Rethinking the Macroscopic Presentation of the Second Law of Thermodynamics

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Abstract: The classical macroscopic presentation of the second law of thermodynamics is an elegant but abstract sequence of very specific thought experiments that utilize reversible processes occurring within heat engines operating between infinite temperature reservoirs. The length, specificity and complexity of this sequence may hamper the understanding of important concepts such as exergy and entropy. The pedagogical problems of this approach have been discussed, followed by an alternative presentation wherein second law concepts and formulations have been derived from thought experiments that use real, rather than imaginary processes. The thought experiments involve classifying heat transfer at any local point for any arbitrary process involving work-heat interactions into different categories, and then collecting terms for each category throughout the control volume in order to relate property changes to external heat transfer and/or work. They embrace the spatial non-uniformity present in any real process, are consistent with contemporary computational approaches, and can potentially serve as building blocks for the development of computational thinking in students. An assessment plan with limited sample size has been described. The primary purpose of this paper to interest other thermodynamics instructors in the proposed presentation so that the assessment can be performed with a large number of students.

1. Pedagogical Problems with the Classical Presentation: The approximate sequence of the classical macroscopic presentation of second law concepts and results has not changed for more than a century. Figure 1 shows a schematic of the sequence of steps followed by engineering textbooks used in introductory thermodynamics courses over the last half-century, all based on the edifice constructed by Carnot, Clausius and Kelvin. The sequence commencing with the Kelvin-Planck/Clausius statements of the Second Law and culminating with Exergy analysis is long, sometimes spanning more than 200 pages in recent textbooks, complex and completely based on imaginary reversible processes. Although the classical presentation is stimulating in an abstract intellectual sense, it has a number of shortcomings from a pedagogical perspective:

a. Derivation is unrelated to application: Mathematical formulations for calculating exergy, entropy generation and irreversibilities follow from the Clausius inequality, all of which are derived from arguments that utilize imaginary reversible heat engines (RHEs) in imaginary situations. RHE efficiency in turn originates from a seemingly arbitrary choice of temperature function used to define the Thermodynamic Temperature Scale (TTS). Ultimately, all second law formulations are derived using infinitely slow reversible processes during which all properties are spatially uniform. The insight gained by following and understanding the derivation is not directly transferable to the second law analysis of any real system.

b. Specific-to-general approach: The derivations are undertaken with specific devices (heat engines) and processes (reversible processes) but students are expected to apply the second law to general problems that do not use these particular devices or processes, e.g. exergy analysis of a real (irreversible) fuel cell. This specific-to-general approach is an exception to the general pedagogical practice of deriving results for a general situation that is then applied to specific cases.
c. Entropy is an abstract concept: Determining the entropy change between two states requires traversing an imaginary reversible path between them. Entropy might have been an abstract concept in the twentieth century but it is defined, understood and used as a measure of dispersion in real systems, in many contemporary fields such as data mining and information theory. The proposed derivation is consistent with this modern approach; Entropy is defined at an infinitesimal point for a real process so that entropy generation is understood fundamentally in terms of dispersion of heat resulting from spatial non-uniformity.

d. Irreversibility is poorly understood: The classical presentation precedes the development of computational approaches that describe spatial non-uniformities. All derivations require spatially uniform (and therefore infinitely slow) processes. Irreversible processes are simply as processes that are not reversible. If future engineers are going to design devices with high second law efficiency by minimizing irreversibilities, they need to understand irreversibilities in terms of spatial non-uniformity of processes and properties.

Outside the universe of engineering textbooks, the second law has been expressed and formulated in many different ways for different audiences, e.g. works by Morales11, Macdonald12, Muschik13, Thomsen14 and Baerlein15. A discussion of different second-law approaches can be found in a review paper by Muschik16. None of these approaches address the four pedagogical shortcomings listed above; they are still based on RHE’s operating between temperature reservoirs. Many Introductory physics textbooks at the college level have modified their presentation of the second law by introducing entropy from a molecular perspective, while using an abridged version of the sequence shown in figure 1 to discuss only RHE’s (exergy is generally not covered). Some introductory physics textbooks17-20 skip the Clausius theorem altogether, and derive RHE efficiency starting from $\Delta S=0$. Others derive the Clausius theorem from RHE efficiency21, which is presented as the upper limit of efficiency (without the RHE corollaries presented in almost all engineering textbooks) after being derived for an ideal gas.

The motivation for the current work is to address the four shortcomings listed above by deriving all macroscopic second law results for any arbitrary real process involving heat and/or work transfer.

2. Proposed Derivation of Second Law Formulations for any Arbitrary (Real) Process

The derivation is divided into two parts; the Local Heat Category (LHC) equation introduced in this work is presented first. It is then used to derive the standard second-law results found in introductory textbooks.

2.1 Local Heat Category (LHC) Equation

Consider heat transfer across the surfaces of an infinitesimally small volume inside a finite control volume (CV) as shown in figure 1.

Energy transferred as heat at this infinitesimal point can be classified into three exclusive categories:

a. **Internal** heat transfer from another internal point excluding the external source. This positive heat transfer term will be denoted by $dQ^+$.

b. **Internal** heat transfer to another internal point excluding the external sink. This negative heat transfer term will be denoted by $dQ^-$.

c. **External** heat transfer from/to the external source/sink. This can happen at points located along the boundary of the CV, or through radiation to/from internal points. This term will be denoted by $dQ_{\text{boundary}}$. 

The terms of the LHC equation shown at an infinitesimal point inside a finite CV. Heat transferred from and to other interior points are denoted by $dQ^-$ and $dQ^+$ respectively. Heat transfer to or from external sources/sinks is denoted by $dQ_{\text{boundary}}$. For simplicity, each term has been shown to act across one face only. In general however, each term is comprised of flux from all faces, as per equation 2.

The net heat energy gained/lost at any point inside the CV is then given by:

$$\Delta Q = dQ^- + dQ^+ + dQ_{\text{boundary}}$$  

This is the Local Heat Category (LHC) equation. Each term represents the infinitesimal amount of energy transferred across the surfaces of an infinitesimal volume over an infinitesimal time duration. For example:

$$dQ^- = \sum_{i=1}^{n} q_i'' dA_i dt$$  

where $q_i''$ is the instantaneous negative heat flux across an infinitesimal surface of area $dA_i$. Heat energy rather than heat flux terms will be henceforth used because of simplicity, so equation (2) is not part of the derivation.

Since $dQ^-$ is internal by definition, every $dQ^-$ term across the surface of every infinitesimal point must be part of a $dQ^+$ term elsewhere (also internal by definition), and vice-versa, as shown simplistically by figure 2. The sum of all $dQ^-$ terms across all faces of all infinitesimal points must be equal in magnitude to the corresponding sum of $dQ^+$ terms. This is shown by equation (3):
Equation (3) simply says that the sum of positive internal heat transfer throughout the CV is equal to the sum of negative internal heat transfer. It can be integrated over a finite time duration:

\[ \int_{t_1}^{t_2} \int_{CV} dQ^- + \int_{t_1}^{t_2} \int_{CV} dQ^+ = 0 \]  

(4)

Note that the double integral produces finite terms because the \( dQ \) terms are products of two differential quantities as per equation (2). Second law results will be derived for finite processes, so double integral will be used henceforth.

An important result follows directly from equation (4), and the Second Law statement that heat transfer can only occur from higher to lower temperature. Since the temperature at the internal source(s) of the \( dQ^- \) term must exceed the temperatures at the locations corresponding to the \( dQ^+ \) term, \( \frac{dQ^-}{T} \) must be smaller than \( \frac{dQ^+}{T} \). Therefore:

\[ \int_{t_1}^{t_2} \int_{CV} \frac{dQ^-}{T} + \int_{t_1}^{t_2} \int_{CV} \frac{dQ^+}{T} \geq 0 \]  

(5)

because, the first term is positive while the second is negative. This result will be used later.

2.2 Derivation of \( ds \geq \frac{dQ}{T} \) for any Arbitrary (Real) Process

Consider any arbitrary process involving external heat transfer to or from any CV as shown in figure 1. Multiple heat sources and/or sinks might exist and external work may/may not be done on/by the CV. If \( q^{\text{source}} \) is the instantaneous heat flux at any point on the surface of the CV, then the net external heat transfer is given by:

\[ Q^{\text{External}} = \int_A q^{\text{source}} dA dt = \int_A \int_{CV} dQ^{\text{External}} \]  

(6)

The external heat flux is integrated over the surface area of the CV, denoted by \( A \). All of the external heat transfer must occur across the boundary of the CV. Therefore:

\[ \int_{t_1}^{t_2} \int_{CV} dQ^{\text{boundary}} = \int_{t_1}^{t_2} \int_A dQ^{\text{External}} \]  

(7)

where \( dQ^{\text{boundary}} \) is the last term of the LHC equation, see equation (1). Note that integration of \( dQ^{\text{boundary}} \) over the CV implies integration over the surfaces of infinitesimal points as per equation (2). This leads to the second important result following equation (5):

\[ \int_{t_1}^{t_2} \int_{CV} \frac{dQ^{\text{boundary}}}{T} \geq \int_{t_1}^{t_2} \int_A \frac{dQ^{\text{External}}}{T} \]  

(8)
The argument identical to the one used to obtain equation (5); the temperature of any boundary point inside the CV has to be lower than the external source temperature, or higher than the external sink temperature. For the latter case, the left-hand-side will be a smaller negative number than the right-hand-side.

Adding the two important results, equations (5) and (8):

$$
\iint \int \int \int \int \int \int \frac{dQ^+}{T} + \iint \int \int \frac{dQ^-}{T} + \iint \int \int \frac{dQ^{\text{boundary}}}{T} \geq \iint \int \int \frac{dQ^{\text{External}}}{T} \quad (9)
$$

Re-organizing terms and using the LHC equation (1), we obtain:

$$
\iint \int \frac{dQ^+ + dQ^- + dQ^{\text{boundary}}}{T} = \iint \int \frac{dQ^-}{T} \geq \iint \int \frac{dQ^{\text{External}}}{T} \quad (10)
$$

If the term $\frac{dQ}{T}$ is denoted by the variable $dS$:

$$
\iint dS \geq \iint \frac{dQ^{\text{External}}}{T} \quad (11)
$$

It can be easily shown that the variable $dS$ is a point function; therefore ‘S’ is a property that will be called entropy. Equation (11) is the familiar mathematical statement of the second law, derived from heat engine arguments in the classical presentation. The proposed approach reverses this specific-to-general approach, and uses equation (11) to derive all the mathematical results of the second law, including reversible heat engine (RHE) efficiency, as illustrated in the next sub-section 3.3.

2.3 Mathematical Results Following from the Equation (11)

For any cyclic process, the property change $\Delta S=0$ and equation (11) reduces to the Clausius Inequality:

$$
\iint \frac{dQ^{\text{External}}}{T} \leq 0 \quad (12)
$$

It is evident that in order to convert heat into work, at least one heat sink would be required in order for the left-hand-side to be negative. This is consistent with the Kelvin-Planck statements of the second law. For the limiting case where the CV encloses a cyclic and reversible heat engine (RHE) operating between a single source and a single sink of constant temperature, equation (12) reduces to:

$$
\frac{\Delta Q^{\text{Source}}}{T^{\text{Source}}} + \frac{\Delta Q^{\text{Sink}}}{T^{\text{Sink}}} = 0 \quad (13)
$$

This results in the familiar expression for the thermal efficiency of a RHE operating between two temperature reservoirs:

$$
\eta_{\text{reversible}} = 1 - \frac{T^{\text{Source}}}{T^{\text{Sink}}} \quad (14)
$$
The second law equation (11) can also be used to determine the exergy of a substance. If the CV encloses the substance (without a heat source), it can be seen that a heat sink will be required to achieve a change of state, i.e. non-zero $\Delta S$. Equation (11) then integrates to:

$$\Delta S \geq \frac{\Delta Q_{\text{sink}}}{T_o}$$ \hspace{1cm} (15)

where $\Delta S$ corresponds to the change between current and dead state. Maximum work production will correspond to minimum heat rejection, i.e. the limiting equality corresponding to an imaginary reversible process:

$$\Delta Q_{\text{reversible}}^{\text{Sink}} = T_o \Delta S$$ \hspace{1cm} (16)

The mathematical expressions for exergy of any closed or open system readily follow from equation (16) when combined with the first law. The $\Delta S$ term must include the entropy change of the flow terms if mass crosses the CV boundaries.

3. Pedagogical Implications of Proposed Derivation: The proposed derivation makes it easier to understand (ir)reversibility, entropy, entropy generation and exergy destruction in real and arbitrary systems that are not heat engines. The only second law statement used for the derivation is that heat is transferred from higher to lower temperatures. Students understand this intuitively and can appreciate that everything else follows from this. Reversibility can be mathematically defined using the LHC equation as any process in which:

$$dQ^- = dQ^+ = 0$$ \hspace{1cm} (17)

at every point and every instant throughout the process. This is because every kind of irreversibility within a CV, including frictional dissipation, will ultimately result in irreversible internal heat transfer. The definition unites the different kinds of irreversibilities that are described in current textbooks as any process violating equation (17). In that case it is easy to see that every violation results in the loss of work potential. The differential amount of exergy lost when $dQ^-$ becomes $dQ^+$ across temperature difference $dT$ can be easily derived from equation (14):

$$dX = \frac{dQ^+}{T^2}dT$$ \hspace{1cm} (18)

Students can then understand why reversible processes conserve work potential while irreversible processes do not. They can appreciate that $dQ^+$ and $dQ^-$ terms will be non-zero for a real process, but minimizing them can reduce exergy destruction. They can intuitively understand that $dQ^+$ and $dQ^-$ terms can be minimized by minimizing temperature gradients within the system, by designing processes that are spatially uniform. For example, the exergy destruction in any combusting system is greatly reduced if combustion occurs uniformly throughout the combustion chamber.

Entropy is defined at an infinitesimal point, see equation (11), and calculating entropy change does not require a parallel reversible process. Entropy generation can be understood to result from $\frac{dQ^+}{T}$ and $\frac{dQ^-}{T}$ terms, and ultimately from spatial non-uniformity. A more detailed discussion of defining entropy in this manner can be found elsewhere, and is best suited to a graduate thermodynamics course.
The derivation can also be used to reduce confusion between the different temperature scales. Unlike the classical presentation which requires defining a Thermodynamic Temperature Scale (TTS), see figure 1, the proposed derivation can be based on the more easily understood Ideal Gas Temperature Scale (IGTS). The TTS (or the Kelvin scale) can then be derived from equation (14) to show that the IGTS coincides with the TTS. Again, the reader is pointed elsewhere for a more detailed discussion on this topic.

4. Assessment: A simple assessment method would be to compare two cohorts of students who have been taught the classical and proposed presentations respectively, using a well-validated measurement tool. One such tool is the Concept Inventory for Engineering Thermodynamics (CIET) developed by Vigeant et al. Reliability data for the CIET was collected from 15 institutions nationwide. This data shows that the CIET has sufficient reliability to be used as a research instrument for post-testing. No pre-testing is being proposed in the current work. At the author’s institution, classes in mechanical engineering run double sections because classes are capped at 24 students. Hence the CIET will be administered to both sections but only one section will be instructed using the proposed presentation. The primary purpose of this paper is to interest other thermodynamics instructors in the proposed presentation so that the assessment can be performed with a large number of students, and the normal distribution can be used (not possible with n=24) to assess the effect of the proposed approach on the population of students studying thermodynamics.

5. Conclusions: A number of shortcomings in the classical presentation of the second law of thermodynamics as found in contemporary engineering textbooks have been pointed out from a pedagogical perspective. A new presentation that uses thought experiments about real rather than imaginary processes to derive second-law results has been proposed. The proposed derivation has conceptual implications. The effectiveness of the proposed presentation can therefore be measured using a reliable concept inventory. The author urges fellow thermodynamics instructors to examine the problem described, and consider an educational experiment with the proposed solution.

REFERENCES


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