Second law and lost work

Kent W. Mayhew[a)]
68 Pineglen Cres., Ottawa, Ontario K2G 0G8, Canada

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Abstract: The concept of energy lost by expanding systems is reconsidered. The implications to thermodynamic are profound especially to concepts such as reversibility and the second law thermodynamics. © *2015 Physics Essays Publication.*
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Résumé: Le concept d'énergie perdue par systèmes en expansion est reconsidéré. Les implications dans la thermodynamique sont profondes surtout dans les concepts comme la réversibilité et la deuxième loi de la thermodynamique.

Key words: Entropy; Second Law; Lost Heat; Lost Work

I. INTRODUCTION

The second law was conceived in the 19th century to explain the "lost work" (i.e., lost energy and lost heat) associated with idealized heat engine,[1] i.e., the Carnot cycle. A traditional consideration of the second law is:[2] "An equilibrium macrostate of a system can be characterized by a quantity S (called entropy), which has the following properties:

(1) In any infinitesimal quasistatic process in which a system absorbs heat, its entropy changes by an amount

$$dS = dQ/T, \tag{1}$$

where T is a parameter characteristic of the macrostate of the system and is called its absolute temperature.

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

$$\Delta S \geq 0'' \tag{2}$$

where dS and dQ, respectively, represent entropy change and heat exchanged.

A summation: "The second law of thermodynamics states that the entropy of an isolated system never decreases, because isolated systems always evolve towards thermodynamic equilibrium, which is a state of maximum entropy."[3] Interestingly, Nikulov and Sheehan[4] give a good summation of the challenges to the second law. Sheehan[5] states: "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."

A reversible process is one that can readily return to its original state. Reversibility is an idealistic concept for a system's state, wherein it can be changed, and then readily returned to its original state. It is idealistic because few, if any real processes, mechanical, or otherwise, are truly reversible.[6]

Conversely, an irreversible process is one that cannot return to its original state without the expenditure of energy. Another way of viewing an irreversible process is to consider it as some process wherein energy is irretrievably lost, i.e., lost work (dW_{lost}), and then write

$$dS = (dQ + dW_{lost})/T \tag{3}$$

Lost work can be due to many phenomena, such as those resulting in dissipation of energy, i.e., friction. If: $dW_{lost} = 0$, then the process is reversible, i.e., Eq. (1).

In terms of energy, Eq. (3) can be rewritten as

$$TdS = dQ + dW_{lost} \tag{4}$$

Traditionally, work lost by expanding systems is considered as being a boundary effect, i.e., performed onto a system's walls,[2,6–8] which can be real or imaginary. Mayhew[6,7] realized that work is always done through the system's walls. Moreover, when a system expands, then its expansion must include work done onto the atmosphere. This simpler explanation of work going through the walls was equated to

$$W = PdV. \tag{5}$$

Entropy has been contemplated in numerous ways, such as: "Randomness of matter in incessant motion"[9] or "The dispersal of a system's molecular energy."[10] Both statements are based upon its thermodynamic conception. More recently, Ben-Naim[1] has reconsidered thermodynamics, by discussing how the concept of randomness is ambiguous, thus emphasizing Shannon's information-based thermodynamics. Of interest to this author is the fact that Ben-Naim[1] discussed the plausibility that entropy may be misguided in its traditional application. Certainly, he considers that entropy's definition's lack of clarity allows for information to be considered as better terminology. Moreover, he treats entropy as a mathematical contrivance.[1] Interestingly in a brief email correspondence, Ben-Naim did agree with this author that it is, albeit he stressed an important one.

[a)]Kent.Mayhew@gmail.com

II. LOST WORK BY EXPANDING SYSTEMS

One consideration for lost work that has been traditionally omitted is as follows. Consider the work, which is generally lost by expanding systems. Begin by asking some simple questions:

(1) Does the Earth's atmosphere have mass?
(2) Is the Earth's atmosphere primarily contained by gravity?
(3) Does an expanding system displace some of the atmosphere's gases against gravity?

If you answer yes to the above questions, then you must accept that the upward displacement of Earth's atmosphere requires work. Why upward? Certainly a volume increase means displacement, and this displacement cannot be downward into the Earth. Perhaps, it results in a pressure increase. If it does then this pressure increase would only exist momentarily as it pushes the atmosphere's gases upward. Ultimately, the displacement can only be in one direction, that being upward.

Certainly, the displacement of our atmosphere means that the potential energy of the atmosphere's gas molecules has increased, albeit generally by a small amount when compared with the atmosphere's total energy. Moreover, this must signify "lost work." If one chooses to calculate the total work required to displace our atmosphere, then the result would be given by Eq. (5) as was shown by Mayhew[7] to be

$$dW_{\mathrm{lost}} = PdV. \tag{6}$$

Neither man nor his machines can ever harness the work lost by expanding systems! Specifically, when atmospheric molecules are upwardly displaced they experience a potential energy increase. Interestingly, if the expanding system collapses then the potential energy increases, as experienced by the upwardly displaced gas molecules transform into kinetic energy of these molecules, which in most cases results in an increase to our atmosphere's heat.

Is the above not a simple undeniable explanation for some of the energy lost by the 19th century idealized heat engines? Certainly, such a cyclic engine has at least one cycle wherein its system is expanded, thus displacing our atmosphere, and resulting in "lost work." The vast majority of engines that power our lives possess at least one step, which involves the expansion of a system. Accordingly, this concept of lost work applies to most systems of interest, irrelevant to that system being considered open or closed.

III. APPLICATIONS OF LOST WORK BY EXPANDING SYSTEM

Consider a high-pressure gas filled vessel, whose temperature is isothermal with the surrounding atmosphere. Opening a valve on such a vessel will result in a cool zone forming at the location of gas expansion. This is a case of an expanding gas doing work, i.e., lost work (PdV). Traditionally, this was explained in terms of either an entropy increase, or work done onto imaginary walls.[7] Certainly, the simplest and most logical explanation is that the temperature decrease is due to the lost work, i.e., it involves our atmosphere's upward displacement. Note: The actual temperature changes may vary depending upon factors, such as the pressure change, rate of change, and the nature of the gas.

A more common occurrence is the previously discussed cyclic engine. Consider a steam engine. Herein, the steam's pressure is moderately higher than the surrounding atmosphere, thus this pressure is used to first drive a piston in one direction, then valves open and close, allowing the steam's pressure to next drive the piston in the other direction. Therefore, with every movement of piston, the volume within the piston-cylinder increases thus displacing our atmosphere. Hence, one result is continuous lost work: PdV.

Certainly, the steam engine does more work than just displace the atmosphere. Like any cyclic engine, the total work done by the steam engine is the summation of the work lost onto the atmosphere, plus work in moving the machine, plus all the other dissipative energy losses. Obviously, useful expanding systems that move man, and/or machine, inevitably do suffer the fate of lost work.

Interestingly, not all expanding systems necessarily result in "lost work." Consider a hermetically sealed piston-cylinder apparatus whose volume is increased by pulling on the piston thus creating a vacuum within. If the piston is then released, atmosphere's pressure will drive the piston back into the apparatus. Accordingly, this process returned to its original state. Seemingly, when an external force expands a system while its internal pressure decreases, then work is not necessarily lost. Herein, it may be best to contemplate in terms of the displacement of the volume of gas against a gravitational field in the manner discussed by Mayhew.[6,7,11] Interestingly, due to the law of atmospheres, the displacements, as a function of height, is logarithmic.[6,11]

IV. WALLS

There will be those who adhere to the traditional conceptualization that work is lost into the expanding system walls. As previously stated, arguments against were presented by Mayhew.[7] If one insists on such conjecture, then you must answer why all walls would require the same amount of work irrelevant of how they are constructed. Sure, it can be mathematically deduced that the work is given by PdV. But PdV is also the same answer one obtains if one considers the work lost in displacing our atmosphere.[4,6] So what makes more sense: (A) work by expanding systems is lost into the surrounding atmosphere, or (B) work is mysteriously lost into walls?[6,7]

If you prefer (B) then you must be able to explain: Why then is the work not returned, if the system's volume decreases, i.e., walls shrink? And why is the answer: PdV irrelevant of whether the walls are imaginary or real, and irrelevant of what the walls are made of. Certainly, (A) is a simpler and is enveloped in common sense, i.e., the acceptance that when a system does work, that this work is done by the system through its walls.

V. ENTROPY

There will be those whose preference is to consider that the work lost by an expanding system is associated with an entropy increase. Interestingly, Ben-Naim[1] correctly discusses that the concept of randomness has nothing to do with energy, moreover, he correctly points out that the actual perception of matter's randomness in any system is really up to one's own interpretation. As was the case with work lost into walls, entropy based explanations are due to our fixation on the system without consideration to the surroundings.[6] Sadly, if our eyes were not so transfixed upon the expanding system, then these issues could have been resolved over century and a half ago.

VI. REVERSIBILITY

If we heat a system and allow for isobaric expansion, then that system must experience lost work. This applies to many useful processes. Based upon our new understanding concerning expanding systems, and Eq. (3), such processes are irreversible. Furthermore, living on mother Earth means that we live a fundamentally isobaric existence. Thus most useful work is obtained from expanding systems, hence most useful processes are not reversible!

The exception being, when a closed system expands due to an external force, wherein the process may be reversible. But how useful is such a process?[6] This also makes one ponder, do we really need entropy to explain reversibility? Traditional belief centers about a process being reversible if infinitesimal changes to a system occurs without entropy production. Reconsider the expansion of the hermetically sealed piston-cylinder apparatus. If entropy is about randomness of matter, then the entropy of the gases within the piston-cylinder apparatus must increase. Yet this process was obviously reversible, thus seemingly befuddling traditional understanding. Okay, one could argue that no energy was dissipated, and they would be right (to a degree).[6]

Perhaps, we should remove the concept of entropy from our traditional understanding of reversibility, and simply say: A system's process is irreversible if energy is irretrievably lost by that system.

VII. CONSEQUENCES TO THE SECOND LAW

As stated, Ben-Naim[1] points out that the second law was derived to help explain the work lost by expanding systems. Does this mean that the second law needs re-evaluation? This author believes so.

Begin by considering our understanding of an isolated system, that being a system which is completely enclosed by walls through which no energy, nor matter, can pass. Accepting that an expanding system must displace our atmosphere, and this constitutes work, then can expanding systems be considered isolated? Certainly not for the majority of processes that involve expansion! The reason being that most expanding system, must work onto our atmosphere, hence must either receive or expend energy in order to expand. This has gone unacknowledged for too long!

Certainly as written, the second law applies to only isolated systems, therefore, it cannot possibly apply to useful expanding systems here on Earth, i.e., those that experience isobaric expansion. Perhaps we should add to the second law: If a system experiences isobaric expansion and its surroundings contain mass in a gravitational field, then that system cannot be deemed isolated. Of course if we do, then the relevance of the second law becomes extremely limited. It verges upon irrelevant!

Interestingly for previously discussed reversible expansion of the hermetically sealed piston-cylinder apparatus, this as a system can be considered isolated because an external force expands the system, hence it does not necessarily change the amount of energy within that system.

Consider the classical interpretation that entropy represents the randomness of matter. As great as the second law sounds, consider the statement "equilibrium, which is the state of maximum entropy." Could "maximum entropy" not simply be replaced with "maximum dispersion"? Certainly dispersion is not necessarily associated with energy in the same manner as entropy is, but still if you leave an isolated system of matter to its own devices, then dispersion will occur. If we say the net result is maximum dispersion then this is nothing profound. But strangely, maximum entropy is deemed profound.

Certainly, if one accepts that expanding systems displace some of our atmosphere's gases, thus increasing those gases' potential energy, thus resulting in the system's lost work, then one must begin to question the second law and all that follows. Never forget that the second law was originally devised to help explain energy lost by expanding systems. In other words, it explains things in traditional thermodynamics because we formulated it to do so. The fact that empirical data are used to validate it becomes circular logic, demonstrating the power of the mathematics, rather than a logical sequence. Even more disturbing is the fact that this poorly conceived second law forms the foundation of traditional thermodynamics. The implications become profound, almost unbelievably so.

VIII. CONSEQUENCES TO ENTROPY

Should entropy retain its demigod status? Based upon Eq. (4), entropy can remain something that when multiplied by temperature gives energy, just as 19th century scientists such as Rudolf Clausius first envisioned it to be, i.e., a mathematical contrivance. Can we downgrade entropy to simply being a mathematical contrivance? Certainly, this author believes so, and perhaps, others such as Ben-Naim[1] have alluded to. Although left for discussion on another day, this author further realizes that there exists another simple explanation for why something whose change, when multiplied by temperature, defines the thermal energy change within matter.[6] If one chooses to call that something entropy, so be it, in which case we should alter our traditional conception of entropy.

IX. CONCLUSIONS

In its simplest context, the energy lost by an ideal heat engine during its volume expansion step of its cycle can be explained in terms of the displacement of the Earth's atmosphere and this is a form of "lost work." To deny this is to deny that Earth's atmosphere has mass, which exists in a gravitational field, which must be displaced by expanding systems! Moreover, this displacement of our atmosphere requires work, which is generally lost onto Earth's atmosphere's gases.

Understand that concepts, such as entropy and the second law, were formulated in the 19th century to explain the previously unexplainable, namely, the work lost by the Carnot engine. Sure the second law is empirically proven here on Earth, but only because it is poorly conceived and mankind designed it that way, using circular logic. And just because we formulate definitions to explain what we witness, does not render that definition as the simplest and most logical explanation.

The fact that the very definition of entropy remains controversial to this day, a century and a half after its conception, demonstrates an inherent weakness in its structure. As for our formulating the second law, if we concerned ourselves with a system's surrounding as much as we did with the system itself, then the second law may have never needed to be written. There is no denying that the second law applies to isolated systems, but what constitutes an isolated system was questioned. Based upon our realizations, the applicability of the second law becomes too limited to bestow any true value. The implications to thermodynamics are profound!

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