

# **New Thermodynamics vs Problematic Traditional**

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## ***Abstract***

Thermodynamics is written in both classical and statistical formats. It will be shown that misunderstanding has allowed the science to become overly complicated. The concept of lost work in both expanding and compressed systems will be examined classically, showing why processes are irreversible here on Earth due to expanding system's interactions with the surrounding atmosphere. This new classical explanation allows for a simplification of the science, which should lead to the questioning and possible rewrite of statistical thermodynamics.

## ***Introduction***

To most scientists, thermodynamics is an inarguably mature science. To some this is not the case<sup>1, 2, 3</sup>, although different authors have proposed vastly different considerations as to why this is so, with some proposing rather complex theories<sup>1</sup>. This author realized something was wrong with the traditional construct of work when writing his paper concerning nucleation that was the first to correctly explain the energy required for bubble nucleation<sup>4</sup>, wherein work/energy for nucleation was considered in terms of<sup>4</sup>:

$$W = dE + d(PV) \quad (1)$$

With  $dE$  includes the energy required to form a tensile layer while  $P$  and  $V$  respectively represent pressure and volume of a given system of nucleating molecules.

Although similar, eqn (1) challenged the conscript of bubble nucleation which throughout the 20<sup>th</sup> century was illogically believed to take the form<sup>4,5,6,7,8</sup>:

$$W = dE + VdP \quad (2)$$

Which puzzled this author because bubble nucleation involved both a volume and pressure increase, yet eqn (2) limits bubble nucleation to an isometric pressure increase. This all led to the questioning the construct of thermodynamics, wherein this author realized that work goes through a system's walls rather than into a system's walls, as was traditionally taught<sup>9</sup>. This also led to the understanding that a system can do work onto either a neighbouring system, and/or its surroundings, but not onto a vacuum<sup>10</sup>. Which led to the reasoning that Enrico Fermi's statement that the work associated with an expanding universe "goes into the hands of god"<sup>10</sup>, was a statement based upon misconceptions<sup>9</sup>, although it being mathematically plausible.

The accepted writing of energy change and work associated with an expanding system, in terms of isothermal entropy change is<sup>11</sup>:

$$TdS = dE + PdV \quad (3)$$

Where  $T$  is temperature,  $S$  is entropy,  $E$  is internal energy. Eqn (3) is readily rewritten in terms of the first law by considering that the energy input ( $dQ$ ) into an expanding system signifies isothermal entropy change, i.e.<sup>11,12</sup>:

$$dQ = dE + PdV \quad (4)$$

There are inherent problems with both eqn (3) and (4). As written,  $PdV$  lacks clarity, and, as such, many may think that the work is done within the expanding systems and/or in its walls.

Realizing that work has to be done through the walls, this author realized that the work as defined by  $PdV$ , is done onto the surrounding atmosphere<sup>13</sup> by the expanding system. Moreover such work is irreversible, hence, is “lost work”.

Interestingly, if one searches, one may find websites that now realize that work ( $PdV$ ) is done onto the surrounding atmosphere but do not understand that it is lost work. Accepting that the atmosphere is a massive heat sink/bath then as such, measureable change to its parameters does not occur when normal real processes give or extract energy from it. I.e., the atmosphere tends to be isobaric, isothermal and/or isometric, from a perspective of measurement. Clearly, if an abundance of such real processes occurs, then the parameter change will become measureable. Another way of viewing this is that real processes affect the atmosphere in a similar manner that infinitesimal processes affect real systems.

So although the real expanding system does work onto the atmosphere, the atmosphere remains both isobaric and isothermal. Accordingly, the atmosphere cannot return the work done onto it by real expanding systems. Yet another way of viewing this: A gaseous system can only do work onto its neighbouring system (or surroundings) if that system is at a higher pressure than its neighbouring system. Similarly: A system can only pass thermal energy onto its neighbouring system (or surroundings) if that system is at a higher temperature than its neighbouring system.

Since, after expansion, the system is at the same pressure and temperature as the atmosphere, then the atmosphere cannot return either work or energy back into the expanded system. Thus  $PdV$  is lost work (i.e., irreversible work).

There is yet another issue with associating  $PdV$  in equations (3) and/or (4) with the expanding system. Since the internal energy change ( $dE$ ) is a summation of the microscopic energies of the expanding system, it represents the change of the system's total energy! Therefore the work as defined by  $PdV$  can only be external to that system. Seemingly defining  $dE$  in terms of summation of microscopic energies has allowed for confusion, although it is just a fancy way of saying total energy!

In order to avoid confusion, eqn (4) should be rewritten as<sup>13</sup>:

$$dQ_{sys} = dE_{sys} + (PdV)_{atm} = dE_{sys} + P_{atm}dV_{sys} \quad (5)$$

Eqn (5) clarifies that the work done onto the atmosphere is an increase to its potential energy, that being an isobaric upward displacement of its mass. However, this is not exactly the case, because in reality an expanding system may cause a regional pressure increase within the atmosphere, and this may then result in an isobaric expansion of the atmosphere - i.e.,  $PdV$  (Note: Here the expanding system is now considered as being part of the atmosphere as a system). Or the regional pressure increase may result in heat associated with viscous dissipation<sup>14</sup>, due to the inelastic intermolecular collisions!

Eqn (5) also clarifies that the expanding system is a subsystem of some massive system that being Earth's atmosphere. And as a massive system the Earth's atmosphere behaves as a heat sink, thus it does not experience a measurable temperature and/or pressure increase due to the expanding system. Of course if a massive number of such expanding processes did occur then the atmosphere's energy increase would be measureable!

Inelastic intermolecular collisions mean that momentum is physically conserved but not kinetic energy. Thus heat (thermal

photons) will also be radiated, thus maintaining conservation of energy. Of course, this goes against accepted kinetic theory wherein all collisions are considered to be elastic. Interestingly, this author has shown that by considering the wall molecules to be massive energy pumps that pump their energetics onto colliding gas molecules then a new kinetic theory can be written<sup>15,16</sup>. A theory that no longer relies upon equipartition and most importantly, it better explains empirical findings, without the need of all those exceptions that are currently employed, so that traditional theory somewhat matches known empirical findings.

Moreover, we now can understand that intermolecular collisions are inelastic. Not only does this improve our understanding of kinetic theory, it also allows us to now understand why pressure-temperature relationships exist<sup>14,15,16</sup>, i.e., a pressure increase is due to and/or:

- 1) An increase to the number of intermolecular collisions
- 2) An increases to the kinetic energy per molecule

Both of the above 1) and 2) will lend itself to the creation of more heat due to inelastic intermolecular collisions.

The above also fits with our understanding that electron collisions are inelastic<sup>17</sup>.

It should also be stated that statistical ensembles, such as those for entropy, are wrongly based upon the collisions being elastic, hence, will require new considerations.

It is also of interest that one the many 20<sup>th</sup> century definitions for entropy is the “randomness of molecules in incessant

motion”<sup>18</sup>. Ben-Naim<sup>19</sup> rightfully points out that randomness is in the eye of the beholder, hence, is not particularly scientific!

Furthermore, associating randomness with energy changes and/or work done to the gaseous molecules within the expanding system, may also lend itself to the incorrect assumption that all variables/parameters in eqn (4) has to do with those within the expanding system. This now raises the question: What exactly does the isothermal entropy change in eqn (3) concern? Sadly this remains impossible to answer until the definition of entropy is clarified.

Isothermal entropy change is accepted to never decrease - i.e., the basis of the second law of thermodynamics for isolated systems. This brings up the question of “*Are any systems here on Earth truly isolated?*” Reconsider any expanding system doing work onto the surrounding atmosphere. Certainly such systems are NOT isolated<sup>13,14</sup> because they do work onto their surrounding atmosphere! Accordingly, the second law does not apply to expanding systems here on the Earth’s surface<sup>13,14</sup>.

Since many useful systems depend upon expansion to power man and/or machine, then they are not isolated hence the second law does not apply to them. This is definitely the case for Carnot cycle and the steam engine, both of which are 19<sup>th</sup> century inventions for which the second law was devised.

In his 1917 “*Treatise on Thermodynamics*”<sup>20</sup> Planck acknowledges that there are two ways to formulate thermodynamics. A): “*We may take for granted the correctness of the mechanical view of nature, and assume that all changes in nature can be reduced to motions of materials points between which there act forces which have a potential. Then the principle of energy is simply the well-known mechanical*

*theorem of kinetic theory, generalized to include all natural processes.” Or B): As was done; “leave open the question concerning the possibility of reducing all natural processes to those of motion, and start from the fact which has been tested by centuries of human experience and repeatedly verified” ...” no way possible to have perpetual motion”.*

Thermodynamics followed B) crafting the second law into the supreme postulate! In an interesting email exchange with Jeremy Dunning-Davis, Jeremy rightfully pointed out that the basic conscript for the second law did not necessitate the statistical form it now has. This implies that it was the simple understanding, as Planck states in B).

It must now be questioned whether or not our forefathers would had taken the stance they did if it was realized that work as defined in eqn (4) is irreversible, i.e., lost work that provides a description, which suits both of Planck’s A) and B). Accordingly, this paper will investigate the application of the first law, i.e., equation (4), to both expansion and compression of ideal gases, incorporating our understanding of lost work.

For those who believe that irreversibility can only be explained by statistical arguments, I will assert the following. I am sure that statistical thermodynamics can be rewritten by the willing. And we are better served by formulating constructive logic and then finding a mathematical construct that fits that logic, rather than the other way around as the science is currently written/taught.

Before continuing, free energy must be discussed. In deriving his free energy, Gibbs started off with eqn (3), and then subtracts the following total differential:

$$d(TS) = dE + d(PV) \quad (6)$$

Logic dictates that we should start off with a total differential, from which we determine its partial derivatives. The only reason the absurdity of subtracting a total differential from a partial differential to obtain the other parts<sup>3</sup> was acceptable is it gave eqn (3) [the isothermal entropy change relation] a sense of being supreme, which obviously it is not.

Furthermore, Gibbs famous paper<sup>6</sup> “On the equilibrium of heterogeneous substances” was published in two forms: A long 350 page paper followed by its short 50 page treatise. There is nothing wrong with this, however, they are both published in the same book under the same title. And this is confusing as well as, not particularly scientific<sup>4</sup>. When deriving his free energies both papers give a similar result, however, the same cannot be said of nucleation theory<sup>4</sup>! This has led this author to wonder how much other confusion exists due to this method of publication.

Getting to the heart of the problem, one must ponder: If  $dE$  is the change to the system's energy then what is  $d(PV)$ . In Gibbs derivation, he treats both  $dE$  and  $d(PV)$  as if they are part of the same system, as seemingly described by eqn (6). Logic dictates that if  $PdV$  in eqn (4) is work done external to the expanding system, then  $d(PV)$  is similarly external, i.e., part of the surroundings. This further begs the question: What does eqn (6) mean?

There are other plausible explanations for free energies as are given in my book<sup>14</sup>. Free energies amongst other concepts may be a case of getting things somewhat right for the wrong reasons. Anyhow in order to keep this paper from becoming a



book, I will leave the free energies, solubility as well as numerous other considerations to future discussions.

***A: Expanding Systems: Insulated:  $dQ > 0$***

Consider a hermetically sealed expanding piston-cylinder filled with an ideal gas, as in Fig 1. As the vertically oriented piston-cylinder expands by a distance/height  $dh$ , its volume increases by  $dV$  and the work done is  $PdV$ . By understanding that the work is done onto the surrounding atmosphere, one avoids the confusion that students often have of:  $PdV = -VdP$ , inside of the piston-cylinder, i.e., why choose an isobaric volume increase over an isometric pressure decrease?

Since work done is through the expanding system's walls, then herein the expanding wall is the moving piston which does work into the surrounding atmosphere! And this is lost work, i.e., irreversible work!

In the above, we never discussed what drove the expansion. Let us say that the expansion was driven by heating as shown in Fig 2, hence, Eqn (4) applies. As we heat the insulated piston-cylinder then its temperature increases thus increasing its internal energy ( $dE$ ) resulting in a pressure increase, which drives the piston outward from within the cylinder, thus doing work onto the surrounding atmosphere.

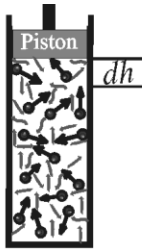
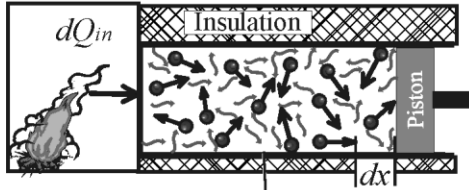


Fig.1

Shows an expanding piston-cylinder filled with an ideal gas and thermal radiation.



System 1: Piston-cylinder apparatus

Fig. 2 Shows a heated piston-cylinder whose temperature increase drives an isobaric volume increase. Hence, irreversible work is done onto the surrounding atmosphere.

Of importance: If the piston-cylinder is considered as a zero frictionless device, then the pressure in the piston-cylinder needs only be infinitesimally greater than that of the atmosphere, hence:

$$(PdV)_{pistoncylinder} \approx (PdV)_{atm} \quad (7)$$

In terms of the ideal gas's isometric heat capacity ( $C_v$ ), eqn (4) can be rewritten as:

$$dQ_{in} = (C_v dT)_{sys} + (PdV)_{atm} \quad (8)$$

And in terms of its isobaric heat capacity ( $C_p$ ) eqn (8) can be rewritten as:

$$dQ_{in} = (C_p dT)_{sys} \quad (9)$$

Obviously, a gas's isometric heat capacity equals its isobaric heat capacity plus the work done onto the atmosphere ( $PdV$ ) by the expanding isobaric system. Thus giving a simple explanation for the well-known empirical relation:

$$(C_p dT)_{sys} = (C_v dT)_{sys} + (PdV)_{atm} \quad (10)$$

Eqn (10) previous explanation was based upon more complex entropy change arguments.

Note: In Fig 2,  $dx$  was used instead of  $dh$ . The reality is that it does not matter what direction the volume expands, because the Earth's atmosphere when displaced can only move in one direction that being upwards.

**B: Expanding Systems: Insulated:  $dQ=0$**

Next consider that fifteen pebbles act as a weight on top of the piston-cylinder, as is shown in Fig 3. Five pebbles are then removed so the system isothermally expands. Again eqn (4) applies, but now  $dQ=0$ . Accordingly, the work comes from within the piston-cylinder. If the piston-cylinder is fully insulated, then, as it expands, it cools down in which case the work comes from the ideal gas's internal energy. Therefore, one might write for the expanding system:

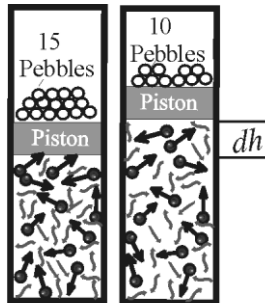


Fig 3 Shows a piston-cylinder expanding due to the removal of some weight (5 pebbles)

$$(dE)_{sys} = -(PdV)_{atm} = -P_{atm}dV_{sys} \quad (11)$$

The gaseous system is doing the work hence its temperature must decrease as it does work onto the surrounding atmosphere!

**C: Expanding Systems: Not-Insulated:  $dQ=0$**

Consider a quasi-static expanding piston-cylinder that is not insulated. Since there is enough time for thermal energy to pass through the piston-cylinder walls into the expanding gas, then the process can be isothermal. Herein, thermal energy from the

surrounding atmosphere is “freely given” into the expanding system. This freely given energy consists of both an increase to the gas molecule’s kinetic energy (translational & rotational) plus its vibrational energy, as well as any increase in thermal radiation in the freespace between gas molecules, which is generally minute when compared to the other energies. Note: The realization that the gas’s kinetic energy is the summation of it’s translational plus rotational energy. This is a key element in making this author’s new kinetic theory<sup>15,16</sup> a better fit to empirical findings.

Conversely, if the same not-insulated piston-cylinder rapidly expands, it will cool down. And once fully expanded, the piston-cylinder’s contents will slowly warm up as freely given thermal energy passes through its walls from the atmosphere back into the cooled expanded ideal gas.

This all becomes interesting because it gives us new insights into rapid processes, which are often deemed non-equilibrium processes. It also helps us understand why quasi-static processes are considered as processes that are in thermal equilibrium!

#### ***D: Mathematical Confusion***

The traditional way to express the work done for the case of the expanding non-insulated piston-cylinder is to write:

$$W = -NkT \ln(V_f / V_i) \quad (12)$$

where the subscripts “*f*” and “*i*” represent the expanding system’s final and initial state. Eqn (12) is based upon the ideal gas law (setting  $P=NkT/V$ ) and integrating work in terms of the expanding system’s parameters.

Eqn (12) is often considered as being reversible work. This is illogical since the expanding system does irreversible work (A.K.A. lost work) onto the surrounding atmosphere! Of interest: The magnitude of work as defined by eqn (12) does equal  $(PdV)_{atm}$  for infinitesimal work but not for real processes!

Let us now investigate eqn (12)'s limitations. Firstly: Eqn (12) assumes that the expansion was isothermal, hence eqn (12) is limited to infinitesimal isothermal work i.e. quasi-static expansion by non-insulated systems. Secondly: Eqn (12) is wrongly written in term of the expanding system's parameters rather than the work that is done onto the surrounding atmosphere, i.e.  $(PdV)_{atm}$ .

In order to better understand the above second point, again consider the heating of the piston-cylinder, as was shown in Fig 2. The heat in  $(dQ_{in})$  drives the expansion.  $dE_{sys}$  is the change to the expanding system's total energy, while  $(PdV)_{atm}$  is the irreversible lost work. For this process the first law based relation becomes is correctly written as:

$$dQ_{in} = dE_{sys} + (PdV)_{atm} = dE_{sys} + P_{atm}dV_{sys} \quad (13)$$

Now consider wrongly writing this in terms of eqn (12) i.e. one might wrongly write the following:

$$dQ_{in} = dE_{sys} + [(NkT) \ln(V_f / V_i)]_{sys} \quad (14)$$

The only way that eqn (14) could be contemplated as being correct is if  $dE_{sys}$  represented all the system's energy changes except for those associated with the system's mechanical parameters i.e. its pressure and/or volume change! And then it

would still be lacking because it does not include the lost work!  
Including the lost work done one would need to now write:

$$dQ_{in} = dE_{sys} + [(NkT) \ln(V_f / V_i)]_{sys} + P_{atm} dV_{sys} \quad (15)$$

Of course if  $dE_{sys}$  remains the changes to the expanding system's total energy i.e. summation of all its microscopic energy changes, then the only correct way to write the equation remains eqn (13)!!!

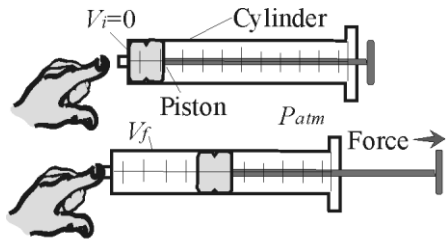
### ***E: Work in Creating a Vacuum***

Consider the expansion of a vacuum by an external force. For example, take a syringe and place the plunger all the way to the bottom, then hermetically seal the syringe's opening with your finger as illustrated in Fig 4. Next apply a volume expanding force. Since the internal pressure is not a function of the system's volume, then the required work is:

$$W = P_{atm} dV = (PdV)_{atm} \quad (16)$$

### ***F: Negative Work***

“Negative work” conceptually feels counterintuitive; it can be mathematically expressed by placing a negative sign in front of the work term. The volume inside of the expanded piston-cylinder in Fig 4 represents negative work done onto that volume of space.



**Fig. 4** Shows a hermetically sealed piston-cylinder being expanded by an external force.

Reconsider the work done in creating a vacuum, but instead of thinking in terms of the work done onto the atmosphere, think in terms of the newly created volume of vacuum. Ignoring any blackbody/thermal radiation that enters through the cylinder's walls then the final kinematic energy state within that created volume is zero. Accordingly, "negative work" was done ( $W_{neg}$ ) onto the vacuum volume within the piston-cylinder:

$$W_{neg} = -W_{atm} \quad (17)$$

Ask: Has the total energy of the atmosphere changed? No, it has not! Potential energy ( $PdV$ ) was added to the atmosphere while negative work was done onto the expanded volume within the piston-cylinder, which is really a subsystem of the atmosphere. In other words, the total energy associated with planet Earth and its surrounding atmosphere was not changed, even though the atmosphere's mass was upwardly displaced. Thus the addition of a *volume of nothingness* (VON) did not alter the atmosphere's total energy!

Negative work tends to create unstable volumes. In the case of the expanded syringe, once the piston is released, then the piston will come crashing down into the cylinder eradicating the recently created volume within the syringe. The mechanical understanding: This is due to the pressure inside of the syringe being less than the atmosphere's.

This raises the question what happens to the energy used to form the vacuum? From a mechanical perspective, you could attach a string to the piston and do work when the plunger is released. From a thermodynamic perspective, things are slightly different. As the piston crashes into the cylinder, the gas molecules associated with the atmosphere potential increase

comes crashing downwards. I.e. some of the atmosphere's potential energy is transformed into kinetic energy, which is similar to heating the atmosphere. And this heating would be infinitesimally small when compared to the atmosphere's total thermal energy, i.e., the atmosphere is a heat sink.

Now consider that the piston-cylinder contained an ideal gas before expansion, then the work done onto the atmosphere would still be  $(PdV)_{\text{atm}}$ . However, in terms of the expanded system's parameters one could write:

$$W_{\text{neg}} = -(NkT)\ln(P_i/P_f) = -(NkT)\ln(V_f/V_i) \quad (18)$$

Eqn (18) is limited in the same ways that eqn (12) was.

### ***G: What about Entropy Change?***

Consider the way chemists like to write entropy change for isothermal reactions.

$$dS = k \ln(V_f/V_i) \quad (19)$$

One must now accept that eqn (19) is limited in the very same way both eqn (18) and eqn (12) are! Most importantly one can not use eqn (19) in any first law based equation, yet it is done throughout thermodynamics!! This needs to stop!

### ***H: Logarithmic Functionality***

What happens if we consider the rate of expansion? Consider expansion driven by an input of thermal energy. Then the rate of work depends upon the pressure difference between the expanding gas and surrounding atmosphere! In terms of some constant ( $A$ ), the change in work rate (power) would be of the form:



$$dW / dt = -A \ln(P_{system} / P_{atm}) \quad (20)$$

Do we really need entropy to explain such empirically known natural logarithmic functionality in thermodynamics?

Consider: For any two systems in thermal contact, changes in heat transfer will depend upon variables such as surface area of contact, mass, heat capacity, and thermal conductivity. And it will be a logarithmic function of temperature. As the system's temperature difference decreases, the rate of heat transfer decreases logarithmically. In other words, the rate of heat transfer should be a decreasing logarithmic function of time in terms of some constant ( $B$ ), i.e.:

$$dE / dt = -B \ln(T_{hot} / T_{cold}) \quad (21)$$

If one really thinks about it, correlations can be witnessed with other considerations of entropy change such as Atkins<sup>21</sup> claim that entropy signifies the quality of a system's energy. Even so, perhaps temperature better defines this quality because as an isolated energy source dissipates, its temperature decreases. Similar arguments apply to Lambert's consideration of entropy being "the dispersal of a system's molecular energy"<sup>23</sup>.

What about an exothermic reaction? The rate of heat transfer from the reaction into its surroundings will decline logarithmically as the reaction's energy disperses, i.e., cools. Again, this questions whether or not entropy is really needed!

### ***I: Compression of a NOT insulated Piston-Cylinder***

Consider that an ideal gas within a regular piston-cylinder is compressed. If the compression is quasi-static, then the compression can be an isothermal process, i.e. if sufficient time is given for any heat created by viscous dissipation to radiate

out through the walls of the piston-cylinder i.e. infinitesimal compression of a gas in a non-insulated system.

As the ideal gas's volume decreases, its pressure increases. When done isothermally, then, in terms of the gas within the piston cylinder, the work required for compression is:

$$W_{\text{compression}} = (NkT) \ln(P_f / P_i) = (NkT) \ln(V_i / V_f) \quad (22)$$

As the plunger moves down into the piston-cylinder, potential energy within the atmosphere again changes into kinetic energy, i.e., infinitesimal heating. Of course, if the plunger is released, it can do work and if this work is only done onto the atmosphere  $[(PdV)_{\text{atm}}]$ , then it's magnitude equals the kinetic energy increase experienced by the atmosphere during compression. Ultimately, the atmosphere's total energy remained constant during compression although potential energy transformed into kinetic energy.

Of interest: For the case of isothermal compression, an ideal gas's total energy remains constant. So one cannot use work as defined by eqn (22) in any first law based relation!

### ***J: Compression of an insulated Piston-Cylinder***

Consider that an ideal gas within an insulated piston-cylinder is compressed. Now the ideal gas's temperature increases as the pressure increases. This can be viewed as either viscous dissipation i.e. due to the fact that intermolecular collisions are inelastic. Since the temperature of the compressed ideal gas has increased, then eqn (22) no longer applies.

If the insulated compressed gas is then allowed to expand, it will cool down. Assuming that the piston-cylinder is frictionless, then when the ideal gas returns back to atmospheric

pressure it will also be isothermal with respect to the atmosphere. Again, in terms of the atmosphere, everything stated for the not insulated compression will apply to the insulated.

***K: Quantum Arguments:***

There are numerous studies out there showing that quantum effects defy the second law<sup>23</sup>. Instead of questioning the statistically based second law, perhaps the question should be do these quantum processes disturb the natural state of our atmosphere? Certainly, some might, but the vast majority should not!

***L: Global Warming:***

The formation of our atmosphere involved work through processes like accretion. And as an approximation, we can think of our atmosphere as being in a state of approximate states of equilibrium. Or, at least, it is constantly trying to attain a state of both thermal equilibrium (temperature) and mechanical equilibrium (pressure). Any time that this is disturbed there should be consequences, some of which were described herein.

Whether this changes our understanding of man's influence concerning global warming, I cannot say. I can, however, attest to the likelihood that our models for global warming are based upon a poorly conceived thermodynamics and probable misunderstanding of greenhouse gases. Accordingly, the models may require a complete rethink if we are to improve the understanding.

***M: Conclusions:***

The concept that thermodynamics is a well-understood mature science has been challenged and shredded. However, rather than continue with the over complication, the simplest approach conceivable was taken, namely, because simple arguments remain the best, and trying to direct entropy based arguments remain futile until thermodynamic entropy receives clarity.

Our new perspective explains Fermi's misconception concerning the expanding universe. Most importantly, it adheres to both Planck's<sup>20</sup> "mechanical view of nature" and his understanding that there is "no way possible to have perpetual motion". It also fits this author's explanation of nucleation theory<sup>4</sup>, wherein the energy required for bubble nucleation was finally explained thus matching empirical findings.

By understanding how expansion and compression affect our atmosphere, we now can visualize why processes here on Earth's surface are irreversible. Accordingly, statistical based second law arguments are no longer required to explain this. The consequences of this will be unfathomable to many readers, especially those who are intimately familiar with currently accepted thermodynamics theory.

Specifically, we examined lost work<sup>13</sup> that being the transfer of the potential and/or thermal energy into the atmosphere by expanding systems, whose total is defined by  $(PdV)_{\text{atm}}$ . This is best explained in terms of the atmosphere having mass within a gravitational field, hence, its displacement generally involves this irreversible work. For expanding systems, it can be thought of in terms of an atmospheric potential increase. However, in reality intermolecular collisions are not elastic as was discussed in this author's papers concerning kinetic theory<sup>15,16</sup>, where a superior fit to known empirical data was obtained. Hence,

viscous dissipation often results in infinitesimal atmospheric temperature increases. Interestingly, inelastic intermolecular collisions also provides an explanation for pressure-temperature relations.

Whether we consider a volume increase (potential energy increase) and/or a temperature increase (viscous dissipation), for real processes that are generally experienced here on Earth, such increases can be thought as infinitesimal when compared to our atmosphere's total energy. However, if a large, significant number of such real processes do occur, then we may have to reconsider how this all influences our planet's warming.

It was shown that not clearly defining which parameters define the work done by expanding systems, has allowed the over complication of the science. It is this author's opinion that the thermodynamics needs an overhaul and that statistical thermodynamic can be rewritten to match our new enlightenment.

Interestingly lost work clearly explains the difference empirically known between isobaric and isometric heat capacity. Importantly, it does so without the complication of entropy change. Furthermore, we saw how logarithmic functions may be part of thermodynamics without the necessity of entropy.

What about the second law, wherein entropy of the universe is a "non-decreasing function of time"<sup>24</sup>? It is a false postulate. What about thermodynamic entropy itself? We discussed some plausible misunderstandings that may have led to entropy's rise and for its attendant unnecessary complexity.

I would like to thank Nick Percival for making this paper possible. Further thanks to Nick, and Dennis Allen for their input. And a final thanks goes to Jeremy Dunning-Davis for his insights although we tended to disagree on the significance of certain aspects.

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