

**NEW THERMODYNAMICS: INELASTIC COLLISIONS, LOST
WORK, AND GASEOUS INEFFICIENCY**

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Abstract

Abstract: This paper examines scientific “certainties” established during the 19th and 20th centuries regarding entropy and the second law. Indoctrinated thermodynamics is structured around elastic collisions. The realization that molecular collisions tend to be inelastic brings into question the validity of accepted thermodynamics. Boltzmann’s inspired and brilliant mathematical edifices based upon elastic collisions remain a good approximation for many systems, especially those where the illusion of elastic collisions exists, e.g., most gaseous experimental systems. But, the laws of thermodynamics cannot be built around approximations which this author believes is currently the case. Explanations based upon lost work, friction and drag can explain why perpetual motion is an unrealistic notion. Gaseous inefficiency also occurs when one tries to use a gaseous system to perform work. An improved understanding based upon inelastic collisions alters how one views our universe. The possibility of using Hadronic mathematics to describe a world undergoing inelastic collisions will be briefly discussed.

Keywords: Inelastic collisions, lost work, gaseous inefficiency, latent heat, kinematic heat transfer, radiative heat transfer, Hadronic mathematics

1. Introduction

Thermodynamics saw its 19th century creators include the likes of Sadi Carnot, Rudolf Clausius and Lord Kelvin. Ludwig Boltzmann in the 1890's provided a mathematical link between the atomic nature of matter and thermodynamics [1] with his statistical probability-based mathematics, whose ensembles were based upon elastic collisions, e.g., Boltzmann distribution a.k.a. Gibbs distribution.

The resulting mathematical genius has not enunciated thermodynamics with clarity. As stated by Sommerfield [2]: “Thermodynamics is a funny subject. The first time you go through it, you do not understand it 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”

More recently, Haddad [3] has conveyed a similar sentiment: “In fact, 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. With few notable exceptions, more than a century of mathematicians have turned away in disquietude from classical thermodynamics, often overlooking its grandiose unsubstantiated claims and allowing it to slip into an abyss of ambiguity.”

A goal of this paper is to provide thermodynamics with more clarity, starting with realistic collisions being inelastic collisions.

2. Elastic Collision

The following analysis for the consideration of an elastic collision is based upon consideration described in this author's book [4]. Consider that mass (M_1) moving with initial velocity (\vec{v}_{1i}) experiencing an elastic collision with mass (M_2) moving at velocity (\vec{v}_{2i}). To simplify the analysis, further consider that the trajectory of the two masses is along a solitary plane that passes through their centers of mass. Based upon conservation of kinetic energy for such an elastic collision, one could write:

$$\frac{M_1 \vec{v}_{1i}^2 + M_2 \vec{v}_{2i}^2}{2} = \frac{M_1 \vec{v}_{1f}^2 + M_2 \vec{v}_{2f}^2}{2} \quad 1$$

Multiplying both sides of Eq. 1 by 2 and rearranging the variables gives:

$$M_1(\vec{v}_{1i}^2 - \vec{v}_{1f}^2) = M_2(\vec{v}_{2f}^2 - \vec{v}_{2i}^2) \quad 2$$

In terms of difference of squares Eq 2 becomes:

$$M_1(\vec{v}_{1i} + \vec{v}_{1f})(\vec{v}_{1i} - \vec{v}_{1f}) = M_2(\vec{v}_{2f} + \vec{v}_{2i})(\vec{v}_{2f} - \vec{v}_{2i}) \quad 3$$

For any collision, conservation of momentum means:

$$M_1\vec{v}_{1i} + M_2\vec{v}_{2i} = M_1\vec{v}_{1f} + M_2\vec{v}_{2f} \quad 4$$

Rearranging Eq. 4 gives:

$$M_1(\vec{v}_{1i} - \vec{v}_{1f}) = M_2(\vec{v}_{2f} - \vec{v}_{2i}) \quad 5$$

Dividing Eq. 3 by Eq. 5 yields:

$$\vec{v}_{1i} + \vec{v}_{1f} = \vec{v}_{2i} + \vec{v}_{2f} \quad 6$$

Rearranging Eq. 6 gives an interesting result:

$$\vec{v}_{1i} = \vec{v}_{2f} + \vec{v}_{2i} - \vec{v}_{1f} \quad 7$$

Eq. 7 states that the relative velocity before the collision equals the negative of the relative velocity after any elastic collision. For example, a super ball will bounce upwards with the same speed it had just before striking the floor.

Inserting Eq. 7 into Eq. 4 gives:

$$M_1(\vec{v}_{2f} + \vec{v}_{2i} - \vec{v}_{1f}) + M_2\vec{v}_{2i} = M_1\vec{v}_{1f} + M_2\vec{v}_{2f} \quad 8$$

Rearranging the terms gives:

$$M_2/M_1 = (\vec{v}_{2f} + \vec{v}_{2i} - 2\vec{v}_{1f})/(\vec{v}_{2f} - \vec{v}_{2i}) \quad 9$$

Eq. 9 does not readily determine what an elastic collision looks like. Accepting its validity renders an elastic collision into a rather rare event. Other equally complex solutions can be found [5,6].

However, setting $M_1=M_2$, does provide the simple solution for Eq. 9:

$$\vec{v}_{1f} = \vec{v}_{2i} \quad 10$$

The simple solution for an elastic collision requires two identical masses with all the momentum being transferred from M_1 to M_2 , where M_2 has an initial velocity of zero in a head on collision. A classic example takes place in a game of billiards. When the cue ball (M_1) hits another ball (M_2) through their centers of mass transferring all the momentum from M_1 to M_2 .

A more interesting example of an elastic collision occurs in Newton's Cradle, where a series of balls hung by equal lengths of string, collide through their centers of mass with one another. Each ball and string act as an independent pendulum, which after colliding passes its momentum and its kinetic energy onto the ball with which it collides. Interestingly, if two balls are lifted and then released, it will be two balls that swing/oscillate, and if three balls are lifted (in a five-ball cradle), three of the five balls will swing/oscillate.

The above implies that an elastic-collision-criteria is that solid spheres of equal mass must collide through the centers of their masses, which seemingly validates Eq. 10. Energy is only lost by the drag of a moving ball in its surrounding atmosphere.

3. Inelastic Collisions

A simple example of an inelastic collision is a bullet hitting and then lodging itself into a piece of wood. In this inelastic collision, energy is conserved only because of the deformation of the bullet and wood, and any created collisional heat. For such an inelastic collision where the two masses become one, based upon Eq. 4, one obtains:

$$M_1\vec{v}_{1i} + M_2\vec{v}_{2i} = (M_1 + M_2)\vec{v}_f \quad 11$$

Eq. 11 signifies a "completely inelastic collision" where the two colliding objects stick together after impact. Other inelastic collisions where the two

colliding objects do not stick together are next to impossible to model with any clarity.

4. The Question

If traditional statistical mechanics/thermodynamics is based upon elastic collisions and molecular collisions are inelastic, then why do the brilliant distributions of Boltzmann (a.k.a. Gibbs) and Maxwell, seemingly correlate with accepted experimental results?

The illusion of elastic collisions exists in most experimental systems [7-10]. Specifically, all inelastic molecular collision (inter and intra) must result in collision induced thermal energy (thermal photons or phonons), in order for energy to be conserved. This induced thermal energy is:

1) reflected back into the system off of reflective coatings often used in experimental apparatus; and/or

2) adsorbed by the experimental system's walls becoming phonons that may eventually be recirculated back into that system as photons.

In other words, many experimental systems suffer from the illusion of elastic collisions. And due to such illusions, the elastic collision based traditional thermodynamics becomes a valid approximation for experimental results.

Furthermore, the total energy associated with thermal phonons in most gaseous systems is often infinitesimal when compared to the total energy associated with the system's gaseous molecule's kinematics, e.g., translational, rotational and vibrational energies.

Moreover, one must keep in mind that photons travel at the speed of light, so their effects can be more significant than one would suspect based solely upon their total energy at a given instant. Effects include heat transfer, and thermal energy lost by open systems, i.e., if experimental walls are removed, the illusions of elastic collisions quickly disappear as most of the collision-induced thermal photons vanish into one's horizons.

It is inarguable that elastic collision-based conjecture enables mathematical simplification. However, a science structured around completely inelastic collisions, also elicits mathematical simplification. Questions arise, such as:

1) How accurate are the approximations of an elastic collision structure, to one's analysis?

2) Does strict adhesion to an elastic collision structure, cause over-complications of one's science?

No matter one's answers, it must be accepted that the sciences based upon the probability function whose basis is elastic collisions, often remains a reasonable approximation especially for systems where the illusion of elastic collisions exists.

5. Real World Elastic Collisions

A thermal photon associated with an inelastic intermolecular collision generally is infinitesimal when compared with the kinematics of a gaseous system. However, an ensemble of such collisions would lend itself to a spectrum of thermal photons. Where would one find such a spectrum?

This author concluded that a good candidate for such a spectrum is a blackbody radiation spectrum [4, 8-10]. Certainly, a cavity surrounded by condensed matter would be filled with such thermal photons from either (or both) inelastic intermolecular or intramolecular collisions. Moreover, the contents within such a cavity would be shielded from much of the wizardry that is generally witnessed here on Earth's surface [4,9,10]. And the placement of a hole into that cavity (e.g., Jean's cube) would expose those very thermal photons, as has been witnessed in the blackbody experiments of the late 19th century [4,9].

Based upon an association of blackbody radiation with collision induced thermal photons, one attains an enlightened explanation for the light emanating from both tungsten lightbulbs, and our Sun [9]. Furthermore, much of the blackbody radiation witnessed in our cosmos could readily be explained in terms of inelastic collisions, e.g., both cosmic microwave blackbody radiation and Hawking's radiation [10].

It is accepted that electron-photon collisions are inelastic [11-12], as well as electron-electron collisions [13,14]. Models for inelastic molecular collisions have even been formulated [15]. Presented with all this, why would one even consider that the vast majority of intermolecular collisions are anything but inelastic? Unlike traditional kinetic theory, inelastic intermolecular collisions fit exceptionally well with this author's kinetic theory [4,16,17], which is a superior match to empirical findings. Moreover, this author's kinetic theory does not require any of the hordes of exceptions that plague traditional kinetic theory.

Unfortunately, most of accepted physics has its foundation vested in elastic collisions. The illusion of elastic collisions extends beyond kinetic theory into

the ideal gas law, Avogadro's hypothesis, and even the Navier-Stokes Equation [18]. Inelastic collisions challenges accepted dogma.

Finally, an interesting question facing physics arises: Why are elastic collisions limited to hard spheres of equal mass, whose collision occurs along a plane through their centers of mass [4]?

6. Traditional Mathematics and Inelastic Collisions

For simplicity's sake, point particles and electromagnetic (EM) waves propagating are traditionally treated as if they are in some homogeneous and isotropic vacuum, e.g., empty space. Such systems can be referred to as "exterior dynamical systems" [19,20], which consists "of particles at sufficiently large distances to [permit their point-like approximation under sole-action-at-a-distance interactions]" [21].

Exterior dynamical systems include those that constantly place of all of a gaseous system's energy solely upon the gas molecules' kinematics, i.e., gaseous systems of elastic collisions. Such elastic collision-based systems conveniently ignore any radiation (residing or generated) within a system. Systems witnessing elastic collisions can be thermodynamically described using statistical thermodynamics, or be dynamically described using either the Hamilton or Lagrange equations.

The Hamiltonian is founded upon conservation energy that being the conservation of a system's kinetic plus potential energy. Here point particles (with kinetic energy) interact with potentials as action-at-a-distance. Certainly, both elastic and inelastic collisions (contact interactions) have zero range hence neither should be strictly Hamiltonian. However, dynamical systems where kinetic plus potential energy is conserved within that system, are really limited to systems undergoing elastic collisions, hence like statistical mechanics is troublesome when applied to real systems undergoing inelastic collisions.

The Lagrange equation considers the generalized forces upon particles/objects (dynamically speaking), hence are sometimes applied to reversible systems (thermodynamically speaking). Like the Hamilton equation, dealing with inelastic collisions within a system would not be ideally suited to the Lagrange equation, except for as a rough approximation. Furthermore, an ensemble of such inelastic collisions results in a thermal spectrum (e.g., a blackbody spectrum), and dealing with a thermal spectrum will add even more complexity to the problem.

Both the Hamilton and Lagrange equations may remain as approximations for systems where the illusion of elastic collisions exists, i.e., systems that recycle photons (or phonons) created by inelastic collisions, back into the system. As was the case of statistical mechanics this requires the blatant oversight of any radiation (thermal or otherwise) residing with a gaseous system.

The generally applied 20th century Hamilton and Lagrange equations are truncated equations i.e., neither considers forces that are not derivable from potentials, e.g., dissipative forces. [20,21]. Real world dynamics do not occur in isotropic vacuums, nor can they all be calculated using such truncated equation.

The above does raise the question: Is the 20th century acceptance of the truncated Hamiltonian and Lagrange equations primarily due to the illusion of elastic collisions in gaseous experimental systems?

It certainly explains why “all known potentials... and therefore all known Hamiltonians, are reversible” [21]. No matter one’s acceptance, real world systems remain irreversible, therefore other considerations are obviously required.

7. Hadronic Mathematics and Inelastic Collisions

Santilli examined Lie’s algebra in his Ph.D thesis (1960’s) [21]. The reality that particles/objects generally experience non-conservative forces, which thermodynamically results in irreversible processes that can be considered using Lie’s algebra. This led to the construction of “Lie-admissible” statistical mechanics [22,23]. Which eventually led to Hadronic mathematics [20,21,24], whose name is based upon the Hadron which is a subatomic composite particle. Note that Lie-admissible algebra is considered to be algebra in its most general form.

Rather than limiting thought to exterior dynamical systems, Hadronic mathematics is structured to deal with the more complex “interior dynamical systems”, where “extended and deformable particles at mutual distances of the order of their size under action-at-a-distance interactions as well as contact nonpotential interactions”. [21]

Interior dynamical systems include non-spherical deformable particles (extended particles) and EM waves that propagate inside of some non-homogeneous anisotropic physical medium. Solutions require unconventional math that is neither linear nor local.

So that there is no misunderstanding, Santilli considered exterior dynamical systems in terms of isomathematics, which dynamically speaking considers “time reversal invariant systems of extended and deformable particles” [20]. This allows for the existence of reversibility in thermodynamic systems undergoing elastic collisions.

Interior dynamical systems are dealt with in genomathematics, which dynamically speaking are intended for “time irreversible systems” [20], e.g., energy releasing processes in open systems. Promising applications for genomathematics has been found in both chemistry and nuclear physics, where resultant discrete energy is released. The benefits in describing the generalities of irreversible thermodynamic systems, is not so clear.

This author is the first to admit that he may not be the best suited to fully understand Hadronic mathematics, hence I recommend that others more qualified at dealing with such conceptualizations, read what has been written herein and then seek the brilliant writings of Santilli and others.

Particles undergoing inelastic collisions could be thought of as extended particles. The witnessed radiation from an ensemble of inelastic collisions results in a spectrum of photons (or phonons) that is non-linear, e.g., a complete blackbody spectrum is not mathematically linear. Part of the explanation for this might lay in the fact that molecules are not spherical balls. However, placing lack of sphericity as the sole explanation is premature, especially in light of the facts witnessed at larger scales, namely concerning Newton’s cradle, where elastic collisions were limited to equal masses colliding along a path through their centers of mass.

Although this author believes that there may be promise with Hadronic mathematics (e.g., genomathematics in particular) when dealing with irreversible thermodynamic systems undergoing real inelastic collisions, the transformations currently used may be too linear, (e.g., eq. 3.65 in Santilli’s paper [20] is for a linear velocity dependent dissipative force). Mind you, dragging an object along the ground can be approximated by a linear velocity dependent dissipative force, although at the molecular level it would be significantly more complex.

Perhaps one could approximate a complete radiated thermal spectrum (blackbody?), due to inelastic collisions, by some linear temperature dependent approximation (along the lines of Wein’s approximation). This then could render Hadronic mathematics into a more suitable approximation for thermodynamic reality than the traditionally accepted mathematics can ever achieve.

Two issues remain. Firstly, when one reasons how thermal radiation results from inelastic collisions. If it concerns is in terms of extended particles undergoing deformations at the atomic scale, then what exactly is deforming? Could it be:

- charge distributions in atoms/molecules?: or
- associated nuclear magnetic moments?

Secondly, deformation during inelastic collisions at larger scales implies permanence. At all scales this may not be the case. Therefore, a basic premise may be to envision:

- an inelastic intramolecular collision as resulting in a loss of vibrational energy within molecules, and
- an inelastic intermolecular collision as resulting in the loss of kinetic energy by molecules in motion

Thermal equilibrium remains meaning that as much thermal energy is lost in creating thermal photons, as is gained in their absorption. Note that this considers that thermal equilibrium is purely radiative in nature.

All energy releasing processes in open systems remain irreversible, unless a mechanism exists that can recycle that energy back into the system. Hence some version of Hadronic mathematics may be determined as a superior mathematical fit when compared to the more traditionally accepted mathematics.

8. Lost Work

Irreversibility found in systems undergoing inelastic collisions, has been discussed. However, irreversibility also exists in expanding systems that experience lost work [4,7,9,17,25,26]. This occurs irrelevant of whether the expanding system undergoes elastic or inelastic molecular collisions.

Lost work provides insights into why entropy and the second law are ill-advised beyond being based upon misguided statistical thermodynamics, which is structured around elastic collisions.

For those not familiar with lost work, consider that one compresses a monatomic gas in a non-insulated piston-cylinder by placing a pair of identical masses (M_1 and M_2) on top of the piston as shown in Fig. 1. All movement will be considered as being frictionless, hence ideal.

The compressed gas can be defined in terms of its mechanical parameters, i.e., pressure (P) and volume (V). Such a PV closed system can often be

modeled in terms of the number of molecules (N), Boltzmann's constant (k) and temperature (T), that being the ideal gas law:

$$PV = NkT \quad 12$$

How much work was required to compress the gas? For infinitesimal compression, in terms of the gas inside of the piston-cylinder, the isothermal work required for compression [$W_{(A \rightarrow B)}$] is an integral of increasing pressures change (dP) over decreasing incremental constant volumes.

$$W_{(A \rightarrow B)} = \int dw = \int_{P_A}^{P_B} V dp = (NkT) \ln \left(\frac{P_B}{P_A} \right) \quad 13$$

As the monatomic gas' pressure increases ($P_A \rightarrow P_B$), an increasing amount of infinitesimal work (dw) is required to compress the gas another incremental volume (V). This explains why in terms of the gas inside the piston-cylinder, the work required is a natural logarithmic function, i.e., Eq. 13.

Consider that both the masses on top of the piston are removed. In terms of the gas inside of the piston-cylinder the isothermal work done [$W_{(B \rightarrow A)}$] is again an integral but this time one contemplates it as incremental pressures (P) multiplied by infinitesimal volume increases (dV), i.e. ($V_B \rightarrow V_A$), hence:

$$W_{(B \rightarrow A)} = \int dw = \int_{V_B}^{V_A} P dv = (NkT) \ln \left(\frac{V_A}{V_B} \right) \quad 14$$

Eq 14 is based upon the fact that as the gas' incremental pressure (P) decreases, the amount of work that an infinitesimal volume (dV) of gas can do, decreases.

The work required to lift [$W_{(lift)}$] those masses a height [$dh_{(B \rightarrow A)}$], i.e., back to their original position is:

$$W_{(lift)} = (M_1 + M_2) \vec{g} dh_{(B \rightarrow A)} \quad 15$$

The energy described by $W_{(lift)}$ was performed by someone or something external to the piston-cylinder, therefore that work remains external to the system's energy.

Whether considering infinitesimal compression or expansion, one often thinks that work is either being done onto the compressed gas, or being done

by the expanding gas. However, if work is actually done onto the compressed gas, or by the expanding gas, why has its temperature not changed?

In order to answer that question, one must realize that the piston-cylinder is a system inside of another system with the second system being our atmosphere. As the gas was infinitesimally compressed, any heat generated was allowed to escape out through the piston-cylinder walls, thus keeping the process isothermal, i.e., our atmosphere behaved as a heat sink.

Conversely, during infinitesimal expansion any heat lost by the expanding monatomic gas is replaced with thermal energy entering the gas through the piston-cylinder's walls, i.e., our atmosphere behaves as a heat bath. Obviously, one cannot simply consider work done by a system (e.g., piston-cylinder) without considering its interactions with the surrounding atmosphere.

As an open system, our atmosphere's pressure is really determined by its overlying weight (mass in gravitational field), thus it does not constitute a PV closed system in the same manner that a closed system does. At a given elevation, the work is volume change (dV) multiplied by the pressure at that elevation. On Earth's surface work done onto our atmosphere is defined by:

$$W_{atm} = (PdV)_{atm} \qquad 16$$

Reconsider the monatomic gas' expansion, surrounded by the atmosphere. As the gas inside of the piston-cylinder expands, it must lift upwards the surrounding atmosphere's overlying mass, as is defined by Eq 16. This work results in a potential energy increase of our atmosphere.

Conversely, a piston-cylinder's volume decreases results in the atmospheric potential energy transform into atmospheric kinetic energy which is a form of heat as defined by kinetic theory (both the traditional and this author's). In other words, a contracting system witnesses an increase in the surrounding atmosphere's kinetic energy. The compression was due to the placement of the masses on top of the piston-cylinder, rather than any work from the atmosphere itself. Just as the lifting of those masses back to their original position required work, that was external to the system as defined by Eq 15.

9. Boiling

Consider what happens if one boils a liquid, as illustrated in Fig 2. The Hot System provides thermal energy (dQ_m) which heats the liquid and surrounding gas (dE_{sys}) that being System 1. Hence in terms of number of moles of liquid

(n_{liq}), number of moles of gas (n_{gas}), their isometric molar heat capacities (C_v) and temperature change (dT):

$$dQ_{in} = dE_{sys1} = (n_{liq}C_{v_{liq}} + n_{gas}C_{v_{gas}})dT \quad 17$$

Eq. 17 assumes that both the gas and liquid experience the same temperature changes and that their relative quantities remain constant.

At the liquid's boiling point, steam/vapours rapidly form inside of the piston-cylinder, i.e., a mass transfer from the liquid to gaseous state. The piston-cylinder now expands, hence does work onto the surrounding atmosphere (W_{atm}). Therefore:

$$dQ_{in} = dE_{sys1} + W_{atm} \quad 18$$

There is no thermal energy from the surrounding atmosphere entering the insulated piston-cylinder during its expansion, i.e., all input thermal energy comes from the Hot System. Accordingly, no thermal energy leaves the atmosphere even though the atmosphere's potential energy is continually increasing, as the piston-cylinder expands. Now, the work done onto the atmosphere (W_{atm}) becomes lost work (W_{lost}), i.e., an irreversible energy lost into the surrounding atmosphere resulting in an irreversible atmospheric potential energy increase.

Therefore, the expansion of any heated enclosed system can now be rewritten in a more general form:

$$dQ_{in} = dE_{sys} + W_{lost} = dE_{sys} + (PdV)_{atm} \quad 19$$

With the Hot System and any insulation around System 1 removed (see Fig. 3), heat radiates out through System 1's walls (Q_{out}) into the surrounding atmosphere, hence System 1 cools down. As System 1 cools there is also a mass transfer from the vaporous state back into the liquid state. This lowers the pressure inside the piston-cylinder, allowing the atmosphere to drive the piston back into the piston.

Some might argue that the atmosphere is doing work onto the contents in the piston-cylinder but this is not the case. If the atmosphere is doing work onto System 1, either its pressure or temperature must increase. Since, the pressure is atmospheric, while its temperature is decreasing, then no work is being done onto System 1.

The equation that describes what is happening to System 1 is simply:

$$dQ_{out} = dE_{sys1} \quad 20$$

Eq. 20 could be rewritten in terms of heat capacities and number of moles, as Eq. 17 is written.

As the piston-cylinder's volume decreases, some of our atmosphere's potential energy is transformed into kinetic energy, which as was previously stated, is a form of heat.

10. Vaporization vs Condensation

Based upon Eq. 19, the latent heat of vaporization can be rewritten as [4]:

$$L_{(l \rightarrow g)} = dU + (PdV)_{atm} = dU + W_{lost} \quad 21$$

Where "L" signifies the latent heat, "(l → g)" indicates that the change is from liquid to gas, (i.e., vaporization), and "dU" is the change in bonding energy.

Since lost work is irreversible, the latent heat of condensation becomes [4]:

$$L_{(g \rightarrow l)} = -dU \quad 22$$

Where "(g → l)" signifies condensation.

Traditionally, it was incorrectly asserted that the latent heat of condensation is equal and opposite to the latent heat of vaporization, i.e., negative of Eq 21. Since no work can be done in condensation, it is logical to conclude that Eq 22 is correct. Why was this not previously realized?

One never actually measures the latent heat of condensation. Instead, the latent heat of vaporization is measured in an isobaric calorimeter, and then it is incorrectly assumed that the magnitude of latent heat of condensation is equal and opposite. Note that in 1887, John Joly [27] discussed using a gravimetric calorimeter for measuring condensation, but to this author's knowledge such a line of thought has not been rigorously applied.

The fact that many expanding systems perform lost work, while all contracting systems do not, broadens one's understandings. Many useful

systems that power our devices involve expansion, e.g., the steam engine. Irreversible lost work inevitably ends up heating our atmosphere, whether the end result is direct or indirect. This can be taken as part of one's analysis for debunking the second law. Before that is done, entropy must be discussed.

11. Entropy

Accepting the Equation written on Boltzmann's tombstone, which defines entropy in terms of the number of microstates (Ω), i.e., the Boltzmann-Planck entropy Equation [4,28]:

$$S = k \ln \Omega \quad 23$$

Eq 23 relates entropy to statistical ensembles that are based upon elastic collisions, whose validity is limited to experimental systems where the illusions of elastic collisions reside.

The notion of entropy (S) began with Rudolf Clausius, as something which when multiplied by temperature (T) gives energy, i.e., $TS = \text{Energy}$.

Entropy increases (e.g., entropy production) is traditionally accepted as the explanation for thermodynamic irreversibility. Mathematically, discussion of entropy increases can become complex, as demonstrated by Hasegawa [29]. Herein, it has been argued that simpler explanations exist for irreversibility. Accordingly, simpler enlightenment for entropy increases is also needed.

Consider the traditionally accepted Equation for the isothermal entropy change in an expanding system. Let " dE " be the internal energy change, then one would write [4,28]:

$$TdS = dE + PdV \quad 24$$

Eq 24 lacks clarity. Specifically, one might incorrectly infer that PdV represents work done in terms of the expanding system [4,30,31], when in fact it is work done by the expanding system onto the surrounding atmosphere. Therefore, clarity is only obtained by rewriting Eq 24 as:

$$(TdS)_{sys} = dE_{sys} + (PdV)_{atm} = dE_{sys} + W_{atm} \quad 25$$

Although Eq 25 possesses clarity, it is not founded upon sequential logic. The isothermal entropy change has been equated to the expanding system's

energy change plus work done by that expanding system onto the surrounding atmosphere. Since no one really knows what entropy is, this has to be the beginnings of circular logic [4].

Specifically, to claim that something equals something measured, and then to claim that something now proves why the something measured actually exists is circular logic. To then bury this logic in an ever increasing complicated array of probability-based statistical mathematics, does not alleviate the fact that it is now fully circular logic.

For a better understanding consider what TdS represents beyond Clausius's assertion. Consider Eq 25 as a version of Eq 19, except now a heat bath is providing the required energy. Now consider Fig.4 where a heat bath drives the expansion of a fully insulated piston-cylinder.

The heat transferred from the heat bath into System 1 in terms of its isometric heat capacity (C_v) and number of molecules (n) is $[(nC_vdT)_{bath}]$. The heat bath's temperature decreases, hence assuming no phase change ($dU=0$) a first law equation describing this process is:

$$(nC_vdT)_{bath} = -[(nC_vdT)_{gas} + (PdV)_{atm}] \quad 26$$

Consider that the thermal energy associated with the heat bath is orders of magnitude greater than the thermal energy required to increase System 1's temperature plus perform lost work. One understands why the heat bath's temperature remains constant, i.e., $dT_{bath}=0$, as measured by a thermometer. Just because the temperature decrease is immeasurable, does not mean that thermal energy did not exit the heat bath, i.e., the temperature drop is infinitesimal.

Upon observing this process, one might incorrectly conclude that the process, is an infinitesimal isothermal process, hence $T_{gas}=T_{bath}$. Obscure rationality may lead to the claim that this process can be explained in terms of the expanding gas' isothermal entropy change (TdS), i.e.:

$$(TdS)_{gas} = (nC_vdT)_{gas} + (PdV)_{atm}] \quad 27$$

Eq. 27 is based upon the fact that the temperature change is immeasurable, rather than it did not occur. Hence, Eq. 27 becomes erroneous. Yes, Eq. 27 does allow for natural logarithmic functionality, but so too does Eq. 28, as will be discussed.

Emphasizing the above point. The heat bath has so much thermal energy in comparison to the expanding system, that the heat bath (and expanding system) seemingly remains isothermal throughout the process of expansion. Just because one's thermometer is not accurate enough to measure the heat bath's temperature change does not mean that the heat bath did not experience an infinitesimal temperature change [4,32].

In other words, the notion of isothermal entropy change, associated with a heat bath experiments, is a misguided supposition that further buries entropy's misguided circular logic origins. No wonder that entropy actually falters when perceived in terms of adiabatic processes [4,32]. No wonder, no one really knows what thermodynamic entropy means [33,34]. How could anyone? Of note, others have also questioned entropy's conscripts [34,35].

All aspects of heat transfer into an expanding system can be dealt with using Eq 19 (or Eq. 26). The bold misguided employment of Eq. 25 (or Eq. 27), hides the fact that one really does not know, and the over-complication hidden behind a mathematics contrived for elastic collisions is the icing on the cake. This was all backed by experimental systems that gave the illusion of elastic collisions.

12. The Second (so-called) Law

The origin of the second law was described in the 19th century, by Lord Kelvin: "It is impossible to transform an amount of heat completely into work in a cyclic process in the absence of other effects" [36]. This fundamental realization concerning the irreversibility of certain systems, basically describes perpetual motion, as an unrealistic notion. The 20th and 21st century conscripts of the second law are upheld in Reif's [28] statement: "In any process in which a thermally isolated system changes from one macrostate to another, its entropy tends to increase, i.e., $\Delta S \geq 0$ ".

This author has challenged the above statistical based assertion, with the realization that no expanding system here on Earth's surface can be an isolated system [4,25,26]. Specifically, the fact that all expanding systems must do work onto the surrounding atmosphere tells us with absolute certainty that any notion of an isolated expanding system must be limited to systems that are not surrounded by matter in a gravitational field, e.g., our atmosphere. Perhaps an isolated system remains applicable to a closed expanding system in outer space.

How does one now explain Lord Kelvin's inarguable statement? Lost work clearly explains why the running of a useful expanding system, such as an engine (steam or petroleum powered), is an irreversible process. Therefore, useful expanding systems cannot power a perpetual motion device. To the condition of not having perpetual motion, one can further add friction (both internal and external) to a mechanical system, resulting in the production of heat, which ultimately ends up in our heat sink e.g., our atmosphere and oceans. One could further add drag, a combination of resistance to motion and frictional heat generated by inelastic collisions, between a moving object and its surrounding atmosphere. This helps to explain why perpetual motion cannot occur here on Earth's surface.

Another interesting second law-based statement is Haddad's [3] "the usable energy in an adiabatically isolated dynamical system is always diminishing in spite of the fact that energy is conserved". Realizing that useful expanding systems that do work onto their surrounding atmosphere also diminishes the notion of an "adiabatic isolated dynamical system". Moreover, one can envision that, as an expanding system does work onto the surrounding atmosphere, its ability to do more work diminishes as its pressure decreases, even if the expanding gas remains isothermal. And this may be deemed a degradation of the system's energy, as Haddad implies.

A more pragmatic understanding may be deduced by considering two systems in thermal and physical contact, e.g., System A is at both a higher temperature and pressure than System B, i.e., $T_A > T_B$ and $P_A > P_B$. Then:

- 1) hotter System A can pass thermal energy onto System B, i.e., $dQ_{(A \rightarrow B)}$.
- 2) higher-pressure System A can do work onto System B, i.e., $dW_{(A \rightarrow B)}$.

Importantly, the rate of heat transfer will decrease as $T_A \rightarrow T_B$, hence in terms of some constant "C":

$$\frac{dQ_{(A \rightarrow B)}}{dt} = -C \ln \left(\frac{T_B}{T_A} \right) \quad 28$$

If System A was a heat bath, then T_A would be considered as being constant. Similarly, the rate of work will decrease as $P_A \rightarrow P_B$, hence in terms of some constant "A":

$$\frac{dW_{(A \rightarrow B)}}{dt} = -A \ln \left(\frac{P_B}{P_A} \right) \quad 29$$

If System B was our atmosphere, then P_{atm} would be considered as constant.

The above formulas lead to two important considerations. Firstly, choosing to use the entropy based second law to explain a system's energy degradation is another over-complication. Certainly, a system's capability to transfer thermal energy, or do work, can be explained in simpler terms. Secondly, the natural logarithmic functionality that is so often associated with entropy in thermodynamics, can now be explained with a superior clarity allowing for the dismissal of Clausius' notion of entropy.

13. Gaseous Inefficiency

There is still one more issue that is plain to see yet not so obvious. It concerns the inherent "gaseous inefficiency" when a gas's kinetic energy is transformed into work. Compare the ideal gas law (Eq 12) to the total kinetic energy ($E_{k_{tot}}$) of a gas:

$$E_{k_{tot}} = 3NkT/2 \quad 30$$

As defined by the ideal gas law, the PV space of a gas is 2/3 a gas' total kinetic energy. This is counter-intuitive, but it is our reality.

This author is inclined to believe that the explanation lay in the total molecular "flux" (Φ_{work}) of an enclosed gas that strikes a unit surface area per unit time that can do work. That being:

$$\Phi_{work} = \left(\frac{1}{4}\right) n\bar{v} \quad 31$$

Note Eq 31 is obtained by the summation over all possible speeds ($0 < v < \infty$), over all possible azimuth angles ($0 < \varphi < 2\pi$) and over all possible angles ($0 < \theta < \pi$), [4,28].

In kinetic theory, the flux of energy imposed upon an enclosed gas, is from the system's six orthogonal walls. The energy flux (Φ_{energy}) from any one of those orthogonal walls, in any one of the six plausible directions is:

$$\Phi_{energy} = \left(\frac{1}{6}\right) n\bar{v} \quad 32$$

Eq 31 and Eq 32 imply that two thirds of a gas' kinetic energy can be used for work. It must be emphasized that this is most likely limited to gases in enclosed systems, where the structured rigid wall molecules impose their energetics onto the gas molecules that they enclose, e.g., most gaseous experimental systems.

14. Limitations of the Accepted Sciences

It should be stated that kinetic theory, Avogadro's hypothesis and the ideal gas law are all limited to closed systems of gases that are sufficiently dilute. Sufficiently dilute means that the primary intermolecular inelastic collision is between the gas molecules and their surrounding walls [4,16,17]. Furthermore, a sufficiently dilute system would also be a system where the illusion of elastic collisions can exist.

When the intermolecular collisions are dominated by gas-gas molecule collisions, many accepted fundamentals of the sciences falter, in part because the illusion of elastic collisions is lost [4]. A prime example of systems dominated by gas-gas molecular collisions is the stars, for which the polytropic equations were devised to define their PV space.

Importantly, when the illusion of elastic collisions is lost, Boltzmann's statistical probability-based math falters. This will be the toughest pill of them all for the physics community to even fathom, yet alone swallow.

15. Enhancing One's Understanding of Work

For clarification purposes, consider that an enclosed system's PV space, as defined by the ideal gas law, is actually a representative of a system's ability to do work, i.e., a system's ability to do work (W_{abi}) is:

$$W_{abi} = d(PV) = NkdT \quad 33$$

The system's ability to do work is in relation to a system of zero pressure. So, when differentiated the ideal gas law represents the ability of a system of gas to do work. Another way of looking at this is that the accretion of the dust and particles that formed Earth and its surrounding atmosphere, took work. Therefore, $d(PV)$ becomes a comparison to that result.

On the other hand, a higher-pressure system's potential (W_{pot}) to do work onto our atmosphere becomes:

$$W_{pot} = V(P_{sys} - P_{atm}) \quad 34$$

The potential to do work is the work that can be done in terms of the surrounding atmosphere.

As a final consideration, re-examine Fig. 1 here the compressed piston-cylinder B becomes lower pressure compressed-cylinder C. When M_2 is removed then the work done by the gas [$W_{(B \rightarrow C)}$] in going from B to C, is onto both M_1 and the surrounding atmosphere. Therefore:

$$W_{(B \rightarrow C)} = (PdV)_{atm} + M_1 \vec{g} dh_{(B \rightarrow C)} \quad 35$$

Eq 35 reinforces the understanding that the compressed gas lifts both the surrounding atmosphere and mass (M_1), increasing both their potential energies. And both the work onto the surrounding atmosphere and in raising M_1 are external to the expanding closed system.

Furthermore, this work can be isothermal when thermal energy enters an expanding system through the system's walls from the surrounding walls, or the system is heated infinitesimally from some heat source. Of course, such understanding forgoes the necessity of some isothermal entropy entwined arguments.

Importantly, when the illusion of elastic collisions is lost, Boltzmann's statistical probability-based math falters. This will be the toughest pill of them all for the physics community to even fathom, yet alone swallow.

16. Kinetic vs Radiative Heat Transfer and Coatings

Seim and Olsen [39] hung two folded (envelope shaped) pieces of aluminum foil in a box, whose walls were clear plastic. One folded piece was painted black while the second was untouched. The box was first heated with a tungsten-halogen lamp (500W). As expected, the temperature of the black piece increased faster than the untouched aluminum foil. They then heated the box with a hot plate and found the reverse occurred, i.e., the aluminum piece heated faster than the black piece. No explanation for this unexpected result was provided.

A tungsten-halogen lamp is dominated by radiative heat (thermal photons) from a blackbody radiation spectrum ($T=3,200$ K) [40], which is somewhat redder than our hotter Sun's blackbody spectrum ($T = 5,800$ K). Behaving as a

classical blackbody, the black foil adsorbs most of the thermal radiation, thus explaining why the black foil heated faster. Note that the shiny aluminum foil should reflect 90% (or more) of the incident radiation for the visible through the infrared spectrum (wavelengths: 248 nm to 100 μm [41]). Thus, one can assume that the aluminum foil is primarily heated due to “kinematic heat transfer” from the inelastic collisions with surrounding gas molecules, i.e., heat transfer explained by this author’s kinetic theory of gases [16, 17].

Conversely, when heated by the hot plate, one expects that the thermal energy transfer is primarily due to kinematic heat transfer, i.e., radiative heat transfer becomes a secondary process. This author speculates that the paint must have had a rubber component to it, therefore the surrounding gas molecules bounced off, rather than transferring their kinetic energy onto the blackened foil.

Although unintended, Seim and Olsen [39] have demonstrated that heat transfer into and/or by gases should often be separated into two parts, such as “radiative” and “kinematic heat transfer”.

One can also extend the above findings to experimental systems with thermal reflective coatings, as previously discussed. It becomes apparent that an experimental system with reflective coatings, reflects most thermal photons back into an experimental system, thus enhancing the illusion of elastic collisions.

17. Understanding Radiative Heat Transfer

Radiative heat transfer suffers from similar over-complication as kinematic heat transfer. This is perhaps best demonstrated by discussing the input from our Sun.

Consider Haddad [3] discussing that “the photons absorbed by Earth from the Sun have a much higher frequency... than those dissipated to space by the Earth, it follows from Planck’s formula relating the energy of each photon of light to the frequency of the radiation it emits that the average energy flow into the Earth from the Sun by each individual photon is far greater than the dissipated energy by the Earth to dark space.”

There is nothing wrong with the above consideration. Our Sun emits a blackbody spectrum whose peak is in the visible spectrum (as defined by Wein’s law). Part of our Sun’s incoming visible spectrum is reflected back out into space, therefore not all of our Sun’s visible spectrum is transformed into thermal energy. Furthermore, other parts of our Sun’s visible spectrum is

absorbed and then radially radiated as heat, that being lower frequency photons. Hence, conservation of energy tells us that the number of radially radiated thermal photons must be at a greater number than the absorbed visible photons from our Sun.

It should be emphasized that the above absorption and ensuing radial radiation as heat, is performed by both condensed matter and polyatomic gases, whose temperatures are closer to 300 K than that of our Sun (5,800 K). Condensed matter and/or an ensemble of polyatomic gases, near 300 K radiate a blackbody spectrum whose peak is in the infrared spectrum, which is generally considered as heat.

Furthermore, although our Sun emits a blackbody spectrum whose peak is in the visible spectrum, a significant portion of our Sun's irradiance is in the infrared [8,9,10,42]. And this significant infrared portion of our Sun's blackbody spectrum will be absorbed, and then radially radiated as blackbody spectrum, whose peak is also in infrared spectrum (T near 300 K).

The above understanding is relatively simple. It does become an over-complication when one tries to then explain this in terms of entropy and the second law. This is demonstrated by the following continuation of Haddad's [3] statement (after "Earth to dark Space"). "This implies that the number of different photon microstates is far greater than the number of microstates carrying the same energy from the Sun to the Earth. Thus, it follows from Boltzmann's entropy formula that the incident energy from the Sun is at considerably lower entropy level than the entropy produced by the Earth through energy dissipation"

Haddad's consideration was easy to deal with up until he felt the indoctrinated need to bring Boltzmann's entropy formula (Eq 23) into it. Haddad continues the overcomplication by discussing how the Earth maintains entropy and uses the free energy argument to support his discussion. Is this all necessary? The answer is no, but only if one questions our indoctrination. Note that this author has previously challenged the conscripts behind free energy.[30]

Conclusions

Traditional thermodynamics is based upon a mathematical conscript that incorrectly strictly adheres to the notion of elastic molecular collisions. This has been reinforced by experiments in gaseous systems where the illusion of elastic collisions exists. Gaseous systems displaying such illusions tend to be

those where the intermolecular collisions between gas molecules and the system's walls dominate, and where the walls can adsorb and then recirculate any thermal energy created by molecular inelastic collisions, e.g., collisional induced thermal photons.

“Science” requires a mathematical treatment producing numerical values that can be confirmed by experiments” [21]. One understands the obscurantism, i.e., the overlooking of the illusion of elastic collisions in experimental systems, concluding that experiments back the elastic collisional based mathematics, e.g., statistical mechanics, as well as the truncated Hamilton and Lagrange equations.

Certainly, a thermal photon from an inelastic collision signifies an infinitesimal amount of energy in comparison to that of most systems. However, an ensemble of such collisions forms a spectrum of thermal radiation. It has been postulated that blackbody radiation spectrum could be a thermal spectrum from such an ensemble of inelastic collisions.

Even as a spectrum, the instantaneous energy associated with thermal photons often is infinitesimal when compared to the energies associated with gaseous molecules. However, the speed of gaseous molecules is infinitesimal when compared to the speed of light. Therefore, the rates of heat transfer in closed systems due to thermal photons and/or the rate of thermal energy (heat) loss due to photon (thermal and otherwise) emission from an open system can be significant.

The energetics of many systems may be approximated by mathematics based upon elastic collisions, which simplifies the math. Certainly, rewriting the sciences based upon inelastic collisions at the molecular scale is a monumental task, one that may have no end, especially when dealing with fully open systems, where simple approximations may not exist. The mathematical understanding may start with Hadronic mathematics, but that has been left for others to determine.

In order to appreciate all the dynamics associated with work and energy, one cannot focus upon a given system, rather one must look at most systems as a system within a second system, with the second system being the first system's surroundings, e.g., our atmosphere.

Lost work is irreversible work, that occurs when energy is transferred from most useful expanding systems into the surrounding atmosphere. Realizing that our atmospheric pressure is defined in terms of the overlying weight of the atmosphere at a given elevation, the lost work done onto our atmosphere is defined by: $W_{\text{lost}} = W_{\text{atm}} = (PdV)_{\text{atm}}$.

Lost work signifies a potential energy increase of our atmosphere. Some of our atmosphere's potential energy is readily transformed into atmospheric kinetic energy (heat) when a system's volume decreases. This also means that the latent heat of condensation does not involve work, hence it is not equal in magnitude to the latent heat of vaporization, which involves lost work.

Many useful systems, that power mankind's machinery, involve systematic volume increases hence lost work. This in part helps to explain why the second law based upon increasing entropy, is no longer required when explaining why perpetual motion is not a realistic notion. Other reasons for perpetual motion's vincibility include friction and drag, with drag being a combination of resistance and friction (heat from inelastic collisions) between a moving object and its surrounding atmosphere.

Thermodynamic irreversibility in terms of an isothermal entropy increase is an unnecessary over-complication. Energy losses such as those associated with inelastic collisions and lost work, are better logic-based explanations for irreversibility in systems.

Another reason for inefficiencies is that only 2/3 of a gas's kinetic energy can be used for work. This can be ascertained by comparing a gas' kinetic energy to its ability to perform work. The reasoning most likely has to do with the fluxes of gases, and this means that the maximum efficiency when using a gas' kinetic energy to perform work is 66.667%.

Furthermore, using the second (so-called) law to explain a degradation of a system's energy is another over-complication. Explaining a degradation of a systems energy in terms of lost work, or changes to the rate at which a system can exchange energy, or perform work, elicits a simpler understanding.

Thermodynamics is not the mature science once thought, as it is in need of a rethink. Boltzmann's, Maxwell's and others' distributions that subscribe to elastic collisions remains beneficial, but only as approximations to idealized systems. Real-world approximations should be determined, e.g., modified Hadronic mathematics. Formulating laws, namely the second law, based upon elastic collision approximations, is not great science. Finally, entropy's status, in all of its guises, needs to be re-examined.

Figures

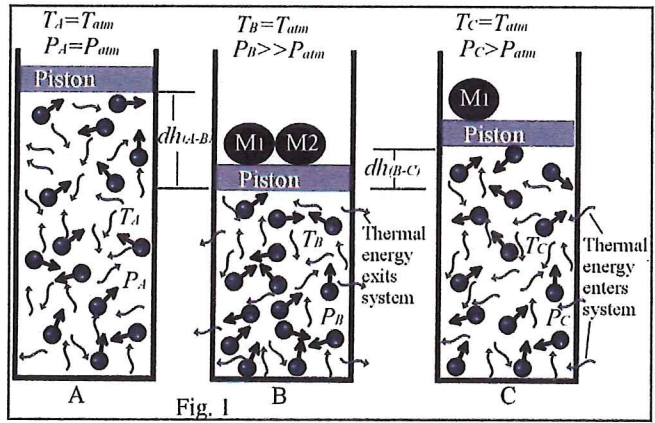


Fig. 1 shows a piston-cylinder at atmospheric pressure and temperature in A. Then at a higher compressed pressure in both B and C, while still remaining at atmospheric temperature (T_{atm}).

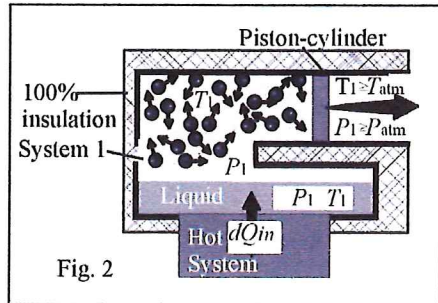


Fig. 2 shows a Hot System heating a liquid in fully insulated System 1, which eventually leads to boiling and the System 1's isobaric expansion using a piston-cylinder apparatus.

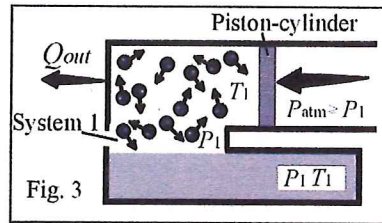


Fig. 3 shows the apparatus of Fig. 2, but now with both the Hot System and with System 1's insulation removed.

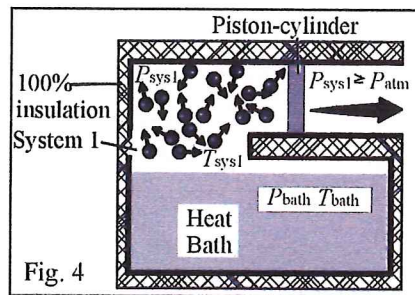


Fig. 4 shows a heat bath driving the expansion of a fully insulated piston-cylinder

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