A General First Law for Thermodynamics

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Dedicated to JAMES B. SERRIN

Introduction

In recent years there has been a lively interest in and discussion around the notions of entropy and absolute temperature, and the proper content of the Second Law of Thermodynamics. With very few exceptions (most notably C. TRUESDELL and M. ŠILHAVÝ), that interest has not encompassed the First Law as well. The idea that every thermal system has a state space and an energy function exactly balancing the heat and work exchanged with the exterior in every process is simply taken as obvious, not requiring serious logical scrutiny, and not worthy of second thought. This is done in spite of difficulties in explaining what the "proper" state space of a system is, and in reducing heat to notions inherited from other physical theories. In some cases, the First Law is considered a mere tautology, equivalent to a definition of heat, disregarding the idea that heat, unlike work and energy, is not a simple scalar quantity but should be specified together with the temperature at which it is received.

However, the principle of conservation of energy is not the only idea normally associated with the First Law. The existence of a mechanical equivalent of heat, the interconvertibility of heat and work in cycles, or the impossibility of perpetual motion machines of the first kind are also thought to be part of this Law. My main purpose here is to study the delicate interplay between these notions, in the context of a formal theory based on axioms of simple physical content. Within this theory there is a natural definition of energy which does not directly involve a balance equation. It is therefore possible to consider energy conservation as an additional restriction on energy, and relate it to other properties of thermal systems. The results suggest that in some cases energy may satisfy an inequality expressing a loss of energy instead of the usual balance equation.

This paper is organized as follows: first we briefly review notions adapted from [1], and originally introduced by SERRIN in [2]. After introducing a statement of the First Law (its weak version), the existence of the quantity I call energy is proved as a corollary, together with an energy inequality and ŠILHAVÝ's weak First Law for cycles. In the first part of this paper the notion of state is used informally, and simply for purposes of illustration. In the second part, state spaces are examined, briefly but rigorously, and their construction based on the primitive notions of this theory is described. Energy conservation is then shown to follow from a reversibility assumption and the weak First Law. We compute lower bounds for energy, and study reversible ideal systems, to show that their theory is a consequence of the weak First Law, as far as energy is concerned. Finally we introduce a second statement of the First Law (its strong version), which allows a slightly unorthodox idea of energy conservation to be considered. Here energy conservation is shown to be equivalent to accessibility both in the past and in the future of states of arbitrarily small energy.

1. Basic Definitions

Thermodynamics has been applied to a great variety of thermal systems, all to some extent modelled using mathematical concepts. Naturally, if the Laws of Thermodynamics are to be phrased independently of the particular details and assumptions made for specific examples of thermal systems, we must begin by abstracting a common core of notions and properties shared by all such examples. It is now quite clear that these revolve around the concepts of process, heat (as a measure on a universal hotness manifold) and work. Moreover, since the First Law treats heat independently of the temperature at which it is absorbed, we may regard here heat and work as merely numbers to be associated with each process of any thermal system, once units and a sign convention have been chosen for these quantities. Thus we regard a *thermal system* $\mathbb{S}$ as simply a set of *processes*, denoted by $\mathbb{P}(\mathbb{S})$, and two functions $Q, W: \mathbb{P}(\mathbb{S}) \to \mathbb{R}$, respectively the *heat* and *work* functions of $\mathbb{S}$ ($\mathbb{R}$ denotes the set of real numbers). Our sign convention is such that if P is a process of $\mathbb{S}$, then $Q(P)$ and $W(P)$ are, respectively, the heat *absorbed* and the work *produced* by $\mathbb{S}$ during P. To illustrate these ideas, if $\mathbb{S}$ is an ideal gas and we restrict our attention to its homogeneous processes, then $\mathbb{P}(\mathbb{S})$ is essentially the set of, say, piecewise smooth paths in the (T, V)-plane and, for each $P \in \mathbb{P}(\mathbb{S})$, $Q(P)$ and $W(P)$ are given by line integrals of differential forms $q = c(T, V)\,dT + \eta(T, V)\,dV$, $w = p(T, V)\,dV$ along the given path.

It is evident that each time a process P is applied to a given system $\mathbb{S}$ the supply of processes immediately available to $\mathbb{S}$ changes correspondingly. In the example above, once the ideal gas follows a path ending at a particular point (T', V'), only those processes which begin at the same point (T', V') can be applied to it. From an abstract point of view, we may say there is a binary relation $\mathbb{F}(\mathbb{S})$ in $\mathbb{P}(\mathbb{S})$, called here the *follow relation*, such that $(P, P') \in \mathbb{F}(\mathbb{S})$ if and only if P' can be applied to $\mathbb{S}$ immediately after P is completed. In such a case we say that P' *follows* P, or P *precedes* P'. Observe also that if $(P, P') \in \mathbb{F}(\mathbb{S})$ then we should regard the *temporal concatenation* of P and P', denoted by PP', and called P *followed by* P', as another process in $\mathbb{P}(\mathbb{S})$. In other words, there is a *binary operation* in $\mathbb{P}(\mathbb{S})$ whose domain is precisely the relation $\mathbb{F}(\mathbb{S})$. It is true that a a process P of a system $\mathbb{S}$ is normally pictured as a path in a state space, leading the system from some initial state x to some final state y, and P' is assumed to follow P if and only if P' starts at state y. But in reality the notion of state is superfluous and unnecessary at this stage, and accordingly will be omitted. Later in this paper I shall return to it, and discuss simple conditions on the follow relation allowing the introduction of a state space in a straightforward manner.

Each process P takes place in a specific time interval $I \subset \mathbb{R}$. In particular, if PP' takes place in the time interval $I = [t_0, t_2]$, then evidently there is $t_1 \in I$ such that P and P' take place respectively in $[t_0, t_1]$ and $[t_1, t_2]$. With this idea in mind, the *additivity* of Q and W with respect to *time* is evidently expressed by the equations $Q(PP') = Q(P) + Q(P')$, and $W(PP') = W(P) + W(P')$, valid whenever P' follows P. The above observations are summarized in the following formal definition:

Definition 1.1 (Thermal system). A thermal system $\mathbb{S}$ is a triple $(\mathbb{P}(\mathbb{S}), Q, W)$, where $\mathbb{P}(\mathbb{S})$ is a set and $Q, W: \mathbb{P}(\mathbb{S}) \to \mathbb{R}$ are functions. In addition,

1. there is a binary operation defined on a subset $\mathbb{F}(\mathbb{S})$ of $\mathbb{P}(\mathbb{S}) \times \mathbb{P}(\mathbb{S})$, denoted by juxtaposition, and associative in the sense that $(PP')\,P''$ and $P(P'P'')$ are defined and equal if and only if PP' and $P'P''$ are both defined.

2. if $(P, P') \in \mathbb{F}(\mathbb{S})$ then

$$Q(PP') = Q(P) + Q(P') \quad \text{and} \quad W(PP') = W(P) + W(P').$$

Our discussion should be interpreted as involving thermal systems in a fixed set $\mathbb{U}$, which is the *universe* of systems under consideration. Note also that, strictly speaking, the functions Q and W are functions of two variables, namely $\mathbb{S} \in \mathbb{U}$ and $P \in \mathbb{P}(\mathbb{S})$, but their dependence on $\mathbb{S}$ will never be explicitly indicated[1]. It is convenient to introduce for any given $P \in \mathbb{P}(\mathbb{S})$ the sets Foll (P) and Pred (P), respectively the sets of *followers* and *predecessors* of P, naturally given by:

$$\mathrm{Foll}\,(P) = \{P' \in \mathbb{P}(\mathbb{S}) \colon (P, P') \in \mathbb{F}(\mathbb{S})\},$$

$$\mathrm{Pred}\,(P) = \{P' \in \mathbb{P}(\mathbb{S}) \colon (P', P) \in \mathbb{F}(\mathbb{S})\}.$$

The set Foll (P) should be thought of as the *future cone* of $\mathbb{S}$ when P is completed. Analogously, Pred (P) is the *past cone* of $\mathbb{S}$ when P starts. I shall always assume that both Pred (P) and Foll (P) are non-empty, but this assumption, although natural, is made merely for the sake of simplicity. Note also that when a state space is given one normally expects Foll (P) and Pred (P) to be determined by, respectively, the final and initial states of $\mathbb{S}$ when P is applied to it.

The operation of combining two given thermal systems $\mathbb{S}_1$ and $\mathbb{S}_2$ so as to form a third and composite system $\mathbb{S}_1 \oplus \mathbb{S}_2$ is a fairly standard device for constructing thermodynamical arguments. The system $\mathbb{S}_1 \oplus \mathbb{S}_2$ must be thought of as a kind of *disjoint* union of $\mathbb{S}_1$ and $\mathbb{S}_2$, so that its operation really consists in operating $\mathbb{S}_1$ and $\mathbb{S}_2$ independently of each other, merely adding up their exchanges of heat and work with the outside world, but not changing the family of processes

[1] To compare the definition above with that used by Coleman & Owen in [6], observe that (topological considerations aside) Q and W are *actions*, but the word "process" is used in [6] in a different way. In particular, $\mathbb{P}(\mathbb{S})$ does *not* correspond to the set of "processes" in the sense of [6], denoted there by Π, but to the set $\Pi \diamond \Sigma$.

available to each individual system. It is of course possible that $\mathbb{S}_1 \oplus \mathbb{S}_2 \notin \mathbb{U}$ for some pairs of thermal systems $\mathbb{S}_1$ and $\mathbb{S}_2$ in $\mathbb{U}$, so this operation will be introduced here as a definition, following [2].

Definition 1.2 (Compatible thermal systems). Let $\mathbb{S}_1$ and $\mathbb{S}_2$ be two thermal systems in $\mathbb{U}$, and for convenience denote the pairs (P, Q) in $\mathbb{P}(\mathbb{S}_1)\times\mathbb{P}(\mathbb{S}_2)$ by $P \oplus Q$. We say $\mathbb{S}_1$ and $\mathbb{S}_2$ are *compatible* if there is a third system $\mathbb{S}$ in $\mathbb{U}$, denoted by $\mathbb{S}_1 \oplus \mathbb{S}_2$, and such that:

1. $\mathbb{P}(\mathbb{S}_1 \oplus \mathbb{S}_2) = \mathbb{P}(\mathbb{S}_1)\times\mathbb{P}(\mathbb{S}_2)$,
2. For all $P_1 \oplus P_2$ in $\mathbb{P}(\mathbb{S}_1 \oplus \mathbb{S}_2)$ we have $Q(P_1 \oplus P_2) = Q(P_1) + Q(P_2)$ and $W(P_1 \oplus P_2) = W(P_1) + W(P_2)$.
3. $(P_1 \oplus P_2)(P_1' \oplus P_2') = (P_1P_1') \oplus (P_2P_2')$ if and only if the right-hand side is defined.

The equalities in 2. and 3. above are not strictly necessary for the arguments presented in this paper. In reality, these equalities can be replaced by inequalities similar to, but stronger than, those used in [2]. Moreover, the inequalities actually needed naturally depend on the axiom chosen as the First Law. Note in passing that $\mathbb{S}_1 \oplus \mathbb{S}_2$ does satisfy the conditions in definition 1.

Before proceeding with a discussion of the First Law, it is convenient to recall a number of additional notions defined in [1] and [2], which play an important role here as well. Classical thermodynamical arguments repeatedly use the notion of *cyclic process*, or *cycle*. From an intuitive point of view, these are processes which can be replicated an arbitrary number of times, both before and after themselves. This description is easily turned into a precise definition.

Definition 1.3 (Cycles). $P \in \mathbb{P}(\mathbb{S})$ is a *cyclic* process, or a *cycle*, if and only if there are sequences $\{P_n\}$ in Pred(P) and $\{P^n\}$ in Foll(P) such that $Q(P_n) = Q(P^n) = nQ(P)$ and $W(P_n) = W(P^n) = nW(P)$.

The set of all cyclic processes of $\mathbb{S}$ is denoted by $\mathbb{P}_C(\mathbb{S})$. Note that the above definition, similar to that used in [2], does not require the processes P_n and P_n to be exact replicas of P.

Finally, and again following [2], I shall say that a process P in $\mathbb{P}(\mathbb{S})$ is *weakly reversible* if there is another process P' in $\mathbb{P}(\mathbb{S})$ such that $Q(P) = -Q(P')$ and $W(P) = -W(P')$. In this case, P' is called a *weak reversal* of P. If P is a cycle, also P' is required to be a cycle.

2. The Weak First Law

At the most elementary level, the First Law is supposed to state that no machine is capable of producing work out of nothing. In fact, and independently of the way this Law might be phrased in a formal treatment of Thermodynamics, this is probably the way a scientist would try to explain its content to a non-scientist. Clearly, the use of the word "nothing" in the statement above is meant to exlude both a supply of heat, and any possible changes in the internal state of the machine. This latter condition (that there be no change in internal state) can be dealt with by requiring the machine to operate in a cyclic process. Once this is recognized, the idea above becomes the following statement:

$$\text{If } P \in \mathrm{P_C}(\mathbb{S}) \text{ and } W(P) > 0, \text{ then } Q(P) > 0. \qquad (2.1)$$

In words, a system operated in a cycle and doing work must absorb heat. This statement was introduced by M. ŠILHAVÝ, and will be refered to as the *Weak First Law for Cycles* (WFLC). In spite of its qualitative content (note that the units of heat and work are clearly arbitrary), it can be used to derive the existence of Joule's constant J (the mechanical equivalent of heat), and to prove the existence of internal energy for a wide variety of thermal systems, including the reversible ideal systems of classical thermodynamics. It should be noted, however, that ŠILHAVÝ himself never considered this to be a *complete* statement of the First Law, proposing instead:

$$\text{If } P \in \mathrm{P_C}(\mathbb{S}), \text{ then } W(P) > 0 \text{ if and only if } Q(P) > 0. \qquad (2.2)$$

This is called the *Strong First Law for Cycles* (SFLC). Observe that the spirit of (2.2) is quite different from that of (2.1). According to our conventions of sign for Q and W, (2.1) really expresses the idea that work cannot be *created* out of nothing, while (2.2) adds to it the notion that heat cannot be *destroyed* (at least in cycles) without the production of work.

Leaving aside for the moment the question of the existence of cycles with $Q(P) > 0$ and $W(P) \leqq 0$, one may still regard both (2.1) and (2.2) as incomplete, simply because neither one says anything applicable to processes which are not part of a cycle. It is certainly possible to think the First Law should contemplate nothing but the properties of cyclic processes, but that will not be the position taken here. My main objective is precisely to explore different statements of the First Law, stronger than (2.1) but possibly weaker than (2.2), without reference to cycles but at same time phrased as prohibitions against certain types of perpetual motion machines. To understand the kind of statements I have in mind, consider the following three examples, necessarily expressed in somewhat vague terms, and organized from strongest to weakest:

It is impossible to build a machine which, once set in some arbitrary, but *fixed*, initial configuration, will be capable of producing *arbitrarily large* amounts of work,

1) without using *arbitrarily large* amounts of heat, or
2) without using *some* heat, or
3) while producing *arbitrarily large* amounts of heat.

I find it difficult to doubt any of these statements. Moreover, the clear absence of any reference to cycles makes them, in my opinion, closer to actual empirical evidence.

To give a precise form to these thoughts, one must understand how the simple ideas listed in the preceding section can be used to formalize its various elements. The setting up of a machine, *i.e.*, a system $\mathbb{S}$, in some arbitrary initial configuration, clearly corresponds to the choice and execution of a given process $P \in \mathbb{P}(\mathbb{S})$.

Once P is completed, the system can be *operated* by choosing any one of the processes in Foll (P), that is, any one of the possible alternatives in the future cone of $\mathbb{S}$ at the time P is completed. Naturally, there are a number of logically equivalent ways of expressing the indicated impossibilities, but it is interesting to begin with essentially literal translations of the alternatives above. In each case, $P \in \mathbb{P}(\mathbb{S})$ is a *fixed* process of $\mathbb{S}$, and $\{P_n\} \subset \mathrm{Foll}(P)$ is a *sequence of followers* of P. These translations then become

(2.3.1) If $W(P_n) \to +\infty$ then $Q(P_n) \to +\infty$, or

(2.4.1) If $W(P_n) \to +\infty$ then $Q(P_n) > 0$ for all sufficiently large n, or

(2.5.1) There is *no* sequence $\{P_n\}$ such that $W(P_n) \to +\infty$ and $Q(P_n) \to -\infty$.

The statements above are in turn equivalent to:

(2.3.2) There is a function $F_0 : \mathbb{P}(\mathbb{S}) \times \mathbb{R} \to \mathbb{R}$ such that if $P' \in \mathrm{Foll}(P)$ then

$$Q(P') \leqq q \Rightarrow W(P') \leqq F_0(P, q).$$

(2.4.2) There is a function $F_1 : \mathbb{P}(\mathbb{S}) \to \mathbb{R}$ such that if $P' \in \mathrm{Foll}(P)$ then

$$Q(P') \leqq 0 \Rightarrow W(P') \leqq F_1(P).$$

(2.5.2) There is a function $F_2 : \mathbb{P}(\mathbb{S}) \to \mathbb{R}$ such that if $P' \in \mathrm{Foll}(P)$ then

$$Q(P') \geqq -F_2(P) \text{ or } W(P') \leqq F_2(P).$$

Statements (2.3.1), (2.4.1) and (2.5.1) are clearly pairwise equivalent to (2.3.2) (2.4.2) and (2.5.2), and it is apparent that (2.3) $\Rightarrow$ (2.4) $\Rightarrow$ (2.5). (Note in particular that we can take $F_1(P) = F_0(P, 0)$ and $F_2(P) = \min\{F_1(P), 0\}$). However, and perhaps more surprisingly, one can also prove (2.3) and (2.4) from (2.5), given some additional and very mild hypotheses.

It is also interesting to compare these statements, and those of Šilhavý, from the point of view of symmetry in the roles of Q and W. Quite clearly, the *only* statement invariant under the change $Q \to W$, $W \to Q$ is SFLC. Naturally, any statement involving Q and W can be made symmetric in these functions, if one simply restates it interchanging Q and W. As an example, if one starts with WFLC, *i.e.*,

$$\text{If } P \in \mathbb{P}_C(\mathbb{S}), \text{ then } W(P) > 0 \Rightarrow Q(P) > 0,$$

the resulting symmetric statement is

$$\text{If } P \in \mathbb{P}_C(\mathbb{S}),\ W(P) > 0 \Rightarrow Q(P) > 0 \text{ and } Q(P) > 0 \Rightarrow W(P) > 0,$$

which is of course SFLC. However, if a similar procedure is applied to *any* of the statements (2.3)–(2.5), the end result is obviously wrong on physical grounds: it is indeed quite possible for a system started in a given state to absorb arbitrarily large amounts of heat without ever producing work. On the other hand, since our conventions of sign for heat and work are different, one can also argue that a statement really treats heat and work in the same manner only if it is invariant with respect to the change $Q \to -W$ and $W \to -Q$. From this point of view, (2.5) is the *only* statement which treats heat and work equally, although theories based on any of the other alternatives lead to conclusions which are also symmetric with respect to this latter change of variables.

To a large extent, the choice of a basic axiom for a theory among all physically realistic possibilities is essentially a matter of personal taste. Naturally, one prefers to start with the weakest and physically most obvious assumption, so I shall take (2.5.1), refered to as *Weak First Law* (WFL), as my *Axiom I*. For clarity, let me restate it here:

Axiom I (Weak First Law). If $\mathbb{S} \in \mathbb{U}$ and $P \in \mathbb{P}(\mathbb{S})$, there is *no* sequence $\{P_n\} \subseteqq \text{Foll}\,(P)$ such that $W(P_n) \to +\infty$ and $Q(P_n) \to -\infty$.

In any case, we shall see that the price one pays for using (2.5) as a basic axiom is really very small (in terms of additional hypotheses), as compared to either (2.3) or (2.4). Again let me point out that Axiom I does treat heat and work equally, and expresses an idea firmly grounded on our experience: it is impossible to build a machine capable of producing *simultaneously* arbitrarily large amounts of work and arbitrarily large amounts of heat. At the same time, this axiom simply ignores any possible prohibitions concerning the *destruction* of heat and work, a point to which I shall return after exploring its main logical consequences.

3. The Work-Heat Inequality and Energy

The results derived in this section involve in an essential way Joule's constant J (the mechanical equivalent of heat), which must be introduced by assuming the existence of a definite special system in $\mathbb{U}$. There is a certain degree of freedom in the properties assigned to this special system, but the simplest possibility corresponds to the following axiom:

Axiom II. There is a system $\mathbb{J} \in \mathbb{U}$ with a weakly reversible *cycle* $R \in \mathbb{P}_C(\mathbb{J})$ such that $W(R) \neq 0$ and $Q(R) \neq 0$.

Let R' be a weak reversal of R. Since $W(R') = -W(R)$, we can suppose without loss of generality that $W(R) > 0$. If we denote by R^{-n} the process $(R')^n$, it is clear that, for any *integer* $n \in \mathbb{Z}$, $R^n \in \text{Foll}\,(R) \cup \text{Foll}\,(R')$, $W(R^n) = nW(R)$ and $Q(R^n) = nQ(R)$. Naturally, *Joule's constant* J is defined by $J = W(R)/Q(R)$, but to insure that $Q(R)$ and J are both positive we need a version of WFL for cycles.

Lemma 3.1. *There is no cycle P with $W(P) > 0$ and $Q(P) < 0$.*

Proof. Let $\{P^n\} \subseteqq \text{Foll}\,(P)$ be the sequence mentioned in definition 1.3. If $W(P) > 0$ and $Q(P) < 0$, it is obvious that $W(P^n) = nW(P) \to \infty$ and $Q(P^n) = nQ(P) \to -\infty$, contradicting WFL. QED.

Note that the same kind of argument applied to either (2.3) or (2.4) immediately produces ŠILHAVÝ's WFLC as a corollary. Note also that if either one of these statements is chosen as a basic axiom then the condition $Q(R) \neq 0$ in axiom II becomes superfluous. In fact, this condition on $\mathbb{J}$ is precisely the price we pay for using the weaker statement (2.5), if we disregard the slightly different versions of definition (1.2) which are strictly required in each case.

The next argument is applicable to any thermal system compatible with $\mathbb{J}$. Its conclusion is both a strengthening of (2.3)–(2.5) and a generalization of the inequality $W(P) \leqq JQ(P)$, proved by ŠILHAVÝ for cycles.

Theorem 3.2 (Work-Heat Inequality). *If* $\mathbb{S}$ *is compatible with* $\mathbb{J}$ *and* $P \in \mathbb{P}(\mathbb{S})$, *then* $\operatorname{Sup}\{W(P') - JQ(P') : P' \in \operatorname{Foll}(P)\} < \infty$.

Proof. If $\{P_n\}$ is a sequence of followers of P and $\{m_n\}$ is a sequence of integers, then $P_n \oplus R^{m_n}$ is a sequence in $\operatorname{Foll}(P \oplus R) \cup \operatorname{Foll}(P \oplus R')$ with

$$W(P_n \oplus R^{m_n}) = W(P_n) + m_n W(R) \quad \text{and} \quad Q(P_n \oplus R^{m_n}) = Q(P_n) + m_n Q(R).$$

Hence, if the integers m_n can be chosen such that

$$W(P_n) + m_n W(R) > n \quad \text{and} \quad Q(P_n) + m_n Q(R) < -n, \tag{3.3}$$

then $W(P_n \oplus R^{m_n}) \to \infty$, $Q(P_n \oplus R^{m_n}) \to -\infty$ and $\mathbb{S} \oplus \mathbb{J}$ violates WFL. It is clear that (3.3) is equivalent to

$$m_n > (n - W(P_n))/W(R) \quad \text{and} \quad m_n < -(n + Q(P_n))/Q(R),$$

and hence there is a sequence of integers m_n satisfying (3.3) if and only if

$$-(n + Q(P_n))/Q(R) - (n - W(P_n))/W(R) > 1 \quad \text{for all } n.$$

Since $W(R) = JQ(R)$, the inequality above can be written as

$$-J(n + Q(P_n)) - (n - W(P_n)) > W(R),$$

which is the same as $W(P_n) - JQ(P_n) > (1 + J)\,n + W(R)$. It is therefore obvious that $\mathbb{S} \oplus \mathbb{J}$ violates WFL if the set $\{W(P') - JQ(P') : P' \in \operatorname{Foll}(P)\}$ is unbounded above. QED.

If P is a cycle, it is clear that

$$W(P) - \mathbb{J}Q(P) > 0 \Rightarrow W(P^n) - JQ(P^n) \to +\infty,$$

and so the preceding theorem implies

Corollary 3.4 (Work-Heat inequality for cycles). *If* $P \in \mathbb{P}_c(\mathbb{S})$ *is a cyclic process and* $\mathbb{S}$ *is compatible with* $\mathbb{J}$ *then* $W(P) \leqq JQ(P)$. *In particular,* $W(P) > 0 \Rightarrow Q(P) > 0$.

Finally, this theorem also shows that both (2.3) and (2.4) are simple consequences of (2.5), given our auxiliary axiom II.

Corollary 3.5. *If* $P \in \mathbb{P}(\mathbb{S})$ *and* $\{P_n\} \subseteq \operatorname{Foll}(P)$, *then* $W(P_n) \to +\infty \Rightarrow Q(P_n) \to +\infty$ *and* $Q(P_n) \to -\infty \Rightarrow W(P_n) \to -\infty$.

In words, the generation of arbitrarily large amounts of work (heat) does require arbitrarily large amounts of heat (work).

The supremum of the set $\{W(P') - JQ(P'): P' \in \text{Foll}\,(P)\}$ is obviously an important quantity associated with the system $\mathbb{S}$ when P is completed. The next definition, although different from classical ideas, certainly gives it a most natural name.

Definition 3.6. The function $E: \mathbb{P}(\mathbb{S}) \to \mathbb{R}$ given by

$$E(P) = \text{Sup}\,\{W(P') - JQ(P'): P' \in \text{Foll}\,(P)\}$$

is called the *energy* of $\mathbb{S}$ at (the conclusion of) P.

Normally, energy is introduced after a specific state space has been chosen for the thermal system under consideration, and one simply assumes that if P takes the system $\mathbb{S}$ from state x to state y then the obvious *balance* equation holds, i.e.,

$$JQ(P) - W(P) = E(y) - E(x). \tag{3.7}$$

Even ignoring the fact that no state space has yet been mentioned, we see that our situation here is markedly different. We are committed to a definition of energy which, although natural, does not mention any possible balance equations. It is of course possible to regard Foll (P) as equivalent for all practical purposes to the *final* state of $\mathbb{S}$ when P is completed, but it is possible to obtain a property of E comparable to (3.7) without introducing states. Observe first that any follower P' of a fixed process P must satisfy the obvious inequality $W(P') - JQ(P') \leqq E(P)$. If we now fix both P and P' and consider the definition of $E(P')$ we easily obtain:

Theorem 3.8 (Energy inequality). *If* $P' \in \text{Foll}\,(P)$, *then*

$$JQ(P') - W(P') \geqq E(P') - E(P).$$

Proof. If R is a follower of P', then $P'R$ is a follower of P, and as noted above we have:

$$W(P'R) - JQ(P'R) \leqq E(P).$$

Since $JQ(P'R) - W(P'R) = JQ(P') - W(P') + JQ(R) - W(R)$, this can also be written as

$$W(R) - JQ(R) \leqq E(P) + JQ(P') - W(P') \quad \text{for all } R \in \text{Foll}\,(P').$$

It follows immediately from the definition of $E(P')$ that

$$E(P') \leqq E(P) + JQ(P') - W(P'). \quad \text{QED.}$$

To compare the preceding result with (3.7), we interpret P and P' as labels for (respectively) the initial and final states of $\mathbb{S}$ associated with P' (but note that $E(P')$ and $E(P)$ really depend only on Foll (P') and Foll (P)). Hence (3.8) corresponds to an inequality like

$$JQ(P') - W(P') \geqq E(y) - E(x),$$

and thus clearly expresses the fact that energy cannot be *created.* As might be expected from our initial axioms, the question of its possible destruction is left essentially open. However, if P is a weakly reversible cycle it is easy to see that we must have $JQ(P) = W(P)$, by applying (3.4) to a weak reversal of P. Hence, the value of J can be obtained from any system compatible with $\mathbb{J}$ and satisfying Axiom II. Another simple but important case where a balance equation can be obtained from the Weak First Law will be discussed in the next section.

4. State Spaces

Applications of Thermodynamics always involve a choice of a proper state space, to serve as domain for functions like energy and entropy. This choice is neither trivial nor obvious, except in the simplest cases. As an example, observe that in the case of a continuum, where its processes are regarded as paths in a certain function space, this space is *not* the state space used, which generally corresponds to fields of *local* states. If one does not wish to resort to simple faith, it is clearly important to find conditions guaranteeing the existence of "useful" state spaces, and rules for their construction from the structural elements already in the theory.

Normally a state space structure is pictured as a set of states Ω, together with functions $\boldsymbol{i}, \boldsymbol{f}: \mathbb{P}(\mathbb{S}) \to \mathbb{R}$, where $\boldsymbol{i}(P)$ and $\boldsymbol{f}(P)$ are the states of $\mathbb{S}$ when P respectively, starts and ends. Such structures can be used to specify the follow relation, if one assumes that P' follows P if and only if $\boldsymbol{f}(P) = \boldsymbol{i}(P')$. However, the existence of a state space with this property clearly represents an additional requirement on the follow relation, in principle absent from definition (1.1). My purpose here is to determine conditions on a thermal system $\mathbb{S}$ equivalent to the existence of such a state structure, and to prove a simple uniqueness result. Let me begin with a definition borrowed from [2]:

Definition 4.1 (State structures). A *state structure* for a thermal system $\mathbb{S}$ is a triple $(\Omega, \boldsymbol{i}, \boldsymbol{f})$, where Ω is a set and $\boldsymbol{i}, \boldsymbol{f}: \mathbb{P}(\mathbb{S}) \to \Omega$ are functions. These functions must satisfy the condition:

$$\text{If } P' \text{ follows } P, \text{ then } \boldsymbol{i}(P') = \boldsymbol{f}(P).$$

The structure is called *deterministic* if it satisfies:

$$P' \text{ follows } P \text{ if and only if } \boldsymbol{i}(P') = \boldsymbol{f}(P).$$

The elements of Ω are called *states*, and Ω is a *state space*. Naturally $\boldsymbol{i}(P)$ and $\boldsymbol{f}(P)$ are called, respectively, the *initial* and *final* states of $\mathbb{S}$ when P is applied to it. Since by assumption each process P has at least one follower and one predecessor, we have $\boldsymbol{i}(\mathbb{P}(\mathbb{S})) = \boldsymbol{f}(\mathbb{P}(\mathbb{S}))$, and I shall also assume for simplicity that both $\boldsymbol{i}$ and $\boldsymbol{f}$ are *onto*. As an example of a (non-deterministic) state structure one can take $\Omega = \mathbb{R}$, and $\boldsymbol{i}(P)$ and $\boldsymbol{f}(P)$ respectively equal to the initial and final time instants of the duration of P.

Naturally, a state structure is only useful from the point of view of the First Law if the *energy hypothesis* (see [2]) is satisfied, *i.e.*, if there is a function $U: \Omega \to \mathbb{R}$ such that for any process P one has at least:

$$JQ(P) - W(P) \geqq U(f(P)) - U(i(P)).$$

It is quite clear that the particular example of a state structure given above cannot be particularly useful, since it seems unlikely that the energy of a system will depend only on time. Moreover, the consideration of very simple examples shows that without added assumptions about a given thermal system it is *impossible* to prove the existence of a state structure satisfying the energy hypothesis.

To see how the existence of a deterministic state structure can be used to prove the energy hypothesis, note that in this case one always has

$$\text{Foll}(P) = \{P' \in \mathbb{P}(\mathbb{S}) : i(P') = f(P)\}. \tag{4.2}$$

In particular, if $x = f(P)$, then

$$\text{Sup}\{W(P') - JQ(P') : P' \in \text{Foll}(P)\} = \text{Sup}\{W(P') - JQ(P') : i(P') = x\}.$$

If we now define $U: \Omega \to \mathbb{R}$ by $U(x) = \text{Sup}\{W(P') - JQ(P') : i(P') = x\}$, the preceding equation becomes:

$$E(P) = U(f(P)) \quad \text{for all } P \in \mathbb{P}(\mathbb{S}).$$

The energy inequality can be rewritten as

$$JQ(P') - W(P') \geqq U(f(P')) - U(f(P)), \tag{4.3}$$

where the reference to P can be eliminated by noting that $f(P) = i(P')$. In summary, we have:

Theorem 4.4. *The energy hypothesis holds for any deterministic state structure* (Ω, i, f), *with a state energy function* $U: \Omega \to \mathbb{R}$, *given by*

$$U(x) = \text{Sup}\{W(P) - JQ(P) : i(P) = x\}.$$

Observe that (4.3) can be obtained independently of the assumption of determinism, and would hold for *every* system, if we simply let $\Omega = \{\text{Foll}(P) : P \in \mathbb{P}(\mathbb{S})\}$ and define $f: \mathbb{P}(\mathbb{S}) \to \Omega$ by $f(P) = \text{Foll}(P)$. The difficulty in obtaining (4.4) from (4.3) resides solely in defining the function i in such a way that $i(P') = f(P)$, for *every* predecessor P of P', while maintaining inequality (4.3).

Before establishing conditions for the existence of a deterministic state structure, let us settle the corresponding uniqueness problem.

Theorem 4.5 (Uniqueness). *Let* (Ω^*, i^*, f^*) *and* (Ω, i, f) *be two state structures for a system* $\mathbb{S}$, *and assume* (Ω^*, i^*, f^*) *is deterministic. Then there is a surjection* $\phi^*: \Omega^* \to \Omega$ *such that* $\phi^* \circ i^* = i$ *and* $\phi^* \circ f^* = f$. *In particular,* Ω *is isomorphic to a quotient set of* Ω^*. *If* (Ω, i, f) *is also deterministic, the function* ϕ^* *is a bijection,* i.e., Ω *and* Ω^* *are isomorphic.*

Proof. We begin by showing that

$$f^*(P) = f^*(P') \Rightarrow f(P) = f(P').$$

Choose a follower P'' of P, and note that

$$i^*(P'') = f^*(P) = f^*(P') \quad \text{and} \quad f(P) = i(P'').$$

Since (Ω^*, i^*, f^*) is deterministic, we conclude that P'' is also a follower of P', and hence $f(P') = i(P'') = f(P)$. In particular, the relation $\phi^* \circ f^* = f$ defines ϕ^*. To check that $\phi^* \circ i^* = i$, consider any process P, and suppose P'' is now one of its predecessors. It follows immediately that

$$\phi^* \circ i^*(P) = \phi^* \circ f^*(P'') = i(P).$$

If (Ω, i, f) is also deterministic, then naturally there is a surjection $\phi: \Omega \to \Omega^*$ such that $\phi \circ i = i^*$ and $\phi \circ f = f^*$, and ϕ is clearly the inverse of ϕ^*. QED.

Note that a "state" in Ω correponds to a *set* of states in Ω^*. Typically, the reduction of Ω^* onto a smaller quotient set Ω would result from discarding state variables which are irrelevant for the calculation of U.

It is (unfortunately) very easy to show that an arbitrary thermal system $\mathbb{S}$ need not have a deterministic state structure. In fact, from (4.2) one gets:

Lemma 4.6. *If* $\mathbb{S}$ *has a deterministic state structure* (Ω, i, f) *then*

$$\text{Foll}(P') \cap \text{Foll}(P'') \neq \emptyset \Rightarrow \text{Foll}(P') = \text{Foll}(P'') \quad \text{for all } P', P'' \in \mathbb{P}(\mathbb{S}).$$

Proof. If $P \in \text{Foll}(P') \cap \text{Foll}(P'')$ then $f(P') = f(P'') = i(P)$, and hence

$$\text{Foll}(P') = \text{Foll}(P'') = \{Q \in \mathbb{P}(\mathbb{S}): i(Q) = i(P)\}. \text{ QED.}$$

In words, if a system has a deterministic state structure then any two processes with a common follower have exactly the same followers. The same idea can also be expressed by saying that $\{\text{Foll}(P): P \in \mathbb{P}(\mathbb{S})\}$ is a *partition* of $\mathbb{P}(\mathbb{S})$. It is also easy to see that the condition in the preceding lemma guarantees the existence of a deterministic state structure. Suppose the system $\mathbb{S}$ satisfies

$$\text{Foll}(P') \cap \text{Foll}(P'') \neq \emptyset \Rightarrow \text{Foll}(P') = \text{Foll}(P'') \quad \text{for all } P', P'' \in \mathbb{P}(\mathbb{S}), \tag{4.7}$$

and define Ω^* and $f^*: \mathbb{P}(\mathbb{S}) \to \Omega^*$ by

$$\Omega^* = \{\text{Foll}(P): P \in \mathbb{P}(\mathbb{S})\} \quad \text{and} \quad f^*(P) = \text{Foll}(P).$$

Note that if P' and P'' are both predecessors of P then (4.7) implies $\text{Foll}(P') = \text{Foll}(P'')$. Hence we can define $i^*: \mathbb{P}(\mathbb{S}) \to \Omega^*$ by setting

$$i^*(P) = f^*(P') \quad \text{if } P \text{ follows } P'.$$

In particular, (Ω^*, i^*, f^*) is a state structure for $\mathbb{S}$, and $P \in i^*(P)$. To verify that (Ω^*, i^*, f^*) is a deterministic structure, note that if $i^*(P) = f^*(P')$ then

$$P \in i^*(P) \Rightarrow P \in f^*(P') \Rightarrow P \in \text{Foll}(P'), \quad \textit{i.e.}, \ P \text{ follows } P'.$$

The above results are partially summarized in:

Theorem 4.8. $\mathbb{S}$ *has a deterministic state structure* $(\Omega, \boldsymbol{i}, \boldsymbol{f})$ *if and only if it satisfies* (4.7). *In this case there is a bijection* $\phi: \Omega \to \{\mathrm{Foll}\,(P): P \in \mathbb{P}(\mathbb{S})\}$ *such that* $\phi \circ \boldsymbol{f}(P) = \mathrm{Foll}\,(P)$ and $\phi \circ \boldsymbol{i}(P) = \mathrm{Foll}\,(P')$, for any $P' \in \mathrm{Pred}\,(P)$.

The existence of a deterministic state structure is, as we just saw, equivalent to (4.7). It is interesting to note that this condition can also be phrased in terms of predecessors, as follows:

$$\mathrm{Pred}\,(P') \cap \mathrm{Pred}\,(P'') \neq \emptyset \Rightarrow \mathrm{Pred}\,(P') = \mathrm{Pred}\,(P'') \quad \text{for all } P', P'' \in \mathbb{P}(\mathbb{S}). \tag{4.9}$$

Consider the set of *future* cones $\Omega^* = \{\mathrm{Foll}\,(P): P \in \mathbb{P}(\mathbb{S})\}$ and the set of *past* cones $\Omega^{**} = \{\mathrm{Pred}\,(P): P \in \mathbb{P}(\mathbb{S})\}$. If a system $\mathbb{S}$ has a deterministic state structure $(\Omega, \boldsymbol{i}, \boldsymbol{f})$, both Ω^* and Ω^{**} are partitions of $\mathbb{P}(\mathbb{S})$. Moreover, there is a bijection $\psi: \Omega^* \to \Omega^{**}$ given by

$$\psi\,(\mathrm{Foll}\,(P)) = \mathrm{Pred}\,(P'), \quad \text{where } P' \in \mathrm{Foll}\,(P). \tag{4.10}$$

In other words, each future cone uniquely determines a past cone, and each past cone uniquely determines a future cone. This unambiguous association is possible because every process in Foll (P) has the same predecessors, and every process in Pred (P') has the same followers. A *state* in a deterministic structure is simply a label for such a *pair* of cones. The Weak First Law as stated here refers only to a future cone, but it should be noted that the Second Law (as stated in [1]) refers to a past cone.

Given states x and y in Ω, it is sometimes necessary to consider the set of states accessible from y, and the set of states from which x is accessible. If $(\Omega, \boldsymbol{i}, \boldsymbol{f})$ is deterministic and P satisfies $\boldsymbol{i}(P) = x$ and $\boldsymbol{f}(P) = y$, these sets are respectively given by

$$\mathbb{F}(y) = \boldsymbol{f}(\mathrm{Foll}\,(P)) \quad \text{and} \quad \mathbb{P}(x) = \boldsymbol{i}\,(\mathrm{Pred}\,(P)).$$

As already noted, in this case we may define a state energy function U by

$$U(x) = \mathrm{Sup}\,\{W(P) - JQ(P): \boldsymbol{i}(P) = x\}, \tag{4.11}$$

and every process $P \in \mathbb{P}(\mathbb{S})$ satisfies

$$JQ(P) - W(P) \geqq U(\boldsymbol{f}(P)) - U(\boldsymbol{i}(P)). \tag{4.12}$$

Combining (4.4) with (4.8), we conclude that WFL and the additional condition (4.7) imply the energy hypothesis, in a state space Ω which is *unique* up to an isomorphism. Naturally it may be possible and convenient to replace Ω by one of its quotient sets without losing (4.12), but such a procedure should be explicitly described, if one wants to understand the connection between the resulting energy inequality and WFL.

Assuming $(\Omega, \boldsymbol{i}, \boldsymbol{f})$ is a state structure for which the energy hypothesis holds, let us now consider the problem of proving balance equations for energy. As mentioned before, there really is no hope of proving a form of the energy conservation principle valid for all processes. However, and as we know from the example of entropy, there is absolutely no difficulty in proving balance equations if we restrict ourselves to reversible processes. Note that the definition below involves a *fixed* state structure.

Definition 4.13 (Reversible processes). P is *reversible* (with respect to a given state structure) if there is a weak reversal P' of P with $\boldsymbol{i}(P) = \boldsymbol{f}(P')$ and $\boldsymbol{f}(P) = \boldsymbol{i}(P')$. In this case (P, P') is called a *reversible pair.*

If (P, P') is a reversible pair, from the inequalities

$$JQ(P) - W(P) \geqq U(\boldsymbol{f}(P)) - U(\boldsymbol{i}(P)) \text{ and}$$

$$JQ(P') - W(P') \geqq U(\boldsymbol{f}(P')) - U(\boldsymbol{i}(P'))$$

we immediately obtain the *energy balance equation*

$$JQ(P) - W(P) = U(\boldsymbol{i}(P)) - U(\boldsymbol{i}(P)). \tag{4.14}$$

In other words, the Weak First Law implies energy conservation in the presence of a form of reversibility, and in this case for very simple reasons. Apart from everything else, this suggests that WFL is all we need to recover the classical theory of reversible systems.

5. Lower Bounds for Energy

In some cases, it is possible to compute the greatest lower bound of U directly from the definition of energy. Let $\mathbb{S}$ be a system with a deterministic structure, and assume that every process $P \in \mathbb{P}(\mathbb{S})$ is *reversible*, and hence satisfies the balance equation

$$JQ(P) - W(P) = U(\boldsymbol{f}(P)) - U(\boldsymbol{i}(P)).$$

If this equation is combined with (4.11), we obtain

$$U(x) = \operatorname{Sup}\{U(x) - U(y) : y \in \mathbb{F}(x)\} = U(x) - \operatorname{Inf}\{U(y) : y \in \mathbb{F}(x)\}. \tag{5.1}$$

It is therefore obvious that

$$\operatorname{Inf}\{U(y) : y \in \mathbb{F}(x)\} = 0, \quad \text{for all } x \in \Omega, \tag{5.2}$$

and, in particular,

$$\text{the infimum of } U \text{ over all of } \Omega \text{ is also } 0. \tag{5.3}$$

The above results can also be easily proved in a slightly more general context. Instead of assuming that all processes of $\mathbb{S}$ are reversible, suppose only that for every $P \in \mathbb{P}(\mathbb{S})$ there is a reversible process $R \in \mathbb{P}(\mathbb{S})$ with the same initial and final states (such processes are normally used to compute entropy changes). In other words, if $x = \boldsymbol{i}(P)$ and $y = \boldsymbol{f}(P)$ then there is a reversible process R with $x = \boldsymbol{i}(R)$ and $y = \boldsymbol{f}(R)$. In this case,

$$W(P) - JQ(P) \leqq U(\boldsymbol{i}(P)) - U(\boldsymbol{i}(P)) = W(R) - JQ(R).$$

Clearly, $U(x)$ can be computed using only reversible processes (strictly speaking, one reversible process for each state y in $\mathbb{F}(x)$) and,

$$U(x) = \operatorname{Sup}\{W(R) - JQ(R) : i(R) = x,\ R \text{ reversible}\}.$$

In particular, statements (5.1)–(5.3) hold without alterations.

If we do not assume any reversibility, (5.1) must be rewritten as the inequality

$$U(x) \leqq U(x) - \operatorname{Inf}\{U(y) : y \in \mathbb{F}(x)\},$$

yielding

$$\operatorname{Inf}\{U(y) : y \in \mathbb{F}(y)\} \leqq 0. \tag{5.4}$$

For the systems usually considered in continuum mechanics, it is always possible to choose processes starting at x, of arbitrarily short duration, and for which $W - JQ$ is arbitrarily close to zero. Hence the energy of these systems must be non-negative. In such cases (5.4) evidently implies both (5.2) and (5.3).

These observations suggest the correctness of our definition for U. This definition eliminates in all cases the ambiguity reflected in the presence of an arbitrary additive constant in the energy function, and provides a natural greatest lower bound for this function, at least in the cases mentioned above. Moreover, it gives an easily understandable physical interpretation to energy. From a slightly different point of view, however, these same observations also suggest that the principle of energy balance is less simple than it seems, and may be inextricably linked to accessibility conditions.

To clarify this latter comment, suppose there is *some* function $V : \Omega \to \mathbb{R}$ satisfying the balance equation

$$JQ(P) - W(P) = V(f(P)) - V(i(P)), \quad \text{for all } P \in \mathbb{P}(\mathbb{S}),$$

and define $I(x) = \operatorname{Inf}\{V(y) : y \in \mathbb{F}(x)\}$. Applying the definition of U, we obtain

$$U(x) = V(x) - \operatorname{Inf}\{V(y) : y \in \mathbb{F}(x)\} = V(x) - I(x).$$

It is evident that if $\mathbb{F}(x) = \Omega$ for all $x \in \Omega$ then I is constant in Ω and U is conserved as well as V. But if accessibility is not perfect we only have

$$y \in \mathbb{F}(x) \Rightarrow \mathbb{F}(y) \subsetneqq F(x) \Rightarrow I(y) \geqq I(x),$$

with the energy loss reflected in the energy inequality for a process going from x to y precisely equal to $I(y) - I(x)$.

In other words, when an attempt is made to define energy in a natural and unambiguous way, one immediately recognizes that the question of its conservation cannot be settled by the usual argument involving the "path independence" of the quantity $JQ(P) - W(P)$, and the lack of a general balance equation for energy does not seem to be such a negative feature of the theory.

6. Classical Ideal Systems

It is interesting to apply the ideas already discussed to a classical ideal system, both as a simple illustration of the theory and as a check that it does contain elementary results among its corollaries. To be specific, consider a system consisting of a fixed mass of a given gas, to be modelled by a triple $\mathbb{S} = (\mathbb{P}(\mathbb{S}), Q, W)$. Naturally, we make no attempt to include in $\mathbb{P}(\mathbb{S})$ *all* processes which may actually be available to the given physical system. Either by ignorance, technical incapacity or simplifying choice we always work with restricted classes of processes, and the classical theory of ideal systems is no exception to this rule.

Suppose first that $\mathbb{P}(\mathbb{S})$ contains only the *homogeneous* processes of the ideal system under consideration. As we know, these processes can be identified with the piecewise smooth functions $P: [a, b] \to \Sigma$, where $[a, b]$ is an interval in the real line (the duration of P), and Σ is an open connected subset of $\mathbb{R}^n$. There are continuous differential forms q and w defined in Σ such that $Q(P)$ and $W(P)$ are (respectively) the line integrals of q and w along $P([a, b])$ with the obvious orientation. If $P' : [a', b'] \to \Sigma$ is another homogeneous process, then P' *follows* P if and only if $b = a'$ and $P(b) = P'(a')$, in which case PP' is the concatenation (or pasting) of the functions P and P'. It is clear that P is a *cycle* if $P(a) = P(b)$, that is, if $P([a, b])$ is a closed curve. To see that any homogeneous process P is *weakly reversible*, it suffices to consider the process $P' : [b, 2b - a] \to \Sigma$ given by $P'(t) = P(2b - t)$, and to use elementary properties of line integrals.

Clearly, the set $\{\text{Foll}\,(P): P \text{ homogeneous}\}$, *i.e.*, the set of all future cones in $\mathbb{P}(\mathbb{S})$ is isomorphic to $\Sigma \times \mathbb{R} = \{(\sigma, t): \sigma \in \Sigma, t \in \mathbb{R}\}$, since the homogeneous followers of $P: [a, b] \to \Sigma$ are determined by $\sigma = P(b)$ and $t = b$. In particular, there is a deterministic structure (Ω^*, i^*, f^*) with $\Omega^* = \Sigma \times \mathbb{R}$

According to (4.11), we can compute $U: \Omega^* \to \mathbb{R}$ by

$$U(\sigma, t) = \text{Sup}\,\{W(P) - JQ(P): P \text{ homogeneous, } i^*(P) = (\sigma, t)\}.$$

Since line integrals are independent of the parametrization used to describe the path of integration, U is independent of t, and hence the state space Ω^* can be replaced by the non-deterministic space $\Omega = \Sigma$, with $\phi: \Omega^* \to \Omega$ given by $\phi(\sigma, t) = \sigma$. It is easy to see that with this simplification every homogeneous process becomes reversible, and writing $u(\sigma)$ instead of $U(\sigma, t)$, (4.14) implies that

$$Jq - w \text{ is exact, with potential } u.$$

Moreover, (5.3) implies that U has infimum 0, and therefore

$$u \text{ is the unique potential of } Jq - w \text{ with infimum } 0.$$

If $\mathbb{P}(\mathbb{S})$ is enlarged so as to contain all processes which have homogeneous predecessors and homogeneous followers and, in addition, we assume that (4.7) holds for $\mathbb{S}$, it is still possible to show (as done after (5.3)) that U is the energy of $\mathbb{S}$. However, we can only prove that energy is conserved in all homogeneous processes in $\mathbb{P}(\mathbb{S})$.

7. The Strong First Law and Energy Conservation

As I said before, WFL expresses only the impossibility of producing heat and work out of "nothing", disregarding completely the question of their destruction. Hence one may feel WFL is incomplete as an expression of the First Law, with its incompleteness reflected in the lack of a general energy balance equation. It is therefore important to investigate the consequences of statements forbidding as well the absorption of arbitrarily large amounts of heat and work by a given system.

To state WFL we considered the *future* of a system after a given process has been completed, and placed upper bounds on the heat and work the system might produce in that future. Quite clearly, we can only place upper bounds on heat and work absorption if we look at the *past* of the system before one of its processes can be started. If we choose to believe that it is impossible to sink arbitrarily large amounts of heat and work into a system if its final state is fixed, the First Law might be phrased as

Axiom 1′. Strong First Law (SFL). If $\mathbb{S} \in \mathbb{U}$ and $P \in \mathbb{P}(\mathbb{S})$, then

- there is *no* sequence $\{P_n\} \subseteq \mathrm{Foll}\,(P)$ such that $W(P_n) \to +\infty$ and $Q(P_n) \to -\infty$ and
- there is *no* sequence $\{P_n\} \subseteq \mathrm{Pred}\,(P)$ such that $Q(P_n) \to +\infty$ and $W(P_n) \to -\infty$.

Note that the second half of this statement is obtained from the first half by exchanging heat and work, and simultaneously exchanging past and future. In spite of this symmetry, it is undoubtedly true that SFL is less convincing than WFL, carrying with it an element of optimism entirely absent from the original statement. Once this latter axiom is assumed, however, one easily gets in addition to those results already proved a new set of theorems which are their mirror images.

Theorem 7.1. *If* $\mathbb{S}$ *is compatible with* $\mathbb{J}$ *and* $P \in \mathbb{P}(\mathbb{S})$, *then*

$$\mathrm{Sup}\,\{JQ(P') - W(P') \colon P' \in \mathrm{Pred}\,(P)\} < \infty .$$

If one applies the preceding result to a cycle P, the inequality in (3.4) is immediately reversed:

Corollary 7.2. *If* $P \in \mathbb{P}_C(\mathbb{S})$ *is a cyclic process and* $\mathbb{S}$ *is compatible with* $\mathbb{J}$ *then* $JQ(P) \leqq W(P)$. *Hence for any cycle* $P \in \mathbb{P}_C(\mathbb{S})$ *we have* $JQ(P) = W(P)$.

In particular, SFL implies Šilhavý's SFLC, and hence the interconvertibility of heat and work in cycles. The definition of E can certainly be copied, but it produces *another* energy function.

Definition 7.3. The function $E^* \colon \mathrm{P}(\mathbb{S}) \to \mathbb{R}$ is given by

$$E^*(P) = \mathrm{Sup}\,\{JQ(P') - W(P') \colon P' \in \mathrm{Pred}\,(P)\}.$$

The inequality corresponding to (3.8) is now

Theorem 7.4. *If* $P' \in \mathrm{Pred}\,(P)$, *then* $E^*(P) - E^*(P') \geqq JQ(P') - W(P')$.

Given a deterministic state structure for $\mathbb{S}$, we can write

$$E^*(P) = U^*(\boldsymbol{i}(P)) = \text{Sup}\{JQ(P') - W(P'): \boldsymbol{f}(P') = \boldsymbol{i}(P')\}.$$

In words, E^* should be associated with the *initial* state of $\mathbb{S}$ when P is applied to it. In terms of processes, one must compare $E(P)$ with $E^*(P')$, when P' follows P. Naturally, if (7.4) is combined with (3.8) using a deterministic state structure one simply obtains two inequalities which do not yield any general balance equations:

$$U^*(\boldsymbol{f}(P)) - U^*(\boldsymbol{i}(P)) \geqq JQ(P) - W(P) \geqq U(\boldsymbol{f}(P)) - U(\boldsymbol{i}(P)). \qquad (7.6)$$

Note in passing that interconvertibility of heat and work in cycles is weaker than energy conservation, and requires a smaller set of axioms to hold.

It is very tempting at this stage to try to argue that $U = U^*$, so that (7.6) can be turned into a balance equation for a single energy function. But the fact remains that U and U^* are computed using two entirely *different* classes of processes, and nothing in the axioms used this far requires these functions to be the same. We can certainly prove the equality $U = U^*$ for some systems, but always at the expense of assumptions which in one way or another express symmetry between past and future.

To see this in detail, suppose first that *all* processes of $\mathbb{S}$ are reversible. In this case, since

$$U^*(x) = \text{Sup}\{JQ(P) - W(P): \boldsymbol{f}(P) = x\},$$
$$U(x) = \text{Sup}\{W(P) - JQ(P): \boldsymbol{i}(P) = x\},$$

and the two sets at right are identical, we obviously have $U = U^*$. Moreover, for such a system SFL follows from WFL. In a sense, there is no difference between its past and its future, these being mirror images of each other. In particular, $\mathbb{F}(x) = \mathbb{P}(x)$ for all x in Ω.

If there are irreversible processes in $\mathbb{P}(\mathbb{S})$, the existence of U^* can be established only if SFL holds. In this case, balance equations can be obtained for all processes P for which $\boldsymbol{i}(P)$ is accessible from $\boldsymbol{f}(P)$. In fact, if $\boldsymbol{i}(P) = \boldsymbol{f}(P') = x$ and $\boldsymbol{f}(P) = \boldsymbol{i}(P') = y$, (7.6) applied to both P and P' yields

$$U^*(y) - U^*(x) = JQ(P) - W(P) = U(y) - U(x) = W(P') - JQ(P').$$

Phrased in a slightly different way, this becomes

Theorem 7.7. *If* SFL *holds and* $\mathbb{F}(x) = \mathbb{P}(x)$ *for all* x *in* Ω, *then* $U = U^*$ *and energy is conserved in every process.*

Proof. We simply observe that the sets $\{JQ(P) - W(P): \boldsymbol{f}(P) = x\}$ and $\{W(P) - JQ(P): \boldsymbol{i}(P) = x\}$ are once again identical. QED.

If $\mathbb{P}(x) \neq \mathbb{F}(x)$ for some $x \in \Omega$, SFL does not imply $U = U^*$, and we must accept the existence of *two* energy functions for the system $\mathbb{S}$. This naturally introduces unexpected difficulties in any discussion about energy conservation, since it becomes necessary to consider two different balance equations! A natural way to avoid this latter difficulty is to define energy conservation as a relation between U and U^*:

Definition 7.8. Energy is *conserved* if and only if $U = U^*$.

When energy is conserved for a given system $\mathbb{S}$, then evidently $\mathbb{S}$ has for all purposes a single energy function satisfying a balance equation for every $P \in \mathbb{P}(\mathbb{S})$. However, it is easy to verify that even if both U and U^* always satisfy a balance equation it does necessarily follow that energy is conserved in the sense of (7.8). As it turns out, the simplest necessary and sufficient conditions on U and U^* equivalent to (7.8) again involve specific lower bounds for these functions, which apart from everything else should definitely be considered as accessibility conditions. These are as follows:

Theorem 7.9 (Energy conservation). *If* SFL *holds for* $\mathbb{S}$, *then* (7.8) *is equivalent to* $\operatorname{Inf}\{U(y): y \in \mathbb{P}(x)\} = \operatorname{Inf}\{U^*(y): y \in \mathbb{F}(x)\} = 0$ *for all* $x \in \Omega$.

Proof. Fix $x \in \Omega$ and suppose $y \in \mathbb{P}(x)$. There is then a process P with $\boldsymbol{i}(P) = y$ and $\boldsymbol{f}(P) = x$, and hence

$$U(x) - U(y) \leqq JQ(P) - W(P) \leqq U^*(x), \quad \text{for all } y \in \mathbb{P}(x).$$

A similar argument produces the inequality

$$U^*(x) - U^*(y) \leqq W(P) - JQ(P) \leqq U(x), \quad \text{for all } y \in \mathbb{F}(x).$$

If $U = U^*$ then clearly both these functions satisfy general balance equations, and the two left inequalities above are equalities. Hence

$$U(x) - \operatorname{Inf}\{U(y): y \in \mathbb{P}(x)\} = U^*(x),$$

and

$$U^*(x) - \operatorname{Inf}\{U^*(y): y \in \mathbb{F}(x)\} = U(x).$$

We conclude that if $U = U^*$ then $\operatorname{Inf}\{U(y): y \in \mathbb{P}(x)\} = \operatorname{Inf}\{U^*(y): y \in \mathbb{F}(x)\} = 0$. If we don't assume $U = U^*$ the inequalities above yield

$$U(x) - \operatorname{Inf}\{U(y): y \in \mathbb{P}(x)\} \leqq U^*(x),$$

and

$$U^*(x) - \operatorname{Inf}\{U^*(y): y \in \mathbb{F}(x)\} \leqq U(x).$$

In this case it is obvious that $\operatorname{Inf}\{U(y): y \in \mathbb{P}(x)\} = \operatorname{Inf}\{U^*(y): y \in \mathbb{F}(x)\} = 0$ imply $U = U^*$. QED.

The content of the statement above should not be overlooked. Even if SFL is assumed, energy conservation is *not* automatic, and is in fact *equivalent* to an accessibility condition. In reality, $U = U^*$ holds if and only if every state is accessible from states of arbitrarily small U, and can access states of arbitrarily small U^*. In the case of *perfect* accessibility, *i.e.*, when $\mathbb{P}(x) = \mathbb{F}(x) = \Omega$, for all $x \in \Omega$, then $U = U^*$ and $\inf U = 0$.

8. Conclusions

It is possible to set up a simple axiomatic framework where different interpretations of the First Law can be precisely phrased and compared. When this is done, one recognizes without difficulties that, as far as this Law is concerned, the theory of reversible processes is a consequence of a simple axiom (the Weak First Law), which forbids the simultaneous generation of arbitrarily large quantities of heat and work. Such an axiom also provides a definition of energy with a clear physical interpretation, free from the traditional ambiguity concerning arbitrary additive constants, and applicable to all thermal systems which can be fitted into a very general model, without special assumptions about either reversibility of processes or accessibility of states. At the same time, this axiom allows energy losses in irreversible processes, a conclusion obviously violating one of the basic hypotheses of Physics.

If energy conservation is to be regarded as a general property of all thermal systems in the context of an axiomatic theory, it must clearly be reduced to axioms of compelling physical evidence. Such a task is harder than it might appear. An attempt in this direction was made here, by exploring another natural (but less convincing) assumption, the Strong First Law. In this case, energy conservation fails only for a special class of irreversible processes, precisely when a certain accessibility condition also fails.

Regardless of the axioms chosen to express the First Law, there is always an intriguing connection between energy conservation for a given system and forms of symmetry between its past and its future. If this connection is real, it suggests that SFL itself may simply be a consequence of WFL and reversibility, not a general physical law. At least from an aesthetic and philosophical point of view, that is a very interesting possibility, leading to a simple and convincing version of the First Law, unexpectedly much closer to the Second Law than it is usually conceived.

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