

Entropy: An ill-conceived mathematical contrivance?

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Abstract: Entropy remains a part of so many thermodynamics relations, yet its true identity lacks clarity. We shall show that entropy may be nothing more than a mathematical contrivance, one that is illogically used to explain too many phenomena. In so doing, we shall question many traditional thermodynamic conceptualizations, as well as provide a unique understanding as to how Boltzmann's constant relates to a system's ability to do work. © 2015 Physics Essays Publication. [<http://dx.doi.org/10.4006/0836-1398-28.3.352>]

Résumé: L'entropie continue à faire partie de bien des relations thermodynamiques, bien que sa vraie nature ne soit pas claire. Nous montrerons que l'entropie n'est qu'un stratagème mathématique, un qui est illogiquement utilisé pour expliquer beaucoup trop de phénomènes. En ce faisant, nous mettrons en doute bien des concepts thermodynamiques traditionnels, tout en fournissant une compréhension unique du rôle de la constante de Boltzmann dans la capacité d'un système à fournir du travail.

Key words: Entropy; Lost Work; Second Law; Boltzmann's Constant; Ideal Gas Law; Enthalpy; Ability; Disorder.

I. INTRODUCTION

A quote from Sommerfeld,¹ “Thermodynamics is a funny subject. The first time you go through it, you do not understand it at all. The second time you go through it, you think you understand it, except for one, or two points. And the third time you go through it, you don't know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore.”

Entropy is the parameter inherent to modern thermodynamics. Remarkably, its definition has not attained clarity 150 years after Rudolf Clausius' declaration that entropy is something which when multiplied by temperature gives energy, which led to the enthalpy relation^{2,3}

$$TS = \varepsilon + PV, \quad (1)$$

where the thermal parameter's temperature (T) and entropy (S) are equated to the internal energy (ε) plus the mechanical parameters pressure (P) and volume (V). Herein, ε represents all the energy within a system that is not directly attributable to the mechanical parameters (P, V); this variation of how some view ε simplifies the science.

Clausius' declaration has also led to a system's entropy change (dS) being equated to its energy change (dQ) divided by its temperature (T)^{2,3}

$$dS = dQ/T. \quad (2)$$

Entropy's mid-20th century guise was it represents the⁴ “randomness of matter in incessant motion,” which was based upon Boltzmann's entropy^{2,3,5,6} (1877)

$$S = k \ln \Omega, \quad (3)$$

where Ω is the total number of system microstates, while k is Boltzmann's constant.

Accordingly, entropy is often accepted as a measurement of a system's disorder to which Ben-Naim⁵ rightfully discusses that the concept of disorder is not particularly scientific. Ben-Naim wrote his evolutionary books^{5,6} on thermodynamics, as a marriage between thermodynamics and Shannon's information theory. Basically assuming that information is carried through thermodynamics processes, thus attempting to explain why the probability functions combined with an altered entropy^{5,6} may explain our unarguable empirical data.

Another 21st century consideration for entropy is⁷ “the dispersal of a system's molecular energy.” Although terms such as “randomness,” “disorder,” “freedom,” “spread,” or “dispersal” are great descriptors for what molecules within closed expanding systems experience, they are subjective terms that do not give entropy clarity.

Consider that a closed system simply prevents mass transfer with its surroundings. Since closed expanding systems must upwardly displace our atmosphere's mass, then such systems must perform work onto the atmosphere, thus explaining, “lost work” by both real and idealized systems,^{8,9} i.e., Sadi Carnot's cycle (1824). Accordingly, entropy and its accomplice, the second law must be queried at their fundamental levels, i.e., Mayhew's^{8,9} assertion that entropy may be nothing more than a mathematical contrivance.

Some may argue that expanding systems are small in comparison to Earth's atmosphere, hence may not actually displace our atmosphere. I ask you: How big does the expansion have to be before you accept its relevance? Certainly, expansion may result in an initial local pressure increase but eventually mechanical equilibrium will prevail, rendering the process into an isobaric volume increase, hence the lost work (W_{lost}) is^{8,9}

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$$W_{\text{lost}} = PdV. \tag{4}$$

Of course when any system loses energy in a given process, then that process cannot be deemed reversible no matter how it is lost.^{8,9} The implication of Eq. (4) becomes that a mistake on a grandiose scale was made by 19th century greats such as Clausius, Kelvin, Maxwell, and Boltzmann. Followed by all of us who have adhered to their assertions into the 21st century.

II. EXPANSION INTO VOLUME

Figure 1 shows four different forms of a gas attaining a volume increase. Most texts^{2,3,5,6} analyze such volume increases in terms of an entropy increase as defined by

$$\Delta S = k \ln(V_3/V_1), \tag{5}$$

where V_3 is the final volume, V_1 is the initial volume, and $\Delta V = V_2$, i.e., $V_3 = V_2 + V_1$.

Treating Eq. (5) as valid, irrespective of the state of the increased volume ($\Delta V = V_2$) is unrealistic, i.e., Fig. 1 case (I) is not universally applicable to Eq. (5) for all volume increases.

Consider Fig. 1 case (II). Herein, the partition simply separates two equal volumes of identical ideal gas, at the same temperature, volume, and pressure. When the partition is lifted, although each gas molecule has a larger total volume in which it can reside, the mean molecular volume remains constant. Certainly, the partition can be replaced at any moment and on average we would return to the original state, assuming that the particles are indistinguishable.

Hence, the process can be deemed as reversible, i.e., Eq. (5) does not apply, as no work is done in this process of partition removal. Obviously, the universal application of Eq. (5) to nondescript volumes makes little or no sense.

Consider Fig. 1 case (III). Assume that the pressure in system 1 is higher than the surrounding atmosphere. As the gas molecules push the piston outward, the Earth’s atmosphere is upwardly displaced. Herein, the work lost by system 1 is defined by Eq. (4). If one wanted to consider this in terms of an entropy change of system 1 then they would be empirically correct in using traditional Eq. (5), although logically compromised.

Is the process reversible? No it is not reversible because system 1 lost work in displacing the surrounding atmosphere. Specifically, system 1 has experienced an irretrievable energy decrease, as defined by Eq. (4). If the expanding closed system 1’s walls are 100% insulated, then the temperature within system 1 will decrease, due to the work done. Conversely, if system 1 expands quasistatically and heat can readily flow through the said walls, then system 1 can expand isothermally.

Of course, this reasoning of lost work was not understood by the 19th century greats. Hence, their insistence in equating entropy change to lost work

$$W = TdS = dE + PdV. \tag{6}$$

Boltzmann formulated his interpretation of entropy Eq. (3), such that Eq. (6) was valid, thus attaining his famous Boltzmann’s constant (k).

To enhance our understanding: Consider that for case (I), V_2 is a vacuum. Is there any work done? Mayhew^{9,10}

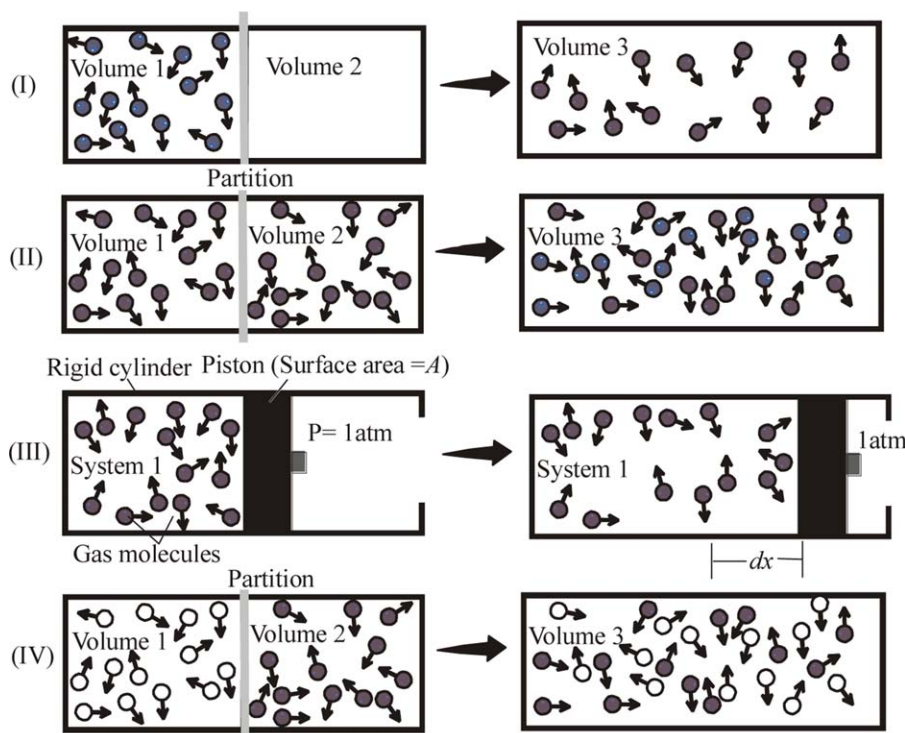


FIG. 1. (Color online) Shows four cases for the increase of a gas’s volume: (I) Lift partition: expansion into a nondescript volume, (II) lift partition: expansion into similar volume, (III) expansion of closed system, i.e., a piston cylinder, (IV) lift partition: mixing of two gases.

discusses that no work can be done onto a vacuum. Accordingly, as long as the V_2 's pressure approximates zero, then as gaseous molecules enter the vacuum, in which case no work is actually done. Ultimately, the end state is going to be a larger V_3 at a lower pressure. Since no work is actually done, then neither Eq. (4), nor Eq. (5), nor Eq. (6) should apply. Is the process reversible? If V_1 starts off at 1 atm pressure, and the final volume (V_3) has the ability to shrink under the atmosphere's weight, then yes. For example, consider that V_2 is a vacuum created by pulling a piston outward from a hermetically sealed piston cylinder, then remove the expanding force (pulling), then the atmosphere's pressure will drive the piston back into the cylinder returning everything their initial states, thus the process is reversible.

In the above process, the system's ability (PV) to do work never changes,⁹ i.e.,

$$W = d(PV) = 0. \quad (7)$$

The above equation confounds tradition, so it will be explained in Section III.

Consider Fig. 1 case (IV). Herein, the partition separates two equal volumes of differing noninteracting ideal gases (no chemical potential change), at the same temperature, volume, and pressure. Lift the partition and the two gases mix. Ben-Naim⁵ rightfully points out that most texts get mixing wrong by claiming that there is an entropy increase in such a mixing process. Furthermore, Ben-Naim⁵ shows that in order for there to be an entropy increase during mixing, then there must be a real expansion, i.e., the type of volume increase shown in case (III). Although Ben-Naim⁵ uses other more complex arguments than given herein, what he actually has shown is this; mixing only has an entropy increase if there is a displacement of our atmosphere, as professed by this author.

Concerning the traditional interpretations for mixing, Ben-Naim writes:⁵ "It is admittedly shocking to learn that what we have seen everyday as mixing and what we thought we have fully understood is only an illusion." Interestingly, Ben-Naim was still thinking in terms entropy, rather than: Although each gas molecule has a larger total volume in which it can reside, the mean molecular volume remains constant.

III. ABILITY TO DO WORK AND BOLTZMANN'S CONSTANT

Equation (7) represents the change in the ability of a system to do work. A system's ability (PV) to do work is basically the amount of work a system can do when the surrounding pressure approaches zero. Why this restriction? A system can only do work against another system/surrounding, which is at a lower pressure. Accordingly, if we consider two closed gaseous systems at equal pressures (mechanical equilibrium), then the system with a greater volume would have a greater ability to do work.

Reconsider the ideal gas law in terms of an ideal gaseous system's ability to do work

$$PV = NkT. \quad (8)$$

In terms of Boltzmann's constant (k), we can write

$$k = PV/NT. \quad (9)$$

Consider a unit cube whose volume is " V " and surface area is " A ". If " M " represents the mass of overlying atmosphere, and " g " is gravitational constant. Then the pressure exerted by the Earth's atmosphere on the top surface of the unit cube is

$$P = Mg/A. \quad (10)$$

Accordingly, Eq. (9) can be rewritten

$$k = (Mg/A)(V/NT). \quad (11)$$

For a unit cube: (V/A) = h , wherein " h " is the cube's height. Rewriting Eq. (11)

$$k = (Mg/T)(h/N), \quad (12)$$

which can be rewritten as

$$kTN = Mgh. \quad (13)$$

Limit any the volume change to only vertical expansion. Then differentiating both sides, we obtain the change in temperature with height as

$$NkdT = Mgdh. \quad (14)$$

Thus

$$k = (1/N)Mgdh/dT. \quad (15)$$

The above equation implies that Boltzmann's constant (k) is the molecular proportionality for the work required to displace Earth's overlying atmosphere by a height of dh , per degree of temperature change, in Earth's gravitational field. There have been other attempts to correlate gravity and thermodynamics,¹¹ but none are as straightforward as this.

IV. AN ALTERNATE PROOF

When two competing theories elicit identical empirical results, it becomes awkward to demonstrate one being superior to the other, beyond Occam's razor style arguments. This is the situation faced by this author, along with the 150 plus years of indoctrination may render my task insurmountable. This author¹² had shown that the energy required to nucleate a bubble could only be properly obtained by equating work to

$$W = d\epsilon + PdV + VdP. \quad (16)$$

The proof was based upon other researcher's empirical data that they admitted could not be explained by traditional theory.¹³ When nucleation theory is based upon Eq. (16), it becomes constructive logic, in complete agreement with empirical findings¹² and for the first time nucleation processes can be explained in simple terms! What is amazing is that no one had realized before.

V. A CONTINUATION OF THE MISTAKE

By limiting the concept of work to isobaric volume change, we unwittingly elevate the importance of entropy change (dS) and volume change (dV), over and above changes to the other parameters. Texts^{2,3,9} start with Eq. (6) from which they subtract

$$SdT + TdS = d\varepsilon + PdV + VdP. \tag{17}$$

In so doing, numerous thermodynamic relations are obtained, i.e., Maxwell’s equations. This rendered thermodynamics into the unique case wherein we start with a part Eq. (6) and then subtract a whole Eq. (17) from that part, to obtain all the other parts.^{9,12} In most every other application of partial derivatives, one starts with a whole Eq. (17) from which they then determine its various parts. The only logical reason for doing so is the belief that lost work could only be explained in terms of entropy change.

VI. ENTROPY AND CIRCULAR LOGIC

Our traditional consideration of entropy is founded upon circular logic.^{8,9} Specifically, Eq. (6) was equated the empirical data for lost work, i.e., was equated to TdS . To then claim that since our empirical data now equate to TdS , therefore, all future solutions must be based upon the inherent logic behind TdS , is circular rather than constructive logic. I would like to believe that this mistake would have not occurred if the 19th century greats had realized that the work required to upwardly displace our atmosphere is PdV thus explaining *Wlost*. Boltzmann’s mathematics, i.e., Eq. (3), only solidified the circular logic!

Understandably, Mach and others were not convinced, which sadly resulted in Boltzmann taking his life. This is not to defer from the Boltzmann’s brilliance! Rather it shows the powers of his math, and how probabilities give results, i.e., deal a deck of cards and there are probabilities of getting a full house, or a pair, etc. The reason is the dealing of the cards; the results are defined by probabilities.

Reasons should be based upon first fundamental principles, such as the displacement of our atmosphere and lost work. The resulting volume increase, simply increases the number of plausible energy states hence Boltzmann’s entropy increase is a result, rather than the reason, as it is wrongly professed in traditional thermodynamics.

VII. ENTROPY AND HEAT CAPACITIES

Consider heat capacity (C_y)^{2,3} or if one prefers the molar specific heat (c_y) for n moles

$$C_y = (dQ/dT)_y \text{ or } c_y \equiv (1/n)C_y = (1/n)(dQ/dT)_y, \tag{18}$$

where the subscript “y” signifies the constant parameter. Comparing Eq. (2) with Eq. (18), one might be inclined to then argue that entropy is simply the heat capacity for a complex system. With complex system meaning a nonhomogeneous system in terms of state and type of matter, isometric (isochoric) (C_V) entropy can be calculated by¹⁴

$$SX = \int_0^{T_X} (C_V/T)dT, \tag{19}$$

where T_X is the temperature in the state X . Note Eq. (19) had led to the postulate known as third law of thermodynamics (at $T \rightarrow 0$, entropy only tends to zero).

As simple as Eq. (19) seems, there remain inherent problems with our use of Boltzmann’s entropy as a type of heat capacity. Reconsider Eq. (1). Does TS , or $\varepsilon + PV$, actually represent the total energy of a system? Consider an ideal gas’s total energy (E_{total}), as defined by kinetic theory^{2,3,9}

$$E_{total} = 3PV/2. \tag{20}$$

Equation (1) does not equate to Eq. (20) unless one concludes that for some magical reason that the energy, which is not directly attributable to the mechanical parameters (P,V), is $\varepsilon = PV/2$. Which makes no sense! Perhaps this in part explains why some prefer to treat ε as if it is something more than simply all the energy within a system that is not directly attributable to (P,V). Furthermore, treating ε as some total energy is illogical because the energy associated with the mechanical parameters (P,V) is part of that system’s energy.

Since enthalpy does not define an ideal gas’s total energy, then neither SdT nor TdS should define a system’s total energy change, unless we rewrite the enthalpy relation without entropy. Thermodynamics circumnavigates the possible that entropy entertains more than one guise by using various unnecessary complex arguments, thus preventing entropy from achieving a single simple definition. Ultimately, confusing what should be a simple constructive science.

Simplicity can be attained if the enthalpy relation ($\varepsilon + PV$) defines the ability of a gaseous system to do work while equations such as Eq. (20) defines the total energy of the system. Should TS remain part of enthalpy? Certainly not, if SdT or TdS represent a system’s energy change, i.e., entropy remains a sort of heat capacity for what, nonhomogeneous systems? This separation of work from a system’s total energy does provide clarity and helps explain inefficiencies.^{9,10}

VIII. ISOBARIC VERSUS ISOMETRIC HEAT CAPACITY

To enhance our understanding, consider the difference between isobaric (C_P) and isometric (isochoric) (C_V) heat capacity. Since the isometric heat capacity is constant volume, then there is no work done onto our surrounding atmosphere.⁹ Conversely, isobaric heat capacity involves an expanding closed system hence the displacement of our atmosphere, hence requires lost work, as defined by Eq. (4). In other words,

$$C_P = C_V + W_{lost} = C_V + PdV. \tag{21}$$

Equation (21) is equivalent to the accepted molar heat capacities⁹ (c_y), which is written in terms of molar ideal gas constant (R) as

$$c_P = c_V + R. \tag{22}$$

IX. ORDER VERSUS DISORDER AND THE SECOND LAW

Many associate Boltzmann's entropy and the second law with disorder.^{2,3,5,6} Certainly Boltzmann's use of the term disorder in describing what happens over time⁶ has led to this belief resulting in concepts like systems always moves toward greater entropy.

Kinetic theory would have gas molecules spreading out from their last collision, if it were not for the containment by surrounding matter,^{9,10} i.e., system's walls, or dense cloud of gas molecules. Energy radiates outwardly from locals of highest concentration. Do we really need traditional interpretations of entropy, or the second law to explain what we witness? At best Boltzmann's entropy remains a result, not a reason!

Seemingly forgotten; forces such as gravity tend to put order back into systems. Certainly, the formation of galaxies, planets, stars, and all other cosmological bodies defy entropy's traditional guise. Arguably, events such as supernova result in matter spreading out, but the dust of such explosions ultimately form future galaxies. Moreover, since lost work by expanding systems is readily explained in terms of our atmosphere's displacement, then should entropy even apply to our universe? This author thinks not!^{9,10}

Since closed expanding systems tend to displace our atmosphere, then no such system can be deemed isolated.^{8,9} Yet isolated is fundamental to the conceptualization of the second law,^{8,9} hence this law falters in too many ways. Useful processes/systems are those that can move man and/or machine.⁹ Since most useful processes involve the system expansion, then it becomes rather difficult to even fathom how the second law even applies to most useful systems, i.e., cyclic engines.⁹ Does the second law even apply to our universe? Assuming that it is as Hubble surmised, then it depends upon what surrounds our universe. If our universe is surrounded by nothingness then no work can be done onto that volume,⁹ hence in terms of lost work there should be none.

Many believe that maximum entropy production governs chemistry and life.¹⁴ Martyushev¹⁴ points out that nature goes against the very notion of randomness, and the possibility of a difference between animate and inanimate objects, as first conceived by Schrodinger. Martyushev¹⁴ then uses complex arguments showing that it may be due to the differences in interpretations between experts and nonexperts. Martyushev,¹⁴ Ben-Naim,^{5,6} and I agree that disorder belongs to the eye of the beholder. Beyond that the second law's limitations, and entropy's lack of clarity, make this author muse; are complex arguments even warranted?

X. INFORMATION

When trying to decide what to call his information theory function, Shannon toyed with words such as "uncertainty" or "information."⁶ It was Von Neumann who recommended to Shannon:⁶ "You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under the same name. In the second place, and more important, no one knows what

entropy really is, so in a debate you will always have an advantage." How scientific is that?

I do agree with Ben Naim⁶ that Shannon's use of the term entropy has further complicated an unfortunate situation. As for Ben-Naim's marriage of information and thermodynamics,^{5,6} I remain troubled at the prospect of molecules carrying the burden of information.

XI. THERMODYNAMICS WITHOUT ENTROPY

Traditional thermodynamics is more complex than is necessary. This author has published a book⁹ that simplifies thermodynamics without any real reliance upon entropy. Although far from perfect, this author likes to think that it provides a new beginning, one that will require the input from many, hopefully resulting in a simpler, constructive logical science, one that Sommerfeld would appreciate!

XII. CONCLUSIONS

Equating one's theory to empirical data, and then saying that all future empirical data now proves that theory, is circular logic, that being the foundation of traditional thermodynamics! Specifically, entropy was devised to help explain, lost work. Boltzmann then added his brilliant mathematics to the fray, thus enlightening the idea of disorder, and unwittingly enforcing traditional misconceptions.

Lost work occurs as expanding systems displace our atmosphere's weight.⁸ Hence, Boltzmann's increase in number of microstates is a result of volume change rather than a reason for energy loss, as is wrongly traditionally professed. Accordingly, a new differing thermodynamic theory⁹ arises, one that does not rely upon terms such as disorder, yet renders the identical empirical results. The new theory enlightens us to Boltzmann's constant simply relating a gaseous system's ability to do work to its local gravitational field. This requires our acceptance that grandiose mistakes were made, mistakes that we have all followed, and many still endorse.

Could entropy simply be an ill-conceived mathematical contrivance, thus complicating the simple? Seemingly, this is the case. Moreover, thermodynamics can become a simple constructive science all that is required is a willingness to make it so.

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