New Thermodynamics: Inefficiency of a Piston-Cylinder

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Abstract—Inefficiencies of expanding systems are traditionally taught in terms of entropy, and the second law. Herein, it will be shown that such traditional explanations are an over-complication of reality. This will be accomplished by providing a simpler understanding as to why such inefficiencies exist in a piston-cylinder apparatus. This introduces the reader to a new perspective which is founded on lost work, and the inherent inefficiencies when converting a gas's kinetic energy into work.

Index Terms—Efficiency, lost work, second law, new thermodynamics

I. INTRODUCTION

A. Lost Work

An equation traditionally applied to expanding isothermal isobaric expanding systems, is:

\[ TdS = dE + PdV \]  (1)

Too often the purveyors of (1) contemplate that \( PdV \) is the work as described in terms of the system’s isobaric volume increase. This author has stated that such an isothermal volume increase is actually lost work that is being work done onto the surrounding atmosphere [1]. This does challenge the illogical mathematical-driven traditional assertion that such work is done into the expanding system’s walls, irrelevant as to whether the walls are real, or imaginary. Our reality is that work is done through the system’s walls, onto its surroundings [1,2].

Furthermore, this author has stated that better clarity is obtained by rewriting equation (1) as [3]:

\[ (TdS)_s = dE_s + (PdV)_atm \]  (2)

Where \((TdS)_s\) represents the expanding system’s isothermal entropy change, \(dE_s\) is the expanding system’s energy change, and \((PdV)_atm\) is the work done onto the surrounding atmosphere.

It should be emphasized that for such an isobaric process; \(P_s \equiv P_{atm}\). Furthermore, the expanding system can be considered as a subsystem within the atmosphere, e.g. a larger surrounding system. Therefore, the atmosphere’s volume increases theoretically equals the expanding system’s volume increase, i.e., \(dV_{atm} = dV_s\). Accordingly, one realizes that:

\[ (PdV)_s \equiv (PdV)_atm \]  (3)

When comparing (3) to (2), one can readily understand how the confusions of (1) can be overlooked. For emphasis, (2) gives the lucidity of knowing that work done is external to the expanding system.

Furthermore, this author does not appreciate the so-called virtues of isothermal entropy, accordingly I prefer to rewrite (2) in terms of a first law style equation. Herein, the system’s energy input \(dQ\) replaces \(TdS\), hence one can use the following accepted equation, i.e. [3,4,5]:

\[ dQ = dE + PdV \]  (4)

As was the case with (1), (4) also lacks the clarity as to onto what is the work done. Once more, lucidity is readily obtained by rewriting (4) as follows [3]:

\[ dQ_{sys-in} = dE_{sys} + (PdV)_{atm} \]  (5)

The work done onto the surrounding atmosphere \([PdV]_{atm}\) is lost work [1,3,6]. The reason it is lost work, is that the atmosphere remains both isobaric and isothermal. Accordingly, the atmosphere cannot return any lost work by an isothermal isobaric expanding system, i.e., “A gaseous system can only do work onto its neighboring system (or surroundings) if that system is at a higher pressure than its neighboring system. Similarly: a system can only pass thermal energy onto its neighboring system (or surroundings) if that system is at a higher temperature than its neighboring system” [3]. Therefore, lost work is irreversible work.

There is another issue with associating \(PdV\) in equations (1) and/or (4) with the expanding system. That being; the internal energy change \((dE)\) is a summation of the microscopic energy changes within a system, which is a fancy way of saying the system’s total energy change! Therefore, the work, as defined by \(PdV\) can only be external to that system. I.e. if the total energy of a gaseous system is defined in terms of its mechanical parameters \((P,V)\), then one often invites complete confusion by similarly defining its external work in terms of the same system’s mechanical parameters.

Equation (5) acknowledges that lost work represents an increase to the atmosphere’s potential energy, i.e., an isobaric upward displacement of part of the atmosphere’s mass. The reality is that an expanding system may result in a regional atmospheric pressure increase, which then results in either, and, or:

a) an isobaric expansion of the atmosphere [1,3]
b) in heat associated with viscous dissipation [3]

In order to better understand b), one must accept that intermolecular collisions are inelastic [3,6,7,8]. A byproduct of inelastic intermolecular collisions, is heat (thermal photons), thus ensuring that the inelastic collision obeys the law of conservation of energy.

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Although, lost work is expressed as a potential energy increase, i.e., \((PdV)_{\text{ext}}\), it manifests itself as a combination of potential energy, and/or heat, which can be equated to molecular kinetic energy \([1,3,6]\).

The above does challenge accepted traditional kinetic theory, which is wrongly based upon elastic collisions. Specifically, this author has shown that by considering the wall molecules as massive energy pumps that impose their energetics onto the smaller gas molecules, allows for an improved new kinetic theory \([6,7]\). A theory that relies upon neither equipartition, nor degrees of freedom. Moreover, it better explains accepted empirical findings, without any of the numerous exceptions that plague the traditionally accepted kinetic theory.

Note that: In general, the Earth’s atmosphere is comparatively massive, hence it acts like a heat sink/bath, i.e., it does not experience a measurable temperature, and/or pressure increase.

**B. Shrinking Systems**

The kinetic energy \((E_k)\) of monatomic gas consisting of \(N\) molecules is defined by \([6,7]\):

\[
E_k = \left(\frac{3}{2}\right) NkT = \left(\frac{3}{2}\right) PV
\]  

(6)

Note that (6) represent the gas’s kinetic energy that being its translational plus rotational, and this differentiates this author’s kinetic theory from the traditional one based upon degrees of freedom \([6,7]\).

One may ponder what happens when a system contracts/shrinks, i.e., a gas is compressed by an external force. If the compression is quasi-static, and the system is not insulated, then any heat associated with the pressure increase can freely escape through the contracting gaseous system’s walls. And hence the process will appear isothermal \([3]\).

Based upon (6) the gas’s energy does not change in such an isothermal process. However, due to its pressure increase, the potential of the gas to do work will increase. Again, if the compressed system does work, then this work is always external to the system, and generally will be lost work.

What is particularly interesting is that when the system compresses, then some of the surrounding atmospheric molecules also move downwards, thus experience a change to some of their potential energy into kinetic energy. And such kinetic energy can be viewed as, and/or be readily transformed into, heat (thermal energy).

**C. Second Law**

Consider the following traditional statements from reference \([5]\): “An equilibrium macrostate of a system can be characterized by a quantity \(S\) (called entropy), which has the following properties:

i) In any infinitesimal quasi-static process in which a system absorbs heat, its entropy changes by an amount:

\[
dS = dQ/T
\]  

(7)

Where \(T\) is a parameter characteristic of the macrostate of the system, and is called its absolute temperature

ii) In any process in which a thermally isolated system changes from one macrostate to another, its entropy tends to increase, e.g.

\[
\Delta S \geq 0
\]  

(8)

The concept of isothermal entropy always increasing is fully indoctrinated into the sciences, as the second law of thermodynamics. This author has previously pointed out that the second law only applies to isolated systems, which is something that does not readily exist here on Earth.

Just re-consider (1); since there is no clarity one might unwittingly think that an expanding isobaric, isothermal system can be isolated. But as clearly expressed in (2), the expanding system must do work onto the surrounding atmosphere, hence it cannot be isolated, as has been previously discussed by this author. \([1,3,6,7]\).

If the second law in its most fundamental conscript falters, then how does one now explain the witnessed inefficiencies? Certainly, part of it is the previously described lost work, but there is more to it than this, as will now be explained.

**II. WORK BY A GAS**

Based upon (6), if the gas’s temperature was to change then the change in the monatomic gas’s kinetic energy \((dE_k)\) becomes:

\[
dE_k = \left(\frac{3}{2}\right) NkdT = \left(\frac{3}{2}\right) d(PV)
\]  

(9)

The ability to do work, can be considered as how much work a system can do onto an imaginary surrounding, whose pressure approaches absolute zero. Accordingly, the change in a system’s ability to do work \((dW_{\text{abi}})\) as based upon the ideal gas law \((PV=NkT)\) becomes \([3]\):

\[
dW_{\text{abi}} = d(PV)_{\text{sys}} = NkdT
\]  

(10)

Comparing (9) to (10), one will notice that the change in the monatomic gas’s ability to do work is 2/3 of its kinetic energy change.

Does the above mean that the change to a system’s ability to do work is only 66.67% of its change in kinetic energy? It certainly does, and this fact is lost in the Gordian knot of the sciences, i.e., traditional thermodynamics.

The best way to understand is this. For a gas enclosed by six walls, i.e., inside of a cube, the molecules of the six walls all impose their kinetic energies onto the enclosed gas \([6,7]\). In other words, the gas’s kinetic energy is a summation of the energy imparted onto them by all six walls. But the actual flux of the gas onto any one wall is defined by \([5]\):

\[
\Phi_0 = \left(\frac{1}{4}\right)n \bar{v}
\]  

(11)

The flux \(\Phi_0\) represent the total number of molecules that strike a unit surface area \((dA)\) over a unit of time \((dt)\). Equation (11) is obtained by the complex analysis of integrating over \([4]\):

a) all possible speeds,

b) all possible azimuth angles.

c) all possible angles.
Note that: The complete derivation of (11) is given in [5] on page 271. It is of interest that in traditionally accepted kinetic theory, the flux in any one direction used to explain what is witnessed is wrongly accepted, as being:

\[ \Phi_0 = (1/6)n\bar{v} \]  

(12)

The above crude analysis, (12), for the flux of gas molecules impacting a wall is found in various thermodynamics [4,5, 9] and/or kinetic theory texts. It is based upon the simple premise that 1/6 of the total flux is directed along a given direction, with the six directions being (+/-) (x,y,z).

Amazingly, (12) is 2/3 of (11). This fact has been ignored by most all texts, when deriving their accepted kinetic theory. And in so doing they all have conveniently allowed for the confusion.

The bottom line is that we now begin to understand why the change to the ability of a gas to do work is only 66.67% of that gas’s kinetic energy change. In simplest terms: When one heats a gaseous system in order to perform work, then the highest possible efficiency of that heated gas to do work is only 2/3 of its gas’s kinetic energy increase.

It should be noted that when a system expands, it can expand in most any direction. No matter what direction the expansion occurs in, the atmosphere can only be displaced in one direction that being upwards. According, all work has a sense of direction e.g., lost work is upwards e.g., work in moving a car is along one given direction. In other words, work has a sense of direction that thermal energy lacks.

III. HEATED PISTON-CYLINDER

Consider heating of a closed piston-cylinder apparatus filled with \( N \) monatomic gaseous molecules, as illustrated in Fig. 1.

The piston is locked in position, and heat is added, then based upon (9), the thermal energy \( (\Delta Q_m) \) required to raise the cylinder’s internal temperature \( (\Delta T_{cyl}) \) is:

\[ Q_m = \left( \frac{3}{2} \right) N k d T_{cyl} \]  

(13)

As the gas’ temperature increases, its kinetic energy increases, hence its pressure increases, i.e., \( P_{cyl} > P_{atm} \) and this increases its ability to do work. Based upon (10), when written in terms of infinitesimal changes, the change to the ability to do work \( (dW_{abl}) \) can be written as:

\[ dW_{abl} = N k d T_{cyl} \]  

(14)

Equation (14) is 2/3 of (13), hence \( \eta < 66.67\% \).

If the piston is unlocked as shown in Fig 2, then the piston-cylinder’s volume will increase \( (dV_{cyl}) \), and then the work done could be written as:

\[ dW = d(PV)_{sys} \approx (VdP)_{sys} + (PdV)_{sys} \]  

(15)

Equation (15) is problematic, i.e., it is expressed in terms of the expanding system. Rewriting in terms of lost work done:

\[ dW \approx (VdP)_{sys} + (PdV)_{atm} \]  

(16)

The lost work done is \( (PdV)_{atm} \). What about \( (VdP)_{sys} \)? Prior to heating, and after expansion the piston-apparatus was at 1 atm pressure. In other words, \( (VdP)_{sys} \) can be thought as becoming irrelevant, for this case.

Think of it another way; if the piston was never locked, then as the piston-cylinder is heated it experiences isobaric expansion, hence \( (VdP)_{sys} \approx 0 \). Hence (16) becomes:

\[ dW = (PdV)_{atm} \]  

(17)

Consider that the heat is continuous during expansion, as illustrated in Fig 2. The piston-cylinder will expand so long as the gas’s pressure within the piston-cylinder remains greater than that of the surrounding atmosphere, e.g., it drives the piston outwards. Assuming frictionless and massless, hence the pressure inside the piston-cylinder only needs to be infinitesimally greater than the surrounding atmosphere. Then based upon (5) and (13) the minimal required thermal energy \( (Q_{min}) \) becomes:

\[ Q_{min} = \left( \frac{3}{2} \right) N k d T_{cyl} + (PdV)_{atm} \]  

(18)

Can the process be fully idealistic, i.e., isothermal \( (dT=0) \) and isobaric \( (dP=0) \)? NO! Because in order for gas to expand then its mean molecular volume must have increased, hence the gas’ temperature must have increased.

Even so, one could still imagine a frictionless massless piston-cylinder and, then imagine an idealistic process the result being no temperature change \( (dT_{cyl}=0) \). For this overly idealistic imaginary case, (18) becomes:

\[ Q_{min} = (PdV)_{atm} \]  

(19)

IV. LIFTING A MASS

The above crude analysis, (12), for the flux of gas molecules impacting a wall is found in various thermodynamics [4,5, 9] and/or kinetic theory texts. It is based upon the simple premise that 1/6 of the total flux is directed along a given direction, with the six directions being (+/-) (x,y,z). Amazingly, (12) is 2/3 of (11). This fact has been ignored by most all texts, when deriving their accepted kinetic theory. And in so doing they all have conveniently allowed for the confusion.

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\[ dW_{abl} = N k d T_{cyl} \]  

(14)

Equation (14) is 2/3 of (13), hence \( \eta < 66.67\% \).
Next consider that the piston has mass \( M \) and moves vertically, as shown in Fig. 3. The potential energy increase \((dE_p)\) of its mass is: \( dE_p = M \dot{g}h \).

Adding \( M \dot{g}h \) to the energy requirements as defined by \((18)\), one obtains:

\[
Q_{\text{min}} = \left( \frac{2}{\gamma} \right) Nk dT_{\text{cyl}} + (PdV)_{\text{atm}} + M \dot{g}h \tag{20}
\]

The piston’s mass means that the final pressure within the system must always be higher than the surrounding atmosphere, i.e., \( P_{\text{sys}} > P_{\text{atm}} \). And this applies to the final pressure of the system, even if the piston’s movement was perfectly frictionless.

Since the final pressure within the piston-cylinder must be higher, then the temperature increase also must be greater than it would be for the zero-mass piston-cylinder, i.e., \( dT_{\text{cyl-mass}} > dT_{\text{cyl-massless}} \).

Certainly, if the piston was to suddenly become massless then the piston-cylinder would expand further, and the lost work \([PdV]_{\text{atm}}\) would increase.

Instead of just lifting the piston’s mass, consider that the piston-cylinder’s ideal monatomic gas also performs work for man, such as powers a mechanical device \((W_{\text{dev}})\). Then one could replace the work required in \((18)\) with the total work done \((W_{\text{done}})\), i.e.:

\[
Q_{\text{min}} = \left( \frac{2}{\gamma} \right) Nk dT_{\text{cyl}} + W_{\text{done}} \tag{21}
\]

However, the total work done is the lost work onto the atmosphere, plus the work of the device, i.e.: \( W_{\text{done}} = W_{\text{dev}} + W_{\text{atm}} \). Therefore, there would be clarity by writing:

\[
Q_{\text{min}} = \left( \frac{2}{\gamma} \right) Nk dT_{\text{cyl}} + W_{\text{dev}} + W_{\text{atm}} \tag{22}
\]

It becomes apparent that the when actually doing work, other than lost work onto the atmosphere, that the final pressure, and temperature, of a gas must be higher than that of the surrounding atmosphere. In other words, any notion of it being an idealistic isobaric, isothermal, process quickly fades.

What does this mean to traditionally taught isothermal, isobaric \((1)\), and or \((4)\). Obviously, they are not valid for most realistic processes.

V. EFFICIENCY

Consider the maximum efficiency \((\eta_{\text{max}})\): 

\[
\eta_{\text{max}} = \frac{W_{\text{dev}}}{Q_{\text{min}}} \tag{23}
\]

Substituting in \((22)\) gives:

\[
\eta_{\text{max}} = \frac{W_{\text{dev}}/\left[\left( \frac{2}{\gamma} \right) Nk dt_{\text{cyl}} + W_{\text{dev}} + W_{\text{atm}}\right]}{\left( \frac{2}{\gamma} \right) Nk dT_{\text{cyl}}} \tag{24}
\]

Equation \((24)\) is based upon an ideal monatomic gas, which is also not particularly realistic for a combustion engine, here on Earth.

The total energy of a polyatomic gas includes its rotational, translational and vibrational energy, all of which was determined by this author to be \([6,7]\):

\[
E_T = NkT(n'' + 1/2) \tag{25}
\]

where \( n'' \) is the number of atoms in the molecule.

Our atmosphere is primarily diatomic gases (\(N_2\) and \(O_2\)). For such diatomic gases \( n'' = 2 \). Then based upon \((25)\), the diatomic gas’s total energy is:

\[
E_T = \frac{5}{2} NkT \tag{26}
\]

And the change to a diatomic gas’s total energy \((dE_T)\), as a function of temperature, becomes:

\[
dE_T = \left( \frac{5}{2} \right) Nk dT \tag{27}
\]

Accordingly, the minimum required energy \((Q_{\text{min}})\) becomes:

\[
Q_{\text{min}} = \left( \frac{2}{\gamma} \right) Nk dT_{\text{cyl}} + W_{\text{dev}} + W_{\text{atm}} \tag{28}
\]

And the maximum efficiency becomes:

\[
\eta_{\text{max}} = \frac{W_{\text{dev}}/\left[\left( \frac{2}{\gamma} \right) Nk dt_{\text{cyl}} + W_{\text{dev}} + W_{\text{atm}}\right]}{\left( \frac{2}{\gamma} \right) Nk dT_{\text{cyl}}} \tag{29}
\]

Equation \((29)\) describes why expanding systems, such as piston-cylinders, are generally so inefficient. And these are unavoidable factors.

If considering a combustion engine, wherein the piston has mass and its movement involves friction (both internal and external), then the actual efficiency will be somewhat less than that as described by \((29)\). Note, although heating heat was shown to be from an external source, the principles discussed herein should also apply to the internal combustion engine.

VI. COMMENTARY

It is this author’s belief, that entropy-based thermodynamics is an over-complication that places mathematical innuendos ahead of constructive logic.

The reason that it lasted throughout the 20th and into the 21st century speaks more to the powers of statistical theory, rather than the virtues of its logic.

Of note: Its math was equated to lost work, via \((1)\), and then in its various forms, was claimed to explain that lost work. This is nothing short of circular logic.
We are taught that probabilities give results, e.g., deal a deck of cards, and the various plausible results are expressed by probabilities. However, when probabilities become reasons, as is too often the case in the sciences, then one walks a rather precarious road.

What is this author’s new thermodynamics? It is the process of clearly demonstrating that simpler perspectives exist. Perspectives that provide more clarity, while equally explaining all the accepted empirical findings. Moreover, it also explains that, which previously lacked lucidity. It now becomes a case for Occam’s razor.

No wonder that 170, or so, yrs after its inception that the definition of entropy still lacks any real transparency. Accepting that entropy is nothing short of a mathematical contrivance [10], be hard for some. Arguably, entropy has too often been illogically applied, all part of making its mathematical based enterprise function.

It is also very important to understand how the various inefficiencies, generally result in the heating of our atmosphere. And how this becomes a major constituent in a new understanding of global warming [11]. Never forget: Intermolecular collisions are inelastic, therefore most all forced changes to our atmosphere’s natural state will result in its heating.

VII. CONCLUSION

The efficiency of a piston-cylinder was examined in terms of new thermodynamics. It became obvious as to why the combustion engine is so inefficient, as can be inferred from (29).

The above inefficiency was primarily due to lost work, and the inefficiency in converting a gas’s kinetic energy changes into work. These factors for inefficiency are unavoidable, unlike the more readily accepted factors such as friction, both internal and external!

Importantly, our improved lucidity started with the understanding that lost work is irreversible work done onto the surrounding atmosphere, by an isothermal, isobaric, expanding system. It was then followed by the understanding that not all of gas’s kinetic energy can be readily converted into work, with an upper limit being approximated by an idealistic 66.67%.

Interestingly, it was discussed that the traditionally accepted isothermal, isobaric based equation for an expanding system, (1), seemingly falters when applied to real processes that involve real work.

This all does not exactly allow us to completely expunge the entropy-based over-complication from the sciences. But it certainly represents another deadly arrow that requires a proper explanation by the indoctrinated, e.g., those who subscribe to it.

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