

New Thermodynamics: Pictet, Epistemology and Philosophy

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Abstract

Pictet's experiment was front and center in the 18th/19th century debate concerning whether heat is a wave, or a particle. Pictet's experiment is best understood by realizing that thermal radiation energy plays a significant role in heat transfer. It is argued that this readily ignored experiment should have long ago alerted us to issues concerning our understanding of thermodynamics. This questions the rationale behind modern statistical thermodynamics, which describes all of a gaseous system's energy purely in terms of the kinematics of that system's gas. Not only is the philosophy of statistical mechanics now questioned but so too are those associated with entropy and its mathematical accomplice the second law. After raising questions, a simpler explanation as to what is witnessed will be discussed. An explanation that relegates statistical mechanics to a valid approximation for sufficiently dilute closed systems of gas, such as those often used in experiments. An explanation that remains void of the mathematical simplifications that statistical mechanics provides. Ultimately, the accepted epistemology of our sciences will be verbally challenged.

Keywords: Pictet's experiment, Radiative heat transfer, Wave-particle duality, Statistical thermodynamics, Entropy, Second law. **

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**Received on December 28, 2022. Accepted on June 21, 2023, Published on June 30, 2023. doi:10.23756/sp.v11i1.1037. ©K.W.Mayhew. This paper is published under the CC-BY licence agreement.

1. Introduction

The fine line between scientific theory and philosophy is often a matter of social importance and time. The concept of radiant heat (radiative energy transfer) originates with the legend of Archimedes focusing the Sun's rays onto invading ships, thus allegedly destroying the Roman fleet. Although founded in such illustrious history, our understanding of radiative heat and its transfer remains problematic.

The term “radiant heat” was envisioned by Swiss chemist C.H. Scheele, with the understanding that it adheres to the same laws as rays of light. [1] This was based on experiments performed in the last quarter of the 18th century, which demonstrated that radiant heat transfer differs from both convection and conduction [2]. The debate arose as to whether heat is a fire-like element called “phlogiston” (followed by “caloric”) or is it a wave (undulation) i.e., similar to light.

The above predates wave-particle duality conceptualizations that are now accepted throughout physics, e.g., quantum physics. Note that conduction has been coined “kinematic heat transfer” [3] to clearly separate it from “radiative heat transfer”.

Standing in the sunlight, one witnesses the warmth of radiant heat. Our Sun's rays that penetrate through our atmosphere are predominantly in the visible spectrum. That being the part of our Sun's blackbody spectrum that tends to be partially reflected and partially absorbed (as heat) by most matter.

In Marc-Auguste Pictet's (1752-1825) experiment, two concave metallic mirrors (9" dia.) were placed 10 ft apart. They faced each other, [2] as shown in Fig.1. A hot (or cold) object is placed at mirror 1's focal point, while a thermometer is placed at mirror 2's focal point.

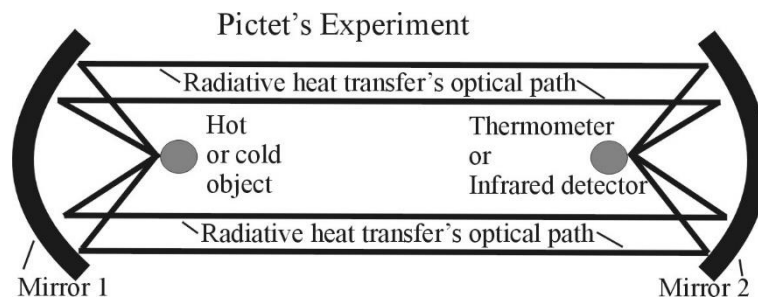


Fig. 1: Shows Pictet's experiment of placing two mirrors such that Mirror 1's focal point is towards an object (hot or cold) and Mirror 2's focal point is towards a thermometer (or infrared detector).

Radiated heat from hot objects causes the thermometer's temperature to increase. Conversely, the placement of cold objects resulted in the decrease of

the thermometer's temperature. This sparked research for "frigorific rays" those being cold particles. This also led to Pictet's colleague, Pierre Prevost writing in 1791: "Memoire sur l-equilibrium du feu". That being a description of heat transfer as some two-way transfer of particles.

Due to the reflections to a focal point, a contemporary interpretation should consider that the heat transfer in Pictet's experiments involves heat transfer behaving as waves rather than particles. Note that for both the hot and cold object's placement, the mirror's temperature remained constant [2].

A modern version of Pictet's experiment has been described using an infrared detector in place of the thermometer [1]. The flux of infrared radiation increased when a hot item was placed at mirror 1's focal point. Conversely, the flux of infrared radiation decreased when cold ice was placed at the mirror 1's focal point [1]. Confirming that:

- Infrared radiant heat obeys optical laws of propagation.
- Changes to infrared radiation is what was witnessed.
- Infrared radiation is associated with radiative heat transfer and temperature.

There is nothing revolutionary about the above points. However, accepting the statistical thermodynamic principle that all of a gas' thermal energy can be defined solely in terms of the gas molecule's kinematics, has just become troublesome. Obviously, both heat transfer and temperature change have a radiative component that is not properly described in statistical thermodynamics, which limits all of a system's energy to its kinematics.

We shall return to statistical thermodynamics, but before we do let us discuss two enshrined concepts based upon statistical paradigms.

2. Entropy

Entropy-founded arguments are too readily accepted. This is especially troublesome when one considers all its various definitions, each lacking full intelligibility. Entropy (S) signifies the disorder within a system. Its definitions include, "randomness of matter in incessant motion" [4], "the dispersal of a system's molecular energy" [5], " S is a measure of the quality of that energy; low entropy implies higher quality, while high entropy implies lower quality" [6].

Intermolecular collisions do result in the dispersal of gas. Is this an entropy increase, or, is it simply a dispersal of those gas molecules? Entropy remains a mathematical construct first described by Clausius and eventually emboldened in statistical mechanics. Yet it remains a contrivance [7],[8] without any real tangible philosophy.

Various discussions concerning entropy can be found. The Stanford Encyclopedia of Philosophy points out that "Even in phenomenological

thermodynamics, the definition of thermodynamic entropy is difficult ” (first written 2009). The encyclopedia also discusses that entropy is the arrow time, processes all move from order to disorder etc. This has led to claims of pessimism such as the inevitable “thermal death” of either our planet or the universe. Such asymmetry of time concepts become embedded in entropy and its change. Embedded in the thermodynamic parameter (S) that remains void of any verbal clarity.

Philosophical debate concerning entropy tends to focus upon the notion of disorder and its representation as the arrow of time [9]. This author agrees with Ben-Naim that the concept of randomness is an arbitrary concept, with the description of randomness laying in the eyes of the beholder [10],[11]. Hence, randomness as a concept is not particularly scientific.

A reason entropy (both Clausius’s and Boltzmann’s) has been embraced is it enables logarithmic functionality. This endowment is required throughout thermodynamics. This author has pointed out that logarithmic functions in thermodynamics generally concern rates. For two systems in thermal contact, the rate of heat transfer decreases as the temperatures of two system’s approach each other [7]. For two systems in physical contact, the rate that one system can perform work upon another, decreases as the two system’s pressures approach one another [7].

Furthermore, entropy-based equations and their differential shuffling lend themselves to free energies, as used in physical chemistry. Other, simpler explanations for free energies exist, please see [12]. Their relations to physical chemistry should be reconsidered by those involved.

Due to Shannon’s endeavors, entropy has transitioned from thermodynamics to information theory. When Shannon asked what to call his measure of information, Von Neumann famously answered “You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, no one really knows what entropy really is, so in a debate you will always have the advantage” [13]. The term entropy is now shared because they share a similar mathematical structure.

3. The Second Law

Pictet’s experiments could be claimed as proof that heat transfer is from hot to cold, with the accepted reasoning being the second law i.e., entropy always increases. This also lends itself to arguments such as all higher quantum microstates of a hotter body are already filled and cannot be raised by lower

energy photons from some lower energy body [14]. Such arguments ignore radiative heat transfer.

Second law challenges exist [15],[16]. Recent defiance considers the Meissner Effect in superconductivity [17]. These all dare the wisdom of Arthur Eddington's famous statement (1915): "The law that entropy always increases holds, I think, the supreme position among the laws of Nature" [18]. A bold statement in light of entropy's ambiguity.

Based on lost work ($W_{lost}=PdV$) being energy lost by an expanding system into the surrounding atmosphere, this author has challenged the second law at its most fundamental level [7]. Our atmosphere has mass, therefore any expanding system must lift that mass. This results in a potential energy increase of the overlying atmosphere [19]-[23]. Any work involved in lifting that mass is forever lost by that expanding system [7],[22].

The second law is also used to explain why perpetual motion cannot exist. Lost work, friction (both internal and external, e.g., drag) [7],[19]-[23], along with the inherent inefficiency of using expanding gases to power devices [19], is often all that is necessary to understand our reality. Lost work also helps one understand why thermodynamic processes are irreversible and differentiates the magnitudes for the latent heat of vaporization from condensation [7].

Although enshrined in our epistemology, any concept of the second law being theoretically validated is superficial. As Daniel Sheehan wrote, "the second law of thermodynamics is an empirical law. It has no fully satisfactory theoretical proof. This being the case, its absolute validity depends upon its continued experimental verification in all thermodynamic regimes." [24]. Have we been measuring inefficiencies due to lost work, friction and/or the inherent inefficiencies of powering devices with expanding gases, and incorrectly attributing it all to the second law's mathematical enormity?

The currently accepted philosophies concerning the second law parallel those discussed concerning entropy in Section 2.

4. Statistical Thermodynamics

Statistical mechanics relies upon probabilities. This has led to many philosophizing the true meaning of its probabilistic assertions. Due to its thermodynamic ramifications, one often loses sight of the possibility that probabilities may only be a grand method for approximation.

Statistical thermodynamics expresses all of a gas' energy in terms of its kinematics (gas' translational, rotational and vibrational energies). Yet, Pictet's experiment clearly demonstrates a significant temperature change resulting from radiative heat transfer.

The total energy associated with photons dispersed between gas molecules tends to be minute in comparison to the total energy of a gas' kinematics. Thus,

in terms of a gaseous system's total energy there is validity in approximating the system's total energy by its kinematics [25], i.e., statistic mechanics.

Photons travel at the speed of light, thus although having a minute total energy, the importance of radiative heat transfer cannot simply be ignored. This queries statistical mechanics as some universally applicable justification.

Statistical thermodynamics is founded upon unquestionable brilliant math envisioned by a combination of Boltzmann and Maxwell. Like Clausius, Boltzmann wanted to show that entropy always increases, while Maxwell was more concerned with atomic theory.

Accepted statistical mechanics is enshrined in assumptions [7],[26], e.g.:

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

Such assumptions enable mathematical simplification. The fact that gas molecules are not some dimensionless point, raises concern. Is statistical thermodynamics an abstraction or clarification of reality?

Consider that molecular collisions are inelastic. Inelastic collisions imply that other forms of energy reside in gaseous systems, e.g., radiative energy (photons). The mathematics required to describe a gaseous system where both gas molecules and photons scatter/interact with each other, would be horrendously complex (perhaps untenable).

From its outset, statistical thermodynamics has remained oblivious to both radiative heat and photons transferring energy into matter. Again, Pictet's experiment clearly shows the importance of radiative heat transfer.

Without its assumptions the simplification that statistical thermodynamics provides, fails. Why does statistical thermodynamics not falter on a more regular basis? Again, statistical thermodynamics provides a good approximation when describing a gaseous system's total energy. Its validity depends upon:

- How closely a gas approximates dimensionless points particles.
- The gas' kinematic energies must be significantly greater than that associated with surrounding photons (radiation).
- Gas-wall molecule collisions dominate the interactions in the system, e.g., sufficiently-dilute closed gaseous systems [20],[25].

It should be emphasized that:

- Theoretically: Elastic collisions enable one to express all of a gaseous system's energy solely (and forever) in terms of its gas molecule's kinematics.
- Mathematically: Elastic collisions enables a two-particle distribution function to be reduced to a product of one-particle distributions.

Up to this point the reader has been enlightened concerning why Pictet's experiments challenge the very foundations of accepted thermodynamics. Let us enhance our new understandings.

5. Inelastic, Illusion and Blackbody Radiation

We have discussed that statistical thermodynamics is valid as an approximation for sufficiently-dilute closed gaseous systems, e.g., most experimental systems. Those being systems where the "illusion of elastic collisions" exists. Our reality is that collisions (molecular and otherwise) tend to be inelastic. Conservation of energy tells us that inelastic molecular collisions (both inter and intra) result in the creation of photons, [7],[20],[25].

An ensemble of such inelastic molecular (and/or atomic) collisions will result in a spectrum of radiation. Often a blackbody spectrum, as defined by the Stefan-Boltzmann equation. The illusion exists because the spectrum's photons are either reflected or absorbed by the closed system's walls. The reflected photons simply return inwards back towards the gas molecules.

The energy of the absorbed photons adds to the wall's vibrational energy, thus increasing the wall's temperature. In thermal equilibrium, this energy is eventually returned back into the gas through gas-wall molecular collisions, or through the colliding wall molecules emitting blackbody radiation [7],[25].

This challenges accepted doctrine, which considers blackbody radiation as residing inside a Jean's cube. That being a box with a hole in it, through which observers can witness any blackbody radiation within. The implication being that blackbody radiation resides in closed systems surrounded by crystalline walls. Strangely, all sufficiently warm objects (enclosed or otherwise) emit blackbody radiation. This includes everything from a rat in a field to our glorious Sun. Complex explanations for this can be had. Are they necessary?

What is the mechanism by which collisions generate photons? At this point, one can only speculate. Perhaps, it has to do with distortions of electron clouds around molecules/atoms. Perhaps, it is something else. Whatever the final conclusion, one should accept that collisions tend to be inelastic.

6. Wave-particle duality and Thermal Photons

It is accepted that infrared photons behave as waves, hence interact with lopsided charge distributions in gases. This is the basis of infrared spectrometry where the absorption of discrete frequencies is well-known. Such discreteness enables infrared spectrometers to identify gases.

Photons possess a particle-wave duality. Acting as a particle, one only has to consider the photo-electric effect, photons pushing some solar sail through outer space, or even the pressure exerted by a photon gas [27]. It has been

pointed out that infrared photons acting as particles increase one's understanding of radiative heat transfer [7], [25].

As a particle, a photon's momentum/energy is absorbed by matter (both condensed and gaseous). These absorbed photons are "thermal photons", those being photons that become part of the absorbing matter's vibrational energy [7],[25]. This signifies an infinitesimal temperature increase within that matter.

Thermal photons universality helps one to understand matter's heat capacities. Specifically, the heat capacities of gases are more dependent upon the number of atoms in a specific gas molecule [28],[29] than that gas' charge distribution [7], [25]. Similar principles apply to the heat capacities of condensed matter. Accordingly, thermal photons better explain the empirically measured heat capacities of all matter, then lopsided charge distribution (photons acting as waves) ever could.

Blackbody radiation emitted by matter is countered by the absorption of thermal photons. This enables thermal equilibrium to exist both in terms of thermal radiation and kinematics of matter. Without this, the concept of thermal equilibrium approaches nonsensical, i.e., matter emitting but not absorbing radiation is too one-sided. One might argue that matter radiates energy while absorbing kinematic energy. Then ask them to imagine equilibrium of matter in a vacuum, radiating while not absorbing.

Therefore, in thermal equilibrium matter:

- Radiates radiation (often blackbody) [25].
- Absorbs thermal photons [25].
- Pass energy onto its surrounding matter via molecular collisions.
- Absorbs energy from its surrounding matter via molecular collisions.

Understandably the first two points concern radiative heat transfer, while the last two concern kinematic heat transfer (conduction, if one prefers). Convection also distributes heat by the flow of matter.

Consider kinematic heat transfer. Higher temperatures imply greater vibrational energies within matter (condensed or polyatomic gas). Therefore, hotter matter has a greater ability to pass kinematic energy onto objects in thermal contact, than colder matter. Again, there is no need for the over-complications associated with expressing the directional heat transfer in terms of entropy, or its change.

If the hotter matter is condensed while the colliding objects are gas molecules, then the condensed matter (e.g., system walls) will tend to impose their kinematics upon the gas molecules. This is similar to the mechanism described by this author in his new improved kinetic theory, where the larger structured wall molecules impose their kinematics upon the smaller gas molecules. In this author's new kinetic theory, the resultant equations are a superior fit to known empirical findings for all heat capacities of gases, when compared to the accepted equations of traditional kinetic theory [28],[29]. Note

that traditional kinetic theory is founded upon degrees of freedom, that now arguably becomes mathematical conjecture.

7. Infrared Spectrometry Blunder

In infrared spectrometry one evacuates the system, then measures its blackbody radiation. The gas in question is inserted and measurements are taken. The initially measured blackbody radiation is automatically subtracted, creating the final output spectrum. This innocuous act has led enabled confusion in the sciences.

Accept that blackbody radiation is created and absorbed by any polyatomic gases within a spectrometer. When in thermal equilibrium the gas' absorbed radiation energy equals the gas' radiated energy. The gas is also in equilibrium with the spectrometer's walls. This means that the system's walls and gas molecules are all absorbing and radiating a similar blackbody spectrum, i.e., related to the same temperature. Remember this spectrum is one associated with photons acting as particles.

Obviously, the blackbody spectrum that was subtracted thus creating the final output. This often being the subtraction of both the spectrometer's and the gas' radiative heat signatures. That being their interactions with photons behaving as particles. Accordingly, the spectrometer's final output only concerns photons acting as waves.

Another way of viewing this is that the sciences have incorrectly been treating the blackbody radiation as if it is not part of a gas' energetics. However, in thermal equilibrium it is the gas's thermal radiative signature [7], [25].

Is this a theoretical, or philosophical mistake? Whatever the answer. One understands that statistical thermodynamics mathematically places all a gases energy upon its kinematics. Thus, by the time one is taught how to use a spectrometer, he/she is not even considering the existence of thermal photons, yet their interactions with gases.

The infrared spectrometer blunder is not the subtraction of the blackbody spectrum. Rather, it is not fully comprehending what one is subtracting. Imagine that the blackbody radiation was not subtracted. Then all resulting spectrums of all gases would be dominated by their temperature defined blackbody spectrum. In which case their similarity would prevent one from determining what gases are present.

The real blunder is thinking that the resultant spectrum shows which gases absorb infrared photons and which gases do not. This will make more sense after reading Section 11 (Radiative Heat and Allmendinger).

8. Probabilities

If statistical thermodynamics is challenged, then what of its probability-based foundations? Interestingly in 1894 Planck wrote [30]: “It is completely unfounded, simply to assume that changes in Nature always proceed in the direction of lesser to greater probability.”

Although Planck inevitably altered his position. The debate as to what degree probabilities govern the universe may need a rethink. Furthermore, whether or not quantum mechanics is actually a complete theory actually is still debated into the 21st century. This includes EPR (Einstein, Podolsky and Rosen) arguments [31].

Interestingly this author has realized that the probability of a molecule evaporating in a boiling process should consider the likelihood that a molecule obtains sufficient energy from all of its neighboring molecules, at some instance. This is contrary to the accepted Boltzmann factor-based probabilities, which only considers the act of obtaining energy from a solitary neighbor. The energy exchanged (kT , k being Boltzmann constant) from a solitary neighbor being more than several times too small when compared to the energy required for vaporization.

This does not remove probabilities from the sciences but it only questions how one writes and theorizes them [32]. Again, a valid mathematical approximation or something else. Herein, [33] probabilities are briefly discussed by this author. A major issue being that when using functions like Boltzmann’s factor, one could use the wrong energy function and still be able to normalize it to match one’s empirical findings. Such is both the power and weakness of using logarithmic functions.

9. Quick Discussion

Again, by showing the true importance of radiative energy, Pictet’s experiment strikes at the very heart of accepted thermodynamics.

Consider the incorrect yet accepted notion that a vacuum has no temperature. A vacuum’s temperature is not readily definable in statistical mechanics, simply because there are no gas molecules/atoms to define. However, if one places a thermometer in a vacuum, one measures a temperature. If the blackbody radiation is isotropic, then mathematically a vacuum’s temperature can be clearly defined by taking the fourth root of the Stefan-Boltzmann’s equation. This applies to systems that are vast enough that a thermometer’s thermal energy does not alter one’s temperature measurement.

Note that issues do arise when measuring temperatures in systems dominated by anisotropic radiation, e.g., upper atmospheric measurements [34].

For emphasis, consider one standing on the moon. No lunar atmosphere means no kinematic energies, hence statistical thermodynamics physics does not apply. Yet, the dark side of the moon it is too cold, while on the bright side it is too hot, for man to survive without some thermal protection. All due to the anisotropic radiation emanating from the Sun (too hot).

Arguably, no gas near the moon's surface thus there is no temperature. Unfortunately, one is then riddled by, what did too hot, or too cold, actually mean?

10. Pictet and New Thermodynamics

All emitted blackbody spectrums have a temperature dependence as defined by the Stefan-Boltzmann equation. The hotter an object is, then the:

- Higher its radiated energy's peak frequency is (defined by Wein's law).
- Greater the total flux of emitted energy will be.

In Pictet's experiment; when a comparatively hot object is placed at mirror 1's focal point, it radiates a greater amount of thermal photon's total energy towards mirror 2. Mirror 2 focuses that energy and the thermometer heats up. This is all due to radiative heat transfer.

Accept that both the thermometer and the hot object radiate thermal energy (generally blackbody radiation). Then it is just a case of the radiative energy flux from the hot object being greater than the radiative heat flux from the cooler thermometer. The result being the heating of the thermometer and the cooling of the hot object.

Conversely, when a comparatively cold object is placed at mirror 1's focal point, it radiates less thermal radiation energy towards mirror 2's focal point, than the thermometer radiates from its location at mirror 2's focal point. This is not the cooling by "cold emanations from a flask of snow" [2] (or frigorific rays). It simply concerns a non-equilibrium situation where the thermometer absorbs less radiative energy than it emits.

The explanation for what is witnessed in Pictet's experiment is that simple. Hotter objects radiate a greater flux of thermal radiation energy than colder objects do. This applies to both the thermometer and the object.

One does not require the over-complications elicited by statistical mechanics, i.e., entropy or the second law. It is temperature alone (not entropy) that determines the net direction that heat flows when considering heat transfer (both radiative and kinematic).

In thermal equilibrium the total thermal energy (heat) into a system must equal the total thermal energy out of that system. The total thermal energy (in or out) being some combination of radiative and kinematic heat transfer. Once more, using either entropy or the second law to explain what is witnessed will

lead to unnecessary over-complications. Note that the absorbed and radiated spectrums may not always be exactly the same but the total energy in must equal the total energy out.

If heat transfer only involved kinematic heat transfer (as is traditionally insinuated), then the temperature changes in Pictet's experiments would be immeasurable. The total energy associated with thermal photons remains minute in comparison to the kinematic energies of the surrounding gas. However, as previously stated, it is the immensity of a photon's speed that renders it relevant when contemplating heat transfer.

It is inarguable that photons reflecting off of the mirrors represent photons acting as waves. Furthermore, the fact that the mirror did not heat up (hot object case) or cool down (cold object case) means that for the case of reflection, photon's acting as waves did not result in the transfer of thermal energy. Hence, photon's acting strictly as waves does not explain the witnessed universality in radiative heat transfer.

Pictet's experiment should have raised red flags to those mathematical geniuses writing science. It seems strange that this has gone unrealized over the centuries.

11. Radiative Heat and Allmendinger

The exact mechanism of photon absorption or its radiation by matter, is presently not fully understood. However, some experiments do provide insights. Of particular interest are Thomas Allmendinger's experiments [35], [36], which clearly show the absorption of thermal photons by gases [25].

Seemingly, such absorption is related to the gas molecule's size, specifically its scattering cross-section [25]. Whatever the final understanding, photons acting particles provide certain universality. Note that a photon's size probably has a frequency dependence, something that has yet to be determined.

Allmendinger shone directional lights (with a strong infrared component) into various gas filled tubes. The tested gases include carbon dioxide (CO₂), air, oxygen (O₂), nitrogen (N₂) as well as some noble gases namely helium (He), neon (Ne), and argon (Ar). All tested gases witnessed a temperature increase.

Allmendinger's findings challenge traditionally accepted notions (philosophy or theory?) that only gases with lopsided charge distributions absorb infrared radiation. Specifically, O₂, N₂ and all the noble gases are supposedly transparent to infrared radiation. This notion of transparency is based upon infrared spectrometry, which only considers photons as waves. Note that the term "opaque" was incorrectly used by this author instead of "transparent" [25].

Allmendinger also determined that different gases had different experimental limiting temperatures. This is most likely due to the experimental

apparatus, i.e., if the tube was infinite in length, or the infrared light's intensity was infinite in intensity, there would be no limiting temperature. Given similar intensity and duration, the differences in limiting temperatures would be due to differences in the various gas's infrared absorption cross-sections [25].

A traditionalist might argue that it was the tube's walls that heated up rather than the gas. Such an argument fails to provide clarity concerning the mechanism by which the infrared photons heat the walls. "Moreover, if the infrared radiation only heated the tube's walls, then based upon accepted traditional kinetic theory, the expectation would be that the temperature increase would be independent of the gas inside of the tube" [25].

Based upon Allmendinger's experiments (namely his Fig. 25 and Fig. 26 [34]) this author has concluded that it is the gaseous atom's/molecule's size that determines both the various gas' rates of heating and their limiting temperatures. Specifically, the larger the gaseous atom's/molecule's size is, then the faster that gas heated, and the higher its limiting temperature was. In other words, larger atoms/molecules have greater scattering cross-sections, thus more photons impact them, thus more momentum/energy is passed onto that gas [25].

This challenges the philosophy/theory behind traditionally accepted radiative heating (based upon photons acting as waves). The implication being that thermal photon's momentum/energy is passed onto the atoms within the gas molecules. Certainly, this fits better with our understanding of heat as it fits with the witnessed universality of heat and its transfer.

12. Greenhouse Gas Experiment

Allmendinger's experiments challenge the notion of the greenhouse effect, in climate change. Other experiments show gases absorbing infrared photons. Google "greenhouse gas experiment," and one finds researchers shining infrared lights upon vessels filled with either CO₂ or air. They claim that so-called greenhouse gases [carbon dioxide (CO₂), water vapor (H₂O), methane (CH₄)] absorb infrared photons while other gases [oxygen (O₂), nitrogen (N₂) and noble gases] do not. This claim is founded upon infrared spectrometry, i.e., previously discussed photons acting as waves with the greenhouse gas molecule's lopsided charge distribution.

As emboldened as they tend to be, scientists and philosophers of climate change [36], tend to be oblivious to certain facts. In greenhouse gas experiments, both the air and CO₂ heat up, with the heating of the CO₂ always being at a slightly higher rate with a greater limiting temperature.

Since air is 99% O₂ and N₂, the heating of air confirms Allmendinger's findings. Specifically, both N₂ and O₂ are claimed to be transparent to infrared radiation. This means that the minute concentration of CO₂ in air (0.04%) is

supposedly enough to enable air to heat at a rate that is approximately 65% that of pure CO₂ [25]. Such an widely embraced explanation is ridiculous.

Consider that air is primarily diatomic (N₂ and O₂) while carbon dioxide (CO₂) is triatomic. Could one not infer that the 65% rate may be indicative of the fact that O₂ and N₂ may roughly be 2/3 the size of CO₂? This rudimentary analysis indicates that their ratio of scattering cross-sections could better explain what is witnessed.

Note that climate change still is anthropogenic. It is just that man's total energy use and not so-called green-house gases (philosophy of greenhouse gases [37]), becomes the root cause [38], [39]. It is inarguable that man's energy use is only a small fraction of our Sun's energy that reaches our outer atmosphere. However, with new insights this author has shown that man's energy use does explain what is known concerning Earth's climate change [39]. This alters our understanding of climate change, bringing it into the context of new thermodynamics understanding as described herein by this author.

Accepting that man's energy use is a root cause of climate change, one must then question the wisdom of using recently proclaimed fusion nuclear energy. The reckless use of such a relatively clean and possibly cheap source of energy may lend itself to a disastrous reality.

13. Seim and Olsen

Seim and Olsen [40] hung two folded pieces of aluminum foil, one untouched and the other painted black, in a box. The box was then enclosed with clear plastic. The box was heated by a 500 W tungsten-halogen lamp emitting radiative heat [25]. The black foil's temperature increased at a faster rate than the untouched foil.

The black foil acted as a blackbody absorbing most thermal photons. Thus, explaining the fact that the black foil heated faster when exposed to infrared radiation. Conversely, the shiny aluminum foil reflects the majority of incident thermal radiation, thus heated much slower.

Just as in Pictet's experiment, the importance of thermal photons is again witnessed. Again, all this is not readily explained using traditionally accepted thermodynamics, which places all the energy upon the gas molecule's kinematics. Our philosophies (or theories) concerning heat transfer has to change, as well as thermodynamics in general.

The concept of wave-particle duality is founded in the differences in math that is used to describe a wave versus that used to describe a particle. A philosophical question being: Is this a weakness in our math, i.e., our math cannot properly describe both phenomena at the same time?

Note that both Allmendinger's and Seim & Olsen's experiments were devised to show that climate change is not a result of so-called greenhouse gas.

They all conclude that climate change is not anthropogenic, a position that this author disagrees with (as previously discussed).

14. Unnoticed Radiative Heat

Why has radiative heat's importance not been previously noticed in closed systems? Imagine blackbody radiation emanating from the walls of a closed experimental system. The radiation will be isotropic. Therefore, on average the energy/momentum from thermal photons will strike a gaseous molecule (or atom) equally from all directions, over the duration that it takes a gas molecule (or atom) to travel across the system. Therefore, on average there will be no net energy passed onto the gas molecule (or atom) between its gas-wall molecule collisions [25]. Therefore, the translational (and probably rotational) energy of the gas atoms/molecules will not be affected.

However, the effects on molecular vibrational energy may be quite different. Realizing that molecules vibrate in and around 10^{13} Hz, means that thermal photons can be absorbed. This assumes that each atom within a molecule is not struck equally from all directions in the duration of its vibration [25].

One might ponder, what happens to the energy of thermal photons that collide with atoms (or molecules) at the same instant from opposite directions? A plausible interesting debate.

15. Conclusions

One may choose to consider what has been discussed as issues with our epistemology, philosophies of sciences, or scientific theory. Nothing was proven, however issues with traditional theory were discussed. Lucidity was provided by improved understanding. Ultimately, the door to questioning our indoctrination has been torn wide open.

Pictet's experiment influenced the 18th-19th century debate as to whether or not heat involves particles or waves. Modern thermodynamics focuses upon statistical mechanics. Thus, the kinematics of matter has become the foundation for explaining both a system's total energy, and processes of heat transfer. Radiative heat transfer is now treated as some addendum.

Lucidity of Pictet's experiment is only obtained by realizing the significance of radiative heat transfer. Although often obscure, radiative heat transfer's true importance lay in a photon's speed rather than the energy associated with all the photons dispersed amongst a system's gas molecules. Implications to our philosophies in sciences become profound. This includes how one envisions

climate change. Note that other experiments also confirm radiative heat transfer's importance, e.g., Allmendinger's, Seim and Olsen's.

Misconceptions are founded upon the assumptions that enabled mathematical simplification by great minds of our forefathers (including Maxwell and Boltzmann). These statistical thermodynamic assumptions have rendered mathematical simplification while manifesting theoretical obscurity.

More realistic understandings are needed. Such as:

- Molecular collisions are inelastic.
- Molecules are not point particles.
- Radiative heat exists and its transfer cannot remain ignored.

Although they improve one's knowledge, such understandings will lend themselves to extremely complex mathematics (possibly untenable).

The existence of thermal photons provides clarity. Thermal equilibrium involves the absorption and emission of thermal photons. An ensemble of inelastic molecular (and/or atomic) collisions will result in a spectrum, e.g., a blackbody spectrum.

Questions arise concerning over-complications asserted in thermodynamics. Entropy remains a parameter, based upon mathematical brilliance without any viable foundation. Like entropy, the relevance of the mathematically described second law comes into question. For emphasis, a math that is founded upon the placement of all a system's energy and heat transfer, upon the kinematics of matter. A math that is indifferent to the radiative energy placed upon us, including that of our Sun.

The association of entropy change with the direction of heat transfer is misleading. Clarity is obtained by realizing that it is temperature alone that determines the direction of heat transfer, i.e., the net flow of thermal energy (heat) is always from hot to cold.

Thermal energy transfer becomes a combination of radiative and kinematic heat transfers. Radiative heat transfer is dominated by photon's acting as particles. This alleviates issues witnessed throughout thermodynamics. Ultimately, Pictet's experiments demonstrate the wave-particle duality of thermal photons. Profound differences exist between photons acting as waves (e.g., reflections off of mirror) vs those acting as particles. As waves, photons do not necessarily result in heat transfer. Heat transfer does involve thermal photons, those being photons acting as particles.

Taking math and forever trying to squeeze theory out of it can, be problematic. Too often one forgets to first observe, and then and only then, to

formulate one's theories. It is only at that point that one should attempt to elicit their observation's best descriptor.

This all brings forth the need for the sciences to step back and philosophize. What have we done? Over-complication is something we humans are good at. Admitting that we do, not so much.

My Apology and Our Dignity

I must apologize for all the self-referencing. However, when one rewrites thermodynamics, one must explain the published path of logic.

A combination of indoctrination, and human indignity too often prevents those who should know better from knowing. Tolstoy said it best "I know that most men, including those at ease with problems of the greatest complexity, can seldom accept even the simplest and most obvious truth, if it be such as would oblige them to admit the falsity of conclusions which they have delighted in explaining to colleagues, which they have proudly taught to others, and which they have woven, thread by thread, into the fabric of their lives" [41].

It raises the question of, just where does this paper belong?

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