is time reversed, the result is a system deviating from equilibrium…*" However, we will not focus on their proposal for a Minus First Law here.

So, the reversed film from Figure 1 shows water form an ice-cube – which could not happen due to spontaneously driven heat transfer from colder-to-hotter in all directions throughout the entire process. Although the beginning and endpoints of the reversed film show equilibrium states for water and ice respectively, this only gives the impression that spontaneously driven colder-to-hotter flow occurred throughout the process, when in fact, it did not.

Key Points: In the forward direction of time, the Clausius statement of thermodynamics holds during the entire duration of a spontaneous heat transfer process. In the reverse direction of time, the Clausius statement holds overall. However, *during* the process, the Clausius statement is not even violated - it does not even have any meaning. The Clausius statement of the second law does not appear to be continuously reversible in time.

If the Clausius statement does not have meaning during time reversal, what can be said about the equivalent statements of the second law, such as the principle of entropy increase? Could

Penrose's assertion that "*Since the entropy increases in the future direction of time, it must decrease in the past direction of time,*" be challenged by Loschmidt's paradox that entropy can increase in both directions of time?

4. Conclusion

The oft-repeated refrain that "entropy increases into the future, and was lower in the past," comes from our experience of a forward direction of time. In our forward direction of time, it has been established that the principle of entropy increase, the Kelvin-Planck statement, and the Clausius statement are all equivalent forms of the second law of thermodynamics. But, in this paper, we have argued that the Clausius statement of the second law does not even have meaning continuously during time reversal. This begs the question, do the equivalent forms of the second law have meaning if time were reversed?

Appendix

Although it is outside the scope of the present article, we mention that some authors have argued that the Second Law/entropy increase is not the cause for the arrow of time, if one even exists. The following text does not claim to indicate all these arguments, but merely indicates that there are objections. One example from Ben-Naim[33] states that: *"…entropy is defined only for the equilibrium state. Entropy is a state function, and as such, it is not a function of time, and whenever it is defined, it does not change with time.*" A remark by Golosz[34] states that: "…*one can conclude that the increase of entropy as it is described by the second law of thermodynamics is only a process which is asymmetrical in time and in no way helps us to explain the asymmetry of time itself.*" In an online article, Siegel[35] states, "*What many don't appreciate is that these two types of arrows — the thermodynamic arrow of entropy and the perceptive arrow of time — are not interchangeable."* As a final note, Uffink[36] has argued "*…for the view that the second law has nothing to do with the arrow of time*" using a discussion that includes irreversibilities, how the Second Law is regarded, historic contexts, and other considerations. Brown[32] later joined Uffink in this position about the Second Law and the arrow of time, which was subsequently adopted by Roberts[31].

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