Chapter 3

 Foundations of the Clausius-Duhem Inequality*

M. Feinberg and R. Lavine

3.1 Introduction

To some extent modern continuum thermodynamics amounts to a collection of "thermodynamical theories" sharing common premises and common methodology. There are theories of elastic materials, of viscous materials, of materials with memory, of mixtures, and so on. It is generally the case that, in the context of each theory, one considers all processes (compatible with classical conservation laws) that bodies composed of the prescribed material might admit, and, moreover, one supposes that there exists for the theory a "Clausius-Duhem inequality". In very rough terms this amounts to an assertion of the following kind: 

For any process suffered by any body composed of the material under study

\[
\int_{\text{end of process}} - \int_{\text{beginning of process}} dq \leq \int_{\text{process}} \frac{\partial q}{\partial \theta}
\]

\(dq\) denoting the element of heat received from external sources and \(\theta\) the temperature of the part of the system receiving it. (This interpretation of the integral on the right side of (3.1) is taken from the opening page of Gibbs's "On the Equilibrium of Heterogeneous Substances").

In fact, one generally supposes something more: that in calculating the various quantities appearing in (3.1) one has available "functions of state" that give instantaneous values of the specific entropy (entropy/mass) and the temperature at a material point within a body once the instantaneous "state" of the material point is specified. More precisely, in a theory of a prescribed material it is usually taken for granted that "states" of material points can be identified with elements of a Hausdorff space \(\Sigma\) (which depends upon the manner in which the notion of "state" is rendered concrete within the theory) and that there exist

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* With very minor differences this article has also appeared as an appendix in the second edition of C. Truesdell's *Rational Thermodynamics* (Springer, Berlin, Heidelberg, New York, Tokyo 1984).

1 A "state" will always be regarded here as an attribute of a material point within a body, never as an attribute of the body as a whole. We say that a material point is in a certain "state" while the body containing it is in a certain "condition".

2 The notion of "state" will vary from one theory to another. In a theory of an elastic material the state of a material point might, for example, be identified with a pair \((e,F)\), \(e\) and \(F\) denoting instantaneous values of the specific internal energy (energy/mass) and the deformation gradient at that material point. In a theory of a particular gas the state of a material point might be identified with a pair \((p,v)\), \(p\) and \(v\) denoting instantaneous values at that material point of the pressure and specific volume.
two functions — a *specific entropy function* \( \eta: \Sigma \to \mathbb{R} \) (where \( \mathbb{R} \) denotes the real numbers) and a *thermodynamic temperature scale* \( \theta: \Sigma \to \mathbb{P} \) (where \( \mathbb{P} \) denotes the positive real numbers) — such that the specific entropy and temperature of a material point in state \( \sigma \in \Sigma \) are given by \( \eta(\sigma) \) and \( \theta(\sigma) \). If, for a body suffering a particular process, one has a specification of the manner in which states of the various material points evolve in time, then the functions \( \eta(\cdot) \) and \( \theta(\cdot) \) permit local and instantaneous calculation of the temperature and specific entropy. In turn these calculations, supplemented with suitable information about the process, permit evaluation of the quantities appearing in (3.1), each by means of an appropriate integration procedure. The crucial supposition here is not only that the functions \( \eta(\cdot) \) and \( \theta(\cdot) \) exist within the context of a particular theory, but also that they are compatible with (3.1) for all processes that bodies considered within the theory might admit. Indeed, for thermodynamical theories of the kind we have in mind, this supposition plays the role of the Second Law.

The Second Law, however, is traditionally invoked in far more basic terms, usually as a simple prohibition against certain kinds of heat receipt by bodies suffering cyclic processes. No initial appeal is made to notions of "entropy" or "thermodynamic temperature", much less to "functions of state" that give instantaneous values of the thermodynamic temperature and specific entropy at a material point. To the extent that these functions exist within the context of a particular theory, their existence is generally expected to be a consequence of the Second Law rather than a precursor of it.

Classical arguments for the existence of specific entropy functions and thermodynamic temperature scales are — at least in spirit — constructive ones, based entirely on consideration of *reversible* (usually homogeneous) processes. These are generally depicted as hypothetical processes, suitably well-approximated by actual processes, which operate so slowly that a body suffering such a process might be regarded to be in an equilibrated condition at every instant. Based on one or another of the primitive statements of the Second Law (and the tacit presumption of a rich supply of reversible processes), these arguments deliver both the existence and the uniqueness (up to inconsequential scale changes) of "functions of state" which give the specific entropy and thermodynamic temperature. However, the very nature of these arguments suggests that the functions so constructed should contain in their domain only those states that might be exhibited within a body during the course of a reversible process.

On the other hand, the methodology of modern continuum thermodynamics requires that the Clausius-Duhem inequality apply to *all* processes that bodies of a particular material under study might suffer, even those processes which involve rapid deformation and heating. Accordingly, states within the domains of the *pre-supposed* functions \( \eta(\cdot) \) and \( \theta(\cdot) \) are generally *not* restricted to those that might be manifested during reversible processes. In effect, results of the classical arguments — in particular the existence of \( \eta(\cdot) \) and \( \theta(\cdot) \) — are lifted from and applied beyond the restricted setting within which they were derived. In discussing modern use of the Clausius-Duhem inequality, Truesdell\(^3\) [3.1] has written that

> "... we are following here the common, tried path of theorists: We have observed a property that summarizes a number of known and understood facts, and we ask if it will serve by itself, stripped of the restricting assumptions by which we were led to it, as an axiom on the basis of which further facts may be explained and further effects predicted."

Nevertheless, it is not unreasonable that more orthodox thermodynamicists should call into question the very premises upon which modern use of the Clausius-Duhem inequality depends. It is our purpose here to address issues of this kind.

In the sense suggested at the outset, we shall continue to view thermodynamics as a collection of thermodynamical theories, each appropriate to a particular material. The notion of "thermodynamical theory" will eventually be made precise. It suffices here to say that we shall regard such a theory to be characterized, first, by specification of the "state space" \( \Sigma \) — that is, of the manner in which the notion of "state of a material point" is rendered concrete within the theory — and, second, by a suitable description of those processes bodies composed of the prescribed material are deemed to suffer. Once the notion of "thermodynamical theory" is made mathematical we shall want to know

i) for *precisely* which theories there exist two "functions of state" — a thermodynamic temperature scale \( \theta: \Sigma \to \mathbb{P} \) and a specific entropy function \( \eta: \Sigma \to \mathbb{R} \) — such that inequality (3.1), made suitably precise, is satisfied for every process the theory contains; and

ii) for precisely which of those theories that admit such functions is it the case that this pair of functions is *unique* (up to inconsequential changes of scale).

Although we wish to address these questions in general terms, we shall circumscribe our considerations in one respect, primordially so that subsequent discussion might have a substantially less technical character. For all theories considered hereafter we shall presume that \( \Sigma \) is a compact Hausdorff space. In effect, for a particular material we are restricting attention to processes wherein no material point experiences a state outside a fixed compact set, perhaps very large.\(^4\) This restriction will be understood throughout.

In this context we show that, among all thermodynamical theories, *existence of functions* \( \eta: \Sigma \to \mathbb{R} \) and \( \theta: \Sigma \to \mathbb{P} \) (compatible with the Clausius-Duhem inequality) is a property of *precisely* those we call Kelvin-Planck theories — roughly, of those thermodynamical theories for which the processes comply with a version of the Kelvin-Planck Second Law. Our proof, which we sketch very briefly, is based on the Hahn-Banach theorem (as are proofs of virtually all other

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\(^3\) That physical theory often proceeds in the way Truesdell suggests has been argued elsewhere by Feynman [3.2].

\(^4\) When \( \Sigma \) is merely required to be *locally* compact, one can obtain results similar but not identical to those obtained here. It should be mentioned, however, that when \( \Sigma \) is not even locally compact our work becomes more problematical. For materials with memory (in which states are identified with "histories" residing in an infinite-dimensional Banach space) the assumption that \( \Sigma \) be compact or even locally compact may be too restrictive to permit consideration of a suitably rich supply of processes.
theorems stated here) and relies not at all on notions of reversibility, slow processes, Carnot cycles, differential forms, equilibrium states or any other apparatus normally built into classical existence arguments. Thus, for theories that admit functions \( p(t) \) and \( \theta(t) \), elements of the domain \( \Sigma \) need not be restricted to those states that might be exhibited in a body during the course of a reversible process. On the other hand, further theorems indicate that, for theories in which these functions not only exist but are also essentially unique, it must be the case that each state in \( \Sigma \) is "exhibited" in some process — if not an actual process then one well approximated by actual processes — which is reversible (in a certain weak sense). Taken together, our theorems suggest that orthodoxy criticism of premises upon which modern thermodynamical methodology is based should perhaps focus less upon questions concerning existence of crucial state functions and more upon questions concerning the extent to which uniqueness of these functions plays a role in applications.

More extensive discussion of the work sketched here as well as additional results can be found in two articles by us [3.3]. These articles had their origin in unpublished notes we wrote for James Serrin in 1978 to show how some of his early ideas, when used in conjunction with the Hahn-Banach theorem, could deliver results similar to his Accumulation Theorem in a rather different way. Our concerns then were much more limited than they are here. We concentrated only on how the Hahn-Banach theorem provides information about the existence and uniqueness of thermodynamic temperature scales suited for the Clausius inequality (i.e. (3.1) restricted to cyclic processes), and then only when the existence of an empirical temperature scale (or hotness manifold) is taken for granted. That the existence of such thermodynamic temperature scales emerges from the Hahn-Banach theorem (in approximately the same limited setting) was apparently observed by Šilhavý at about the same time. Readers are encouraged to consult the contributions to this volume by Serrin and Šilhavý, and also those by Coleman and Owen, for discussion of their research on foundations of the Clausius-Duhem inequality.

### 3.2 Thermodynamical Theories

In this section we make precise what we mean by a thermodynamical theory and, in particular, what we mean by a Kelvin-Planck theory. At the outset our discussion will be informal: words like "theory" and "process" will be used in an intuitive way only to provide motivation for definitions we shall eventually record.

Although thermodynamical theories of different materials may vary greatly in detail, answer to questions posed earlier depend less upon the fine structure of a particular theory than they depend upon certain of its coarse-grained features. For our purposes, then, we regard a thermodynamical theory to be characterized by just those features that bear upon issues connected with existence and properties of specific entropy functions and thermodynamic temperature scales compatible with the Clausius-Duhem inequality. In fact, we regard a theory to be specified by two sets, \( \Sigma \) and \( \mathcal{P} \), that carry precisely the information we require. The first of these is called the set of states for the theory, and the second is called the set of (basic) processes.

The set \( \Sigma \) serves to specify for a particular theory the manner in which the notion of "state of a material point" is made concrete. In effect, specification of \( \Sigma \) amounts to a description of the domain of states that material points might conceivably experience during processes admitted for consideration in the theory. As indicated earlier, we shall always assume that \( \Sigma \) is endowed with a compact Hausdorff topology. For example if, in a theory of a particular gas, a state is regarded to be a pair \((p, v)\), with \( p \) the pressure and \( v \) the specific volume at a material point, then \( \Sigma \) would be identified with a closed and bounded region of \( \mathbb{R}^2 \), perhaps very large. In any case, it should be kept in mind that a "state" is an attribute of a material point within a body, not an attribute of the body as a whole.

To explain the nature of the set \( \mathcal{P} \) and the sense in which it characterizes the processes a theory contains, we shall require a somewhat more extensive discussion. For this purpose we shall consider a theory concerned with all bodies composed of a particular material, and we shall suppose that states of material points are identified with elements of a compact Hausdorff space \( \Sigma \).

We begin by making precise the idea that a body (as distinct from a material point within a body) reveals itself in a certain instantaneous "condition". Consider a body composed of the prescribed material. At some fixed instant each material point within the body manifests itself in some state contained in \( \Sigma \). (We do not presume that all material points are in the same state, although it may in fact be the case that the body is homogeneous throughout.) By the (instantaneous) condition of the body we mean a positive Borel measure on \( \Sigma \) which we denote here by \( \omega_0 \) and which we interpret in the following way: For each Borel set \( A \subset \Sigma \), \( \omega(A) \) is the mass of the part of the body consisting of material points in states contained within \( A \). In rough terms we can imagine \( \omega(A) \) to be determined by removing from the body just those material points in states contained within \( A \) and weighing the material so removed. Thus, the measure \( \omega \) describes the instantaneous distribution of material among the various states. Note that \( \omega(\Sigma) \) is the mass of the entire body. Note also that if a body of total mass \( M \) is homogeneous throughout with all material points in state \( \sigma \in \Sigma \), then the condition of the body is given by \( M \delta_{\sigma} \), where \( \delta_{\sigma} \) is the Dirac measure\(^6\) concentrated at \( \sigma \).

Now we consider a process suffered by some body composed of the prescribed material. During the course of the process the body may suffer deformation, and heat exchange may occur between the body and its exterior. Moreover, each material point within the body may experience a variety of states as the process advances. As a result, the initial condition \( \omega_0 \) of the body (at the beginning of the process) may be very different from its final condition, \( \omega_f \) (at the end of the process). In fact, with the process we may associate the change of condition

\[
\Delta \omega := \omega_f - \omega_0
\]

\[\text{[3.2]}\]

\(^5\) The second article, "Thermodynamics based on the Hahn-Banach Theorem: the Clausius-Duhem inequality" is being prepared for the same journal.
suffered by the body between the beginning of the process and its end. Here $\Delta m$ is a (signed) Borel measure on $\Sigma$; that is, $\Delta m$ may take negative values on some Borel sets. Note, however, that

$$\Delta m(\Sigma) = m_f(\Sigma) - m_i(\Sigma) = 0$$

(3.3)

since both $m_f(\Sigma)$ and $m_i(\Sigma)$ are equal to the total mass of the body suffering the process.

In addition to the change of condition we shall associate with the process under consideration another (signed) Borel measure on $\Sigma$ called the heating measure for the process. We denote the heating measure by $\vartheta$ and give it the following interpretation: for each Borel set $\Lambda \subset \Sigma$, $\vartheta(\Lambda)$ is the net amount of heat received (from the exterior of the body suffering the process) during the entire process by material points in states contained within $\Lambda$. In rough terms, $\vartheta(\Lambda)$ is the net amount of heat one would observe being received by the body from its exterior if, at each instant during the process, one ignored heat receipt by parts of the body in states outside $\Lambda$. Note that $\vartheta$ may be positive (corresponding to net heat absorption) on some Borel sets and negative (corresponding to net heat emission) on others.

Because the measures $\Delta m$ and $\vartheta$ for a process will play significant roles in what follows it is perhaps instructive to consider how these measures derive from a somewhat more traditional (and more detailed) process description:

**Example 1.** For the material under consideration we consider a particular process. With the process we associate

i) a body $B$ that suffers the process. We regard $B$ to be a set (of material points) taken together with a $\sigma$-algebra of subsets of $B$ called the parts of $B$. Moreover, we presume that $B$ comes equipped with a positive measure $\mu$ defined on its parts: for each part $P \subset B$, $\mu(P)$ is the mass of part $P$;

ii) a closed interval $I = [t_i, t_f]$ to be interpreted as the time interval during which the process takes place;

iii) a measurable function $\delta_0: B \times I \rightarrow \Sigma$, where $\delta_0(x, t)$ is to be interpreted as the state of material point $x$ at time $t$;

iv) a real-valued (signed) measure $\delta$ on $B \times I$ with the following interpretation: for each part $P \subset B$ and each Lebesgue measurable set $J \subset I$, $\delta(P \times J)$ is the net amount of heat received (from the exterior of $B$) by part $P$ during instants contained in $J$.

For the process so described the heating measure $\vartheta$ is constructed as follows: for each Borel set $\Lambda \subset \Sigma$,

$$\vartheta(\Lambda) = \delta(\delta^{-1}(\Lambda))$$

(3.4)

To construct the change of condition for the process we proceed in the following way: Let the functions $\delta_i: B \rightarrow \Sigma$ and $\delta_f: B \rightarrow \Sigma$ be defined by

$$\delta_i(\cdot) = \delta(\cdot, t_i) \quad \text{and} \quad \delta_f(\cdot) = \delta(\cdot, t_f)$$

(3.5)

Then the initial condition $m_i$ of body $B$ and its final condition $m_f$ are defined as follows: for each Borel set $\Lambda \subset \Sigma$,

$$m_i(\Lambda) = \mu(\delta_i^{-1}(\Lambda)) \quad \text{and} \quad m_f(\Lambda) = \mu(\delta_f^{-1}(\Lambda)).$$

(3.6)

The change of condition $\Delta m$ for the process is then given by $m_f - m_i$.

We are now in a position to describe the set $\mathcal{P}$ for the theory under consideration. With a process admitted by a body composed of the prescribed material we can associate the pair $(\Delta m, \vartheta)$, where $\Delta m$ is the change of condition and $\vartheta$ is the heating measure for the process. By $\mathcal{P}$ we shall mean the set of all $(\Delta m, \vartheta)$ pairs that derive from processes admitted by bodies composed of the prescribed material.\footnote{The description of a process in terms of what we call the condition of a body was suggested by Noll [3.4]. The use of what we call heating measures in process descriptions and in statements of the Second Law seems to have originated with Serrin [3.5].}

Let $\mathcal{M}(\Sigma)$ denote the vector space of finite signed regular Borel measures on $\Sigma$, and we let $\mathcal{M}^\circ(\Sigma)$ denote the linear subspace of $\mathcal{M}(\Sigma)$ defined by

$$\mathcal{M}^\circ(\Sigma) = \{ \nu \in \mathcal{M}(\Sigma) | \nu(\Sigma) = 0 \}$$

(3.7)

It follows from (3.3) that the change of condition for any process is an element of $\mathcal{M}^\circ(\Sigma)$. Thus we can view $\mathcal{P}$ as a subset of $\mathcal{M}^\circ(\Sigma) \oplus \mathcal{M}(\Sigma)$. Hereafter, for a theory with state space $\Sigma$ we give $\mathcal{M}(\Sigma)$ the weak-star topology\footnote{By the weak-star topology we mean the coarsest topology on $\mathcal{M}(\Sigma)$ such that, for every continuous $f: \Sigma \rightarrow \mathbb{R}$, the function $\mu \mapsto f(\mu)$ is continuous.}. $\mathcal{M}^\circ(\Sigma)$ the topology it inherits as a subspace of $\mathcal{M}(\Sigma)$, and $\mathcal{M}^\circ(\Sigma) \oplus \mathcal{M}(\Sigma)$ the resulting product topology.

There is a certain amount of structure one might expect the set $\mathcal{P}$ to possess. For example, if $(\Delta m, \vartheta) \in \mathcal{P}$ derives from a process suffered by a body composed of the material under study and if $(\Delta m', \vartheta') \in \mathcal{P}$ derives from a process suffered by another such body (perhaps a copy of the first), then one might expect $\Delta m + \Delta m'$ to be an element of $\mathcal{P}$ on the grounds that the two processes executed in separate locations constitute a third process suffered by the "union" of the two separate bodies. (In effect, we are invoking what Serrin has called the "union axiom"). Moreover, if $(\Delta m, \vartheta) \in \mathcal{P}$ derives from a process suffered by a body of mass $M$ and if $\alpha$ is a positive number, one might expect $\alpha \Delta m, \alpha \vartheta$ to be an element of $\mathcal{P}$ as well — an element that derives from a "scaled copy" of the first process, one suffered by a body of mass $\alpha M$. With considerations like these in mind, we shall assume that $\mathcal{P} \subset \mathcal{M}^\circ(\Sigma) \oplus \mathcal{M}(\Sigma)$ is a convex cone.\footnote{In fact, we shall only require that the topological closure of $\mathcal{P}$ be a convex cone. (If $\mathcal{P}$ is a convex cone, if follows that $\text{cl}(\mathcal{P})$ is a convex cone.) Our discussion here is merely intended to make plausible the idea that $\text{cl}(\mathcal{P})$ should have a convex conical structure. Arguments presented in the second of our articles cited earlier are somewhat different and, we think, more satisfactory.}

Because the set $\mathcal{P}$ for a particular theory carries all the information we shall require about the nature of processes the theory contains, we shall find it convenient to speak of "the process $(\Delta m, \vartheta) \in \mathcal{P}$". In fact, we shall go a step further. In classical thermodynamics one attaches significance not only to
actual processes the bodies under consideration admit but also to idealized "processes" which, while perhaps not among the actual processes, are in some sense approximated by them. Indeed, a substantial part of classical methodology is predicated on the tacit supposition that thermodynamical laws restricting actual processes should govern such idealized "processes" as well. With this in mind, we shall designate as processes not only those elements of $\mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma)$ that lie in $\mathcal{P}$ but also those elements that lie in the closure of $\mathcal{P}$ (denoted $\text{cl}(\mathcal{P})$). When we wish to discuss elements of $\mathcal{P}$ in particular, we shall refer to these as basic processes.

**Definition 1.** A thermodynamical theory $(\Sigma, \mathcal{P})$ is specified by

i) a non-empty set $\Sigma$ endowed with a compact Hausdorff topology. Elements of $\Sigma$ are called states (of material points).

ii) a non-empty set $\mathcal{P} \subseteq \mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma)$ such that $\text{cl}(\mathcal{P})$ is a convex cone. Elements of $\text{cl}(\mathcal{P})$ are called processes; in particular, elements of $\mathcal{P}$ are called basic processes. If $\lambda = (\Delta m, \varphi)$ is a process, then $\Delta m \in \mathcal{M}^0(\Sigma)$ is the change of condition for the process $\lambda$, and $\varphi \in \mathcal{M}(\Sigma)$ is the heating measure for the process $\lambda$.

By a Kelvin-Planck theory we shall mean a thermodynamical theory for which the processes comply with a version of the Kelvin-Planck Second Law. In rough terms this amounts to an assertion that for no cyclic process can the body suffering the process absorb heat from its exterior without emitting heat as well. We begin by defining what we mean by a cyclic process.

**Definition 2.** A cyclic process in a thermodynamical theory $(\Sigma, \mathcal{P})$ is a process for which the change of condition is the zero measure. We denote by $\mathcal{C}$ the set of elements of $\mathcal{M}(\Sigma)$ which are heating measures of cyclic processes. That is,

$$\mathcal{C} := \{ \varphi \in \mathcal{M}(\Sigma) \mid (0, \varphi) \in \text{cl}(\mathcal{P}) \}. $$

Elements of $\mathcal{C}$ are called the cyclic heating measures for the theory.

Note that for a process to be cyclic we require only that the initial and final condition of the body suffering the process be identical. We do not impose the stronger requirement that the state of each material point be the same at the beginning and end of the process.

A Kelvin-Planck theory is a thermodynamical theory in which no (nonzero) cyclic heating measure is a positive measure. This is to say that if, for a Kelvin-Planck theory, $\varphi$ is a heating measure for a cyclic process and there exists a Borel set $A \subseteq \Sigma$ such that $\varphi(A)$ is positive (corresponding to heat absorption), then there must exist a Borel set $A' \subseteq \Sigma$ such that $\varphi(A')$ is negative (corresponding to heat emission). We shall denote by $\mathcal{M}(\Sigma)$ the set of positive Borel measures on $\Sigma$ — that is, the set of those elements of $\mathcal{M}(\Sigma)$ (including the zero measure) which are non-negative on every Borel set. Thus, we have

**: Definition 3.** A Kelvin-Planck theory is a thermodynamical theory $(\Sigma, \mathcal{P})$ for which

$$\mathcal{C} \cap \mathcal{M}_+(\Sigma) = \{0\}. $$

We are now in position to supply answers to questions posed earlier.

### 3.3 The Existence of Specific Entropy Functions and Thermodynamic Temperature Scales

The following theorem asserts that, among all thermodynamical theories, the Kelvin-Planck theories are precisely those that admit (continuous) specific entropy functions and thermodynamic temperature scales which are compatible with the Clausius-Duhem inequality in the sense described earlier. Hereafter $C(\Sigma, K)$ will denote the set of real-valued continuous functions on $\Sigma$, and $C(\Sigma, K)$ will denote the set of functions in $C(\Sigma, K)$ that take strictly positive values.

**Theorem 1.** Let $(\Sigma, \mathcal{P})$ be a thermodynamical theory. The following are equivalent:

i) $(\Sigma, \mathcal{P})$ is a Kelvin-Planck theory.

ii) There exist functions $\eta \in C(\Sigma, K)$ and $\theta \in C(\Sigma, K)$ such that

$$\left\{ \eta \ d(\Delta m) \geq \int_{\Sigma} \frac{d\varphi}{\theta}, \quad \forall (\Delta m, \varphi) \in \text{cl}(\mathcal{P}) \right\}. $$

**Remark 1.** It is worth noting that if, for a particular process, $\Delta m_1$ and $\Delta m_2$ are the initial and final condition of the body suffering the process, then $\Delta m = \Delta m_2 - \Delta m_1$ and

$$\int \eta \ d(\Delta m) = \int \eta \ d\Delta m_1 - \int \eta \ d\Delta m_2. $$

We shall of course regard (3.10) as a Clausius-Duhem inequality for a KelvinPlanck theory, with $\eta(\cdot)$ playing the role of a specific entropy function and $\theta(\cdot)$ playing the role of a temperature scale. Thus, the terms on the right of (3.11) become the final and initial total entropy of the body suffering the process. It is also worth noting that if, for a particular process, the pair $(\Delta m, \varphi)$ derives from the data specified in Example 1, Sect. 3.2 then, for that process, the inequality appearing in (3.10) can be "pulled back" to a somewhat more traditional expression of the Clausius-Duhem inequality:

$$\left\{ \eta(\delta_t(X)) d\mu(X) - \int \eta(\delta_t(X)) d\mu(X) \geq \int \frac{d\delta_t(X, t)}{\theta(\delta_t(X, t))}, \right\}. $$

**Proof of the implication** that (ii) implies (i) in Theorem 1 of this section is straightforward, and we shall not give it. We do, however, think it important to give a brief sketch of the proof that (i) implies (ii) if only to demonstrate that it relies not at all on tacit assumptions about equilibrium states, reversible pro-
cesses, Carnot cycles, or any of the other hypothetical physical apparatus built into classical arguments for the existence of entropy functions and thermodynamic temperature scales.

Rather, the proof relies exclusively on ideas in functional analysis which, while now standard, were unavailable to the pioneers of thermodynamics. We shall need a few preliminary facts: First, \( \mathcal{M}(\Sigma) \) is a locally convex Hausdorff topological vector space, as is \( \mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma) \). Second, the compactness of \( \Sigma \) ensures that
\[
\mathcal{M}^1(\Sigma) = \{ \nu \in \mathcal{M}(\Sigma) \mid \mathcal{C}(\nu) = 1 \}
\]
is a compact subset of \( \mathcal{M}(\Sigma) \). Finally, if \( f: \mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma) \to \mathbb{R} \) is a continuous linear functional, then there exist in \( C(\Sigma, \mathbb{R}) \) functions \( \alpha(\cdot) \) and \( \beta(\cdot) \) such that, for every \( (\nu, \omega) \in \mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma) \),
\[
f(\nu, \omega) = \int_\Sigma \alpha(d\nu) + \int_\Sigma \beta(d\omega).
\] (3.13)

**Sketch of Proof.** (i) implies (ii). In a Kelvin-Planck theory no process is of the form \((0, \omega)\) with \( \omega \in \mathcal{M}^1(\Sigma) \). Thus, in \( \mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma) \) the closed convex cone \( \text{cl}(\mathcal{P}) \) is disjoint from the compact convex set \( \{0\} \times \mathcal{M}^1(\Sigma) \). The Hahn-Banach theorem therefore ensures the existence of a continuous linear functional \( f: \mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma) \to \mathbb{R} \) such that
\[
f(\Delta m, \rho) \leq 0, \quad \forall (\Delta m, \rho) \in \text{cl}(\mathcal{P})
\] (3.14)
and
\[
f(0, \omega) > 0, \quad \forall (0, \omega) \in \{0\} \times \mathcal{M}^1(\Sigma).
\] (3.15)
Moreover, there exist in \( C(\Sigma, \mathbb{R}) \) functions \( \eta(\cdot) \) and \( \beta(\cdot) \) such that \( f(\cdot, \cdot) \) has a representation
\[
f(\nu, \omega) = \int_\Sigma (-\eta)(d\nu) + \int_\Sigma \beta(d\omega), \quad \forall (\nu, \omega) \in \mathcal{M}^0(\Sigma) \oplus \mathcal{M}(\Sigma).
\] (3.16)
Since, for each \( \sigma \in \Sigma \), the Dirac measure \( \delta_\sigma \) is a member of \( \mathcal{M}^1(\Sigma) \) it follows from (3.15) and (3.16) that \( \beta(\cdot) \) takes positive values. Taking \( \theta(\cdot) = 1/\beta(\cdot) \), we obtain (3.10) from (3.14) and (3.16).

**Definition 1.** Let \( (\Sigma, \mathcal{P}) \) be a Kelvin-Planck theory. An element \( (\eta, \theta) \in C(\Sigma, \mathbb{R}) \times C(\Sigma, \mathbb{P}) \) that satisfies condition (3.10) will be called a **Clausius-Duhem pair** for the theory. A function \( \theta \in C(\Sigma, \mathbb{P}) \) is a **Clausius-Duhem temperature scale** for the theory if there exists \( \eta \in C(\Sigma, \mathbb{R}) \) such that \( (\eta, \theta) \) is a Clausius-Duhem pair, in which case \( \eta(\cdot) \) is a **specific entropy function** (corresponding to the Clausius-Duhem temperature scale \( \theta(\cdot) \)). We denote by \( \mathcal{F}_{\text{CD}} \) the set of all Clausius-Duhem temperature scales for the theory.


Because we shall be interested in, among other things, the uniqueness of specific entropy functions and Clausius-Duhem temperature scales for a given Kelvin-Planck theory, we shall be concerned with the supply of Clausius-Duhem pairs a particular theory admits. Inspection of condition (3.10) suggests that the supply of Clausius-Duhem pairs is intimately connected with the supply of processes the theory contains. In rough terms, the larger the set \( \mathcal{P} \) for a Kelvin-Planck theory, the more demanding condition (3.10) becomes and the smaller will be the set of \( (\eta, \theta) \) pairs that satisfy its requirements. It is this dual relationship between the supply of processes and the supply of Clausius-Duhem pairs for a Kelvin-Planck theory that we begin to explore next.

### 3.4 Properties of the Set of Clausius-Duhem Temperatures Scales

This section will conclude with a theorem which gives for a Kelvin-Planck theory a condition which is both necessary and sufficient to ensure that all its Clausius-Duhem temperature scales are identical up to multiplication by a positive constant. Even in the absence of such uniqueness we shall want to draw a connection between temperature and "hotness". That is, we shall want to understand the sense in which the Clausius-Duhem temperatures scales of a Kelvin-Planck theory \( (\Sigma, \mathcal{P}) \) assign to states in \( \Sigma \) numbers which reflect the relative hotness of material points in those various states. Thus, we shall require that the set \( \Sigma \) carry some "hotness structure" wherein it makes sense to say that two distinct states are "of the same hotness" or that one is "hotter than" another. We take the point of view that such a structure should be imposed by the processes the theory contains. Therefore, without recourse to the existence of temperature scales we define the notions "of the same hotness" and "hotter than" in terms of existence within the theory of processes having specified properties. Then we ask how the resulting hotness structure on \( \Sigma \) is reflected in the Clausius-Duhem temperature scales the theory admits.

We begin by stating what we mean by a reversible process.

**Definition 1.** A **reversible process** in a thermodynamical theory \( (\Sigma, \mathcal{P}) \) is a process \( (\Delta m, \rho) \in \text{cl}(\mathcal{P}) \) such that \( (\Delta m, -\rho) \) is also contained in \( \text{cl}(\mathcal{P}) \).

Note that a reversible process need not be a member of \( \mathcal{P} \), the set of basic processes; it need only be a member of \( \text{cl}(\mathcal{P}) \). This we believe reflects the usual idea that a reversible process need not be a member of the "actual" processes but should be approximated by them. Note also that our definition of a reversible process is somewhat weaker than the traditional one, in which a process and its reverse trace out "paths" in opposite directions. Here we require no notion of "path".

**Definition 2.** Let \( (\Sigma, \mathcal{P}) \) be a thermodynamical theory. Two states \( \sigma, \sigma' \in \Sigma \) are of the same hotness (denoted \( \sigma \sim \sigma' \)) if there exists in \( \text{cl}(\mathcal{P}) \) a reversible cyclic process with heating measure \( \delta_{\sigma'} - \delta_{\sigma} \). The equivalence relation \( \sim \) induces a partition of \( \Sigma \) into equivalence classes called **hotness levels**.
denote by $\mathcal{H}$ the set of all hotness levels, and we give $\mathcal{H}$ the quotient topology it inherits from $\Sigma$.

In rough terms, the reversible cyclic process described in Definition 2 of this section is such that, for the body suffering the process, heat is absorbed only by material points in state $\sigma'$, heat is emitted only by material points in state $\sigma$, and the amount of heat absorbed is equal to the amount emitted (whereupon the First Law requires that the net amount of work done on the body is zero). Here again it is important to recognize that the process described need not be among the basic (or "actual") processes; it need only be approximated by them.

**Theorem 1.** Let $(\Sigma, \mathcal{F})$ be Kelvin-Planck theory. The following are equivalent:

i) $\sigma' \in \Sigma$ and $\sigma \in \Sigma$ are of the same hotness.

ii) $\theta(\sigma') = \theta(\sigma)$, $\forall \theta \in \mathcal{F}_{CD}$.

Theorem 1 of this section asserts not only that two states of the same hotness are assigned identical temperatures by every Clausius-Duhem scale but also that if two states $\sigma'$ and $\sigma$ are not distinguished by any Clausius-Duhem scale for the theory then the theory must contain a process of the kind described in Definition 2 of this section.

Because two states residing in the same hotness level are assigned identical temperatures by every Clausius-Duhem scale, it makes sense to speak of the "temperature of a hotness level".

**Definition 3.** For a Kelvin-Planck theory $(\Sigma, \mathcal{F})$ let $\theta: \Sigma \rightarrow \mathbb{P}$ be a Clausius-Duhem temperature scale. By $\theta^*: \mathcal{H} \rightarrow \mathbb{P}$ we mean the Clausius-Duhem temperature scale on $\mathcal{H}$ induced by $\theta(\cdot)$ in the following way: For each $h \in \mathcal{H}$

$$\theta^*(h) = \theta(\sigma),$$

where $\sigma$ is any element of $h$. The set of all Clausius-Duhem temperature scales induced on $\mathcal{H}$ by members of $\mathcal{F}_{CD}$ will be denoted by $\mathcal{F}^*_{CD}$.

Next we wish to give meaning to the idea that one hotness level is "hotter" than another. In preparation for that definition we recall that the support of a measure $\nu \in \mathcal{M}_+(\Sigma)$ is defined to be the complement in $\Sigma$ of the largest open set in $\Sigma$ of $\nu$-measure zero. We denote the support of $\nu$ by $\text{supp} \nu$. In terms which are hardly precise, $\text{supp} \nu$ is that part of $\Sigma$ which $\nu$ acts on in a nontrivial way. In particular, if $h \subseteq \Sigma$ is a hotness level, then $\text{supp} \nu \subseteq h$ implies that $\nu(\Lambda) = 0$ for any Borel set $\Lambda \subseteq \Sigma$ disjoint from $h$.

**Definition 4.** For a Kelvin-Planck theory $(\Sigma, \mathcal{F})$ with hotness levels $\mathcal{H}$ we say that $h' \in \mathcal{H}$ is hotter than $h \in \mathcal{H}$ (denoted $h' \succ h$) if $h' \neq h$ and there exists in $\text{cl}(\mathcal{F})$ a cyclic process with heating measure of the form

$$\nu = \nu' - \nu,$$

where $\nu'$ and $\nu$ are members of $\mathcal{M}_+(\Sigma)$ such that $\text{supp} \nu \subseteq h$ and $\nu'(h') > \nu(h)$.

In rough terms, the process described is a cyclic (not necessarily reversible) one wherein heat is emitted only by material points in states within hotness level $h$, and the amount of heat emitted is less than the amount absorbed by material points in states contained within hotness level $h'$. Thus, the total amount of heat absorbed by the body suffering the process is positive (whereupon the First Law requires that the body do work).\(^{12}\)

**Remark 1.** For a Kelvin-Planck theory the relation $\succ$ is a partial order on the set of hotness levels. It need not be the case that the order is total, for the theory may be insufficiently rich in processes to render every pair of hotness levels $\succ$-comparable.

**Theorem 2.** Let $h'$ and $h$ be hotness levels for a Kelvin-Planck theory. The following are equivalent:

i) $h'$ is hotter than $h$.

ii) There exists $\epsilon > 0$ such that

$$\frac{\theta^*(h')}{\theta^*(h)} > 1 + \epsilon, \quad \forall \theta^* \in \mathcal{F}_{CD}. \quad (3.17)$$

Theorem 2 of this section asserts that if $h'$ is hotter than $h$ it is not only true that $\theta^*(h') > \theta^*(h)$ for each $\theta^* \in \mathcal{F}_{CD}$ but also that the ratio of the two temperatures is bounded away from unity as $\theta^*(\cdot)$ ranges over all Clausius-Duhem scales on $\mathcal{H}$. Conversely, if the set of Clausius-Duhem temperature scales for a Kelvin-Planck theory has this property, then the theory must contain a process of the kind described in Definition 4 of this section.

We turn next to a corollary of Theorem 2 of this section. Recall that for us the hotness levels for a Kelvin-Planck theory $(\Sigma, \mathcal{F})$ were defined objects, and the set $\mathcal{H}$ of all hotness levels inherited its topology (Definition 2 of this section) from that of $\Sigma$ even before $\mathcal{H}$ was endowed with a "hotter than" relation. In the absence of special assumptions one cannot say much about the topological nature of $\mathcal{H}$ other than that $\mathcal{H}$, like $\Sigma$, is compact and Hausdorff. If, however, the Kelvin-Planck theory in question is sufficiently rich in processes as to make $\succ$ a total order on $\mathcal{H}$, then one can say quite a bit: that $\mathcal{H}$ looks very much like a subset of the real line.

**Corollary 1.** Let $\mathcal{H}$ be the set of hotness levels for a Kelvin-Planck theory $(\Sigma, \mathcal{F})$. If $\mathcal{H}$ is totally ordered by $\succ$, then $\mathcal{H}$ is both homeomorphic and order-similar to a subset of the real line.\(^{13}\) In particular, if $\Sigma$ is connected then $\mathcal{H}$ is homeomorphic and order-similar to a bounded closed interval of the real line.

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\(^{12}\) A similar, though somewhat more special, notion of hotter than was used by Truesdell [3.7].

\(^{13}\) Corollary 1 of this section gives nontrivial information not only about the topological structure of $\mathcal{H}$ but also about its order structure. It is not generally the case that a totally ordered set is order-similar to a subset of the real line. For a counterexample see [3.3, Sect. 5].
In questions concerning the essential uniqueness of Clausius-Duhem temperature scales we shall find that Carnot processes play an inexorable role.

**Definition 5.** A Carnot process in a thermodynamical theory \((\Sigma, \mathcal{P})\) is a reversible cyclic process \((0, \varphi) \in cl(\mathcal{P})\) with the following property: There exist in \(\Sigma\) hotness levels \(h' \) and \(h\) such that the heating measure \(\varphi\) has a representation
\[ \varphi = \nu' - \nu, \]
where \(\nu'\) and \(\nu\) are non-zero elements of \(\mathcal{M}_+(\Sigma)\) with \(supp \nu' \subseteq h'\) and \(supp \nu \subseteq h\). We say that the Carnot process operates between hotness levels \(h'\) and \(h\).

In rough terms, the process described in Definition 5 of this section is a reversible cyclic one wherein heat is absorbed by material points in states contained entirely in one hotness level and heat is emitted by material points in states contained entirely in another hotness level.

**Theorem 3.** Let \((\Sigma, \mathcal{P})\) be a Kelvin-Planck theory. The following are equivalent:

i) All Clausius-Duhem temperature scales for \((\Sigma, \mathcal{P})\) are identical up to multiplication by a positive constant.

ii) For each pair of hotness levels \(h'\) and \(h\) there exists in \(cl(\mathcal{P})\) a Carnot process operating between \(h'\) and \(h\).

iii) For each pair of states \(\sigma' \in \Sigma\) and \(\sigma \in \Sigma\) there exists in \(cl(\mathcal{P})\) a Carnot process with heating measure \(c' \delta_{\sigma'} - c \delta_{\sigma}\), where \(c'\) and \(c\) are positive numbers.\(^{14}\)

The implications (iii) \(\Rightarrow\) (ii) \(\Rightarrow\) (i) of Theorem 3 of this section are routine. Of real interest here are the implications (i) \(\Rightarrow\) (ii) \(\Rightarrow\) (iii). In rough terms these assert that, in order for a Kelvin-Planck theory \((\Sigma, \mathcal{P})\) to have an essentially unique Clausius-Duhem temperature scale, it is necessary that the theory contain a rich supply of Carnot processes; moreover, every state in \(\Sigma\) must manifest itself in a reversible (Carnot) process.

### 3.5 Properties of the Set of Specific Entropy Functions

Here we examine connections between the set of specific entropy functions for a Kelvin-Planck theory and the set of processes the theory contains. Let \((\Sigma, \mathcal{P})\) be a Kelvin-Planck theory for which \(\mathcal{F}_{CD}\) is the set of Clausius-Duhem temperature scales. For each \(\varphi \in \mathcal{F}_{CD}\) we denote by \(\mathcal{F}_\varphi\) the set of specific entropy functions that correspond to \(\varphi\):
\[ \mathcal{F}_\varphi = \{ \eta \in C(\Sigma, \mathcal{R}) \mid (\eta, \varphi) \text{ is a Clausius-Duhem pair for } (\Sigma, \mathcal{P}) \}. \]

Moreover, we denote by \(\mathcal{F}\) the set of all specific entropy functions the theory admits; that is, \(\mathcal{F}\) is the union of all \(\mathcal{F}_\varphi\) as \(\varphi\) ranges over \(\mathcal{F}_{CD}\).

**Definition 1.** An adiabatic process in a thermodynamical theory \((\Sigma, \mathcal{P})\) is an element of \(cl(\mathcal{P})\) for which the heating measure is the zero measure.\(^{15}\)

**Definition 2.** Let \((\Sigma, \mathcal{P})\) be a thermodynamical theory. Two states \(\sigma' \in \Sigma\) and \(\sigma \in \Sigma\) are adiabatically related if there exists in \(cl(\mathcal{P})\) a reversible adiabatic process for which \(\delta_{\sigma'} - \delta_{\sigma}\) is the change of condition.\(^{16}\)

The process described in Definition 2 of this section can be regarded as a reversible adiabatic one in which the body (of unit mass) suffering the process has initial condition \(\delta_{\sigma}\) and final condition \(\delta_{\sigma'}\). That is, the body begins in a homogeneous condition wherein all material points are in state \(\sigma\) and ends in a homogeneous condition wherein all material points are in state \(\sigma'\).

**Theorem 1.** Let \((\Sigma, \mathcal{P})\) be a Kelvin-Planck theory. The following are equivalent:

i) \(\sigma' \in \Sigma\) and \(\sigma \in \Sigma\) are adiabatically related.

ii) \(\eta(\sigma') = \eta(\sigma),\quad \forall \eta \in \mathcal{F}\).

Theorem 1 of this section asserts not only that two adiabatically related states are assigned identical values by every specific entropy function for the theory but also that if no specific entropy functions distinguishes \(\sigma'\) from \(\sigma\) then the theory must contain a process of the kind described in Definition 2 of this section.

Our next theorem addresses the following question: In a Kelvin-Planck theory for which all Clausius-Duhem temperature scales are essentially identical, what is required — beyond a rich supply of Carnot processes — in order to ensure that the specific entropy functions corresponding to each temperature scale are also essentially identical?

**Theorem 2.** Let \((\Sigma, \mathcal{P})\) be a Kelvin-Planck theory for which all Clausius-Duhem temperature scales are identical up to multiplication by a positive number. The following are equivalent:

i) For each \(\varphi \in \mathcal{F}_{CD}\) the elements of \(\mathcal{F}_\varphi\) are identical up to an additive constant.\(^{17}\)

ii) For each pair of states \(\sigma' \in \Sigma\) and \(\sigma \in \Sigma\) there exists in \(cl(\mathcal{P})\) a reversible process for which the change of condition is \(\delta_{\sigma'} - \delta_{\sigma}\).

As in the discussion following Definition 2 of this section, the process described in (ii) can be regarded to be a reversible one in which the body suffering

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\(^{14}\) In rough terms, the Carnot process described in (iii) is one for which there is net heat absorption only by material points in state \(\sigma'\) and net heat emission only from material points in state \(\sigma\). It should be remembered that such a process need only lie in the closure of \(\mathcal{P}\). In terms of the classical picture it is instructive to think about a sequence of Carnot cycles with isothermal parts of decreasing length.

\(^{15}\) The definition of an adiabatic process given here is somewhat weaker than the usual one. It does not necessarily imply that during the course of the process there is no heat supplied or removed but rather that if there is heat supplied and removed these compensate each other in such a way as to make \(\phi(A) = 0\) for every Borel set \(A \subseteq \Sigma\).

\(^{16}\) The equivalence relation on \(\Sigma\) given in Definition 2 of this section serves to partition \(\Sigma\) into adiabats. In ways we shall not pursue here, these play for specific entropy functions the role that hotness levels play for Clausius-Duhem temperature scales.

\(^{17}\) In the context of the theorem it is not difficult to deduce from (ii) that if \(\eta(\sigma)\) and \(\eta(\tau)\) are any specific entropy functions for the theory, not necessarily corresponding to the same temperature scale, there exist \(c \in \mathcal{R}\) and \(c' \in \mathcal{R}\) such that \(\eta(\tau) = c\eta(\sigma) + c'\).
the process begins with all its material points in state \( \sigma \) and ends with all its material points in state \( \sigma' \). Here, however, the process need not be adiabatic.

That (ii) implies (i) is well known. That (i) implies (ii) is more interesting. In rough terms this last implication requires that, for a Kelvin-Planck theory \((\Sigma, \mathcal{P})\) to have not only an essentially unique Clausius-Duhem temperature scale but also an essentially unique specific entropy function, it is necessary that \( \mathcal{P} \) be so rich that, for each pair of states in \( \Sigma \), there exists in \( \text{cl}(\mathcal{P}) \) a reversible process connecting them. Here, as in Theorem 3 of Sect. 3.4 uniqueness of the specific entropy function requires that each state in \( \Sigma \) manifests itself in some reversible process.

### 3.6 Concluding Remark

Beginning with a statement of the Second Law and the tacit presumption of a rich supply of reversible processes, classical arguments deduce simultaneously both the existence and uniqueness of requisite functions of state. Questions of existence and uniqueness are of course very different, and it should come as no surprise if conditions for one are largely irrelevant to the other. Theorem 1 of Sect. 3.3 ensures the existence of a Clausius-Duhem temperature scale and a specific entropy functions for any Kelvin-Planck theory — roughly, for any thermodynamical theory that carries a Kelvin-Planck Second Law — regardless of the nature of the individual “states” the theory purports to take into account. On the other hand, if these functions are to be essentially unique for a particular theory, Theorems 3 of Sect. 3.4 and Theorem 2 of Sect. 3.5 require that all the states be of the kind that can be exhibited during the course of a reversible process. Thus, there is little in these theorems to support the position of those who would deny the existence of crucial state functions in modern thermodynamical theories. On the contrary, Theorem 1 of Sect. 3.3 calls such a denial into serious question. If, however, uniqueness of these functions is at issue, then the more conservative thermodynamicists would seem to have the weight of Theorem 3 of Sect. 3.4 and Theorem 2 of Sect. 3.5 on their side.

### References

3.7 C. Truesdell: Absolute temperatures as a consequence of Carnot’s general axiom. Arch. History Exact Sci. 20, 357 – 380 (1979)