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New Thermodynamics Starts with Sensible Lost Work

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Abstract

Lost work by expanding systems remains a foundation of thermodynamics, which has been explained in terms of a system's entropy increase. Free expansion experiments actually prove that increasing entropy can't explain lost work. Such experimental results are expected, when one realizes that expanding system near Earth's surface must do work onto the surrounding atmosphere, i.e., sensible lost work. Rewriting thermodynamics with clarity, enables a new scientific understanding that is a superior fit to witnessed realities.

1 Introduction

A litany of grievances against thermodynamics exists [1], e.g., "no other discipline in mathematical science is riddled with so many logical and mathematical inconsistencies, differences in definitions, and ill-defined notation as classical thermodynamics" [2]. Sensible work tends to be an exact differential that is external to the system doing that work [1]. Herein, an elaboration of sensible vs nonsensible work will be provided enabling a plausible new thermodynamics. One that better explains what has been witnessed. Isobaric heating of closed gaseous system involves a volume increase, as described by a first law equation showing the equivalence of work and energy, i.e.:

$$dQ = dE + PdV \tag{1}$$

Eq. 1 lacks clarity. Rewriting in terms of heat in ($dQ_i n$), internal energy change (dE_s), and the work done [$W = (PdV)_s$] gives necessary clarity:

$$dQ_{in} = dE_s + (PdV)_s \tag{2}$$

Eq. 2 remains problematic because it implies that the work [$(PdV)_s$] is done onto the expanding system, which is nonsensible Reality is that the work done, is performed onto a system/object external to the expanding system. Lucidity is gained by writing:

$$dQ_{in} = dE_s + dW_{out} \tag{3}$$

dQ_{in} is the cause, while dE_s and dW_{out} are the effects/results. This is sensible.

For any expanding system near Earth's surface, work is done onto the expanding system's surrounding atmosphere (dW_a).[1]

$$dQ_{in} = dE_s + dW_a \tag{4}$$

Which can be expressed in terms of isobaric atmospheric volume increase [1],[3]-[8], i.e.: $dW_a = (PdV)_a$ Thus, eq. 4 becomes:

$$dQ_{in} = dE_s + (PdV)_a \tag{5}$$

Isobaric work done onto the atmosphere was equated to the work required to lift the mass of the column of atmosphere residing over the expanding system. i.e., $[(PdV)_a = (M\vec{g}dh)_{ca}$ where M_{ca} is the overlying atmospheric column mass, $vecg$ is the gravitational force, and dh_{ca} is the theoretical height that the column of atmosphere is elevated [1],[3]. Therefore, eq. 5 can be rewritten as follows:

$$dQ_{in} = dE_s + (M\vec{g}dh)_{ca} \tag{6}$$

If the expanding system does more work than lift Earth's atmosphere, e.g., an engine's expanding piston-cylinders accelerates a car resulting in the car's kinetic energy $[(Mv^2/2)_{car}]$ increase from $E_k = 0$, then in terms of Wout:

$$dQ_{in} = dE_s + Wout = dE_s + (M\vec{g}dh)_{ca} + (Mv^2/2)_{car} \tag{7}$$

Since W_{out} is an exact differential one can interchange dW_{out} with W_{out} as was the case for an expanding system lifting a mass along with the surrounding atmosphere [1].

In various discussions, some have failed to appreciate W_a. Thus, Section 2 will enhance that understanding. Moreover, eq. 2 has led thermodynamics down the path of entropy change, which will be shown to be challenged by free expansion.

2 Expressing Work in terms of $(PdV)_a$

The simple explanation: Expanding systems near Earth's surface displace the atmosphere. The Earth is a rigid body, hence only direction for expansion is upwards. Lift a spring from its base, at first it compresses. After a duration the spring decompresses and $W_{done} = (M\vec{g}dh)_{spring}$ = the spring's potential energy increase.

The atmosphere is also compressible. Accordingly, as a system expands, it initially compresses the atmosphere [higher pressure zone (HPZ)]. Over a duration, the HPZ decompresses back to 1 atm pressure. Whether or not the atmosphere fully decompresses is irrelevant. The total work is an exact differential $(PdV)_a$ that equates to $(M\vec{g}dh)_c a$.

The complex explanation: The inhomogeneous atmosphere is impossible to fully describe. Even so, the atmospheric pressure exerted upon a surface area (A), is:

$$P_a = (M\vec{g}/A)_{ca} \tag{8}$$

The work done onto the atmosphere results in some combination of: 1) Isobaric work:$dw_a = (PdV)_a$, 2) Isometric work: $dw_a = (VdP)_a$, 3) Thermal energy change: $dE_a = nc_v dT$, where c_v is the molar isochoric heat capacity. The total work done is:

$$W_a = (PdV)_a + (VdP)_a + nC_v dT \tag{9}$$

Each part in eq. 9 is limited to the region where the changes take place, and will disperse throughout the whole atmosphere. For an isothermal atmosphere:

$$W_a = (PdV)_a + (VdP)_a \tag{10}$$

If our atmosphere was contained within rigid walls, then: $W_a = (VdP)_a$. The atmosphere is an open system thus, HPZ's expand, i.e.: $W_a = (PdV)_a$. Ultimately, for an expanding system near Earth's surface, equations 4, 5 and 6 all provide an understanding of sensible work for an isobaric, isothermal atmosphere. Therefore, with all the inherent complexities, Wa can be expressed as follows:

$$W_a = \int dw_a = \int (Pdv)_a = (PdV)_a = (M\vec{g}dh)_{ca} \tag{11}$$

In terms of heat into an expanding system (dQ_{in}), that system's internal energy change (dE_s) and the work done by that system, one can write for an isothermal, isobaric atmosphere:

In terms of dQ_{in}, dE_s and $dW_a = W_a$, for an isothermal, isobaric atmosphere:

$$dQ_{in} = dE_s + W_a = dE_s + (M\vec{g}dh)_{ca} = dE_s + (PdV)_a \tag{12}$$

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Eq. 12 enables an understanding in the same context that M_{ca} enables eq. 8. W_a is infinitesimal when compared to the atmosphere's total energy, i.e., the atmosphere is a heat sink. Thus, W_a cannot be measured in terms of the atmosphere. However, W_a can be measured in terms of the expanding system, i.e., $W_a = (PdV)_s$, which may turn result in using a nonsensible inexact differential [1].

3 Mayer (1842) and Specific Heats

Julius Robert von Mayer postulated work done with respect to the atmosphere, in terms of PdV. Mayer was not necessarily thinking in terms of W_a. Mayer stated, "we must find out how high a particular weight must be raised above the surface of the Earth in order that its falling power may be equivalent to the heating of weight of water from 0oC to 1oC" [9]. Mayer "reasoned that an amount of gas needs to be heated more at constant pressure than at constant volume, because at constant pressure it is free to dilate and not work against the atmosphere; in today's notation we would write" [9]:

$$mc_{P-m}dT - mc_{v-m}dT = P_a dV \tag{13}$$

where m is the mass, c_{p-m} and c_{v-m} are respectively isobaric and isochoric molar heat capacities per gram, i.e., engineer's notation. Scientists prefer using the number of moles (n), isobaric (c_p) and isochoric (c_v) molar heat capacities, i.e.:

$$(nc_p - nc_v)dT_s = (PdV)_a \tag{14}$$

Eq. 14 shows the differences in heat capacities can be based upon work done [10] rather than the accepted explanations based on entropy change. One does not know if Mayer viewed dV as nonsensible dV_s or sensible dV_a. Isobaric expanding systems near Earth's surface are subsystems of the atmosphere, thus, $dV_a = dV_s$. Importantly, W_a was disclosed prior to entropy's supposition.

4 Lost Work: W_a vs TdS

In 1865, Clausius made the following supposition for a system's isothermal entropy change $(TdS)_s$. Note, Rankine had devised a similar "thermodynamic function" in 1855 [9]:

$$(TdS)_s = dQ_{in} \tag{15}$$

Note, Clausius coined the term Entropy but it was Rankine who devised a "thermodynamic function" with similar properties in 1855 [9].

Lost work has traditionally been dealt with by stating that a process is irreversible when:

$$dW_{actual} < dW_{reverse} \tag{16}$$

This has led to a process being deemed irreversible when:

$$dS_s > dQ_{in}/T_s \tag{17}$$

Eq. 17 implies that the expanding system's dS_s explains W_{lost}, i.e., a questionable association between randomness and lost work. Combining eq. 15 and eq. 2, gives:

$$(TdS)_s = dQ_{in} = dE_s + (PdV)_s \tag{18}$$

Eq. 18 fails to acknowledge that: $(PdV)_s$ is nonsensible work. Moreover, How can $(PdV)_s$ be part of the expanding system's energy change? Furthermore, dE_s is the change to the summation of all the energies in the expanding system, therefore what is $(PdV)_s$. Finally, there is no lucidity concerning how/why/where W_{lost} occurs, e.g., when asked where the work associated with an expanding universe goes, Enrico Fermi once replied "into the hands of god" [11], confirming that he had no idea.

Try applying W_a to eq. 16:

$$(TdS)_s = dQ_{in} = dE_s + W_a \tag{19}$$

dQ_{in} is the cause, and the effects are dE_s and dW_a. Does $(TdS)_s$ resolve any issues? No. $(PdV)_s$ and $(TdS)_s$ remain nonsensible. No wonder entropy has no physical meaning [12]. There are no benefits in writing either eq. 18, or eq. 19. Note that if the system did not expand then no work would be done, e.g., $dQ_{in} = dE_s$ and T↑.

Sensible W_a explains W_{lost}, i.e., W_a never returns to the expanded system, i.e., W_a results in an atmospheric potential energy increase $[(M\vec{g}dh)_{ca}]$ [1]. As an exact differential: $[dW_a = W_a = W_{lost}]$.

When systems collapse then overlying atmospheric gas molecules fall downward, converting some of their potential energy into kinetic energy [1],[3]. Hence, any work required for expansion, never returns, i.e., expansion is an irreversible process.

Such kinetic energy increases can be viewed as temperature increases that eventually disperses throughout the atmosphere. Accordingly, eq. 5 becomes:

$$dQ_{in} = dE_s + (PdV)_a = dE_s + dW_a = dE_s + dW_{lost} \tag{20}$$

Eq. 20 is limited to expanding systems in an isobaric, isothermal atmosphere. For the more general case, one writes:

$$dQ_{in} = dE_s + dW_a = dE_s + dW_{lost} \tag{21}$$

Section conclusions: TdS is a mathematical contrivance [10] based upon quasi-static processes. If TdS accomplishes anything, it inadvertently hides the realities of nonsensible work. No wonder entropy and its change, lack physical meaning.

5 Boiling: W_a vs TdS

Consider Fig. 1. If boiling involves isothermal entropy increase, then where is it? The mean molecular volume of both the vapor and liquid molecules remains constant. System 1's isobaric, isothermal volume increases is due to mass transfer, not some mean volume increase of vapor molecules, i.e., not some entropy increase. Furthermore, equations 18 through 21, apply to the latent heat of vaporization. Other heating processes are not isobaric and isothermal. How can TdS be some universal concept? Yet everything from "boiling" to "our expanding universe" to the "arrow of time" all claim that $TdS = dQ$ has validity.

Investigating boiling further. The isobaric expanding system is a subsystem of the atmosphere, thus $dV_s = dV_a$. Therefore:

$$(PdV)_s \approx (PdV)_a \tag{22}$$

Again, although empirically correct, $(PdV)_s$ is nonsensible work while $(PdV)_a$ is sensible work, i.e., $dW_a = (PdV)a$ is theoretically correct. Thus:

$$dQ_{in} = dE_s + (PdV)_s \approx dE_s + (PdV)_a \tag{23}$$

If the work is not considered to result in an atmosphere that remains both isothermal and isobaric, then one should write:

$$dQ_{in} = dE_s + (PdV)_s = dE_s + dW_a \tag{24}$$

Sensible work changes how one envisions $L_{l\to g}$ vs $L_{g\to l}$, [1], [10] i.e., the latent heat of vaporization vs condensation, in terms of bonding potential change (dU):

$$L_{l\to g} = dU_s + dW_a \tag{25}$$

If the atmosphere remains both isothermal and isobaric then the latent heat of vaporization can be approximated by [1],[3], [10]:

$$L_{l\to g} \approx dU_s + (PdV)_a \tag{26}$$

Since there is no work onto the surrounding atmosphere during contraction ($dW_a = 0$), the latent heat of condensation becomes:

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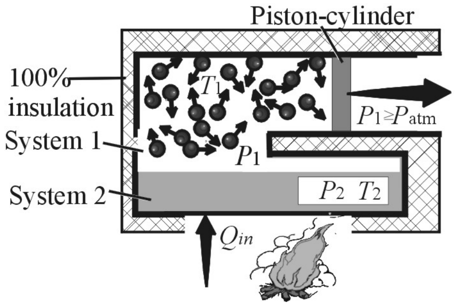

Figure 1: Illustrates a boiling process. If one considers the liquid as System 2 and the vapor as System 1, then there is a mass transfer from System 2 into System 1. Mass transfer implies no mean molecular volume change in either System 1 or System 2, even though the volume of System 1 increases

$$L_{g\to l} = dU_s \tag{27}$$

Due to questioning of the term enthalpy [1],[10], this author's prefers to use the term latent heat (L) rather than enthalpy change (dH). The subscripts "l" and "g" represent the liquid and gas states, while the arrow indicates the direction of change. Why has eq. 27 not been understood? Unlike $L_{g\to l}$, $L_{l\to g}$, can be readily measured using an isobaric calorimeter. It has been incorrectly assumed that: $L_{g\to l} = -L_{l\to g}$. [1],[3], [10]

6 Loschmidt's Paradox

Loschmidt's paradox (1876) puts the time reversal of a macroscopic system's processes at odds with the second law's (TdS¿0) implication for irreversibility. Since isolated systems tend to return to their initial conditions (P,V,T), the second law seems paradoxical. However, if one thinks in terms of equations 25 and 27, then the paradox, along with the accepted second law, both disappear. Specifically, more energy is required for vaporization than will be returned during condensation, the difference being, W_a.

The weight of the overlying atmosphere often forces a system back to its initial volume. This does not mean that all the energy required for system expansion simply returns, i.e., the illusion of reversibility, i.e., from a mechanical perspective the expanded system has returned to its pre-expansion state. However, from an energy perspective it remains irreversible, since $W_{lost} = W_a$.

During contraction some of the atmosphere's potential energy becomes an atmospheric kinetic energy increase which can be viewed as an infinitesimal atmospheric temperature increase that disperses throughout the atmosphere, i.e., atmosphere appears isothermal. Section conclusion. W_a removes the need for both the second law and Loschmidt's paradox.

7 Gay-Lussac's Free Expansion Experiment

Is there any proof that shows which of these two plausible scenarios for the lost work. If W_{lost} was as traditionally described e.g., work as in eq. 18, then energy would be lost by all expanding systems, irrelevant of their surroundings. If lost work is as described by eq. 20, then energy would only be lost only when expanding systems actually does sensible work.

Early in the 19th century, Gay-Lussac considered free expansion where a gas in Flask 1 expands into an equal-sized Flask 2 (a vacuum), as shown in Fig. 2. Both classical and statistical thermodynamics have been used without any acceptable explanation [15] because the theories imply that work is done by all expanding systems.

Both flasks are initially evacuated. Flask 1 was then filled with various gases, e.g., air, hydrogen, carbon dioxide and oxygen. Both vessels started at the same temperature. After opening the cock between both vessels, Gay-Lussac found that once the pressure in both vessels equalized, then the temperature in Flask

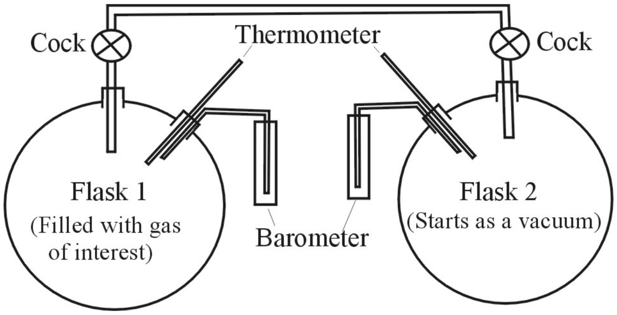

Figure 2: Shows the apparatus used in the Gay-Lussac free expansion experiment

1 decreased, while the temperature in Flask 2 increased. This occurred with all gases, with temperature changes under 1 K [15], [16].

These results were confirmed by James Harry Potter (1959) [15],[17]. Potter had a few changes with argon, air and carbon dioxide being the chosen gases. It was determined that Flask 1's temperature decreased by a few degrees, while Flask 2's temperature increased by similar amounts (over 10 to 30 seconds). All $deltaT$'s were under 10.0 K. i.e., generally 5 to 6 K. After one to two minutes, both flasks reattained thermal equilibrium.

Someone may claim that Flask 1 cooled implies that work is done by the gas during expansion into Flask 2. How, does one then explain gas' temperature increase in Flask 2, i.e., if work is done during the expansion and such work can be explained in terms of TdS, then why did the temperature increase in Flask 2? Moreover, the gas' total energy remained constant with the total being the energy in Flask 1 plus the energy in Flask 2.

Investigating, rewrite eq. 23 in terms of the expanding system' isochoric heat capacity (C_v), number of moles (n) and temperature change (dT), i.e. $dE_s = c_v dT$. Thus:

$$dQ_{in} = nC_v dT_s + (PdV)_s \tag{28}$$

For an expanding ideal gas ($PV = nRT$), and ($dQ_i n = 0$). Then eq. 28 becomes:

$$nC_v dT_s = -(nRTdV/V)_s \tag{29}$$

Collecting the terms, and dividing both sides by T, one obtains:

$$(C_v dT/T)_s = -(RdV/V)_s \tag{30}$$

Integrating eq. 30 one obtains:

$$C_v In(T_2/T_1)_s = -RIn(V_2/V_1)_s \tag{31}$$

Eq. 31 can be rearranged into the accepted Poisson's adiabatic expansion relation:

$$T_2/T_1 = (V_2/V_1)^{(-R/c_v)} \tag{32}$$

Hernandez [15] calculated the expected temperature difference during expansion:

$$\Delta T = T_2 - T_1 = [(P_2/P_1)^{\gamma-1/\gamma} - 1] \tag{33}$$

Hernandez [15]: For diatomic molecules the adiabatic index is: γ=7/5 and $(\gamma - 1)/\gamma$=2/7. Since the pressure is reduced by 50

A version of the Gay-Lussac free expansion experiment was performed by James Prescott Joule in 1845. According to Mares et al [18] the theoretical expected temperature change in Joule's experiment should be 73 K, but the determined temperature change was only 1.3 K. Thus, confirming the findings in the Gay-Lussac experiments.

8 Free Expansion Discussion

In free expansion experiments Flask 1's temperature decreased while Flask 2' temperature increased. The decreases and increases were equally diminutive, i.e., an order of magnitude lower than was theoretically expected, with the total energy remaining constant. Therefore, no actual work was done in any of the free expansion experiments.

The expansion into a vacuum does not involve actual work, i.e., no lost work. This proves that lost work is not due to the expansion by any system into any surroundings, as predicted by entropy change thermodynamics.

Consider sensible lost work. Since, in a vacuum there is: No mass to lift (or displace) against gravity therefore $(PdV)_{vac} = 0$. No gas to compress therefore, $(VdP)_{vac} = 0$. Therefore, no work can be done onto the vacuum. Reality is work has to be done onto something tangible. Why the Gay-Lussac's experiment didn't prevent entropy-based classical thermodynamics' rule, is left to the historians.

Hugo Hernandez provides an interesting insight [15]. The gas molecules that initially escape from Flask 1 into Flask 2, will be those gas molecules with higher velocities, i.e. higher mean kinetic energy, explains Flask 2's small temperature increase. Conversely, Flask 1's temperature decrease, would be due to the loss of such high energy gas molecules.

Furthermore, Flask 2 had a temperature before the valve was opened. This temperature measurement would be based on the thermometer's adsorption and emission of thermal radiation. This confounds the statistical thermodynamics notion that a vacuum has no temperature. Thermal radiation will be discussed further in Sections 15 and 17. Ultimately, free expansion experiment fits with the understanding that sensible lost work is work that is done onto the atmosphere by an expanding system, i.e.: $W_lost = W_a$.

Section conclusion: Free expansion proves that work has to be done onto something (e.g. with weight) that resides external to the expanding system, e.g., $W_{lost} = W_a$

9 Isentropic Relations

Accepting the reality of sensible lost work, one not only question entropy change, but one must question the relations for adiabatic expansion. Is calling equations 31 and 32 isentropic relations unnecessary over-complications? Simpler understanding being relations for "no heat in expansion processes", i.e.: $dQ_{in} = 0$, hence eq. 2 becomes:

$$0 = dE_s + (PdV)_s \tag{34}$$

Thus:

$$dE_s = -(PdV)_s \tag{35}$$

If the system is an ideal gas whose internal energy is strictly defined in terms of its isochoric (isometric) heat capacity and temperature, then eq. 35 can be rewritten as:

$$nc_v dT_s = -(PdV)_s \tag{36}$$

The so-called isentropic equations can be derived from eq 36, just as was done for equations 29 through 32.

In terms of the sensible work onto the atmosphere, eq. 36 becomes:

$$nc_v dT_s = -W_a \tag{37}$$

Eq. 37 informs us that the energy required for sensible work onto the surrounding atmosphere, must come from the expanding system's internal energy.

If the atmosphere is considered to remain both isobaric and isothermal, then:

$$nc_v dT_s \approx -(PdV)_a = -(M\vec{g}dh)_{ca} \tag{38}$$

Unlike eq. 36, equations 37 and 38 give lucidity concerning where the work goes, just as eq. 7 provided clarity for the work being transformed into the car's kinetic energy. Seemingly the lack of lucidity became a cornerstone of accepted classical thermodynamics. Again ask, is entropy change required? What about the term isentropic?

10 Kinematic Energy

Herein, kinematic energy signifies the translational, rotational and/or vibrational energy associated with the system's molecules/atoms motions, i.e., as defined by kinetic theory, whether it be this author's kinetic theory [21] or traditionally accepted kinetic theory. Kinetic energy has been limited to translational energies and elastic collisions. This seems strange because translational energy can result in rotational energy during a molecular collision, and visa-versa. Similarly, the rotational energy of a molecule can involve heat transfer. Although semantics, this author favors kinematic energy.

11 Work During Compression and Inelastic Collisions

Isothermal compression can occur when one quasi-statically compresses a gas in a non-insulated closed system, e.g., a piston-cylinder. Although the gas' energy density increases during isothermal compression, the mean energy associated with each ideal gas molecule/atom remains constant, e.g., a monatomic gas' mean energy remains: 3kT/2. The temperature can be independent of the system's kinematic energy density. Two plausible explanations for isothermal compression are:

Molecular collisions are elastic. Hence an increase in kinematic energy density doesn't result in a measured temperature increase. This is due to each molecule independently exchanging its energy with a thermometer during the gas molecule-thermometer collisional energy exchanges. Thus, a higher system energy density simply means more energy exchanges, rather than higher temperatures.

Molecular collisions are inelastic, i.e., heat is generated, i.e., thermal radiation is created during molecular collisions. Quasi-static compression: As the piston is driven inwards, the gas compresses and any heat that is generated escapes out through the cylinder's walls, i.e., the illusion of being an isothermal process.

Elastic collisions adheres to traditional theorization. If true, would it matter if the compression was quasi-static, or if the cylinder's walls were insulated? This author sees no reason for it to matter, i.e. if collisions are elastic then all compression would simply result in an isothermal kinematic energy density increase, i.e., $dT = 0$.

Inelastic collisions imply rapid compression generates thermal radiation (heat), hence $dT > 0$ if the walls are insulated or compression is too rapid for heat escape to escape.

Inelastic intermolecular collisions [3],[5],[19]-[23] result in the distortions of the electron clouds that surround molecules/atoms. The result being the emission of thermal photons (a form of heat). Thermal photons tend to be radiated and/or absorbed by matter. An ensemble of radiated thermal photons forms a thermal radiation spectrum.

As one compresses a gaseous system there will be an increase in the number of collisions, hence, an increase in the number (and/or mean energy) of thermal photons created, hence a possible increase in temperature associated with that system. Thermal photons can be absorbed/radiated by the system walls and the gaseous molecules within [3], [21]-[25].

A thermometer not only exchanges kinematic energy with the gas molecules in its surrounding system, it also exchanges radiative energy associated with thermal photons (often blackbody in nature). Accordingly, inelastic collisions play a significant role in a system's temperature increase. One can envision work resulting in heat, as measured by a temperature increase, i.e., a form of friction generated heat. Furthermore, inelastic collisions can improve one's understanding of the pressure-temperature relationships, e.g., in the Earth's interior.

12 Isothermal Compression

Reconsider isothermal compression of an ideal gas. If there is:

1. No inelastic collision generated heat retained by the compressed system.
2. No energy changes of that compressed system, i.e. ideal monatomic gas' system's energy $\approx 3NkT/2$.

3. There is a pressure increase: $dP = \Delta P = P_{final} - P_{intial} > 0$.

Is the above work? If one simply defines work in terms of either an increase in the kinematic energy, or the potential energy, then the answer is no.

If one's definition of work includes an increase to a system's potential to do work, then the answer becomes yes. An isothermal pressure increase of a gas is an increase in that gas' potential to do work, rather than an increase in its energy. The work required (W_{req}) to isothermally compress a gas approximates the increase in that gas's potential to do work. The work required for the isothermal pressure increase can be approximated in terms of path-dependent work. For an ideal gas, $V = NkT/P$, thus W_{req} can be determined by:

$$W_req = \int dw_req \approx NkT \int dP/P \tag{39}$$

Such work results in (effect) an increased potential to do work (W_{pot}), as defined by:

$$W_{pot} = \int dp_{pot} = (VdP)_s \tag{40}$$

Reconsider localized compression of the atmosphere. Eventually that compressed region will expand, thus becoming work in terms of PdV.

One must remain cognizant of the fact that in isothermal compression, can occur as some quasi-static process. Thus, heat can freely radiate out through the system's walls. This "freely radiated heat/energy" is often small in comparison to the total energy associated with the gas molecules, thus in terms of a system's total energy it often can go unnoticed.

13 Non-Isothermal Compression

Consider that the gas' compression is not isothermal. The energy required (E_{req}) should include the work for compression plus the energy to increase that gas's temperature, i.e.:

$$E_{req} = W_{req} + nC_v\delta T = NkT \int dP/P + nC_v(T_f - T_i) \tag{41}$$

Eq. 41 is nonsensible/cumbersome because E_{req} and $W - [req]$ are causes while $nC_v\delta T$ is an effect. A better way of writing would be having the R.H.S. all effects, i.e.:

$$E_{req} = (V_{final}dP)_s + nC_v dT \tag{42}$$

14 Isothermal Expansion

Reconsider an expanding compressed gas in a non-insulated piston-cylinder, where $dQ_in = 0$. As the expanding gas displaces the surrounding atmosphere, that gas naturally wants to cool due to W_a.

Again, quasi-static expansion can be isothermal, i.e., thermal energy (heat) from the atmosphere passes through the system walls thus, isothermal expansion, i.e., atmosphere is a heat bath. Such energy is "freely-given energy", or, "freely-given heat" [3]. Herein:

$$W_a = (PdV)_a = E_{freely} \tag{43}$$

The freely-given energy is thermal energy lost by the atmosphere (dE_a):

$$W_a = (PdV)_a = -dE_a \tag{44}$$

For emphasis, when the atmosphere acts as a heat bath/sink, $dT_a \approx 0$, i.e., the energy lost or gained by the atmosphere is infinitesimal in comparison to the atmosphere's total energy.

15 Other Concerns

The concept of thermal photons has been discussed when rewriting kinetic theory [3],[24]. Unlike traditionally accepted kinetic theory, this author's kinetic theory allows for inelastic collisions, because the system's wall's molecules impose their kinematic energies onto the enclosed gas molecules. Traditional kinetic theory considers all gas molecules to have similar kinematic energies, without any clarity concerning those energies origins. It is as if all molecules magically possess energetics related to temperature. Note that this author's kinetic theory a superior fit to empirical findings, plus it requires none of the exceptions that have plagued accepted theory.

A plausible understanding as to what constitutes thermal energy has been obtained [25]. Thermal energy, (including thermal photons) likely reside in the longer infrared wavelengths, i.e. $\lambda_{cut} > 10\ \mu$m. Although a preliminary analysis, the cut-off wavelength represents a theoretical limit for thermal energy, i.e., the energy associated with the matter's kinematic energies.

Thermal radiation would be readily emitted and/or absorbed by matter. Although speculative, it could be the photon's momentum that tends to be absorbed by atoms in most matter (including gases). Conversely, the emission of photons may involve distortions of electron clouds. The absorption and emission mechanisms do not have to be identical, the rule being; in thermal equilibrium the thermal "energy in" equals thermal "energy out". This has yet to be proven but it may add to our understanding as to why our atmosphere is opaque to thermal infrared photons (currently accepted explanation being atmospheric dust [26], [27]). This may also alter one's understanding of climate change.

Inelastic collisions explain thermal radiation, including the blackbody radiation from our Sun [22], [23], i.e., the hotter the object, the more intense the molecular collisions, hence the greater the mean collisional energy, hence the spectrum's higher frequencies.

16 Irreversibility

Since all expanding systems near Earth's surface witness lost work, then no expanding process can be reversible, at least from an energy perspective. Of course, from a mechanical perspective one still has the illusion of reversibility, e.g., Loschmidt's paradox. It has to be emphasized that as a system's energy disperses, then resources are often required to reconcentrate that energy. Is this simple dispersal of energy, or is it some complicated association with magical entropy?

This questions entropy-based second law as the explanation for irreversibility ($TdS > 0$), as previously discussed by this author [1], [3]-[7], along with Hernandez [10]. Reversible processes have been described as being isentropic ($dS = 0$). As was discussed in Section 11, the math behind isentropic relations can be explained in the simpler terms of: $dQ_in = 0$. Arguably, entropy change is no longer required.

Modern thermodynamics started out with the need to understand the steam engine. There are numerous factors that contribute to its inefficiency. Including:

1. W_a means irreversible
2. Not all of an expanding gas's energy can be used for work, i.e. monatomic gas's energy is $3NPV/2$, while its ability to do work is NPV, i.e. a monatomic gas's efficiency is only 66.67
3. Mechanical friction, creates heat that is lost, i.e., an inefficiency and irreversibility.
4. Energy expelled from the engine during the exhaust step in its cycle. Hence an inefficiency and irreversibility.

One realizes that TdS or dS is not required, i.e., accepted second law falters

17 Pictet's Experiment

Marc-Auguste Pictet's (1752-1825) placed two concave metallic mirrors 10 ft apart and facing each other as shown in Fig.3. A hot object was placed at mirror 1's focal point, and a thermometer was placed at the focal, point of mirror 2. The hot object radiated heat causing the thermometer's temperature to increase.

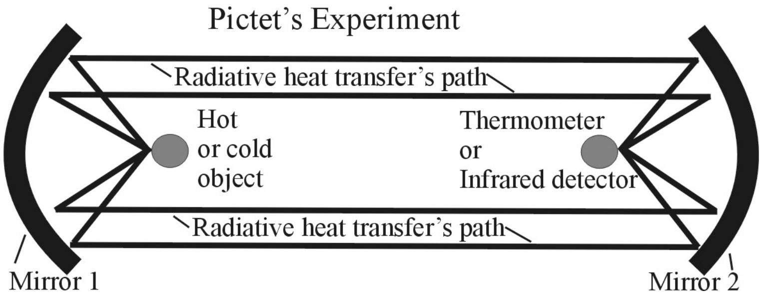

Figure 3: Shows Pictet's experiment. Two mirrors are placed such that Mirror 1's focal point is towards a hot object while Mirror 2's focal point is towards a thermometer

What Pictet's experiments shows is that radiative heat (thermal photon's) cannot be ignored when considering heat transfer. Such radiative heat has been forgotten when contemplating heat transfer in both classical and statistical thermodynamics [19]. Like free expansion, Pictet's experiment has been conveniently ignored.

18 Statistical Thermodynamics

It is inarguable that as a mathematical entity, statistical thermodynamics has certain powers that other mathematical constructions lack. Its weakness lay the fact that it is built upon assumptions. As with any mathematical construct built upon assumptions, at its very best, it is an approximation. Assumptions include:

1. Equidistribution of microstates: All accessible microstates are equally likely
2. Stochastic microstate energy changes: Upon collision, a system's microstates changes
3. Ergodicity theorem: Long term average of fluctuating properties remains the same
4. H-Theorem: An ensemble of states will evolve towards maximum entropy.

The above are statistical theorem assumptions. More fundamental assumptions that allow for mathematical simplification include [19]:

1. The colliding molecules/atoms can be treated as point particles.
2. The velocities of such colliding point particles are not correlated.
3. Their velocities are independent of both their position and origins.
4. The point particle collisions are elastic.

The fact that gas molecules are not dimensionless points invites concern. The one that particularly concerns this paper is elastic collisions. I.e., inelastic molecular collisions imply that energy other than kinematic energy interact in gaseous systems. Consider the plausibility of radiative energy residing in a gaseous system. A mathematical description where both gas molecules and thermal photons interact with each other, may be untenable for humans. Perhaps there will be hope in artificial intelligence (AI).

Statistical thermodynamics work so well as an approximation for determining the energy of system. It is because, the energy associated with a gas' kinematics ¿¿¿¿ energy associated its surrounding thermal radiation. [19]

This raises other issues such as the statistical thermodynamics assertion that a vacuum has no temperature, e.g., thermal photons are absorbed by thermometers then one must question the notion that a vacuum has no temperature. If one does not appreciate the concept of thermal photons then ask, why does a thermometer even measure a temperature when placed in a vacuum? Statistical thermodynamics remains a wonderous approximation but approximation should not form a universal theory's foundation.

19 Planck's Statement

Planck stated that there were two ways to formulate thermodynamics. Firstly: "We may take for granted the correctness of the mechanical view of nature, and assume that all changes in nature can be reduced to motions of materials points between which there act forces which have a potential. Then the principle of energy is simply the well-known mechanical theorem of kinetic theory, generalized to include all natural processes." Or secondly: "leave open the question concerning the possibility of reducing all natural processes to those of motion, and start from the fact which has been tested by centuries of human experience and repeatedly verified "…"no way possible to have perpetual motion"[28].

Choosing the second over the first, has led the sciences down a path where the entropy change based second law reigns supreme. It has been shown that embracing the reality of sensible lost work onto the atmosphere allows for both of Planck's stated ways of writing thermodynamics to hold true. Envisioning work onto the atmosphere as Mayer did in 1842, may have saved thermodynamics from almost two centuries of over-complications. Lost work also helps one to understand why the difference between the way that physicists and engineers view thermodynamics?

Of course, one has to draw one'd own conclusions concerning whether or not accepted thermodynamics has placed/taught their preferred mathematical implications ahead of logical consequences. Accepting what has been stated may be difficult

20 Conclusions

Many believe that classical thermodynamics is rudimentary science that doesn't explain all of what has been witnessed, e.g., free expansion. This paper turns accepted thermodynamics is turned on its head, while rendering a plausible new perspective.

First law equations for expanding systems tend to lack clarity, e.g. eq. 1, i.e., they incorrectly imply that work by an expanding system is done onto itself, e.g., eq 2, where $PdV)_s$ signifies nonsensible work that is done onto the expanding system.

Moreover, eq. 18 applies the supposition $TdS = dQ$ to expansion processes that are both isothermal and isobaric, e.g., boiling without the any concern as to what isothermal entropy change (TdS) means. TdS only hides the issues concerning eq. 2. Furthermore, TdS incorrectly implies that all expanding systems do work, irrelevant of their surroundings. This is illogical because work by an expanding system is done onto its surroundings.

For expanding systems near Earth's surface, the surroundings include the atmosphere. Hence sensible work includes work onto the atmosphere $[W_a = (PdV)_a]$, plus any other work done in some process. Furthermore, work tends to be lost by the expanding systems. This includes W_a that is lost by all systems that expand near the Earth's surface, i.e., $W_a = W_lost$.

Traditionally, W_lost has been incorrectly explained in terms TdS. $W_lost = W_a$ releases classical thermodynamics from all the burdens that the parameter with no physical meaning (entropy) creates. One is no longer faced with the scientific indignity of work disappearing "into the hands of god". Moreover, this challenges the currently accepted second law, which is founded upon: $TdS > 0$.

TdS and the isentropic equations incorrectly imply that an expanding system does work onto a vacuum, i.e., theoretical predictions include significant temperature decreases by the gases that expanded into the vacuum. Both the Gay-Lussac and Joules 19th century free expansion experiments had comparatively minute temperature changes. Moreover, any temperature drop in Flask 1 was countered by a temperature increase in Flask 2, thus the gas' total energy never changed. Thus, proving that no work is done when a gas expands into a vacuum. Thus, challenging the very essence of accepted thermodynamics.

Since W_a is infinitesimal when compared to the atmosphere's total energy, W_a is immeasurable in terms of the atmosphere's parameters. Therefore, when analyzing experiments, one may utilize the fact that $(PdV)_a = PdV)_s$ and then use the so-called isentropic equations in their analysis. However, one is best to base their theoretical analysis on sensible work, e.g., $W_a = (PdV)_a = (M\vec{g}dh)_{ca}$, where the atmosphere can be approximated as remaining both isothermal and isobaric. Note that work in similar terms was previously described by Mayer (circa 1842), where the difference between isobaric and isochoric heat capacities were first described in terms of W_a.

A broader context for expanding systems near Earth's surface may consider that Wa should be expressed in terms of eq. 9: $W_a = (PdV)_a + (VdP)_a + nC_v dT$. Again, if our atmosphere is considered to remain both isothermal and isobaric then the work done onto the atmosphere can be idealized by: $W_a = (PdV)_a$. A first law equation for a heating process where a system expands in an isobaric atmosphere is eq. 5: $dQ_i n = dE_s + (PdV)_a$. Note, in reality an expanding system initially creates a high pressure zone (HPZ). The HPZ disperses from around the expanded system, eventually returning to 1 atm pressure.

It seems strange that scientists chose to ignore the fact that the free expansion experiments disprove their preferred theory. A theory founded upon TdS's supposition, which led to the second law assertion that increasing entropy signifies irreversibility. Instead, our forefathers took the stance that classical thermodynamics is an imperfect science and that statistical thermodynamics provides the only real explanation. All the while admitting that entropy has no physical meaning.

Interestingly, Pictet's experiment actually challenges statistical thermodynamics. This should be expected due to statistical thermodynamics being founded upon so many assumptions. Such an array of assumptions allows the brilliant mathematics to be manageable, however they also render it into a great approximation. Accepting that sensible lost work onto the atmosphere explains both boiling and free expansion leaves one to ponder, can a New Thermodynamics be found? The answer is yes.

Although up for debate, a plausible New Thermodynamics involves the acceptance that:

1. Molecular collisions are inelastic.
2. A superior kinetic theory has validity.
3. Not all of a gas' energy can be used for work

Added to the above is this author's intuition that thermal photons exist. Thermal photons being photons that are readily absorbed and/or radiated by matter. Based upon a rudimentary analysis thermal photons/phonons would predominately reside in the thermal infrared part of the EM spectrum.

This all raises doubts concerning the veracity of our currently accepted entropy-based doctrine. Unfortunately, accepting this will also present challenges to statistical thermodynamics. Challenges that some may not be willing to embrace.

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22 Copyright Notice

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