



Serrin's accumulation function, the First and the Second Laws of Thermodynamics

R.R. Huilgol

College of Science and Engineering, Flinders University of South Australia, GPO Box 2100, Adelaide, SA 5001, Australia

ARTICLE INFO

Keywords:

Temperature
Thermodynamic systems. First and Second Law
Accumulation function
Engineering cycles

ABSTRACT

Beginning in 1979, the First and Second Laws of Classical Thermodynamics were given a new lease of life through the researches of Serrin. The definition of a positive, empirical temperature scale was shown to depend on the ideas of Maxwell and Mach. Next, a thorough description of thermodynamical systems and product systems was given, and the internal energy was defined as a function which acts as a lower potential for the difference between the heat transferred and the work done for each process. Using simple mathematics and the First Law for cycles, the existence of the internal energy function for reversible systems was derived through a well known theorem from multivariable calculus. Further, the accumulation function which defines the heat transferred between the working substance and its surroundings up to and equal to a given temperature was introduced. From this, it emerged that Clausius' inequality for a cycle was equivalent to an integral inequality involving the accumulation function over the open, positive real numbers. It was demonstrated that this inequality leads to the definition of the absolute temperature scale. From this, entropy was defined as an upper potential to the integral appearing in the Accumulation Theorem, for each process. The existence of the entropy function for reversible processes was also proved. In addition, it was shown by Huilgol that the First Law for a cycle can be represented by an inequality, which places bounds on the work done in a cycle. Moreover, the First Law and the entropy function derived from the Second Law can be used to derive an upper bound on the work done in a cycle which is sharper than that due to Carnot. Specifically, if the cycle is irreversible, the bound includes the product of the change in entropy over the adiabatic parts of the cycle, with the least value of the absolute temperature over the heat rejecting part. In the work presented here, these ideas will be explored with a view to incorporating them, along with newer versions of the Second Law due to Serrin, in the standard curriculum of thermodynamics. In order to facilitate this inclusion, explicit forms for the accumulation function in the Otto, Diesel, Stirling and Ericsson cycles are derived.

1. Introduction

In his Lecture Notes, Serrin (1984) remarked that classical “thermodynamics contains three of the brightest jewels in the diadem of science: the magnificent discovery of the equivalence of work and heat, the strikingly beautiful definition of the absolute temperature scale, and the unexpected, unheralded, but portentous entry onto the scene of that most remarkable of all state functions, entropy.” These words reflected his views after he began to put into simple, but elegant, form the Second Law of thermodynamics in 1979 (Serrin, 1979). In that pioneering work, the mathematics was kept to the barest minimum to introduce the concept of the accumulation function, $Q(P, \theta)$, which is the amount of heat transferred between the working substance and its surroundings up to and equal to a given temperature θ , in any process P . Serrin went on to show that if the integral of $(Q(P, \theta)/\theta^2)$ over the interval $(0, \infty)$ is less than or equal to zero, it leads to the definition of the absolute temperature; that this integral inequality is

the same as Clausius inequality for a cycle; and that the integral of $(Q(P, \theta)/\theta^2)$ over a reversible cycle leads to the definition of entropy. Later on, in 1986, Serrin (1986) provided a fresh statement of the First Law of thermodynamics: if a positive amount of work is done during a homogeneous cycle, the heat transfer during the cycle is also positive, and vice versa. Finally, he gave a precise meaning to quasi-static processes in thermodynamics (Serrin, 1995).

The purpose of this article is to re-examine the concepts of thermodynamics basing most of the arguments on the researches of Serrin. In Section 2, the concept of temperature, θ , is developed using the ideas of Mach and Maxwell. It is also shown that any empirical temperature scale can be turned into one over the positive real axis, i.e., $\theta \in (0, \infty)$. In Section 3, borrowing the ideas from Serrin (Serrin, 1979, 1986), a definition of a thermodynamic system is provided. This system admits a set of processes, which include reversible cycles. The work done by the

E-mail address: Raj.Huilgol@flinders.edu.au.

<https://doi.org/10.1016/j.apples.2021.100057>

Received 15 December 2020; Received in revised form 20 April 2021; Accepted 29 May 2021

Available online 24 July 2021

2666-4968/© 2021 The Author.

Published by Elsevier Ltd This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

material and the heat transfer to it in a process are deemed to be well defined. In addition, the product system of any two thermodynamic systems is defined, giving a precise meaning to the ideas due to Carnot. Moreover, the path followed by a process in the state space associated with the thermodynamic system is defined, along with the work done and the heat transferred along this path.

In Section 4, it is shown that the First Law for a cycle implies an inequality for the work done in it; in particular, an integral similar to the Clausius integral appears in the upper and lower bounds on the work done in a cyclic process, W_c . Moreover, four important temperatures appear in the inequality, viz., the two extrema of temperatures in the heat absorbing processes of the cycle and the other two extrema in the heat rejecting processes. Next, the internal energy function is defined as a lower potential to the difference between the heat transferred and the work done in a process, P . The internal energy function is proven to exist in a reversible process and a formula to determine it is obtained.

In Section 5, the concept of the accumulation function, $Q(P, \theta)$, due to Serrin (1979), is introduced and the forms taken by it when heat is absorbed and when it is rejected are explained. Next, it is shown that the integral of $(Q(P, \theta)/\theta^2)$ over $(0, \infty)$ is the same as that of (dQ/θ) . A second derivation of this equivalence due to Serrin (1984, 1986) is also given. In Section 6, the various forms of the Second Law due to Clausius, Kelvin and Planck are examined and shown to be derived from those due to Serrin (1984, 1979, 1986). Next, the Accumulation Theorem (Serrin, 1979) is stated which has wide ranging implications, including making precise the status of the absolute temperature, T , in thermodynamics. Finally, the entropy function is defined as an upper potential to the integral of $(Q(P, T)/T^2)$ over $(0, \infty)$ in any process P . Once again, the existence of the entropy function can be proved for reversible cycles and processes.

In Section 7, the accumulation functions for four important cycles in thermodynamics, viz., the Otto, Diesel, Stirling and Ericsson cycles, are derived. In particular, the graph of this function is drawn for the Otto cycle to highlight its form. In Section 8, bounds for the work done in a cycle using the existence of the internal energy and entropy functions are obtained. Specifically, this leads to a bound for the work done in an irreversible cycle in which the least temperature over the heat rejecting part of the cycle, and the increase in entropy over the adiabatic process appear. This bound for the work done in a cycle is sharper than that due to Carnot.

Finally, in Section 9, some remarks are offered to summarise the contents of the paper, with a hope that they will lead to a revision of the major texts in engineering thermodynamics, for the mathematical apparatus needed to understand the material presented here forms a part of the usual engineering curriculum.

2. Temperature

The concepts of thermometry and heat transfer between two bodies are central to thermodynamics. Whether they are based on Maxwell's law of equal temperatures (Maxwell, 1872) or on Mach's statement about the sensations of heat (Mach, 1986), one needs to define the temperature of a body. The latter is more perceptive for he (Mach, 1986) stated on page 7 that:

“Of the sensations which we assume to be provoked in us by surrounding bodies, the sensations of heat (cold, cool, tepid, warm, hot) form a distinct series or a particular class of elements bearing a definite relationship to one another. The bodies which produce these sensations likewise exhibit, both as to themselves and as to other objects, a distinctive physical behaviour definitely associated with these sense marks. A very hot body glows, gives forth light, melts, evaporates, or burns away; a cold body congeals. A drop of water on a hot plate evaporates with a hissing noise: on a cold plate it freezes, and so on. The collection of these instances of the physical behaviour of a body, which are connected with the mark of our sensations of heat – the collection of reactions – is termed its thermal state or state with respect to heat.”

On page 48, he says:

“Our sensations of heat,, form a simple series, a simple continuous manifold;”

On pages 53–54, we find that:

“It is remarkable how long a period elapsed before it definitely dawned upon inquirers that the designation of thermal states by numbers rests on a convention.”

Finally, on page 72, Mach (1986) says that:

“The temperature numbers of the common scale are virtually inventorial numbers of the thermal states.”

Motivated by this, Serrin (1979, 1986) has proposed that the concept of hotness be considered as a primitive notion within thermodynamics. This is represented by a *thermal manifold* \mathcal{H} consisting of the set of *hotness levels* L open to material systems. The manifold \mathcal{H} is a *totally ordered set*, with the order relation $>$ corresponding to increased levels of hotness. That is, for any two different hotness levels L_1 and L_2 in \mathcal{H} , either $L_2 > L_1$ or $L_1 > L_2$, not both. In addition, if $L_3 > L_2$ and $L_2 > L_1$, then $L_3 > L_1$. That is, the order is transitive.

Next, the relation $L_2 > L_1$ will be read as “ L_2 is hotter than L_1 ”; alternatively, as “ L_1 is colder than L_2 .” One writes $L_2 \geq L_1$ to indicate that either $L_2 > L_1$, or $L_2 = L_1$.

It is possible to argue that the existence of a hotness manifold has to be proven, not assumed. In this connection, we note that Fosdick and Rajagopal (1983) proposed several axioms to prove the existence of a manifold for temperature and a universal temperature space. They were influenced by the fact that the sensation of heat is experienced through its conduction from one person to another person or from a body to another; radiation plays a similar role. In particular, the following extracts from page 32 of the book by Maxwell (1872) were decisive (Fosdick and Rajagopal, 1983):

“If when two bodies are placed in thermal communication, one of the bodies loses heat, and the other gains heat, that body which gives out heat is said to have a higher temperature than that which receives heat from it..... If when two bodies are placed in thermal communication neither of them loses or gains heat, the two bodies are said to have equal temperatures or the same temperature. The two bodies are then said to be in thermal equilibrium.” This statement, which was reproduced in Serrin (1979), is better known as the Zeroth Law of Thermodynamics.

In the sequel, we shall follow Serrin (1979, 1986) and proceed. Any temperature scale is a strictly increasing map from \mathcal{H} into the reals \mathbb{R} . If ϕ is a temperature scale, then $\phi(L)$ is called the *temperature* of L in the scale ϕ . Thus, in general, the temperature $\phi(L)$ of all of the hotness levels in the thermal manifold \mathcal{H} is such that $-\infty < \phi(L) < \infty$. Since most of the thermodynamics is based on a positive temperature scale, the assumption that the empirical temperature $\phi(L)$ may take on negative values can be circumvented by creating a positive empirical temperature scale θ , such that $0 < \theta < \infty$, through

$$\theta(L) = e^{\phi(L)}. \quad (2.1)$$

Hence, we assume that all values of the temperature are positive. Moreover, we accept that if two positive numbers θ_1 and θ_2 are such that if $\theta_2 > \theta_1$, it follows that θ_2 represents a state of hotness higher than that represented by θ_1 , or that θ_1 represents a state of hotness lower than θ_2 .

3. Thermodynamical systems

Following Serrin (1979, 1986), we turn to the definition of a *thermodynamic system*. For example, consider a body of gas or an elastic solid. Such a system S is endowed with a set $\mathbb{P}(S)$ of *processes*, denoted by P, R, S , etc., which the system may undergo. The set \mathbb{P} of processes has a subset $\mathbb{P}_c(S)$ of reversible and irreversible cycles.

In thermodynamic applications, we assume that the system S is endowed with a finite dimensional state space Σ , which is an open

connected subset of \mathbb{R}^n . A process $P \in \mathbb{P}(S)$ has a unique corresponding path Γ ,

$$\Gamma : I \rightarrow \Sigma, \tag{3.1}$$

where $I = [a, b]$ is a closed time interval, and the function $t \rightarrow \Gamma(t)$ is piecewise smooth. There are other ways of classifying a process, such as that used extensively in thermodynamic cycles. Here, the cycle consists of four processes depicted in the (V, p) plane, where V is the volume of the working substance and p is the corresponding pressure. Each adiabatic process in such a cycle can be described through a function, $p = p(V)$.

To each process P , there are two primitive concepts expressed through real numbers, viz., the work done $\overline{W}(P)$ by the process and the heat transferred $\overline{Q}(P)$ to the process. That is,

$$\overline{W} : \mathbb{P}(S) \rightarrow \mathbb{R}, \tag{3.2}$$

$$\overline{Q} : \mathbb{P}(S) \rightarrow \mathbb{R}. \tag{3.3}$$

We adopt the convention that if $\overline{W}(P) > 0$, the thermodynamic system does work on the surroundings; if $\overline{W}(P) < 0$, work is done on the material. The work done in a cycle is denoted by $\overline{W}_c(P)$. Turning to the heat transfer in a process, if $\overline{Q}(P) > 0$, the working substance absorbs heat from the surroundings; if $\overline{Q}(P) < 0$, the material rejects heat to the surroundings. The heat transfer in a cycle is denoted by $\overline{Q}_c(P)$. To be succinct, we shall adopt the notation that the work done and the heat transfer in a cyclic process (or a cycle) are given, respectively, by W_c and Q_c .

A further structural concept that is needed is that of a process or a cycle following from a former one. On pages 10–11 of his memoir, Carnot (1960) considered the motive power that can be produced by transferring heat from a hotter body to a colder one, and that required to perform the reverse. These two processes did not require that the working substances to be the same. Additional explanations of these ideas were given by Carnot on pages 17–22 of his work (Carnot, 1960).

A precise wording of these statements, due to Serrin (1979, 1986), is as follows. Let S_1 and S_2 be a pair of thermodynamical systems. The product system, $S_1 \oplus S_2$ is defined by its processes, their work done and their heat transfers. They are required to satisfy the following conditions:

1. $\mathbb{P}(S_1 \oplus S_2) = \mathbb{P}(S_1) \times \mathbb{P}(S_2)$
2. $\mathbb{P}_c(S_1 \oplus S_2) = \mathbb{P}_c(S_1) \times \mathbb{P}_c(S_2)$
3. $\overline{W}(P_1 \oplus P_2) = \overline{W}(P_1) + \overline{W}(P_2)$
4. $\overline{Q}(P_1 \oplus P_2) = \overline{Q}(P_1) + \overline{Q}(P_2)$

Here, $P_1 \oplus P_2$ denotes the union process in $\mathbb{P}(S_1 \oplus S_2)$ corresponding to the pair of processes $P_1 \in \mathbb{P}(S_1)$, $P_2 \in \mathbb{P}(S_2)$ and \times denotes the Cartesian product.

An example of a cycle that repeats itself, over and over again, arises in internal combustion engines. Clearly, the work done and the heat transferred in n -cycles, $W^n(\mathbb{P}_c)$ and $Q^n(\mathbb{P}_c)$ respectively, can be found as follows:

$$\overline{W}_c^n(P) = n \times \overline{W}_c(P), \quad \overline{Q}_c^n(P) = n \times \overline{Q}_c(P), \tag{3.4}$$

where $n \in \mathbb{N}$.

An example of a product system can be found in liquid metal cooled fast breeder reactors, where the heat from the reactor is absorbed by a metal in a liquid state and this heat is supplied to water, turning it into steam. The cooled metal is returned to the reactor, undergoing a cycle. The steam is used to drive a turbine to generate electricity, with the exhausted steam cooled down to be part of a second cyclic process.

We assume that S consists of a set Σ , whose elements are called the states of the system. There is a corresponding family of processes $\mathbb{P}_\Sigma(S) \subset \mathbb{P}(S)$, with each process having a well-defined initial state $A \in \Sigma$ and a final state $B \in \Sigma$. Of course, for each process P , there exist two real numbers, viz., the work done $\overline{W}(P)$ and the heat transferred $\overline{Q}(P)$. There is no simple procedure to calculate these two quantities,

for they depend on the constitutive equations of the working substance and the equations of continuum mechanics.

Finally, we turn to reversible systems. Here, the system S is endowed with a finite dimensional state space Σ , which is a connected open subset of \mathbb{R}^n . For each process $P \in \mathbb{P}(S)$, there is a unique path Γ associated with it in Σ , i.e.,

$$\Gamma : I \rightarrow \Sigma, \tag{3.5}$$

where $I = [a, b]$ is a closed time interval and the function $t \rightarrow \Gamma(t)$ is piecewise smooth. The path of a reversible cyclic process is closed, i.e., $\Gamma(a) = \Gamma(b)$.

It is also assumed that there are two differential forms dw and dq defined on Σ , with continuous coefficients. These two lead to the work done and the heat transferred in a process as follows:

$$\overline{W}(P) = \int_\Gamma dw, \quad \overline{Q}(P) = \int_\Gamma dq, \tag{3.6}$$

with Γ being the path corresponding to P .

4. The First Law of Thermodynamics

In June 1845, Joule read his paper, *On the Mechanical equivalent of Heat*, to the British Association at Cambridge. In this report, he described the results of his experiments on the conversion of mechanical work into heat. These experiments had measured the work done by a falling weight due to gravity which, in turn, was used to spin a paddle wheel in an insulated barrel of water, resulting in an increase in temperature of the water. That is, he was able to estimate the mechanical work done in foot-pounds to produce a British Thermal Unit (BTU) of heat.

These experiments and subsequent ones performed with greater precision led to the acceptance that there exists a universal constant $J > 0$, better known as *the mechanical equivalent of heat*, such that $W_c = JQ_c$ for any cyclic process of a thermodynamical system. This equality is called the First Law of Thermodynamics.

For ease of presentation in this work, we shall assume that $J = 1$ and the First Law now becomes:

$$W_c = Q_c. \tag{4.1}$$

In the above formulation, what matters is the amount of heat received and rejected in a cycle, and the work done. The range of temperatures across which heat is absorbed or rejected is of secondary importance. To emphasise this, consider the comments by Gibbs (1961):

“In thermodynamic problems, heat received at one temperature is by no means the equivalent of the same amount of heat received at another temperature. For example, a supply of a million calories at 150° is a very different from a supply of million calories at 50°. But no such distinction exists in regard to work. This is a result of the general law, that heat can only pass from a hotter body to a colder body, while work can be transferred by mechanical means from one fluid to any other, whatever may be the pressures (emphasis added). Hence, in thermodynamic problems, it is generally necessary to distinguish between the quantities of heat received or given out by the body at different temperatures, while as far work is concerned, it is generally sufficient to ascertain the total amount performed.”

These words are taken from Serrin (1979). Elsewhere, on page 29, Serrin (1984) has remarked that the word pressures above is incorrect; and that Gibbs must have meant temperatures (emphasis added) instead.

We shall now demonstrate that the First Law for cycles implies an inequality in which the range of temperatures in the cycle appear, and that an integral similar to the Clausius integral appears. That is, the First Law anticipates, as it were, the importance of this integral in the Second Law as remarked by Huilgol (1979).

We can split Q_c into the heat absorbed by the working substance in a cyclic process, $Q_c^+ \geq 0$; and the heat rejected during the cycle, $Q_c^- \geq 0$. That is,

$$Q_c = Q_c^+ - Q_c^-. \tag{4.2}$$

Hence, the First Law for a cycle becomes

$$W_c = Q_c^+ - Q_c^- \tag{4.3}$$

To begin, consider a thermodynamic cycle over a temperature range $[\theta_1, \theta_2]$, defined through an empirical positive temperature scale such that $0 < \theta_1 \leq \theta \leq \theta_2 < \infty$. Let the finite time interval $I = [0, 1]$ of the cycle be denoted by $I = I^+(t) \cup I^-(t) \cup I^0(t)$, $0 \leq t \leq 1$. That is, I is a disjoint union of the three sub-intervals. We define $I^+(t)$ as the time interval where the rate of heat transfer, $\dot{q}(t) > 0$; on the interval $I^-(t)$, one has $\dot{q}(t) < 0$; and, finally, on $I^0(t)$, the process is adiabatic and $\dot{q}(t) = 0$. Of course, one or two of the sub-intervals may be empty. Now, it is easy to see that (Huilgol, 1979; Diaz, 1978):

$$\frac{Q_c^+}{\theta_2} \leq \int_{I^+(t)} \frac{\dot{q}(t)}{\theta(t)} dt \leq \frac{Q_c^+}{\theta_1}, \tag{4.4}$$

$$\frac{Q_c^-}{\theta_2} \leq \int_{I^-(t)} \frac{(-\dot{q}(t))}{\theta(t)} dt \leq \frac{Q_c^-}{\theta_1}. \tag{4.5}$$

Since $\dot{q}(t) = 0$ over the adiabatic time interval $I^0(t)$, one obtains

$$\int_I \frac{\dot{q}(t)}{\theta(t)} dt = \int_{I^+(t)} \frac{\dot{q}(t)}{\theta(t)} dt - \int_{I^-(t)} \frac{(-\dot{q}(t))}{\theta(t)} dt. \tag{4.6}$$

Now, noting the relevant negative signs, rewrite (4.5) as:

$$-\frac{Q_c^-}{\theta_1} \leq - \int_{I^-(t)} \frac{(-\dot{q}(t))}{\theta(t)} dt \leq -\frac{Q_c^-}{\theta_2}. \tag{4.7}$$

Combining (4.4), (4.6) and (4.7), we see that

$$\frac{Q_c^+}{\theta_2} - \frac{Q_c^-}{\theta_1} \leq \int_I \frac{\dot{q}(t)}{\theta(t)} dt \leq \frac{Q_c^+}{\theta_1} - \frac{Q_c^-}{\theta_2}. \tag{4.8}$$

Next, consider a *regular thermodynamic cycle* where $Q_c^+ > 0$ and $Q_c^- > 0$. That is, a positive amount of heat is absorbed as well as rejected in the cycle. It will be seen that one needs two different temperatures over I_c^+ , where heat is absorbed. These are the respective maximum and minimum: θ_{\max}^+ , θ_{\min}^+ . Similarly, over I_c^- , where heat is rejected, there are two more different temperatures: θ_{\max}^- , θ_{\min}^- . Using these in (4.4) and (4.7), we get

$$\frac{Q_c^+}{\theta_{\max}^+} \leq \int_{I_c^+} \frac{\dot{q}(t)}{\theta(t)} dt \leq \frac{Q_c^+}{\theta_{\min}^+}, \tag{4.9}$$

$$-\frac{Q_c^-}{\theta_{\min}^-} \leq - \int_{I_c^-} \frac{(-\dot{q}(t))}{\theta(t)} dt \leq -\frac{Q_c^-}{\theta_{\max}^-}. \tag{4.10}$$

Thus, we obtain (cf. (4.8)):

$$\frac{Q_c^+}{\theta_{\max}^+} - \frac{Q_c^-}{\theta_{\min}^-} \leq \oint_I \frac{\dot{q}(t)}{\theta(t)} dt \leq \frac{Q_c^+}{\theta_{\min}^+} - \frac{Q_c^-}{\theta_{\max}^-}. \tag{4.11}$$

Hence, the *First Law for a regular cycle implies the inequality* obtained by Huilgol (1979):

$$\left[1 - \frac{\theta_{\max}^-}{\theta_{\min}^+}\right] Q_c^+ + \theta_{\max}^- \oint_I \frac{\dot{q}(t)}{\theta(t)} dt \leq W_c \leq \left[1 - \frac{\theta_{\min}^-}{\theta_{\max}^+}\right] Q_c^+ + \theta_{\min}^- \oint_I \frac{\dot{q}(t)}{\theta(t)} dt, \tag{4.12}$$

where not only do the heat absorbed and the heat rejected appear, so do the four important temperatures in a cycle. Moreover, the First Law and the resulting inequality show us why the integral, $\oint (\dot{q}(t)/\theta(t))dt$, which is similar to the Clausius integral, plays a crucial role in thermodynamics.

We shall now consider the First Law applicable to a process. To address this question, we say that the system S has an *internal energy* associated with the state structure $(\Sigma, \mathbb{P}_\Sigma)$ if there exists a function (Serrin, 1986)

$$U : \Sigma \rightarrow \mathbb{R}, \tag{4.13}$$

such that $\Delta U = U(P_f) - U(P_i)$ is the difference between its final and initial values for each process P , and

$$\Delta U \leq \overline{Q}(P) - \overline{W}(P) \tag{4.14}$$

for each process $P \in \mathbb{P}_\Sigma(S)$. That is, the function U acts as a *lower potential* for the difference between the heat transferred and the work done. Is the internal energy unique?

To answer this, Serrin (1986) argued as follows. Let there exist a base state $\sigma_0 \in \Sigma$ such that for each state $\sigma \in \Sigma$, there exists at least one strongly reversible process P with initial state σ_0 and final state σ . In a strongly reversible process, ΔU satisfies the equality:

$$\Delta U = \overline{Q}(P) - \overline{W}(P). \tag{4.15}$$

Now, U is unique to within a constant, say its initial value at σ_0 .

Finally, does the internal energy U exist for reversible systems, defined in Section 3 above? The answer lies in considering a reversible cycle, and appealing to (3.6). That is, let P_c be a cyclic process and let Γ_c be a closed smooth path associated with it. By the First Law, it follows from (3.6) that

$$\oint_{\Gamma_c} dq = \oint_{\Gamma_c} dw. \tag{4.16}$$

Hence, the differential form $dq - dw$ is exact and there exists a continuously differentiable function U such that

$$dU = dq - dw. \tag{4.17}$$

Thus, for any process P of a reversible system, we see that (4.15) holds, i.e.,

$$\overline{Q}(P) - \overline{W}(P) = \int_\Gamma dq - \int_\Gamma dw = \int_\Gamma dU = \Delta U. \tag{4.18}$$

The conditions under which (4.15) holds, due to Serrin (1986), have to be contrasted with those usually found in the textbooks on engineering thermodynamics.

5. Serrin's accumulation function

Since the range of temperatures have been shown to be important in a cycle, it is necessary to re-examine the role played by the temperature in any process more carefully. Here, motivated by Gibbs' comments, it is clear that one needs a more refined and subtle measure of this heat transfer in which the role of the temperature is paramount. In this context, the *accumulation function* defined by Serrin (1979) plays a crucial role and we turn to this next.

The accumulation function describes the total or net heat transferred to the body in a process P up to a hotness level L' less than or equal to L . If we accept that a positive temperature scale has been chosen, as stated in §2, we can define:

$$Q : \mathbb{P}(S) \times \phi \rightarrow \mathbb{R}. \tag{5.1}$$

The function $Q(P, \cdot)$ is called the *accumulation function* of the process P . That is, given a process P and a temperature θ during the process, $Q(P, \theta)$ is the total or net heat transferred the body in that process up to any temperature less than or equal to θ .

Now, in any process, no heat is exchanged up to a temperature θ_l . And, heat is exchanged up to a higher temperature θ_h and none after. So, one can see that

$$Q(P, \theta) = 0, \quad 0 < \theta < \theta_l; \quad Q(P, \theta) = \overline{Q}(P), \quad \theta_h \leq \theta < \infty. \tag{5.2}$$

where $\overline{Q}(P)$ is the heat transferred in the process P . In the interval $\theta_l \leq \theta \leq \theta_h$, one has to define the way heat is exchanged by the body with its surroundings; for example, consider a constant volume process in an ideal gas.

This function $Q(P, \cdot)$ has some unusual features. First of all, consider an isothermal process at a constant temperature θ_c . Here,

$$Q(P, \theta) = 0, \quad 0 < \theta < \theta_c; \quad Q(P, \theta) = Q(P, \theta_c) = \overline{Q}(P), \quad \theta_c \leq \theta < \infty. \tag{5.3}$$

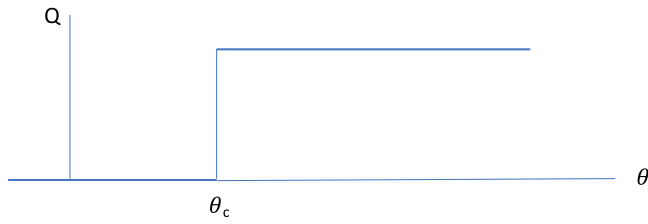


Fig. 1. Accumulation function Q in an isothermal process at a temperature of θ_c .

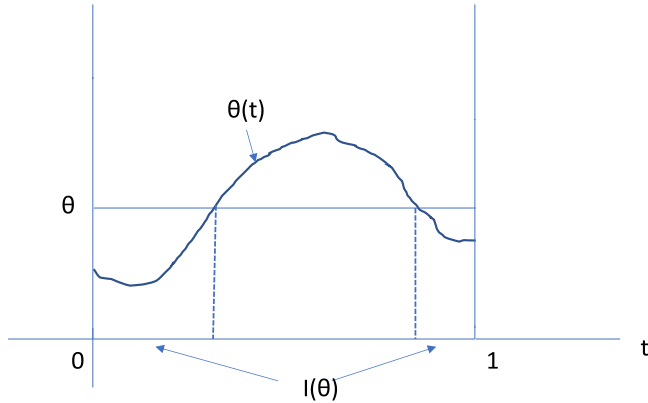


Fig. 2. Process in the (t, θ) plane, with the interval of $I(\theta)$ where $\theta(t)$ is less than or equal to θ .

That is, the function $Q(P, \theta)$ suffers a jump at the temperature $\theta = \theta_c$. Thus, the function $Q(P, \theta)$ is right-continuous. See Fig. 1 for a depiction of this function.

We have yet to consider the definition of the accumulation function in two separate cases: one of heat absorption and another of rejection. Following the approach of Pradas (1994), we define

$$\int_0^\theta dQ^+(P, \xi) = Q^+(P, \theta) \tag{5.4}$$

as the heat absorbed by a body during the process P up to and including the temperature θ . Here, $dQ^+(P, \xi)$ is the infinitesimal amount of heat absorbed by the body in the process P at the temperature ξ , where $0 \leq \xi \leq \theta$.

It follows therefore that if θ_l^+ is the lowest temperature at which any heat is absorbed by the body, we have:

$$Q^+(P, \theta) = 0, \quad 0 < \theta < \theta_l^+. \tag{5.5}$$

If θ_u^+ is the highest temperature at which heat is absorbed by the body, we have:

$$Q^+(P, \theta) = Q^+(P, \theta_u^+) = \bar{Q}^+(P), \quad \theta_u^+ \leq \theta < \infty, \tag{5.6}$$

where $\bar{Q}^+(P)$ is the heat absorbed by the body in the process P . Note that $\bar{Q}^+(P)$ is now a constant. Thus, in any interval $[\theta_l^+, \theta_u^+]$, we can define

$$\bar{Q}^+(P) = Q^+(P, \theta_u^+) - Q^+(P, \theta_l^+), \tag{5.7}$$

as the heat absorbed by the body during the process P . Similarly, during a process up to and including the temperature θ , we define

$$\int_0^\theta dQ^-(P, \xi) = Q^-(P, \theta) \tag{5.8}$$

as the heat emitted during the process. Once again, $dQ^-(P, \xi)$ is the infinitesimal amount of heat emitted by the body in the process P at the temperature ξ , where $0 \leq \xi \leq \theta$.

Thus, the heat emitted during a process P in the interval $[\theta_l^-, \theta_u^-]$ is given by

$$\bar{Q}^-(P) = Q^-(P, \theta_u^-) - Q^-(P, \theta_l^-). \tag{5.9}$$

Note that the differentials, $dQ^+(P, \xi)$ and $dQ^-(P, \xi)$, are both positive and usually different. For instance, in a Diesel cycle, heat is absorbed at a constant pressure and rejected at a constant volume.

From the foregoing, the net heat exchanged in a process up to and including the temperature θ can be defined as the function

$$Q(P, \theta) = Q^+(P, \theta) - Q^-(P, \theta). \tag{5.10}$$

This is Serrin's accumulation function (Serrin, 1979).

At this juncture, one has to seek answers to the following questions: Does the accumulation function lead to a mathematically precise statement of the Second Law? Does it define the absolute temperature scale? Does it place Clausius' inequality for a cycle on a firm footing?

These answers depend to a large extent on the convergence of the following improper integral:

$$\int_0^\infty \frac{Q(P, \theta)}{\theta^2} d\theta = \lim_{\alpha \rightarrow 0} \int_\alpha^c \frac{Q(P, \theta)}{\theta^2} d\theta + \lim_{\beta \rightarrow \infty} \int_c^\beta \frac{Q(P, \theta)}{\theta^2} d\theta, \tag{5.11}$$

provided each limit exists on the right side.

To demonstrate that they do, consider the first integral. Since $Q(P, \theta) = 0$, $0 < \theta < \theta_l$, it follows from L'Hôpital's rule that

$$\lim_{\theta \rightarrow 0^+} \frac{Q(P, \theta)}{\theta^2} = 0, \tag{5.12}$$

which shows that the first integral converges. Similarly, $Q(P, \theta) = Q(P, \theta_u)$, a constant over $\theta_u \leq \theta < \infty$. Hence, we have

$$\lim_{\theta \rightarrow \infty} \frac{Q(P, \theta)}{\theta^2} = 0, \tag{5.13}$$

which proves that the second limit exists. Hence, the improper integral in (5.11) converges, and we may rewrite it as:

$$\begin{aligned} \int_0^\infty \frac{Q(P, \theta)}{\theta^2} d\theta &= \int_{\theta_l}^{\theta_u} \frac{Q(P, \theta)}{\theta^2} d\theta + Q(P, \theta_u) \int_{\theta_u}^\infty \frac{1}{\theta^2} d\theta \\ &= \int_{\theta_l}^{\theta_u} \frac{Q(P, \theta)}{\theta^2} d\theta + \frac{Q(P, \theta_u)}{\theta_u}. \end{aligned} \tag{5.14}$$

Now, let us assume for convenience that the accumulation function is differentiable over $0 < \theta < \infty$. Thus, using integration by parts, we find that

$$\int_0^\infty \frac{Q(P, \theta)}{\theta^2} d\theta = \int_0^\infty \frac{dQ(P, \theta)}{d\theta} \frac{1}{\theta} d\theta. \tag{5.15}$$

For short, one can express the above as

$$\int_0^\infty \frac{Q(P, \theta)}{\theta^2} d\theta = \int_0^\infty \frac{dQ}{\theta}. \tag{5.16}$$

There is another method for the derivation of the above relationship due to Serrin (1984). Suppose that in a thermodynamic process over the time interval $[0, 1]$, the temperature of the body is given by $\theta = \theta(t)$, $t \in [0, 1]$, and its range is given by $\theta(t) \in [\theta_l, \theta_u]$. It is important to realise that at any fixed instant $t_1 \in [0, 1]$, the working substance does not exchange any heat with its surroundings in $0 < \theta < \theta(t_1)$. At $\theta = \theta(t_1)$, exchange of heat occurs and this amount remains constant in $\theta(t_1) < \theta < \infty$. However, if $\theta(t_1) > \theta_l$, heat transfer will occur for all $\theta(t)$ such that $\theta_l \leq \theta(t) \leq \theta(t_1)$. As an example of such a process, see Fig. 2.

To derive Serrin's relationship (Serrin, 1984), let

$$I(\theta) = \{t \in [0, 1] : \theta(t) \leq \theta\}. \tag{5.17}$$

If the rate of heat transfer at time t is given by $\dot{q}(t)$, we can see that

$$Q(P, \theta) = \int_{I(\theta)} \dot{q}(t) dt. \tag{5.18}$$

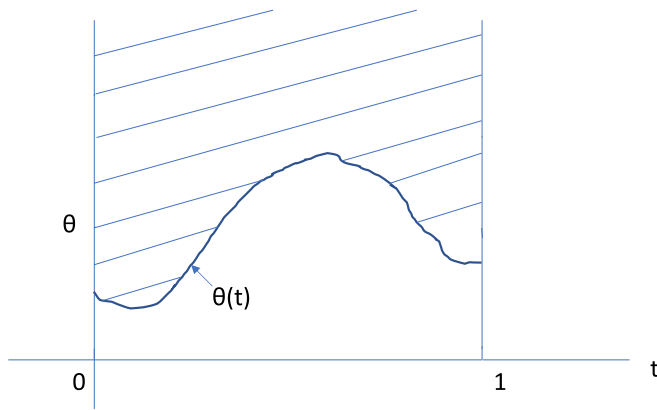


Fig. 3. Iterated integral area for a process in the (t, θ) plane.

Now consider the depiction of the process in the (t, θ) plane. See Fig. 2. Appealing to Fubini's theorem and interchanging the order of integration, one finds that

$$\begin{aligned} \int_0^\infty \frac{Q(P, \theta)}{\theta^2} d\theta &= \int_0^\infty \frac{\int_{I(\theta)} \dot{q}(t) dt}{\theta^2} d\theta \\ &= \int_0^1 \left(\int_{\theta(t)}^\infty \frac{1}{\theta^2} d\theta \right) \dot{q}(t) dt \\ &= \int_0^1 \frac{\dot{q}(t)}{\theta(t)} dt, \end{aligned} \tag{5.19}$$

which is Eq. (5.16). Note that the iterated integrals in the first and second lines above determine the region of points in the (t, θ) plane, defined as the shaded region in Fig. 3.

Finally, if the accumulation function has a finite number of jumps in $\theta_l \leq \theta \leq \theta_u$, Eq. (5.19) is still valid; of course, one has to appeal to Stieltjes integrals.

6. The Second Law: Absolute temperature and entropy

Let us now turn to the Second Law of Thermodynamics. It is well known that statements of this due to Clausius, Kelvin and Planck exist in the literature. It is also believed that they are not all equivalent. Serrin used his accumulation function (Serrin, 1979) to depict each statement pictorially and pointed out the differences between them. In addition, he derived a single statement of the Second Law which encompassed the previous versions and unified them. These matters will be discussed next.

Let us recall the first statement of the second law due to Clausius, proposed in 1850. His description is too long to be reproduced here. We shall restrict ourselves to the following quote from its translation (Clausius, 1867b):

“Hence by repeating both these alternating processes, without any expenditure of force or other alteration whatever, any quantity of heat might be transmitted from a cold body to warm one; and this contradicts the general deportment of heat, which everywhere exhibits the tendency to annul differences of temperature and therefore to pass from a warmer body to a colder one.”

In contrast to the above obscure passage, on page 179, Kelvin (Thompson, Lord Kelvin) proposed the following in 1851:

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the surrounding objects.

On page 181, we find that Kelvin was able to give another interpretation of Clausius's version:

It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.

Subsequently, in 1854, Clausius proposed a different formulation. Its translation appeared in 1856 and reads as follows (Clausius, 1867a):

Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

Much later, in 1897, on page 86, Planck (1903) offered his version:

It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir.

In his paper, Serrin (1979) drew four figures to show that these statements are equivalent to the accumulation function being never negative in a cyclic process, or that it must be positive over an infinite interval. Finally, Serrin (1979) proposed his first version of the Second Law of Thermodynamics:

I. The accumulation function of a non-adiabatic cycle C cannot be non-negative, i.e. $Q_c(\theta) \geq 0$.

He says: “In essence, such an accumulation function corresponds to a process which raises heat from various different low temperatures to various higher temperatures, and simultaneously does work. Thus its impossibility for a cycle process is self-evident.”

Later on, Serrin (1986) proposed the following version for the Second Law:

II. The condition $Q_c(\theta) \geq 0$ can occur for a cycle C of a thermodynamical system only in the exceptional case $Q_c = 0$.

Once again, we have a situation where the accumulated function is always greater than or equal to zero. This is prohibited by this version of the Second Law unless the net heat transfer in the cycle is zero.

Finally in 1995, Serrin (1995) proposed the following version;

III. If the work done $W_c > 0$ in a cycle C , then there is some temperature θ_0 in the hotness manifold for which $Q(P, \theta_0) < 0$.

To understand this version, if $W_c > 0$ in a cycle, then $Q_c > 0$ as well. However, $Q_c(\theta) \geq 0$ cannot hold over the entire cycle as stated above in II. Hence, there must be some temperature in the cycle where heat is rejected.

All of the above were summarised from Serrin's versions (Serrin, 1979, 1986, 1995) by Man and Massoudi (2010), who produced the following mathematical statement of the Second Law:

Second Law of Thermodynamics: The accumulation function of a cycle cannot have the form given by

$$Q_c(\theta) = KH(\theta - \theta_0), \quad 0 < \theta < \infty, \tag{6.1}$$

where $K > 0$ is a constant, θ_0 is some fixed temperature and the Heaviside function H is such that $H(x) = 0, x < 0, H(x) = 1, x \geq 1$.

Having stated the Second Law, we shall examine the relationship between the Clausius' inequality and the accumulation function. To proceed, Eq. (5.19) says that in any cycle, the following is true:

$$\oint \frac{\dot{q}(t)}{\theta(t)} dt = \int_0^\infty \frac{Q_c(\theta)}{\theta^2} d\theta, \tag{6.2}$$

where $\theta > 0$ is any empirical temperature and $Q_c(\theta)$ is the corresponding accumulation function. Thus, the following question arises: of all empirical temperatures scales, which one is the distinguishing feature of the absolute temperature scale T ? If we replace θ in Eq. (6.2) above by T , it becomes the well known Clausius integral $\oint dQ/T$. If this integral satisfies Clausius' inequality for a cycle, the right side must also do the same. Thus, we can reformulate Clausius' inequality and introduce the absolute temperature through the following theorem due to Serrin [2]:

The Accumulation Theorem: There exists an absolute temperature scale T on the hotness manifold with $T > 0$, such that for any cycle C , the corresponding accumulation function $Q_c(\theta)$ must satisfy the inequality

$$\oint \frac{\dot{q}(t)}{T(t)} dt = \int_0^\infty \frac{Q_c(\theta(T))}{T^2} dT \leq 0, \tag{6.3}$$

where $\theta(T)$ is the hotness level corresponding to the absolute temperature T .

The inequality is unaffected if we replace T by $\hat{T} = cT$, where $c > 0$ is any positive constant. That is, the absolute temperature scale T which satisfies the above inequality is unique up to a constant positive multiple.

Now that the absolute temperature scale has been introduced, the accumulation function satisfies the following inequality for all cycles:

$$\int_0^\infty \frac{Q_c(T)}{T^2} dT \leq 0. \tag{6.4}$$

This proves that in every cycle, where the work done is positive or negative, heat has to be rejected. Otherwise, the integrand, $Q_c(T)/T^2$, can never be negative and the above inequality is not satisfied.

How about the converse? In Serrin (1986), Serrin has proved through a detailed argument that if there is a cycle C such that

$$\int_0^\infty \frac{Q_c(T)}{T^2} dT > 0, \tag{6.5}$$

that cycle violates the Second Law. A much simpler proof of the equivalence between the Accumulation Theorem and the Second Law can be given if one assumes that the universe of thermodynamic materials includes the ideal gas (Pradas and Pedregal, 1996; Owen and Pedregal, 1998).

Summarising the arguments so far, it is clear that Clausius' inequality, the definition of the absolute temperature T and the Second Law of Thermodynamics have been formulated in mathematical terms. They transcend the verbal statements available in the literature.

We shall now turn to the entropy function. In a manner similar to that concerning the internal energy, U in Section 4, we say that the system S has an entropy associated with the state structure $(\Sigma, \mathbb{P}_\Sigma)$ if there exists a function

$$S : \Sigma \rightarrow \mathbb{R}, \tag{6.6}$$

such that

$$\Delta S \geq \bar{A}(P), \tag{6.7}$$

for each process $P \in \mathbb{P}_\Sigma$. Here, $\bar{A}(P)$ is called the accumulation integral defined through

$$\bar{A}(P) = \int_0^\infty \frac{Q(P, T)}{T^2} dT. \tag{6.8}$$

That is, S acts as an upper potential for $\bar{A}(P)$. The conditions under which the entropy S is unique, to within a constant, are the same as those which led to Eq. (4.15) concerning the internal energy U .

Assuming that there exists an entropy S , three important consequences arise from (6.7). First of all, if P_c is cyclic, it follows that S returns to its original value, or $\Delta S = 0$. Hence, in all cycles,

$$\bar{A}(P_c) \leq 0. \tag{6.9}$$

Next, in an adiabatic process, we know that $Q(P, T) = 0$, which means that $\bar{A}(P) = 0$. Thus, the change in entropy must be non-negative, i.e.,

$$\Delta S \geq 0. \tag{6.10}$$

Thirdly, if P is strongly reversible, the following holds:

$$\Delta S = \bar{A}(P). \tag{6.11}$$

That is, it is possible find the difference in the entropy along such a path only. This is the common procedure adopted in textbooks on engineering thermodynamics.

Finally, just as in the case of the internal energy function U , one can prove the existence of the entropy function S for reversible systems. In such a system, we observe from (6.9) that in all cycles,

$$\oint \frac{dq}{T} \leq 0. \tag{6.12}$$

However, completing a reversible cyclic process in one direction and executing it in the opposite direction leads to

$$\oint \frac{dq}{T} = 0. \tag{6.13}$$

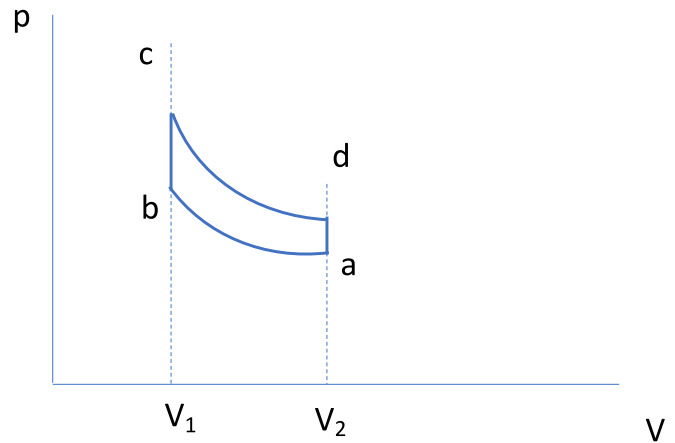


Fig. 4. Otto cycle in the (V, p) plane.

Hence, the differential form dq/T is exact and there exists an entropy function $S : \Gamma \rightarrow \mathbb{R}$ such that

$$dS = \frac{dq}{T}. \tag{6.14}$$

For the special case, when the differential form dw has the single expression $p dv$, we obtain the famous formula from Eqs. (4.17) and (6.12):

$$T dS = dU + p dv. \tag{6.15}$$

7. Serrin's Accumulation Function for Otto, Diesel, Stirling and Ericsson cycles

Engineering cycles, such as the Otto, Diesel, Stirling, and Stirling cycles are mostly depicted as closed curves in the (V, p) plane, where V is the volume of the working substance and p is the corresponding pressure. They are also drawn as closed curves in the (S, T) plane, where S is the entropy and T is the absolute temperature. During the non-adiabatic processes of these cycles, one can determine the amount of heat transferred as a function of the temperature. However, during the adiabatic processes, such a relationship is difficult to determine for the heat transferred is zero. That is, in adiabatic compression, there is no heat transfer while the temperature rises; the opposite occurs in adiabatic expansion.

The accumulation function makes explicit, in each process, the amount of heat transferred up to and including any temperature at any point of the process. Due the Second Law, the graph of such a function over a given cycle must not only include temperature(s) where heat is absorbed, there must exist temperature(s) where it is rejected. Hence, there is a wealth of information about any engineering cycle awaiting to be discovered, and the accumulation function lays it bare.

To start with, we shall turn to the Otto cycle (Man, 2016), determine its accumulation function and draw its graph. Having achieved this aim, we derive the accumulation functions for the Diesel, Stirling and Ericsson cycles.

In an Otto cycle, the working substance is assumed to be an ideal gas and the temperature scale is the absolute temperature scale T . In Fig. 4, the cycle $abcd$ represents an Otto cycle using the volume, V , and the pressure, p , diagram. In this cycle, the process $a \rightarrow b$ represents the adiabatic compression of the ideal gas, $b \rightarrow c$ the rise in temperature at constant volume due to heat supply, $c \rightarrow d$ is the adiabatic expansion and $d \rightarrow a$ is the fall in temperature at constant volume as heat is rejected. The ideal gas has constant heat capacities c_p and c_v at constant pressure and volume respectively. Let $\gamma = c_p/c_v > 1$. The following results concerning the Otto cycle are well known.

$$T_a V_1^{\gamma-1} = T_b V_2^{\gamma-1}, \quad T_d V_1^{\gamma-1} = T_c V_2^{\gamma-1}, \tag{7.1}$$

and

$$\frac{T_c - T_b}{T_d - T_a} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}. \quad (7.2)$$

Since $V_2 > V_1, \gamma > 1$ and $T_b < T_c$, we must have $T_a < T_d$ and

$$T_c - T_b > T_d - T_a. \quad (7.3)$$

Let $H(\cdot)$ be the Heaviside function, i.e., $H(x) = 0, x < 0$, and $H(x) = 1, x \geq 0$. The accumulation function for the Otto cycle must be such that in the absorption process at constant volume,

$$Q^+(P, T) = \begin{cases} 0, & T < T_b, \\ c_v(T - T_b), & T_b \leq T < T_c, \\ c_v(T_c - T_b), & T_c \leq T < \infty. \end{cases} \quad (7.4)$$

That is

$$Q^+(P, T) = \left[c_v(T - T_b)H(T - T_b) - c_v(T - T_c)H(T - T_c) \right], \quad 0 < T < \infty. \quad (7.5)$$

Similarly, in the heat rejection process,

$$Q^-(P, T) = \begin{cases} 0, & T < T_a, \\ c_v(T - T_a), & T_a \leq T < T_d, \\ c_v(T_d - T_a), & T_d \leq T < \infty. \end{cases} \quad (7.6)$$

Hence,

$$Q^-(P, T) = \left[c_v(T - T_a)H(T - T_a) - c_v(T - T_d)H(T - T_d) \right], \quad 0 < T < \infty. \quad (7.7)$$

Thus, over the cycle,

$$\begin{aligned} Q_c(T) &= Q^+(P, T) - Q^-(P, T) \\ &= \left[c_v(T - T_b)H(T - T_b) - c_v(T - T_c)H(T - T_c) \right] \\ &\quad - \left[c_v(T - T_a)H(T - T_a) - c_v(T - T_d)H(T - T_d) \right]. \end{aligned} \quad (7.8)$$

Here $Q^+(P, T)$ and $Q^-(P, T)$ are the respective amounts of heat absorbed and rejected by the gas at temperatures $T' \leq T$ during the process P , which is now the whole cycle.

From Eq. (7.8), it follows that the total heat received by the gas in the Otto cycle is given by

$$Q_c = c_v(T_c - T_b) - c_v(T_d - T_a) > 0. \quad (7.9)$$

It is reasonable to assume that $T_b > T_d$ in an Otto cycle. Thus, one has the following representation of the accumulation function over the positive real axis:

$$Q(P, T) = \begin{cases} 0, & T < T_a, \\ -c_v(T - T_a), & T_a \leq T < T_d, \\ -c_v(T_d - T_a), & T_d \leq T < T_b, \\ c_v(T - T_b) - c_v(T_d - T_a), & T_b \leq T < T_c, \\ c_v(T_c - T_b) - c_v(T_d - T_a), & T_c \leq T < \infty. \end{cases} \quad (7.10)$$

See Fig. 5. I am grateful to Professor C. S. Man, University of Lexington, for the above example (Man, 2016).

One can compute Clausius' integral for an Otto cycle. It is given by

$$\begin{aligned} \oint \frac{dQ}{T} &= c_v \int_{T_b}^{T_c} \frac{1}{T} dT - c_v \int_{T_a}^{T_d} \frac{1}{T} dT, \\ &= c_v \ln\left(\frac{T_c}{T_b}\right) - c_v \ln\left(\frac{T_d}{T_a}\right) = c_v \ln\left(\frac{T_c T_a}{T_b T_d}\right) = 0. \end{aligned} \quad (7.11)$$

Note that the above result follows because one finds from Eq. (7.1) that

$$\frac{T_c T_a}{T_b T_d} = \frac{T_c}{T_d} \cdot \frac{T_a}{T_b} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1. \quad (7.12)$$

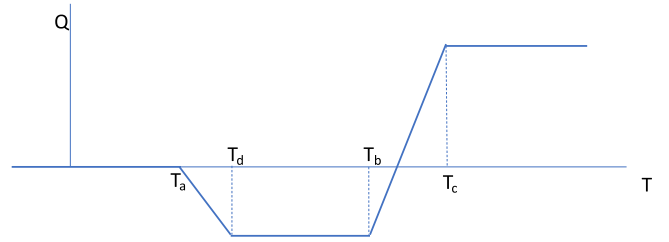


Fig. 5. Accumulation function for an Otto cycle.

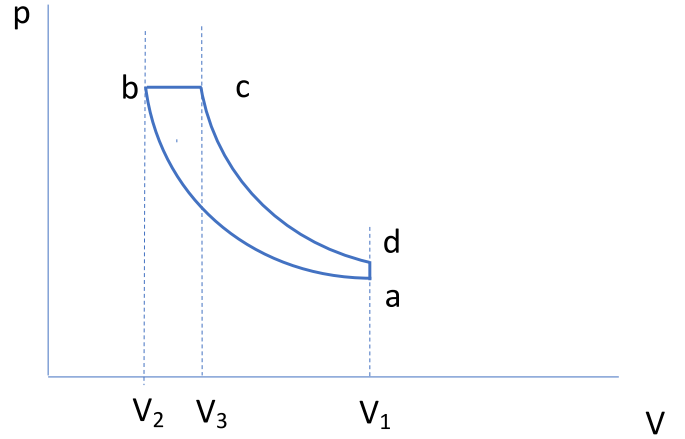


Fig. 6. Diesel cycle in the (V, p) plane.

Of course, since the Otto cycle consists of reversible processes, this is to be expected.

If one were to use the accumulation function $Q(P, T)$ from Eq. (7.10), one finds that

$$\int_0^\infty \frac{Q(P, T)}{T^2} dT = 0, \quad (7.13)$$

after some tedious algebra.

Next, we turn to the Diesel cycle. Once again, we shall use the (V, p) plane. The process $a \rightarrow b$ represents the adiabatic compression of the ideal gas, $b \rightarrow c$ the rise in temperature at constant pressure due to heat supply, $c \rightarrow d$ is the adiabatic expansion and $d \rightarrow a$ is the fall in temperature at constant volume as heat is rejected. See Fig. 6. The following results concerning the Diesel cycle are required.

$$T_a V_1^{\gamma-1} = T_b V_2^{\gamma-1}, \quad T_d V_1^{\gamma-1} = T_c V_3^{\gamma-1}. \quad (7.14)$$

Since heat is supplied in the process $b \rightarrow c$ at a constant pressure $p_b = p_c$, it follows from the ideal gas law $pV = RT$ that

$$p_b V_1 = RT_b, \quad p_c V_3 = RT_c \Rightarrow V_3 = \frac{T_c}{T_b} V_1, \quad (7.15)$$

which means that V_3 is known in terms of the volume V_1 and the temperatures T_b, T_c and T_d . Moreover, it is clear that $T_d < T_b$.

Thus, one has the following representation of the accumulation function for the Diesel cycle:

$$Q(P, T) = \begin{cases} 0, & T < T_a, \\ -c_v(T - T_a), & T_a \leq T < T_d, \\ -c_v(T_d - T_a), & T_d \leq T < T_b, \\ c_p(T - T_b) - c_v(T_d - T_a), & T_b \leq T < T_c, \\ c_p(T_c - T_b) - c_v(T_d - T_a), & T_c \leq T < \infty. \end{cases} \quad (7.16)$$

From this, one can construct the graph of the accumulation function for a Diesel cycle. It is omitted for it is similar to that of the Otto cycle.

Next, we turn to the Stirling cycle; see Fig. 7. Here, once again, it is preferable to use the (V, p) plane. The process $a \rightarrow b$ represents the

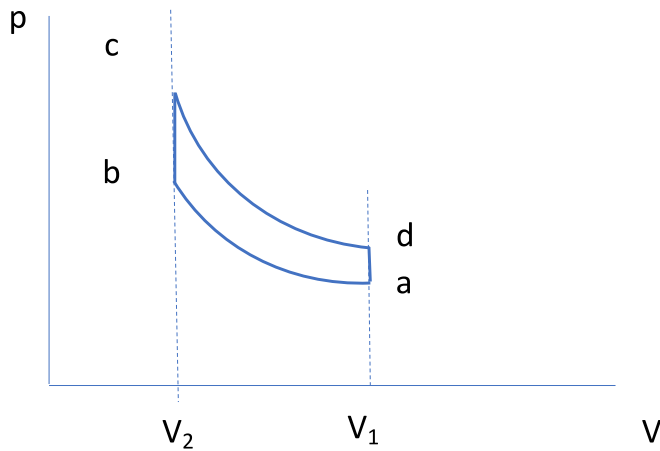


Fig. 7. Stirling cycle in the (V, p) plane.

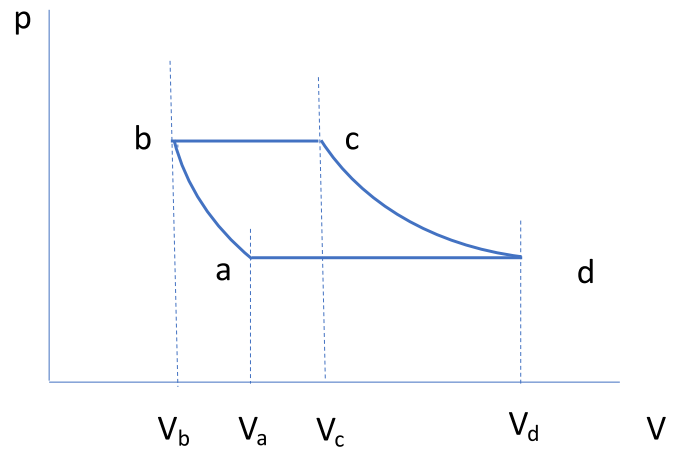


Fig. 8. Ericsson cycle in the (V, p) plane.

isothermal compression of the ideal gas resulting in heat being rejected; in $b \rightarrow c$, there is a rise in temperature at constant volume due to heat supply, $c \rightarrow d$ is an isothermal expansion where more heat is supplied, and $d \rightarrow a$ is the fall in temperature at constant volume as heat is rejected. Hence,

$$T_a = T_b, \quad T_c = T_d, \quad T_c > T_b. \quad (7.17)$$

The amount of heat rejected in the isochoric process $d \rightarrow a$ is given by $c_v(T_d - T_a)$. The heat rejected in the isothermal process $a \rightarrow b$ can be determined by the work done, which is negative. That is

$$W = RT_a \ln(V_2/V_1). \quad (7.18)$$

Thus, the amount of heat rejected is given by $RT_a \ln(V_1/V_2)$. Similarly, in the isothermal expansion defined by the process $c \rightarrow d$, the amount of heat supplied is $RT_c \ln(V_1/V_2)$.

Now, we come to the interesting part concerned with the two processes, each at a constant volume: in the process $b \rightarrow c$, heat is supplied and in the process $d \rightarrow a$, heat is rejected. In the former process, the temperature $T \in [T_b, T_c]$, while in the latter $T \in [T_a, T_d]$. However, we note from Eq. (7.17) that these two intervals are identical. Hence, for any T in these two intervals, the heat supplied is $c_v(T - T_b)$, and the heat rejected is $c_v(T - T_a)$ and they are identical. In other words, there is no change in the accumulation function for any T such that $T_b \leq T < T_c$.

From the foregoing, we can determine the accumulation function for the Stirling cycle:

$$Q(P, T) = \begin{cases} 0, & T < T_a, \\ -RT_a \ln(V_1/V_2), & T_a \leq T < T_c, \\ RT_c \ln(V_1/V_2) - RT_a \ln(V_1/V_2), & T_c \leq T < \infty. \end{cases} \quad (7.19)$$

The graph of this function can be drawn as for the Otto cycle.

Finally, we come to the Ericsson cycle which can be named after Boyle and Charles. This cycle consists of processes arising from the discoveries of the two important persons in thermodynamics. Recall that Boyle's Law says that in an isothermal process, the pressure is inversely proportional to the volume, i.e., $pV = C$, where C is a constant. Charles' Law states that the volume is proportional to the temperature in a process under constant pressure. That is, $V = kT$, where k is another constant. See Fig. 8. In the Ericsson cycle, the process $a \rightarrow b$ is an isothermal Boyle's process of compression where heat is rejected; in $b \rightarrow c$, heat is added at a constant pressure in a Charles' process resulting in an increase in temperature; $c \rightarrow d$ represents an isothermal Boyle's expansion due to heat supply, and finally, a Charles' process at constant pressure $d \rightarrow a$ completes the cycle as heat is rejected.

In a process at constant pressure, the heat transfer is the product of the heat capacity, c_p , at constant pressure and the temperature difference. Since $T_a = T_b < T_c = T_d$, it follows that for any $T \in [T_a, T_c]$, the heat added in the process $b \rightarrow c$ is cancelled out from that lost in the process $d \rightarrow a$. From this information, we can determine the accumulation function for the Ericsson cycle:

$$Q(P, T) = \begin{cases} 0, & T < T_a, \\ -RT_a \ln(V_a/V_b), & T_b \leq T < T_c, \\ RT_c \ln(V_d/V_c) - RT_a \ln(V_a/V_b), & T_c \leq T < \infty. \end{cases} \quad (7.20)$$

We note an interesting fact about the Ericsson cycle. Clearly, the two isothermal processes lead to the following:

$$\frac{V_a}{V_b} = \frac{p_b}{p_a} = \frac{p_c}{p_d} = \frac{V_d}{V_c}. \quad (7.21)$$

Hence, we have:

$$Q(P, T) = \begin{cases} 0, & T < T_a, \\ -RT_a \ln(V_a/V_b), & T_b \leq T < T_c, \\ R[T_c - T_a] \ln(V_d/V_c), & T_c \leq T < \infty. \end{cases} \quad (7.22)$$

The graph of this function can be drawn as for the Otto cycle.

Finally, the Sargent cycle consists of four processes: adiabatic compression, heating at constant volume, adiabatic expansion followed by isobaric cooling. It is similar to the Diesel cycle, although there are differences; in the latter, heat is absorbed at constant pressure and rejected at constant volume. Thus, the accumulation function for the Sargent cycle can be determined, using that of the Diesel cycle as a guide.

8. Bounds on work done in a process and a cycle

Now that a mathematically valid proof the Clausius inequality has been summarised, we can modify the inequality derived earlier in Eq. (4.12). First of all, we replace the empirical temperature θ by the absolute temperature T , and employ (6.2). Thus, for any regular cycle,

$$\left(1 - \frac{T_{\max}^-}{T_{\min}^+}\right) + \frac{T_{\max}^-}{Q_c^+} \int_0^\infty \frac{dQ}{T} \leq \frac{W_c}{Q_c^+} \leq \left(1 - \frac{T_{\min}^-}{T_{\max}^+}\right) + \frac{T_{\min}^-}{Q_c^+} \int_0^\infty \frac{dQ}{T}, \quad (8.1)$$

since $Q_c^+ > 0$. In the right half of the inequality, we know that

$$\int_0^\infty \frac{dQ}{T} \leq 0 \quad (8.2)$$

in all cycles. From this follows the well-known bound:

$$\frac{W_c}{Q_c^+} \leq \left[1 - \frac{T_{\min}^-}{T_{\max}^+} \right], \tag{8.3}$$

which is nothing but the statement that the Carnot cycle has the greatest efficiency when $T_{\min}^- < T_{\max}^+$.

We shall now turn to processes and appeal to the entropy inequality. In turn, this produces a better bound for the work done in a cycle than that in Eq. (8.3). Assuming that an internal energy satisfies Eq. (4.14), one can write the First Law for a process as the following inequality:

$$\overline{W}(P) \leq \overline{Q}^+(P) - \overline{Q}^-(P) - \Delta U. \tag{8.4}$$

Let us write ΔS as the change in entropy during a process as follows:

$$\Delta S = \Delta S^+ + \Delta S^- + \Delta S^0, \tag{8.5}$$

where ΔS^+ is the change in entropy over the time interval $I^+(t)$, where heat is absorbed; ΔS^- is the change over the time interval $I^-(t)$, where heat is rejected, and ΔS^0 is the change over the time interval $I^0(t)$, where the process is adiabatic. This permits us to phrase the composite First-Second Law as:

$$\begin{aligned} \overline{W}(P) \leq & \overline{Q}^+(P) - T_{\min}(\Delta S^+ + \Delta S^0) - (\Delta U - T_{\min} \Delta S) \\ & - (\overline{Q}^-(P) + T_{\min} \Delta S^-). \end{aligned} \tag{8.6}$$

Here, T_{\min} is the minimum value of the absolute temperature of the working substance during the process. Now, the entropy inequality (6.7) tells us that during the interval where heat is rejected, the following holds:

$$\Delta S^- \geq \int_{I^-(t)} \frac{\dot{q}(t)}{T(t)} dt, \tag{8.7}$$

or

$$-\Delta S^- \leq \int_{I^-(t)} \frac{-\dot{q}(t)}{T(t)} dt \leq \frac{\overline{Q}^-(P)}{T_{\min}}, \tag{8.8}$$

which guarantees that

$$\overline{Q}^-(P) + T_{\min} \Delta S^- \geq 0. \tag{8.9}$$

Similarly,

$$\Delta S^+ \geq \int_{I^+(t)} \frac{\dot{q}(t)}{T(t)} dt \geq \frac{\overline{Q}^+(P)}{T_{\max}} \geq 0, \tag{8.10}$$

where T_{\max} is the maximum temperature during the process. Finally, over the adiabatic part of the interval,

$$\Delta S^0 \geq \int_{I^0(t)} \frac{\dot{q}(t)}{T(t)} dt = 0. \tag{8.11}$$

Substituting Eq. (8.9) into the energy inequality, Eq. (8.6), we obtain:

$$\overline{W}(P) \leq \overline{Q}^+(P) - T_{\min}(\Delta S^+ + \Delta S^0) - (\Delta U - T_{\min} \Delta S). \tag{8.12}$$

Next, using Eq. (8.10) in Eq. (8.12), we find that :

$$\overline{W}(P) \leq \left(1 - \frac{T_{\min}}{T_{\max}} \right) \overline{Q}^+(P) - T_{\min} \Delta S^0 - (\Delta U - T_{\min} \Delta S). \tag{8.13}$$

Finally, Eq. (8.13) leads to the following inequality for the work done in a process (Huilgol, 1978):

$$\overline{W}(P) \leq \left(1 - \frac{T_{\min}}{T_{\max}} \right) \overline{Q}^+(P) - (\Delta U - T_{\min} \Delta S). \tag{8.14}$$

It is clear that Eq. (8.13) provides a sharper bound than that in Eq. (8.14), which is due to Truesdell (1976), and Fosdick and Serrin (1975).

Next, the change in the internal energy and the entropy over a cyclic process is zero, i.e., $\Delta U = 0$, and $\Delta S = 0$. Hence, from Eq. (8.13), we

find that the work done in a regular cycle is subject to the following restriction (Huilgol, 1978):

$$W_c \leq \left(1 - \frac{T_{\min}^-}{T_{\max}^+} \right) Q_c^+ - T_{\min}^- \Delta S^0. \tag{8.15}$$

Since the change in entropy over the adiabatic part is non-negative (cf. (6.10)), i.e., $\Delta S^0 \geq 0$, it follows that the inequality in Eq. (8.15) is sharper than the Carnot inequality derived earlier in Eq. (8.3). That is, whenever the cycle has an adiabatic part in it, the change in entropy over this interval reduces the amount of useful work done by the working substance in a heat engine; conversely, it increases the amount of work to be done on the material in a refrigerator.

Given that the upper bound in Eq. (8.15) is expressed in terms of the absolute temperatures and entropy, it is best to view the aforementioned four cycles as well as the Rankine cycle in the (S, T) plane to understand the importance of the upper bound.

9. Concluding remarks

As stated in the Introduction, the ideas behind the meaning of temperature, the internal energy function, U , the absolute temperature scale, T , and the entropy function, S , have been summarised, based mostly on the researches of Serrin (1979, 1986). For those materials which permit reversible cycles, the existence of U and S have also been derived. In addition, the role of the Clausius integral in the First and the Second Law for cycles has been given a new meaning. Newer formulations of the Second Law, which imply the classical versions due to Clausius, Kelvin and Planck, have also been stated. Finally, a bound for the work done in a cycle, which is sharper than the Carnot inequality, has been derived. It is hoped that attempts will be made to incorporate the ideas presented here into books on engineering thermodynamics. This is not going to be an easy task, for the Lecture Notes by Serrin (1984), which expound at length on the material presented here, are difficult to obtain. Similarly, there exists another exposition due to Serrin (1975), which appeared as the Lecture Notes in Mathematics, University of Chicago in 1975; those notes are not easily accessible. However, the book by Owen (1984) on the mathematical foundations of thermodynamics may provide the necessary background to rewrite the material in textbooks on engineering thermodynamics.

Despite the advances listed here, there still exist some confusion in classical thermodynamics about several definitions; consider that of a cycle, for example. Suppose we fill a container with some water, pour it gently into another of different size and shape. After the fluid has come to rest in the second container, one observes that the working substance, viz., the water, has returned to its original state. Can one call this process a cycle (Man, 1995)? Ericksen (1998) has also raised similar questions regarding the meaning of cycles in the thermodynamics of solids.

Turning to broader questions, one has to consider the applications of thermodynamics to continuum mechanics. First of all, can one assert that the internal energy and entropy functions exist for all materials? While there is no general answer to this question, Coleman and Owen (1974) showed that these two functions exist for a certain class of materials only, provided these materials can undergo approximate cycles, at least. For further discussions of these matters, see Man and Massoudi (2010), Coleman et al. (1981), and Serrin (1998).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

I wish to thank the two reviewers for their detailed comments which resulted in a complete rewriting of this article. In addition, I wish to thank Professor K. R. Rajagopal for his help in its submission.

References

- Carnot, S., 1960. Reflections on the motive power of fire. In: Mendoza, E. (Ed.), *Reflections on the Motive Power of Fire and Other Papers on the Second Law of Thermodynamics* By E. Clapeyron and R. Clausius. Dover, New York.
- Clausius, R., 1867a. On a modified form of the second fundamental theorem in the mechanical theory of heat. In: Archer Hirst, T. (Ed.), *Fourth Memoir, Mechanical Theory of Heat with its Applications To the Steam Engine and to the Physical Properties of Bodies*. John van Voorst, London, p. 117.
- Clausius, R., 1867b. On the moving force of heat and the laws of heat itself which may be deduced therefrom. In: Archer Hirst, T. (Ed.), *First Memoir, Mechanical Theory of Heat with Its Applications To the Steam Engine and To the Physical Properties of Bodies*. John van Voorst, London, p. 45.
- Coleman, B.D., Owen, D.R., 1974. A mathematical foundation for thermodynamics. *Arch. Ratl. Mech. Anal.* 54, 1–104.
- Coleman, B.D., Owen, D.R., Serrin, J., 1981. The second law of thermodynamics for systems with approximate cycles. *Arch. Ratl. Mech. Anal.* 77, 103–142.
- Diaz, J.B., 1978. Mathematical prolegomena to every theory of homogeneous heat engines. *SIAM Rev.* 20, 265–277.
- Ericksen, J.L., 1998. *Introduction To the Thermodynamics of Solids*, revised ed. Springer, New York.
- Fosdick, R.L., Rajagopal, K.R., 1983. On the existence of a manifold for temperature. *Arch. Ratl. Mech. Anal.* 81, 317–332.
- Fosdick, R.L., Serrin, J., 1975. Global properties of continuum thermodynamic processes. *Arch. Ratl. Mech. Anal.* 59, 97–109.
- Gibbs, J.W., 1961. *The Scientific Papers of J. Willard Gibbs*, Vol. 1. Dover Publications, New York, p. 10.
- Huilgol, R.R., 1978. Improved bounds for the work done by irreversible heat engines. *Lett. Heat Mass Transf.* 5, 41–45.
- Huilgol, R.R., 1979. The role of clausius' and entropy inequalities in thermodynamics. *Int. J. Mech. Engrg. Ed.* 7, 141–145.
- Mach, E., 1986. In: McGuiness, B. (Ed.), *Principles of the Theory of Heat*, Translation of the Second Ed. of *Die Principien Der Warmelehre* (in German), 1900. Reidel Publishing, Dordrecht, Holland.
- Man, C.-S., 1995. Remarks on global and local versions of the second law of thermodynamics. In: *Thermoelastic Problems and the Thermodynamics of Continua*, ASME. *Appl. Mech. Div.* 33–39, AMD-198.
- Man, C.-S., 2016. Private communication. dated August 3.
- Man, C.-S., Massoudi, M., 2010. On the thermodynamics of some generalized second-grade fluids. *Contin. Mech. Thermodyn.* 22, 27–46. <http://dx.doi.org/10.1007/s00161-009-0123-3>.
- Maxwell, J.C., 1872. *Theory of Heat*, second ed. Longmans, Green and Company, London.
- Owen, D.R., 1984. *A First Course in the Mathematical Foundations of Thermodynamics*. Springer-Verlag, New York.
- Owen, D.R., Pedregal, P., 1998. An elementary proof of the fundamental property of a perfect gas. *Arch. Ratl. Mech. Anal.* 142, 281–292.
- Planck, W., 1903. *Treatise on Thermodynamics*, Ogg, a. (Trans.). Longmans, Green and Co., London.
- Pradas, M.M., 1994. The second law of thermodynamics and optimal bounds for the efficiency of cyclic processes. *J. Non-Equilib. Thermodyn.* 19, 115–134.
- Pradas, M.M., Pedregal, P., 1996. The fundamental property of a perfect gas and the second law of thermodynamics. *Arch. Ratl. Mech. Anal.* 136, 383–408.
- Serrin, J., 1975. *Foundations of Classical Thermodynamics*. In: *Lecture Notes in Mathematics*, Department of Mathematics, University of Chicago.
- Serrin, J.B., 1979. Conceptual analysis of the classical second laws of thermodynamics. *Arch. Ratl. Mech. Anal.* 70, 355–371.
- Serrin, J.B., 1984. *An Introduction to Modern Thermodynamics*, Unpublished Lecture Notes, University of Minnesota.
- Serrin, J., 1986. An outline of thermodynamical structure. In: Serrin, J. (Ed.), *New Perspectives in Thermodynamics*. Springer-Verlag, Heidelberg, pp. 3–32.
- Serrin, J., 1995. On the elementary thermodynamics of quasi-static systems and other remarks. In: *Thermoelastic Problems and the Thermodynamics of Continua*, ASME. *Appl. Mech. Div.* 53–62, AMD-198.
- Serrin, J., 1998. The equations of continuum mechanics and the laws of the thermodynamics. *Meccanica* 31, 547–563.
- Thompson (Lord Kelvin), W., 1882. On the dynamical theory of heat, with numerical results deduced from Mr. Joule's equivalent of a thermal unit, and M. Renault's observations on steam. In: *Trans. Roy. Soc. Edinburgh*, March, 1851, and *Phil. Mag.* IV, 1852. Reprinted As Art. XLVIII in *Mathematical and Physical Papers*, I. Cambridge Univ. Press.
- Truesdell, C., 1976. Irreversible heat engines and the second law of thermodynamics. *Lett. Heat Mass Transf.* 3, 267–290.