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An Axiomatic Foundation for Continuum Thermodynamics

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I. Introduction

During the past several years much progress has been made toward the goal of establishing a general theory of continuum thermodynamics. Coleman and Noll [1963] have developed a rational procedure for systematically establishing those restrictions placed on constitutive relations by the Second Law of Thermodynamics. This procedure has since been applied to various constitutive assumptions,[1] and the results, for surprisingly large classes of materials, seem to be in complete accord with physical experience. As their starting point these studies take the First Law of Thermodynamics in the tradtional form[2]

$$\frac{d}{dt}\int_{\mathcal{Q}} e\,dV = \int_{\partial\mathcal{Q}} \underset{\sim}{q}\cdot\underset{\sim}{n}\; dA + \int_{\mathcal{Q}} r\,dV,$$

and the Second Law in the form of the inequality

$$\frac{d}{dt}\int_{\mathcal{Q}} s\,dV \geq \int_{\partial\mathcal{Q}} \frac{\underset{\sim}{q}\cdot\underset{\sim}{n}}{\theta}\, dA + \int_{\mathcal{Q}} \frac{r}{\theta}\, dV,$$

which is due to Clausius, Duhem, Truesdell, and Toupin[3] and usually referred to as the Clausius-Duhem inequality. Here $\mathcal{Q}$, with boundary $\partial\mathcal{Q}$, is an arbitrary smooth subregion of the body; e is the internal energy density, s the entropy density, θ the temperature, $\underset{\sim}{q}$ the heat conduction vector, and r the radiation density. The success of the above mentioned work has established

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[1] For applications to simple materials see Coleman and Noll [1963], Coleman and Mizel [1963, 1964], Coleman [1964-1,2], Gurtin [1965-1,2; 1967], Gurtin and Williams [1966-1], Wang and Bowen [1966], and Coleman and Gurtin [1967-1,2].

[2] Actually, the above studies include mechanical effects which, for convenience, we neglect. Thus, here and in what follows we assume that the body is rigid and stationary.

[3] This postulate, for the case in which $\underset{\sim}{q} \equiv \underset{\sim}{0}$ and $r \equiv 0$, is due to Clausius [1854, 1862, 1865]; the surface integral was added by Duhem [1901] and the volume integral by Truesdell and Toupin [1960].

that these are appropriate starting assumptions for the study of constitutive relations, at least for those classes of materials to which they have been applied. Because of this it becomes important to develop an axiomatic structure for continuum thermodynamics in which the relation of the above laws to the general axioms of thermodynamics is brought out. In this work we present a complete set of axioms,[1] based upon physically acceptable gross forms of the laws of thermodynamics, which yield appropriate forms of these laws for continuum physics. In particular we give assumptions under which these forms reduce to the classical ones above.[2] Of special interest is the fact that the existence of temperature is seen to be a consequence of the requirement that the entropy flux into one body from another must vanish whenever the two bodies do not exchange heat.

We attempt to maintain throughout the complete rigour which we feel is necessary in any work of this sort. We make no hidden assumptions of smoothness or of any other property; the assumptions necessary for any result, beyond those contained in the axioms, are always stated as hypotheses for the theorem. It also is to be emphasized that nowhere in this work do we find it necessary to consider quasi-static processes, adiabatic processes, reversibility, or any such classical notions. We need to consider only a single body in a single ''process'' to introduce all of the necessary concepts and to demonstrate all of our results.

Aside from the axioms which state the First and Second Laws of Thermodynamics, the basic axioms of the work are those

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[1] For an axiomatic treatment of classical thermodynamics see Arens [1963] and Giles [1964].

[2] Roughly speaking, the assumptions are that there be no internal radiation and that the flow of entropy across any surface be balanced.

typical of continuum physics; first that any physical law postulated as true for a body be true for any ''body-like'' part within the body, and second that all physical quantities defined on such subbodies be extendable to measures.

The plan of the work is as follows: In Section 2 we consider the technical question of which sets contained within a given body are to be considered for the theory. We introduce the notions of internal energy and heat flux in Section 3 and state the First Law in Section 4. Consequences of the First Law are then found and the classical reduced form of this law deduced. In Section 5 we introduce entropy and entropy flux in a manner paralleling the earlier treatment of energy, and in Section 6 we lay down our version of the Second Law. This is then shown to imply the existence of temperature and to lead to a reduction of the expressions for the entropy flux and, in Section 7, to certain heat conduction inequalities. In Section 8, we consider assumptions which are sufficient to reduce the Second Law to the Clausius-Duhem inequality.

Many of the results in Section 4 are analogs of, and based upon, Noll's treatment of continuum mechanics;[1] indeed the realization that measure theory is an appropriate vehicle for the statement of the fundamental axioms of continuum physics is due to Noll.

Although we here treat only the case of non-deforming bodies and hence ignore mechanical effects, it is clear that all of our <u>basic</u> arguments would remain valid for the case of deforming media. Aside from certain obvious alterations to account for the

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[1]Noll [1959, 1963, 1965].

kinematics, the only change we need make is to alter the First Law to read

$$\frac{d}{dt}(E + K) = H + W,$$

where E is the internal energy of an arbitrary subbody $\mathcal{A}$, K the kinetic energy of $\mathcal{A}$, H the heat flux into $\mathcal{A}$ from its exterior, and W the rate of mechanical work done on $\mathcal{A}$. To get all of our results it is then sufficient to assume that the mechanical work W takes the classical form.

II. Bodies, Subbodies, the Material Universe

As we treat here only rigid immobile bodies we dispense with the usual definition of a body[1] and regard it merely as a standard region in Euclidean three dimensional space $\mathcal{E}$. We then consider subbodies of the given body as members of a class of standard subregions of the body. To fix notation let us here point out that we use the term standard region for the closure of an open set $\mathcal{A}$ whose boundary is the union of a closed set of zero area and a finite number of class C^1 two-dimensional manifolds, each of the manifolds having the open set $\mathcal{A}$ on just one side.

We reserve capital script letters for subsets of $\mathcal{E}$ and denote, for $\mathcal{A} \subset \mathcal{E}$, the boundary of $\mathcal{A}$ by $\partial\mathcal{A}$, the interior by $\mathring{\mathcal{A}}$, and the closure by $\overline{\mathcal{A}}$. Given any set $\mathcal{A} \subset \mathcal{E}$ we write

$$\mathcal{A}^e = \overline{\mathcal{E} - \mathcal{A}}$$

and call $\mathcal{A}^e$ the exterior of $\mathcal{A}$ in $\mathcal{E}$.

Henceforth we shall consider a single, fixed body $\mathcal{B}$. Given any other set $\mathcal{A} \subset \mathcal{B}$ we denote the relative exterior of $\mathcal{A}$ in $\mathcal{B}$ by

$$\mathcal{A}^b = \overline{\mathcal{B} - \mathcal{A}} .$$

Of course

$$\mathcal{A}^e = \mathcal{A}^b \cup \mathcal{B}^e .$$

We shall consider a class $\mathcal{M}^{\mathcal{B}}$ of subsets of $\mathcal{B}$; elements of $\mathcal{M}^{\mathcal{B}}$ will be called subbodies. The structure we require on $\mathcal{M}^{\mathcal{B}}$ (which imposes certain smoothness requirements on $\mathcal{B}$) is given in the following axiom. For convenience we consider the null set $\emptyset$ to be a standard region.

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[1] Noll [1959].

Axiom 1: The set $\mathcal{M}^{\mathcal{B}}$ has the following properties:

(i) every element of $\mathcal{M}^{\mathcal{B}}$ is a standard region;

(ii) $\mathcal{A} \in \mathcal{M}^{\mathcal{B}}$ implies $\mathcal{A}^b \in \mathcal{M}^{\mathcal{B}}$;

(iii) $\mathcal{A}, \mathcal{C} \in \mathcal{M}^{\mathcal{B}}$ implies $\mathcal{A} \cup \mathcal{C} \in \mathcal{M}^{\mathcal{B}}$;

(iv) if $\mathcal{C}$ is a solid circular cylinder or a solid prism in $\mathcal{E}$ then $\overline{\overset{\circ}{\mathcal{C} \cap \mathcal{B}}} \in \mathcal{M}^{\mathcal{B}}$;

(v) if $\mathcal{A} \in \mathcal{M}^{\mathcal{B}}$ and $\mathcal{S}$ is any regular surface included in $\partial\mathcal{A}$ there exists a monotone sequence $\{\mathcal{A}_n\}$ of elements of $\mathcal{M}^{\mathcal{B}}$, $\mathcal{A}_n \subset \mathcal{A}$, such that $\bigcap_{n=1}^{\infty} \mathcal{A}_n = \mathcal{S}$;

(vi) if $\mathcal{A} \in \mathcal{M}^{\mathcal{B}}$ and $\underset{\sim}{a}$ is any vector, then $\mathcal{A} + \underset{\sim}{a}$ contained in $\mathcal{B}$ implies $\mathcal{A} + \underset{\sim}{a} \in \mathcal{M}^{\mathcal{B}}$.

The conditions (iv) and (v) ensure that $\mathcal{M}^{\mathcal{B}}$ has sufficiently many elements to generate the Borel sets of $\mathcal{B}$ and of any surface $\partial\mathcal{A}$ with $\mathcal{A} \in \mathcal{M}^{\mathcal{B}}$. The other conditions guarantee a structure on $\mathcal{M}^{\mathcal{B}}$ sufficient to make meaningful all operations carried out in what follows. Note in particular that $\emptyset, \mathcal{B} \in \mathcal{M}^{\mathcal{B}}$. The operation appearing in (iv) occurs sufficiently often that we introduce a special notation for it: for any sets $\mathfrak{F}, \mathfrak{G}$ in $\mathcal{E}$ we define

$$\mathfrak{F} \wedge \mathfrak{G} = \overline{\overset{\circ}{\mathfrak{F} \cap \mathfrak{G}}}.$$

Then it is clear that $\mathcal{A}, \mathcal{C} \in \mathcal{M}^{\mathcal{B}}$ implies $\mathcal{A} \wedge \mathcal{C} \in \mathcal{M}^{\mathcal{B}}$. We will say that two sets $\mathfrak{F}, \mathfrak{G}$ are separate if $\mathfrak{F} \wedge \mathfrak{G} = \emptyset$; it follows that two subbodies $\mathcal{A}, \mathcal{C}$ are separate if and only if $(\mathcal{A} \cap \mathcal{C}) \subset (\partial\mathcal{A} \cap \partial\mathcal{C})$.

One may define, in the manner of Noll [1963, 1965] a material universe as a collection of bodies each of which has the properties of $\mathcal{B}$. This, however, yields more structure than is necessary for the theory; it suffices to consider, besides the elements of $\mathcal{M}^{\mathcal{B}}$, only the exterior, $\mathcal{B}^e$, of $\mathcal{B}$. More precisely we define $\mathcal{M}$, the material universe for $\mathcal{B}$, by

$$\mathcal{M} = \{ \mathcal{D} \mid \mathcal{D} \in \mathcal{M}^{\mathcal{B}} \text{ or } \mathcal{D}^e \in \mathcal{M}^{\mathcal{B}} \}.$$

The structure imposed on $\mathcal{M}^{\mathcal{B}}$ yields a corresponding structure[1] on $\mathcal{M}$: $\mathcal{E}, \emptyset \in \mathcal{M}$; $\mathcal{D} \in \mathcal{M}$ implies $\mathcal{D}^e \in \mathcal{M}$; and $\mathcal{D}_1, \mathcal{D}_2 \in \mathcal{M}$ implies both $\mathcal{D}_1 \cup \mathcal{D}_2 \in \mathcal{M}$ and $\mathcal{D}_1 \wedge \mathcal{D}_2 \in \mathcal{M}$. Of course any element in $\mathcal{M}$ is either a subbody or the union of a subbody and $\mathcal{B}^e$.

We shall be concerned with real-valued set functions defined on $\mathcal{M}^{\mathcal{B}}$ or $\mathcal{M}$. We say that such a function α is separately additive, or simply s-additive, if

$$\alpha(\mathcal{A} \cup \mathcal{C}) = \alpha(\mathcal{A}) + \alpha(\mathcal{C})$$

for every pair of separate elements $\mathcal{A}, \mathcal{C}$ in the domain of α.

Fundamental to this work is the assumption that such functions may be extended to the class of all Borel sets of $\mathcal{B}$. For convenience we shall refer to these sets as parts. Given any part $\mathcal{D}$ we denote the Borel sets of $\mathcal{D}$ by $\mathbb{B}(\mathcal{D})$. We shall use the term measure exclusively to denote finite real-valued Borel signed measure. Except for this convenience we shall use the standard definitions of measure theory; these and all uncited results used herein can be found in the book of Halmos [1950]. We use $<<$ to denote absolute continuity and write $\mu = \mu^+ - \mu^-$ for the Jordan decomposition of the measure μ. We shall use the terms "almost every", "almost everywhere" and "essentially" to denote "except on a set of volume (area) measure zero" (the choice between volume

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[1] With $\cup$ as join and $\wedge$ as meet both $\mathcal{M}^{\mathcal{B}}$ and $\mathcal{M}$ have the structure of a Boolean algebra.

and area will be clear from the context); in all other cases we specify the measure involved. We reserve V for Lebesgue volume measure in $\mathcal{E}$ and A for Lebesgue surface measure on manifolds in $\mathcal{E}$. The only non-standard measure-theoretic concept we need introduce is the following: we say that a measure μ *follows* a measure ν if

$$\mu^+ << \nu^+, \qquad \mu^- << \nu^-;$$

that μ *opposes* ν if

$$\mu^+ << \nu^-, \qquad \mu^- << \nu^+.$$

Clearly μ follows (opposes) ν if and only if any Hahn decomposition for ν is also a Hahn decomposition for μ $(-\mu)$; or if and only if $\mu << \nu$ and the Radon-Nikodym derivative $\frac{d\mu}{d\nu}$ is essentially positive (negative).

We shall reserve the term *surface* for the (relative) closure of an oriented class C^1 two-dimensional differentiable manifold or the finite union of such (closed) manifolds. The boundary of a standard region is taken to be oriented in the positive sense with respect to that region, i.e. with the orientation corresponding to the external normal vector. A surface contained (in the sense of set-inclusion) in another surface is a *positive segment* of that surface if it has the same orientation; if it has the opposite orientation it is called a *negative segment*. We define in an obvious manner the positive and negative normal vectors to a surface; if $\mathcal{S}$ is an oriented surface, then $-\mathcal{S}$ is the same surface taken with the opposite orientation. A point $\underset{\sim}{x}$ in a regular surface $\mathcal{S}$ will be called a *regular point* of $\mathcal{S}$ if $\mathcal{S}$ is smooth at $\underset{\sim}{x}$. A surface $\mathcal{S}$ contained in $\mathcal{B}$ is called a *material surface* if it is a positive segment of the boundary of a subbody. If the (relative) interior of a material surface $\mathscr{S}$ is disjoint from $\partial\mathscr{B}$, then $\mathscr{S}$ is said to be interior to $\mathscr{B}$. If $\mathscr{S}$ is a positive segment of both $\partial\mathscr{P}_1$ and $\partial\mathscr{P}_2$, where $\mathscr{P}_1, \mathscr{P}_2 \in \mathscr{M}$, then $\mathscr{S}$ is also a positive segment of $\partial(\mathscr{P}_1 \wedge \mathscr{P}_2)$.

We shall consider a fixed time interval, i.e., an interval of the real line, and shall denote points of this interval by t. In every assertion involving functions of time we shall imply, without so stating, that the assertion holds for every t.

III. Energy

We now assume that we may associate with the body $\mathcal{B}$ at any time t a scalar $E_t(\mathcal{B})$ which represents the internal energy of the body at that time, and a scalar $H_t(\mathcal{B},\mathcal{B}^e)$ which represents the flux of energy into $\mathcal{B}$ from its exterior $\mathcal{B}^e$. The First Law of Thermodynamics for the body $\mathcal{B}$ is the assertion that the time rate of change of internal energy of $\mathcal{B}$ equals the amount of heat that flows into $\mathcal{B}$ from its exterior:

$$\frac{d}{dt} E_t(\mathcal{B}) = H_t(\mathcal{B},\mathcal{B}^e).$$

The basic continuum hypothesis is then that $E_t(\mathcal{A})$ and $H_t(\mathcal{A},\mathcal{A}^e)$ are defined and satisfy this relation for all subbodies $\mathcal{A}$ contained in $\mathcal{B}$. Beyond this we assume that we can distinguish not only the heat flux $H_t(\mathcal{A},\mathcal{A}^e)$ into $\mathcal{A}$ from its exterior but also the heat flux $H_t(\mathcal{A},\mathcal{D})$ into $\mathcal{A}$ from any other element $\mathcal{D}$ of the material universe, and that $E_t(\cdot)$ and $H_t(\cdot,\mathcal{D})$ are extendable to measures. Further, we make a restriction on E_t and H_t which may be interpreted as requiring that a part of $\mathcal{B}$ of arbitrarily small volume must have arbitrarily small internal energy and can accept only an arbitrarily small amount of direct radiation. Correspondingly, we assume that an arbitrarily small surface of contact can suffer only an arbitrarily small amount of conductive transfer.

Therefore, we assume the existence of two set functions: E_t, which assigns to each part $\mathcal{P}$ in $\mathbb{B}(\mathcal{B})$ at any time t a scalar $E_t(\mathcal{P})$ called the *internal energy* of $\mathcal{P}$; and H_t, which assigns to any $\mathcal{D} \in \mathcal{M}$ and any part $\mathcal{P} \subset \mathcal{D}^b$ a scalar $H_t(\mathcal{P},\mathcal{D})$, the *heat flux* into $\mathcal{P}$ from $\mathcal{D}$.

Axiom 2:

(i) $E_t(\cdot)$ is a measure on $\mathbb{B}(\mathcal{B})$;

(ii) the derivative $\dot{E}_t(\mathcal{P}) = \frac{d}{dt} E_t(\mathcal{P})$ exists for each $\mathcal{P} \in \mathbb{B}(\mathcal{B})$;

(iii) there exists a scalar $\alpha(t)$ such that

$$|E_t(\mathcal{P})| \leq \alpha(t) \; V(\mathcal{P})$$
$$|\dot{E}_t(\mathcal{P})| \leq \alpha(t) \; V(\mathcal{P})$$

for all $\mathcal{P} \in \mathbb{B}(\mathcal{B})$.

Clearly (i) and $(iii)_1$ imply that the restriction of E_t to $\mathcal{M}^{\mathcal{B}}$ is s-additive.

It is possible to state Axiom 2 in a somewhat weaker manner. First, if E_t is assumed defined, s-additive, and compatible with $(iii)_1$ on $\mathcal{M}^{\mathcal{B}}$ then by the theorem in the Appendix it can be extended to a measure on $\mathbb{B}(\mathcal{B})$, and this measure has property $(iii)_1$. Similarly, if $\dot{E}_t$ is assumed to exist for all $\mathcal{Q} \in \mathcal{M}^{\mathcal{B}}$ and to obey $(iii)_2$, it can be shown to be s-additive on $\mathcal{M}^{\mathcal{B}}$ and hence also extendable to $\mathbb{B}(\mathcal{B})$ as a measure. Alternatively, since $|E_t(\mathcal{P})| < \alpha(t)V(\mathcal{P})$ implies $E_t \ll V$, it follows from the Vitali-Hahn-Saks Theorem[1] that if $\dot{E}_t$ exists for every $\mathcal{P} \in \mathbb{B}(\mathcal{B})$ it is also volume-continuous. We leave Axiom 2 in its present form to preserve uniformity with Axiom 3 below.

It is important to note that Axiom 2 implies $\dot{E}_t(\cdot)$ is a measure. Indeed, that $\dot{E}_t(\cdot)$ is a finitely additive finite set function on $\mathbb{B}(\mathcal{B})$ is immediate from (ii); that it is also countably additive and hence a measure follows from the Vitali-Hahn-Saks Theorem. Note that assumption (iii) implies absolute continuity of E_t and $\dot{E}_t$ with respect to V but is stronger: it bears the same relation to absolute continuity that Lipschitz

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[1]See, e.g., Dunford and Schwartz [1958], p. 158.

continuity bears to continuity in the case of functions on the real line. This volume continuity of course rules out point, line, or surface concentrations of energy in the body; by the Radon-Nikodym Theorem it implies the existence of essentially bounded functions $e(\cdot,t)$ and $\dot{e}(\cdot,t)$ on $\mathcal{B}$ such that for every part $\mathcal{P}$

$$E_t(\mathcal{P}) = \int_{\mathcal{P}} e(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}),$$

$$\dot{E}_t(\mathcal{P}) = \int_{\mathcal{P}} \dot{e}(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}).$$

We call $e(\underset{\sim}{x},t)$ the *volume-specific internal energy* at $(\underset{\sim}{x},t)$; conditions under which $\dot{e}(\underset{\sim}{x},t) = \frac{d}{dt}\, e(\underset{\sim}{x},t)$ almost everywhere are obvious.

We now make the corresponding assumptions regarding the heat flux H_t.

Axiom 3:

(i) For each $\mathcal{D}\in\mathcal{M}$ the function $H_t(\cdot,\mathcal{D})$ is a measure on $\mathbb{B}(\mathcal{D}^b)$;

(ii) for each part $\mathcal{P}$ the function $H_t(\mathcal{P},\cdot)$ is s-additive on all elements of $\mathcal{M}$ separate from $\mathcal{P}$;

(iii) there exist scalars $\beta(t)$, $\gamma(t)$ such that

$$|H_t(\mathcal{P},\mathcal{D})| \le \beta(t)V(\mathcal{P}) + \gamma(t)A(\mathcal{P}\cap\partial\mathcal{D})$$

for all $\mathcal{P}\in\mathbb{B}(\mathcal{B})$, $\mathcal{D}\in\mathcal{M}$ which are separate.

Statement (iii) makes precise what was indicated earlier: that to have heat transfer from $\mathcal{D}$ to $\mathcal{P}$ the part $\mathcal{P}$ must have non-vanishing volume (yielding radiative transfer) or a non-vanishing area of contact with $\mathcal{D}$ (yielding conductive transfer). Of course $H_t(\cdot,\mathcal{D})$ is s-additive on those elements of $\mathcal{M}^{\mathcal{B}}$ separate from $\mathcal{D}$.

An interesting consequence of the assumption that $H_t(\cdot,\mathcal{A}^e)$ is a measure is the possibility of sectioning any subbody $\mathcal{A}$ into absorbent and emmittent portions. We say that a part $\mathcal{P} \in \mathbb{B}(\mathcal{A})$ *absorbs* heat from $\mathcal{A}^e$ if $H_t(\mathcal{P},\mathcal{A}^e) \geq 0$, *emits* heat to $\mathcal{A}^e$ if $H_t(\mathcal{P},\mathcal{A}^e) \leq 0$. Then as a consequence of the Hahn Decomposition Theorem $\mathcal{A}$ is the union of disjoint sets $\mathcal{A}^+$ and $\mathcal{A}^-$ such that, with respect to $\mathcal{A}^e$, every part $\mathcal{P} \subset \mathcal{A}^+$ is heat absorbing and every part $\mathcal{P} \subset \mathcal{A}^-$ is heat emitting. Any part $\mathcal{P} \subset \mathcal{A}$ moreover admits the decomposition $\mathcal{P} = \mathcal{P}^+ \cup \mathcal{P}^-$, $\mathcal{P}^+ \cap \mathcal{P}^- = \emptyset$, where $\mathcal{P}^+$ is contained in $\mathcal{A}^+$ and hence absorbs heat from $\mathcal{A}^e$ and $\mathcal{P}^-$ is contained in $\mathcal{A}^-$ and hence emits heat to $\mathcal{A}^e$. Of course the sets $\mathcal{A}^+$ and $\mathcal{A}^-$ are determined only to within sets of $H_t(\cdot,\mathcal{A}^e)$ measure zero.

As a consequence of Axiom 3 we have the following centrally important decomposition theorem for H_t.

Theorem 1: For each $\mathcal{B} \in \mathcal{M}$, $H_t(\cdot,\mathcal{B})$ admits the unique decomposition

$$H_t(\cdot,\mathcal{B}) = R_t(\cdot,\mathcal{B}) + Q_t(\cdot,\mathcal{B}),$$

where $R_t(\cdot,\mathcal{B})$ and $Q_t(\cdot,\mathcal{B})$ are measures on $\mathbb{B}(\mathcal{B}^b)$ with the following property: for any part $\mathcal{P} \subset \mathcal{B}^b$

$$R_t(\mathcal{P},\mathcal{B}) \leq \beta(t)V(\mathcal{P}),$$

$$Q_t(\mathcal{P},\mathcal{B}) \leq \gamma(t)A(\mathcal{P} \cap \partial\mathcal{B}).$$

Moreover

$$R_t(\mathcal{P},\mathcal{B}) = H_t(\mathcal{P} - \partial\mathcal{B},\mathcal{B}),$$

$$Q_t(\mathcal{P},\mathcal{B}) = H_t(\mathcal{P} \cap \partial\mathcal{B},\mathcal{B}).$$

We call $R_t(\mathcal{P},\mathcal{B})$ the *radiative* heat flux into $\mathcal{P}$ from $\mathcal{B}$, $Q_t(\mathcal{P},\mathcal{B})$ the *conductive* heat flux into $\mathcal{P}$ from $\mathcal{B}$.

Before proving this theorem let us note that what we have chosen at this point to call radiative and conductive heat flux need have little or nothing in common with the classical notions of conduction and radiation[1]; we shall see that further special assumptions are necessary before we can identify them with the classical forms.

Proof: If we define R_t and Q_t as above, then $H_t(\mathcal{P},\mathcal{D}) = R_t(\mathcal{P},\mathcal{D}) + Q_t(\mathcal{P},\mathcal{D})$ and by Axiom 3 the measures R_t and Q_t have the desired properties. The uniqueness of the above decomposition follows from the fact that it is a Lebesgue decomposition of $H_t(\cdot,\mathcal{D})$ with respect to volume. This completes the proof.

It is clear that both $R_t(\mathcal{P},\cdot)$ and $Q_t(\mathcal{P},\cdot)$ are, for any part $\mathcal{P}$ of $\mathcal{B}$, s-additive on those elements of $\mathcal{M}$ separate from $\mathcal{P}$.

A direct consequence of Theorem 1 is the fact that $R_t(\cdot,\mathcal{D})$ is absolutely continuous with respect to volume and $Q_t(\cdot,\mathcal{D})$, when restricted to $\mathbb{B}(\partial\mathcal{D})$, is absolutely continuous with respect to area. Thus there exist functions $r_{\mathcal{D}}(\cdot,t)$ and $q_{\mathcal{D}}(\cdot,t)$, the first defined on $\mathcal{D}^b$ and the second on $\partial\mathcal{D}$, such that

$$R_t(\mathcal{P},\mathcal{D}) = \int_{\mathcal{P}} r_{\mathcal{D}}(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}),$$

$$Q_t(\mathcal{P},\mathcal{D}) = \int_{\mathcal{P}\cap\partial\mathcal{D}} q_{\mathcal{D}}(\underset{\sim}{x},t)\,dA(\underset{\sim}{x}),$$

for all parts $\mathcal{P} \subset \mathcal{D}^b$. Note that the energy flux H_t now begins to resemble its classical counterpart. The functions $q_{\mathcal{D}}$ and $r_{\mathcal{D}}$, however, are dependent upon $\mathcal{D}$, as indeed one would expect. The remainder of this section and most of the next is devoted to the problem of isolating the nature of this dependence, especially for the most important case: $R_t(\mathcal{A},\mathcal{A}^e)$ and $Q_t(\mathcal{A},\mathcal{A}^e)$ when $\mathcal{A}$ is a subbody. An immediate consequence of the

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[1] For an axiomatic treatment of radiative transfer, see Preisendorfer [1957].

s-additivity of $R_t(\mathcal{P},\cdot)$ is that for any $\mathcal{D}_1, \mathcal{D}_2 \in \mathcal{M}$ which are separate

$$r_{\mathcal{D}_1}(\underset{\sim}{x},t) + r_{\mathcal{D}_2}(\underset{\sim}{x},t) = r_{\mathcal{D}_1 \cup \mathcal{D}_2}(\underset{\sim}{x},t)$$

for almost every $\underset{\sim}{x} \in (\mathcal{D}_1 \cup \mathcal{D}_2)^b$.

We may prove for the conductive flux a much stronger result: that $Q_t(\mathcal{P},\mathcal{D})$ depends not upon $\mathcal{D}$ but only upon the material surface (in $\partial\mathcal{D}$) in question.

Theorem 2: <u>Corresponding to any material surface $\mathcal{S}$ there exists a scalar $Q_t(\mathcal{S})$ such that</u>

$$Q_t(\mathcal{S}) = Q_t(\mathcal{S},\mathcal{D})$$

<u>whenever $\mathcal{S}$ is a negative segment of the surface $\partial\mathcal{D}$ of $\mathcal{D} \in \mathcal{M}$.</u>

Proof: We shall prove that given any material surface $\mathcal{S}$ there exists a measure $Q_t^{\mathcal{S}}(\cdot)$ on $\mathbb{B}(\mathcal{S})$ such that

$$Q_t^{\mathcal{S}}(\mathcal{P}) = Q_t(\mathcal{P},\mathcal{D})$$

for each $\mathcal{P} \in \mathbb{B}(\mathcal{S})$ whenever $\mathcal{S}$ is a negative segment of $\partial\mathcal{D}$. Then we simply define $Q_t(\mathcal{S}) = Q_t^{\mathcal{S}}(\mathcal{S})$.

Thus let $\mathcal{S}$ be given; since $\mathcal{S}$ is a material surface there exists at least one $\mathcal{D} \in \mathcal{M}$ for which $\mathcal{S}$ is a negative segment of $\partial\mathcal{D}$. For any $\mathcal{P} \in \mathbb{B}(\mathcal{S})$ define

$$Q_t^{\mathcal{S}}(\mathcal{P}) = Q_t(\mathcal{P},\mathcal{D}).$$

Then $Q_t^{\mathcal{S}}(\cdot)$ is a measure on $\mathbb{B}(\mathcal{S})$; we shall show it is independent of $\mathcal{D}$. Suppose $\mathcal{S}$ is also a negative segment of $\partial\hat{\mathcal{D}}$, $\hat{\mathcal{D}} \in \mathcal{M}$. It follows, as noted earlier, that $\mathcal{D}$ and $\hat{\mathcal{D}}$ are not separate and that $\mathcal{S}$ is a negative segment of $\partial(\mathcal{D} \wedge \hat{\mathcal{D}})$. Since $\mathcal{D} \wedge \hat{\mathcal{D}}$ is contained in both $\mathcal{D}$ and $\hat{\mathcal{D}}$, the following lemma then shows $Q_t(\mathcal{P},\mathcal{D}) = Q_t(\mathcal{P},\mathcal{D}\wedge\hat{\mathcal{D}}) = Q_t(\mathcal{P},\hat{\mathcal{D}})$.

Lemma: Let $\mathscr{D}_1, \mathscr{D}_2 \in \mathcal{M}$, $\mathscr{D}_1 \subset \mathscr{D}_2$, and let $\mathcal{P}$ be a part with $\mathcal{P} \subset \partial\mathscr{D}_1 \cap \partial\mathscr{D}_2$. Then

$$H_t(\mathcal{P},\mathscr{D}_1) = H_t(\mathcal{P},\mathscr{D}_2).$$

Proof: Since every element of $\mathcal{M}$ is either a subbody or the exterior of a subbody it follows that the (relative) boundary of $\partial\mathscr{D}_1 \cap \partial\mathscr{D}_2$ is of zero area measure, so we may assume $\mathcal{P}$ (relatively) interior to $\partial\mathscr{D}_1 \cap \partial\mathscr{D}_2$. Next $\mathscr{D}_2 = \mathscr{D}_1 \cup (\mathscr{D}_1^e \wedge \mathscr{D}_2)$, while $\mathscr{D}_1$ and $\mathscr{D}_1^e \wedge \mathscr{D}_2$ are separate; hence

$$H_t(\mathcal{P},\mathscr{D}_2) = H_t(\mathcal{P},\mathscr{D}_1) + H_t(\mathcal{P},\mathscr{D}_1^e \wedge \mathscr{D}_2).$$

Since $\mathcal{P}$ is interior to $\partial\mathscr{D}_1 \cap \partial\mathscr{D}_2$ and thus disjoint from $\mathscr{D}_1^e \wedge \mathscr{D}_2$ and since $V(\mathcal{P}) = 0$ it follows from (iii) of Axiom 3 that $H_t(\mathcal{P},\mathscr{D}_1^e \wedge \mathscr{D}_2) = 0$, which proves the Lemma and hence the Theorem.

It is clear that $Q_t^{\mathscr{S}}(\cdot)$ as defined above is area-continuous on $\mathbb{B}(\mathscr{S})$; hence there exists an essentially bounded function $q_{\mathscr{S}}(\cdot,t)$ on $\mathscr{S}$ such that

$$Q_t^{\mathscr{S}}(\mathcal{P}) = \int_{\mathcal{P}} q_{\mathscr{S}}(\underset{\sim}{x},t)\,dA(\underset{\sim}{x}),$$

or, more pertinently,

$$Q_t(\mathscr{S}) = \int_{\mathscr{S}} q_{\mathscr{S}}(\underset{\sim}{x},t)\,dA(\underset{\sim}{x}).$$

Moreover it is an obvious property of $Q_t^{\mathscr{S}}(\cdot)$ that $\mathscr{S}_1$ a positive segment of $\mathscr{S}_2$ implies $Q_t^{\mathscr{S}_1}(\cdot) = Q_t^{\mathscr{S}_2}(\cdot)$ on $\mathbb{B}(\mathscr{S}_1)$; thus

$$q_{\mathscr{S}_1}(\underset{\sim}{x},t) = q_{\mathscr{S}_2}(\underset{\sim}{x},t)$$

for almost every $\underset{\sim}{x} \in \mathscr{S}_1$. Finally we note the useful fact that if $\mathscr{S}_1$ and $\mathscr{S}_2$ are positive segments of $\mathscr{S}$ such that

$\mathcal{S} = \mathcal{S}_1 \cup \mathcal{S}_2$ and $A(\mathcal{S}_1 \cap \mathcal{S}_2) = 0$, then

$$Q_t(\mathcal{S}) = Q_t(\mathcal{S}_1) + Q_t(\mathcal{S}_2).$$

We shall say that there is no internal radiation if for every pair of disjoint subbodies $\mathcal{A}, \mathcal{C}$

$$H_t(\mathcal{A}, \mathcal{C}) = 0.$$

If this is true then $R_t(\mathcal{A}, \mathcal{C}) = 0$ for every pair of separate subbodies $\mathcal{A}$ and $\mathcal{C}$. But by the theorem in the Appendix $R_t(\cdot, \mathcal{C})$ is determined by its values on subbodies; hence $R_t(\mathcal{P}, \mathcal{C}) = 0$ for every subbody $\mathcal{C}$ and every part $\mathcal{P} \in \mathbb{B}(\mathcal{C}^b)$. Consequently

$$R_t(\mathcal{P}, \mathcal{A}^e) = R_t(\mathcal{P}, \mathcal{A}^b) + R_t(\mathcal{P}, \mathcal{B}^e) = R_t(\mathcal{P}, \mathcal{B}^e)$$

for every subbody $\mathcal{A}$ and hence

$$R_t(\mathcal{P}, \mathcal{A}^e) = \int_{\mathcal{P}} r_{\mathcal{B}^e}(\underset{\sim}{x}, t)\, dV(\underset{\sim}{x}).$$

Thus the absence of internal radiation implies that the radiative transfer R_t is completely determined by the single density $r_{\mathcal{B}^e}$.[1] This is the case that is usually considered in the classical studies in continuum thermodynamics.

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[1]A more general result of this form is given in Theorem 5.

IV. The First Law of Thermodynamics

We now make formally the assumption that the First Law of Thermodynamics holds for subbodies of $\mathcal{B}$.

Axiom 4: (The First Law of Thermodynamics) For every subbody $\mathcal{Q}$

$$\dot{E}_t(\mathcal{Q}) = H_t(\mathcal{Q}, \mathcal{Q}^e).$$

An immediate consequence of Axiom 4 is that the mapping $\mathcal{Q} \rightarrow H_t(\mathcal{Q}, \mathcal{Q}^e)$ is an s-additive function on $\mathcal{M}^{\mathcal{B}}$; i.e.,

$$H_t(\mathcal{Q} \cup \mathcal{C}, (\mathcal{Q} \cup \mathcal{C})^e) = H_t(\mathcal{Q}, \mathcal{Q}^e) + H_t(\mathcal{C}, \mathcal{C}^e)$$

for every pair of separate subbodies $\mathcal{Q}$ and $\mathcal{C}$. From this fact follows a result which may be called the Principle of Detailed Balance. We emphasize that this result has nothing whatsoever to do with the notion of equilibrium.

Theorem 3: (Principle of Detailed Balance). For every pair of separate subbodies $\mathcal{Q}$ and $\mathcal{C}$

$$H_t(\mathcal{Q}, \mathcal{C}) = -H_t(\mathcal{C}, \mathcal{Q}).$$

Proof: The proof is trivial when one observes that since $H_t(\cdot,\cdot)$ is s-additive in each argument and $\mathcal{Q}^e = (\mathcal{Q} \cup \mathcal{C})^e \cup \mathcal{C}$, $\mathcal{C}^e = (\mathcal{Q} \cup \mathcal{C})^e \cup \mathcal{Q}$,

$$\begin{aligned} H_t(\mathcal{Q}, \mathcal{Q}^e) + H_t(\mathcal{C}, \mathcal{C}^e) &= H_t(\mathcal{Q}, (\mathcal{Q} \cup \mathcal{C})^e) + H_t(\mathcal{C}, (\mathcal{Q} \cup \mathcal{C})^e) \\ &\quad + H_t(\mathcal{Q}, \mathcal{C}) + H_t(\mathcal{C}, \mathcal{Q}) \\ &= H_t(\mathcal{Q} \cup \mathcal{C}, (\mathcal{Q} \cup \mathcal{C})^e) + H_t(\mathcal{Q}, \mathcal{C}) + H_t(\mathcal{C}, \mathcal{Q}). \end{aligned}$$

Thus $H_t(\mathcal{Q}, \mathcal{C}) = -H_t(\mathcal{C}, \mathcal{Q})$.

We now establish that this result is also true for Q_t and hence also for R_t.

Theorem 4: (Principle of Detailed Balance for Conductive Transfer) For every material surface $\mathcal{S}$ interior to $\mathcal{B}$

$$Q_t(\mathcal{S}) = -Q_t(-\mathcal{S})$$

Proof: Since $\mathcal{S}$ is interior to $\mathcal{B}$, $-\mathcal{S}$ is also a material surface. Hence by (v) of Axiom 1 there exist decreasing sequences $\{\mathcal{A}_n\}$ and $\{\hat{\mathcal{A}}_n\}$ of subbodies such that $\mathcal{S}$ is a positive segment of $\partial\mathcal{A}_n$ for each n, $-\mathcal{S}$ is a positive segment of $\partial\hat{\mathcal{A}}_n$ for each n, and

$$\bigcap_{n=1}^{\infty} \mathcal{A}_n = \bigcap_{n=1}^{\infty} \hat{\mathcal{A}}_n = \mathcal{S} .$$

Moreover we can choose $\{\mathcal{A}_n\}$ and $\{\hat{\mathcal{A}}_n\}$ such that for each n $\mathcal{A}_n$ and $\hat{\mathcal{A}}_n$ are separate. By Theorem 3, then,

$$H_t(\mathcal{A}_n, \hat{\mathcal{A}}_n) = -H_t(\hat{\mathcal{A}}_n, \mathcal{A}_n)$$

or equivalently, if $\mathcal{S}_n = \partial\mathcal{A}_n \cap \partial\hat{\mathcal{A}}_n$ and $\mathcal{S}_n$ is taken to have the orientation of $\mathcal{S}$,

$$R_t(\mathcal{A}_n, \hat{\mathcal{A}}_n) + Q_t(\mathcal{S}_n) = -R_t(\hat{\mathcal{A}}_n, \mathcal{A}_n) - Q_t(-\mathcal{S}_n) .$$

Since $\bigcap_{n=1}^{\infty} \mathcal{S}_n = \mathcal{S}$,

$$Q_t(\mathcal{S}_n) \to Q_t(\mathcal{S}), \qquad Q_t(-\mathcal{S}_n) \to Q_t(-\mathcal{S})$$

as $n \to \infty$. Thus to complete the proof we have only to show that

$$R_t(\mathcal{A}_n, \hat{\mathcal{A}}_n) \to 0, \qquad R_t(\hat{\mathcal{A}}_n, \mathcal{A}_n) \to 0,$$

as $n \to \infty$. But this follows at once from the inequalities

$$|R_t(\mathcal{A}_n, \hat{\mathcal{A}}_n)| \leq \alpha(t)V(\mathcal{A}_n),$$

$$|R_t(\hat{\mathcal{A}}_n, \mathcal{A}_n)| \leq \alpha(t)V(\hat{\mathcal{A}}_n),$$

of Theorem 1.

Since for every pair of separate subbodies $\mathcal{A}$ and $\mathcal{C}$

$$H_t(\mathcal{A},\mathcal{C}) = R_t(\mathcal{A},\mathcal{C}) + Q_t(\mathcal{S}),$$

where $\mathcal{S}$ is the (possibly empty) positive segment of $\partial\mathcal{A}$ for which $\mathcal{S} = \partial\mathcal{A} \cap \partial\mathcal{C}$, Theorems 3 and 4 imply

Theorem 5: (Principle of Detailed Balance For Radiative Transfer) For every pair of separate subbodies $\mathcal{A}$ and $\mathcal{C}$

$$R_t(\mathcal{A},\mathcal{C}) = -R_t(\mathcal{C},\mathcal{A}).$$

Since

$$R_t(\mathcal{A},\mathcal{A}^e) + R_t(\mathcal{C},\mathcal{C}^e) = R_t(\mathcal{A}\cup\mathcal{C},(\mathcal{A}\cup\mathcal{C})^e)$$
$$+ R_t(\mathcal{A},\mathcal{C}) + R_t(\mathcal{C},\mathcal{A})$$

for every pair of separate subbodies $\mathcal{A}$ and $\mathcal{C}$, we conclude from Theorem 5 that the mapping $\mathcal{A} \to R_t(\mathcal{A},\mathcal{A}^e)$ is s-additive. This conclusion the fact that $|R_t(\mathcal{A},\mathcal{A}^e)| \leq \beta(t)V(\mathcal{A})$ and the theorem in the Appendix imply the following striking result.

Theorem 6: There exists a function $r(\cdot,t)$ on $\mathcal{B}$ such that for every subbody $\mathcal{A}$

$$R_t(\mathcal{A},\mathcal{A}^e) = \int_{\mathcal{A}} r(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}).$$

Hence there exists a single function $r(\cdot,t)$ whose integral yields the volume-continuous part of the right-hand side of the First Law. We remarked at the end of Section 3 that in the absence of internal radiation $R_t(\mathcal{A},\mathcal{A}^e) = R_t(\mathcal{A},\mathcal{B}^e)$. Hence in this case $r_{\mathcal{B}^e}(\cdot,t) = r(\cdot,t)$ almost everywhere. This is of course not true in the presence of internal radiation.

Our next objective is to establish the counterpart of Theorem 6 for Q_t. With this in mind we now introduce certain auxiliary notation. For any well-behaved monotone sequence $\{A_n\}$ of sets which tend to the single point $\underset{\sim}{x}$ (i.e. $\{\underset{\sim}{x}\} = \bigcap_{n=1}^{\infty} A_n$), and which are measurable with respect to some measure μ, it is well known that

$$f(\underset{\sim}{x}) = \lim_{n \to \infty} \frac{\int_{A_n} f d\mu}{\mu(A_n)}$$

for almost every $\underset{\sim}{x}$, provided only that f is μ-integrable. We shall apply this result to the surface integrals that define Q_t. (It is not difficult to show that the sequences of sets we shall use are sufficiently well-behaved.)

Given a point $\underset{\sim}{x} \in \mathring{\mathcal{B}}$ and a unit vector $\underset{\sim}{\lambda}$, we define $\mathcal{C}(\underset{\sim}{x}, \underset{\sim}{\lambda}, r)$ to be that circular cylinder centered at $\underset{\sim}{x}$ with radius r, axis parallel to $\underset{\sim}{\lambda}$, and height $2r$. Now suppose $\underset{\sim}{x}$ is a regular point of the material surface $\mathcal{S}$ and let $\underset{\sim}{n}$ denote the positive unit normal to $\mathcal{S}$ at $\underset{\sim}{x}$. We define

$$\mathcal{S}(r) = \mathcal{S} \cap \mathcal{C}(\underset{\sim}{x}, \underset{\sim}{n}, r),$$

letting the orientation of $\mathcal{S}(r)$ agree with that of $\mathcal{S}$. Since $\mathcal{S}$ is smooth at $\underset{\sim}{x}$ it is clear that for all sufficiently small r

$\mathcal{S}(r)$ intersects the boundary of $\mathcal{C}(\underset{\sim}{x}, \underset{\sim}{n}, r)$ only on the curved segment, i.e., $\underset{\sim}{y} \in [\mathcal{S}(r) \cap \partial\mathcal{C}(\underset{\sim}{x}, \underset{\sim}{n}, r)]$ implies $|(\underset{\sim}{y} - \underset{\sim}{x}) \cdot \underset{\sim}{n}| < r$ (Figure 1). We will call $\underset{\sim}{x}$ a *point of density* of Q_t on $\mathcal{S}$ if $\underset{\sim}{x}$

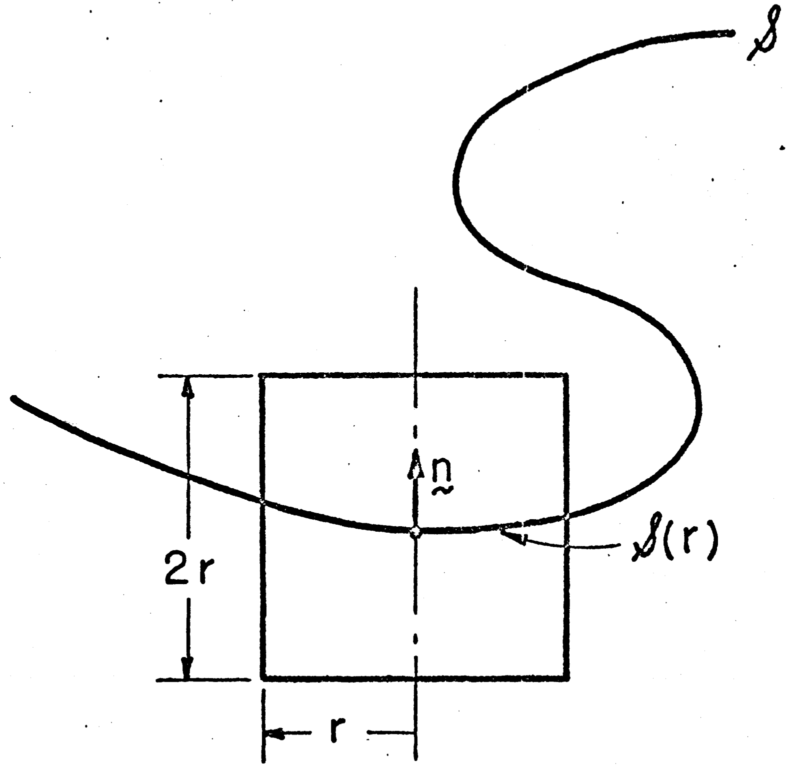

Figure 1

is a regular point of $\mathscr{S}$ and

$$q_{\mathscr{S}}(\underset{\sim}{x},t) = \lim_{r \to 0} \frac{Q_t(\mathscr{S}(r))}{A(\mathscr{S}(r))}$$

Since this relation

holds for almost every $\underset{\sim}{x} \in \mathscr{S}$ and since $q_{\mathscr{S}}(\cdot,t)$ is indeterminate to within a set of measure zero, we may suppose $q_{\mathscr{S}}(\cdot,t)$ to be such that the above relation is valid whenever the limit on the right-hand side exists. Then Theorem 4 implies that if $\underset{\sim}{x}$ is a point of density of Q_t on $\mathscr{S}$, it is a point of density on $-\mathscr{S}$ and

$$q_{\mathscr{S}}(\underset{\sim}{x},t) = -q_{-\mathscr{S}}(\underset{\sim}{x},t).$$

We now have sufficient apparatus at hand to establish the counterpart of Theorem 6 for Q_t. This, a direct analog of a result of Noll [1959] regarding contact forces, is central in the theory of contact effects and provides a basis for a result usually assumed in the classical literature. The proof below is essentially that of Noll.

Theorem 7: For every $\underset{\sim}{x} \in \mathring{\mathcal{B}}$ and every unit vector $\underset{\sim}{n}$ there exists a scalar $q(\underset{\sim}{x},\underset{\sim}{n},t)$ such that for any material surface $\mathscr{S}$ interior to $\mathcal{B}$

$$Q_t(\mathscr{S}) = \int_{\mathscr{S}} q(\underset{\sim}{x},\underset{\sim}{n}(\underset{\sim}{x}),t)\,dA(\underset{\sim}{x}),$$

where $\underset{\sim}{n}(\underset{\sim}{x})$ is the positive unit normal to $\mathscr{S}$ at $\underset{\sim}{x}$. Further, the function $q(\underset{\sim}{x},\cdot,t)$ satisifes

$$q(\underset{\sim}{x},\underset{\sim}{n},t) = -q(\underset{\sim}{x},-\underset{\sim}{n},t).$$

Proof: Recall that for every material surface $\mathscr{S}$ interior to $\mathcal{B}$

$$Q_t(\mathscr{S}) = \int_{\mathscr{S}} q_{\mathscr{S}}(\underset{\sim}{x},t)\,dA(\underset{\sim}{x})$$

and that almost every $\underset{\sim}{x} \in \mathscr{S}$ is a point of density for Q_t on $\mathscr{S}$. Thus it is sufficient to show that for every $(\underset{\sim}{x},\underset{\sim}{n},t)$ there exists a scalar $q(\underset{\sim}{x},\underset{\sim}{n},t)$ such that for any $\mathscr{S}$ interior to $\mathcal{B}$

$$q_{\mathcal{S}}(\underset{\sim}{x},t) = q(\underset{\sim}{x},\underset{\sim}{n}(\underset{\sim}{x}),t)$$

whenever $\underset{\sim}{x}$ is a point of density for Q_t on $\mathcal{S}$.

Choose $(\underset{\sim}{x},\underset{\sim}{n},t)$ arbitrarily and consider the family Ω of all material surfaces through $\underset{\sim}{x}$ with positive unit normal $\underset{\sim}{n}$ at $\underset{\sim}{x}$. If $\underset{\sim}{x}$ is not a point of density for Q_t on any $\mathcal{S}\in\Omega$ we choose $q(\underset{\sim}{x},\underset{\sim}{n},t)$ arbitrarily and set $q(\underset{\sim}{x},-\underset{\sim}{n},t) = -q(\underset{\sim}{x},\underset{\sim}{n},t)$. If it is a point of density for Q_t on some surface $\mathcal{S}_1\in\Omega$ we set $q(\underset{\sim}{x},\underset{\sim}{n},t) = q_{\mathcal{S}_1}(\underset{\sim}{x},t)$. We need now only show that if it is also a point of density for $\mathcal{S}_2\in\Omega$, then $q_{\mathcal{S}_1}(\underset{\sim}{x},t) = q_{\mathcal{S}_2}(\underset{\sim}{x},t)$. Let k be regular for both $\mathcal{S}_1$ and $\mathcal{S}_2$ and consider the cylinder $C(\underset{\sim}{x},\underset{\sim}{n},r)$ and the surfaces $\mathcal{S}_1(r)$ and $\mathcal{S}_2(r)$ defined as above. For sufficiently small r let $\mathcal{A}_1(r)$ denote the subbody whose boundary consists of $\mathcal{S}_1(r)$ and a positive segment of $\partial C(\underset{\sim}{x},\underset{\sim}{n},r)$. Let $\mathcal{A}_2(r)$ be defined in the same manner. Then we may write (see Figure 2)

$$\partial\mathcal{A}_1(r) = \mathcal{S}_1(r) + \mathcal{G}(r) + \mathcal{F}_1(r),$$
$$\partial\mathcal{A}_2(r) = \mathcal{S}_2(r) + \mathcal{G}(r) + \mathcal{F}_2(r),$$

where $\mathcal{G}(r)$ is that portion of $\partial\mathcal{A}_1(r)\cap\partial\mathcal{A}_2(r)$ common to the two subbodies $\big($excluding $\mathcal{S}_1(r)$ and $\mathcal{S}_2(r)\big)$. As r tends to zero we have the estimates

$$A(\mathcal{S}_\alpha(r)) = \pi r^2 + o(r^2),$$
$$A(\mathcal{F}_\alpha(r)) = o(r^2),$$
$$V(\mathcal{A}_\alpha(r)) = o(r^2)$$

for $\alpha = 1,2$.

Using the above decomposition of $\partial\mathcal{A}_\alpha(r)$ we now apply the First Law of Thermodynamics to $\mathcal{A}_\alpha(r)$:

$$\dot{E}_t(\mathcal{A}_\alpha) = R_t(\mathcal{A}_\alpha, \mathcal{A}_\alpha^e) + Q_t(\mathcal{S}_\alpha(r)) + Q_t(\mathcal{G}(r)) + Q_t(\mathcal{F}_\alpha(r)).$$

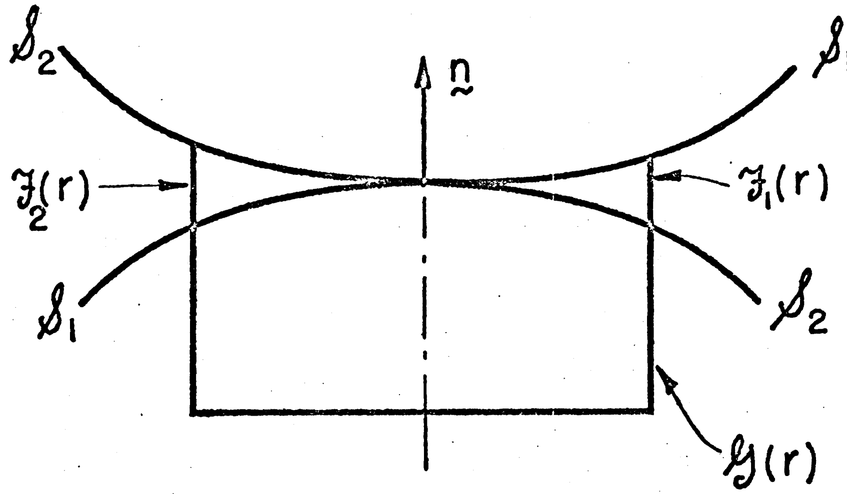
$\mathcal{S}_2$
$\mathcal{S}_1$
$\underset{\sim}{n}$
$\mathcal{J}_2(r)$
$\mathcal{J}_1(r)$
$\mathcal{S}_1$
$\mathcal{S}_2$
$\mathcal{G}(r)$

Figure 2

Then by the above volume and area estimates, together with the boundedness properties of $\dot{E}_t$, R_t, and Q_t given in Axiom 1 and Theorems 1 and 2, we have

$$Q_t(\mathcal{S}_\alpha(r)) + Q_t(\mathcal{C}(r)) = o(r^2),$$

and on subtracting this with $\alpha = 2$ from the same expression with $\alpha = 1$ we arrive at

$$Q_t(\mathcal{S}_1(r)) - Q_t(\mathcal{S}_2(r)) = o(r^2).$$

Thus if we divide by πr^2 and use the area estimate we conclude that

$$\frac{Q_t(\mathcal{S}_1(r))}{A(\mathcal{S}_1(r))} = \frac{Q_t(\mathcal{S}_2(r))}{A(\mathcal{S}_2(r))} + \frac{o(r^2)}{r^2}\ ;$$

since $\underset{\sim}{x}$ is assumed a point of density for Q_t on each of $\mathcal{S}_1$ and $\mathcal{S}_2$, this yields

$$q_{\mathcal{S}_1}(\underset{\sim}{x},t) = q_{\mathcal{S}_2}(\underset{\sim}{x},t)$$

when $r \to 0$, which completes the proof.

We have now established the classic starting point of the theory of heat conduction. A result proved by Cauchy [1823,1827] puts this in a somewhat more familiar form provided the function $q(\cdot,\underset{\sim}{n},t)$ is continuous for every $\underset{\sim}{n}$. In this instance one has the existence of a vector-valued function $\underset{\sim}{q}(\cdot,t)$ such that

$$q(\underset{\sim}{x},\underset{\sim}{n},t) = \underset{\sim}{q}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}$$

for all $\underset{\sim}{x} \in \mathring{\mathcal{B}}$. (A stronger form of Cauchy's theorem is given by Gurtin, Mizel, and Williams [1967].)

We summarize our results in the following theorem.

Theorem 8: (<u>Integral Form of the First Law of Thermodynamics</u>) <u>For every subbody</u> $\mathcal{Q} \subset \mathring{\mathcal{B}}$

$$\int_{\mathcal{Q}} \dot{e}(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}) = \int_{\mathcal{Q}} r(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}) + \int_{\partial\mathcal{Q}} q(\underset{\sim}{x},\underset{\sim}{n}(\underset{\sim}{x}),t)\,dA(\underset{\sim}{x}).$$

<u>If the function</u> $q(\cdot,\underset{\sim}{n},t)$ <u>is continuous on</u> $\mathring{\mathcal{B}}$ <u>for each</u> $\underset{\sim}{n}$, <u>then</u>

$$\int_{\mathcal{A}} \dot{e}(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}) = \int_{\mathcal{A}} r(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}) + \int_{\partial\mathcal{A}} \underset{\sim}{q}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}(\underset{\sim}{x})\,dA(\underset{\sim}{x}).$$

The local form,

$$\dot{e} = r + \operatorname{div} \underset{\sim}{q},$$

follows under obvious smoothness assumptions.

Our theory of the First Law of Thermodynamics is equivalent to the mechanical theory as treated by Noll [1959] (except that his theory necessarily treats vector-valued measures); in his terminology one would write $H_{\mathcal{A}}(\cdot)$ in place of $H_t(\cdot, \mathcal{A}^e)$; $H_{\mathcal{A}}(\cdot)$ corresponds to his "system of forces" while our $E_t(\cdot)$ corresponds to his linear momentum.

Our added assumption that $H_t(\mathcal{P}, \cdot)$ is s-additive over $\mathcal{M}$ allows us to remove one of his axioms (the Lemma to Theorem 2 is his Axiom C.3) and to remove a further assumption he must make (his assumption (b) on p. 278; cf. our Theorem 6) to derive the classical form of the balance law.

V. Entropy

The basic form of the Second Law of Thermodynamics is that the entropy of an isolated system is always non-decreasing in time (modulo an interpretation of the terms "system" and "isolated").[1] This suggests that if a system is not isolated it must in some sense exchange entropy with its surroundings. Hence for our work we are led to postulate the existence of a scalar $M_t(\mathcal{B},\mathcal{B}^e)$, the entropy flux into $\mathcal{B}$ from $\mathcal{B}^e$, which is analogous to the heat flux, $H_t(\mathcal{B},\mathcal{B}^e)$. Then if $S_t(\mathcal{B})$ is the entropy of $\mathcal{B}$ at time t, its rate of increase must always be greater than or equal to the influx from $\mathcal{B}^e$:

$$\frac{d}{dt} S_t(\mathcal{B}) \geq M_t(\mathcal{B},\mathcal{B}^e).$$

Moreover $M_t(\mathcal{B},\mathcal{B}^e)$ must be zero when $\mathcal{B}$ is isolated, which in our formalism is interpreted to mean

$$H_t(\mathcal{P},\mathcal{B}^e) = 0$$

for every part $\mathcal{P}$ of $\mathcal{B}$. With this condition we adopt the above inequality as the appropriate form of the Second Law (Section 6). We then assume (i) that $S_t(\mathcal{A})$ and $M_t(\mathcal{A},\mathcal{A}^e)$ are defined and satisfy the Second Law for every subbody $\mathcal{A}$ of $\mathcal{B}$; (ii) that we can distinguish not only the entropy flux $M_t(\mathcal{A},\mathcal{A}^e)$ into $\mathcal{A}$ from its exterior, but also the entropy flux $M_t(\mathcal{A},\mathcal{D})$ into $\mathcal{A}$ from any other element $\mathcal{D}$ of the material universe; and (iii) that $S_t(\cdot)$ and $M_t(\cdot,\mathcal{D})$ are extendable to measures.

Thus we assume the existence of two set functions: S_t, which assigns to each $\mathcal{P}\in\mathbb{B}(\mathcal{B})$ at any time t a scalar $S_t(\mathcal{P})$ called the *internal entropy* of $\mathcal{P}$; and M_t, which assigns to any $\mathcal{D}\in\mathcal{M}$ and any part $\mathcal{P}\subset\mathcal{D}^b$ a scalar $M_t(\mathcal{P},\mathcal{D})$, the

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[1] An interesting interpretation of the Second Law has been given by Coleman and Mizel [1967] who have shown that when the temporal evolution of a system of thermally interacting particles is governed by a system of ordinary differential equations, the existence of entropy and the validity of the Second Law are consequences of a postulate of asymtotic stability.

rate of entropy transfer (or entropy flux) from $\mathcal{D}$ into .

Axiom 5:

(i) $S_t(\cdot)$ is a measure on $\mathbb{B}(\mathcal{B})$;

(ii) the derivative $\dot{S}_t(\mathcal{P}) = \frac{d}{dt}S_t(\mathcal{P})$ exists for each $\mathcal{P} \in \mathbb{B}(\mathcal{B})$;

(iii) there exists a scalar $\delta(t)$ such that

$$|S_t(\mathcal{P})| \leq \delta(t)V(\mathcal{P})$$
$$|\dot{S}_t(\mathcal{P})| \leq \delta(t)V(\mathcal{P})$$

for all $\mathcal{P} \in \mathbb{B}(\mathcal{B})$.

This is an exact analog of Axiom 2; hence the comments following that axiom also apply here. Thus $\dot{S}_t$ is also a measure on $\mathbb{B}(\mathcal{B})$ and by (iii) there exist essentially bounded functions $s(\cdot,t)$ and $\dot{s}(\cdot,t)$ on $\mathcal{B}$ such that for any part $\mathcal{P}$

$$S_t(\mathcal{P}) = \int_{\mathcal{P}} s(\underset{\sim}{x},t)\,dV(\underset{\sim}{x})$$
$$\dot{S}_t(\mathcal{P}) = \int_{\mathcal{P}} \dot{s}(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}).$$

We call $s(\underset{\sim}{x},t)$ the volume-specific internal entropy at $(\underset{\sim}{x},t)$; under suitable assumptions $\dot{s}(\underset{\sim}{x},t) = \frac{d}{dt}\, s(\underset{\sim}{x},t)$ for almost every $\underset{\sim}{x}$.

The following axiom is the counterpart of Axiom 3, which gave the properties of H_t. Note that although parts (i) and (ii) are exact analogs of the corresponding parts of Axiom 3, we here make no boundedness assumption analogous to (iii) of Axiom 3.

Axiom 6:

(i) For each $\mathcal{D} \in \mathcal{M}$ the function $M_t(\cdot,\mathcal{D})$ is a measure on $\mathbb{B}(\mathcal{D}^b)$;

(ii) for each part $\mathcal{P}$ the function $M_t(\mathcal{P},\cdot)$ is s-additive on all elements of $\mathcal{M}$ separate from $\mathcal{P}$.

One can define, just as for H_t, an absorbent-emittent sectioning of any subbody $\mathcal{Q}$ with respect to M_t. In the following section we shall use the Second Law to derive further properties of M_t.

VI. The Second Law of Thermodynamics, Existence of Temperature

Definition: A part $\mathcal{P}$ of $\mathcal{B}$ is thermally isolated from $\mathfrak{D} \in \mathcal{M}$ at time t if for each part $\mathcal{P}' \subset \mathcal{P}$

$$H_t(\mathcal{P}', \mathfrak{D}) = 0.$$

This condition, which amounts in measure theoretic terms to a statement that the total variation of $H_t(\cdot, \mathfrak{D})$ is zero on $\mathcal{P}$, presents a very clear physical picture: a part is thermally isolated from $\mathfrak{D}$ if no subpart of it exchanges heat with $\mathfrak{D}$. With this notion the Second Law can be stated quite simply.

Axiom 7: (The Second Law of Thermodynamics)

(i) For every subbody $\mathcal{Q}$

$$\dot{S}_t(\mathcal{Q}) \geq M_t(\mathcal{Q}, \mathcal{Q}^e);$$

(ii) if a part $\mathcal{P}$ is thermally isolated from $\mathfrak{D} \in \mathcal{M}$

$$M_t(\mathcal{P}, \mathfrak{D}) = 0.$$

It follows from the first two laws that if a subbody $\mathcal{Q}$ is isolated from its exterior, then

$$\dot{E}_t(\mathcal{Q}) = 0, \qquad \dot{S}_t(\mathcal{Q}) \geq 0,$$

which is the traditional form of the first two laws for "universes".

It should be noted that neither in Axiom 7 nor in the remainder of this work do we say anything about reversibility or irreversibility.

Before we develop the considerable structure induced on the entropy flux M_t by Axiom 7 we make several simple observations. The introduction of the First Law of Thermodynamics allowed us to deduce instantly a principle of detailed balance for the energy flux H_t (Theorem 3), and this led to several striking results. The Second Law, being expressed as an inequality, clearly cannot yield so much; in particular balance of entropy flux does not seem to be a universal rule. (A simple counter-example, not strictly included in this theory but nonetheless relevant, is that of a system of particles at different temperatures radiating between themselves.) We define the *net entropy exchange* between two subbodies $\mathcal{A}$ and $\mathcal{C}$ to be the quantity

$$\overline{M}_t(\mathcal{A},\mathcal{C}) = M_t(\mathcal{A},\mathcal{C}) + M_t(\mathcal{C},\mathcal{A}).$$

If the entropy flux balanced $\overline{M}_t(\mathcal{A},\mathcal{C})$ would be identically zero. Next we define the *entropy production rate* N_t by

$$N_t(\mathcal{A}) = \dot{S}_t(\mathcal{A}) - M_t(\mathcal{A},\mathcal{A}^e).$$

Then the Second Law implies

$$N_t(\mathcal{A}) \geq 0$$

and $N_t(\mathcal{A}) = \dot{S}_t(\mathcal{A})$ when $\mathcal{A}$ is thermally isolated from its exterior.

It is usually assumed in the literature that N_t is s-additive. Our next result shows that such an assumption is equivalent to requiring that M_t balance. As will be seen in Section 7, the assumption of balance of entropy flux is at the foundation of the classical theory of heat conduction.

Theorem 9: For any pair of separate subbodies $\mathcal{A}$ and $\mathcal{C}$

$$N_t(\mathcal{A} \cup \mathcal{C}) - N_t(\mathcal{A}) - N_t(\mathcal{C}) = \overline{M}_t(\mathcal{A},\mathcal{C}).$$

Proof: The above relation follows at once from the definition of N_t, the identity

$$M_t(\mathcal{A},\mathcal{A}^e) + M_t(\mathcal{C},\mathcal{C}^e) = M_t(\mathcal{A} \cup \mathcal{C},(\mathcal{A} \cup \mathcal{C})^e) + \overline{M}_t(\mathcal{A},\mathcal{C})$$

(c.f. the identity in the proof of Theorem 3), and the fact that $\dot{S}_t$ is s-additive.

If we take $\mathcal{C} = \mathcal{A}^b$ in Theorem 9 and use the first part of the Second Law we arrive at the following upper bound for the net entropy exchange between any subbody $\mathcal{A}$ and $\mathcal{A}^b$, its relative exterior with respect to $\mathcal{B}$,

$$\overline{M}_t(\mathcal{A}, \mathcal{A}^b) \leq N_t(\mathcal{B}).$$

The second part of Axiom 7 is equivalent to the assertion that $M_t(\cdot, \mathscr{B})$ is absolutely continuous with respect to $H_t(\cdot, \mathscr{B})$, and this observation leads to the following counterpart of Theorem 1.

Theorem 10: *For any* $\mathscr{B} \in \mathcal{M}$, $M_t(\cdot, \mathscr{B})$ *admits the unique decomposition*.

$$M_t(\cdot, \mathscr{B}) = K_t(\cdot, \mathscr{B}) + J_t(\cdot, \mathscr{B}),$$

where $K_t(\cdot, \mathscr{B})$ *and* $J_t(\cdot, \mathscr{B})$ *are measures on* $\mathbb{B}(\mathscr{B}^b)$ *with* $K_t(\cdot, \mathscr{B})$ *absolutely continuous with respect to the radiative heat flux* $R_t(\cdot, \mathscr{B})$ *and* $J_t(\cdot, \mathscr{B})$ *absolutely continuous with respect to the conductive heat flux* $Q_t(\cdot, \mathscr{B})$. *Moreover*

$$K_t(\mathcal{P}, \mathscr{B}) = M_t(\mathcal{P} - \partial \mathscr{B}, \mathscr{B}),$$

$$J_t(\mathcal{P}, \mathscr{B}) = M_t(\mathcal{P} \cap \partial \mathscr{B}, \mathscr{B}).$$

We call $K_t(\mathcal{P}, \mathscr{B})$ *the radiative entropy flux from* $\mathscr{B}$ *into* $\mathcal{P}$, $J_t(\mathcal{P}, \mathscr{B})$ *the conductive entropy flux from* $\mathscr{B}$ *into* $\mathcal{P}$.

Proof: Let K_t and J_t be defined as above. Then $M_t = K_t + J_t$. Further $J_t(\mathcal{P}, \mathscr{B}) = J_t(\mathcal{P} \cap \partial\mathscr{B}, \mathscr{B})$, and on $\mathbb{B}(\partial\mathscr{B})$ we have

$$J_t(\cdot, \mathscr{B}) = M_t(\cdot, \mathscr{B}) << H_t(\cdot, \mathscr{B}) = Q_t(\cdot, \mathscr{B}).$$

Hence $J_t(\cdot, \mathscr{B}) << Q_t(\cdot, \mathscr{B})$. That $K_t(\cdot, \mathscr{B}) << R_t(\cdot, \mathscr{B})$ follows in a similar manner. Finally, since $M_t(\cdot, \mathscr{B}) = K_t(\cdot, \mathscr{B}) + J_t(\cdot, \mathscr{B})$ is a Lebesgue decomposition with respect to $R_t(\cdot, \mathscr{B})$, it must be unique.

It follows from Theorems 1 and 10 that $K_t(\cdot, \mathscr{B})$ is absolutely continuous with respect to volume and $J_t(\cdot, \mathscr{B})$, when restricted to $\mathbb{B}(\partial\mathscr{B})$ is absolutely continuous with respect to area. The absolute continuity of $K_t(\cdot, \mathscr{B})$ implies the existence of a function

$k_{\mathcal{B}}(\cdot,t)$ on $\mathcal{B}^b$ such that

$$K_t(\mathcal{P},\mathcal{B}) = \int_{\mathcal{P}} k_{\mathcal{B}}(\underset{\sim}{x},t)\,dV(\underset{\sim}{x})$$

for all parts $\mathcal{P} \subset \mathcal{B}^b$. Moreover for any $\mathcal{B}_1, \mathcal{B}_2 \in \mathcal{M}$ which are separate

$$k_{\mathcal{B}_1 \cup \mathcal{B}_2}(\underset{\sim}{x},t) = k_{\mathcal{B}_1}(\underset{\sim}{x},t) + k_{\mathcal{B}_2}(\underset{\sim}{x},t)$$

for almost every $\underset{\sim}{x} \in (\mathcal{B}_1 \cup \mathcal{B}_2)^b$.

Next, Theorem 10 and an argument identical to the one used to prove Theorem 2 yield

Theorem 11: Corresponding to each material surface $\mathcal{S}$ there exists a scalar $J_t(\mathcal{S})$ such that

$$J_t(\mathcal{S}) = J_t(\mathcal{S},\mathcal{B})$$

whenever $\mathcal{S}$ is a negative segment of the surface $\partial\mathcal{B}$ of $\mathcal{B} \in \mathcal{M}$.

By Theorems 1, 10, and 11 there exists, for each material surface $\mathcal{S}$, a function $j_{\mathcal{S}}(\cdot,t)$ on $\mathcal{S}$ such that

$$J_t(\mathcal{S}) = \int_{\mathcal{S}} j_{\mathcal{S}}(\underset{\sim}{x},t)\,dA(\underset{\sim}{x});$$

and $\mathcal{S}_1$ a positive segment of $\mathcal{S}_2$ implies

$$j_{\mathcal{S}_1}(\underset{\sim}{x},t) = j_{\mathcal{S}_2}(\underset{\sim}{x},t)$$

for almost every $\underset{\sim}{x} \in \mathcal{S}_1$.

More important for thermodynamics is the implication of the absolute continuity of the entropy fluxes with respect to the heat fluxes, for this implies through the Radon-Nikodym Theorem the existence of temperature.

Theorem 12: (Existence of Temperature) For every $\mathcal{B} \in \mathcal{M}$ there exists an extended non-zero-valued function $\theta_{\mathcal{B}}(\cdot,t)$ on $\mathcal{B}^b$ such that

$$K_t(\mathcal{P},\mathcal{B}) = \int_{\mathcal{P}} \frac{r_{\mathcal{B}}(\underset{\sim}{x},t)}{\theta_{\mathcal{B}}(x,t)}\,dV(\underset{\sim}{x})$$

<u>for every part</u> $\mathcal{P} \subset \mathcal{B}^b$. <u>For every material surface</u> $\mathcal{S}$ <u>there exists an extended non-zero-valued function</u> $\varphi_{\mathcal{S}}(\cdot,t)$ <u>on</u> $\mathcal{S}$ <u>such that</u>

$$J_t(\mathcal{S}) = \int_{\mathcal{S}} \frac{q_{\mathcal{S}}(\underset{\sim}{x},t)}{\varphi_{\mathcal{S}}(\underset{\sim}{x},t)}\, dA(\underset{\sim}{x}) .$$

<u>Moreover, if</u> $\mathcal{S}_1$ <u>is a positive segment of</u> $\mathcal{S}_2$,

$$\varphi_{\mathcal{S}_1}(\underset{\sim}{x},t) = \varphi_{\mathcal{S}_2}(\underset{\sim}{x},t)$$

<u>for almost every</u> $\underset{\sim}{x}$ <u>in</u> $\mathcal{S}_1$ <u>(with respect to the measure</u> Q_t).

Of course $\theta_{\mathcal{B}}$ and $\varphi_{\mathcal{S}}$ are the reciprocals of the Radon-Nikodym derivatives, respectively, of the radiative and conductive heat flux with respect to the corresponding entropy flux; $\theta_{\mathcal{B}}(\underset{\sim}{x},t)$ is called the *radiative temperature* (corresponding to $\mathcal{B}$) at $(\underset{\sim}{x},t)$ and $\varphi_{\mathcal{S}}(\underset{\sim}{x},t)$ the *conductive temperature* (corresponding to $\mathcal{S}$) at $(\underset{\sim}{x},t)$. It is of interest to note that although zero temperatures are ruled out by Theorem 12, negative and infinite values of the temperature are possible.[1]

Theorem 13: <u>The temperatures</u> $\theta_{\mathcal{B}}(\cdot,t)$ <u>and</u> $\varphi_{\partial\mathcal{B}}(\cdot,t)$ <u>are essentially positive (negative) if and only if the entropy flux</u> $M_t(\cdot,\mathcal{B})$ <u>follows (opposes) the heat flux</u> $H_t(\cdot,\mathcal{B})$.

Proof: We simply note that $M_t(\cdot,\mathcal{B})$ follows (opposes) $H_t(\cdot,\mathcal{B})$ if and only if $K_t(\cdot,\mathcal{B})$ and $J_t(\cdot,\mathcal{B})$, respectively, follow (oppose) $R_t(\cdot,\mathcal{B})$ and $Q_t(\cdot,\mathcal{B})$, and then appeal to the discussion in Section 1 of the notions "follow" and "oppose".

Before proceeding further we remark that if $\mathcal{B}, \mathcal{J} \in \mathcal{M}$ are separate, then

$$\frac{1}{\theta_{\mathcal{B}\cup\mathcal{J}}} = \left(\frac{r_{\mathcal{B}}}{r_{\mathcal{B}} + r_{\mathcal{J}}}\right)\frac{1}{\theta_{\mathcal{B}}} + \left(\frac{r_{\mathcal{J}}}{r_{\mathcal{B}} + r_{\mathcal{J}}}\right)\frac{1}{\theta_{\mathcal{J}}}$$

at almost every point in $(\mathcal{B} \cup \mathcal{J})^b$ at which $r_{\mathcal{B}\cup\mathcal{J}} \neq 0$.

In Section IV we proved that the First Law implied $q_{\mathcal{S}}(\underset{\sim}{x},t) = q(\underset{\sim}{x},\underset{\sim}{n},t)$ and that the radiative heat transfer $R_t(\mathcal{A},\mathcal{A}^e)$

[1]For a discussion of negative temperatures and of the circumstances in which this concept applies see Ramsey [1956].

is determined by a single field $r(\cdot,t)$. This gave us the classical form of the First Law. On the other hand, Theorem 12 implies that the Second Law can be expressed as follows.

Theorem 14: For every subbody $\mathcal{A}$

$$\int_{\mathcal{A}} \dot{s}(\underset{\sim}{x},t)\,dV(x) \geq \int_{\partial\mathcal{A}} \frac{q(\underset{\sim}{x},\underset{\sim}{n}(\underset{\sim}{x}),t)}{\varphi_{\partial\mathcal{A}}(\underset{\sim}{x},t)}\,dA(\underset{\sim}{x}) + \int_{\mathcal{A}} \frac{r_{\mathcal{A}^e}(\underset{\sim}{x},t)}{\theta_{\mathcal{A}^e}(\underset{\sim}{x},t)}\,dV(\underset{\sim}{x})$$

This form of the Second Law is still far from its classical counterpart; we cannot, however, reduce it further without special assumptions. The Second Law by itself is not powerful enough to imply that $\varphi_{\mathscr{S}}(\underset{\sim}{x},t)$ is independent of $\mathscr{S}$, that $K_t(\mathcal{A},\mathcal{A}^e)$ is determined by $r(\cdot,t)$ and a single temperature field $\theta(\cdot,t)$, and that $\varphi(\cdot,t) = \theta(\cdot,t)$. In Section 8 we will show what further hypotheses yield these conclusions.

To a person whose intuition is based on the classical theory of heat conduction the appearance of a conductive temperature $\varphi_{\mathscr{S}}$ dependent upon $\mathscr{S}$ may, at first glance, appear highly artificial. However, such is not the case. A physically reasonable example in which the conductive temperature at certain points may depend upon $\mathscr{S}$ is constructed as follows. Suppose that two separate subbodies $\mathcal{A}_1$ and $\mathcal{A}_2$ of $\mathcal{B}$ are composed of a material which is a good conductor of heat, and that their surface of contact $\mathscr{S}_c$ (taken positive with respect to $\partial\mathcal{A}_1$) is a very poor conductor in the direction normal to it. In the absence of radiation a method of treating such a situation would be to assume that in $\mathring{\mathcal{A}}_1$ and $\mathring{\mathcal{A}}_2$ the temperature $\varphi_{\mathscr{S}}$ is independent of $\mathscr{S}$ $(\varphi_{\mathscr{S}} \equiv \varphi)$, is a smooth function of position, and obeys Fourier's law of heat conduction $\underset{\sim}{q} = k \operatorname{grad}\varphi$; and that across $\mathscr{S}_c$ the temperature is discontinuous and Newton's Law of heat conduction $\underset{\sim}{q}\cdot\underset{\sim}{n} = h(\varphi_2 - \varphi_1)$ applies. Here k and h are positive constants, φ_1 and φ_2 are the limiting values of φ as $\mathcal{S}_c$ is approached from $\mathring{\mathcal{C}}_1$ and $\mathring{\mathcal{C}}_2$, and $\underset{\sim}{n}$ is the positive unit normal to $\partial\mathcal{C}_1$. Then within our framework $\varphi_{\mathcal{S}}$ would be independent of $\mathcal{S}$ within $\mathring{\mathcal{C}}_1$ and $\mathring{\mathcal{C}}_2$, but for points on $\mathcal{S}_c$ we would have $\varphi_{\mathcal{S}_c} = \varphi_1$ and $\varphi_{-\mathcal{S}_c} = \varphi_2$; thus in this special theory $\varphi_{\mathcal{S}}$ depends upon $\mathcal{S}$.[1] In view of the above example we are led to regard the hypotheses which yield classical heat conduction and a single conductive temperature field as a constitutive assumption rather than a general axiom.

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[1]Note that in this example the entropy flux across $\mathcal{S}_c$ is not balanced. Cf. hypothesis (i) in Theorem 18.

VII. Heat Conduction Inequalities

In this section we shall examine some restrictions imposed on J_t by the Second Law. With this in mind we now lay down

Axiom 8: *There exist scalars* $\delta(t)$, $\epsilon(t)$ *such that*

$$|K_t(\mathcal{P}, \mathcal{B})| \leq \delta(t)V(\mathcal{P}), \quad |J_t(\mathcal{P}, \mathcal{B})| \leq \epsilon(t)A(\mathcal{P}\cap\partial\mathcal{B}),$$

for any $\mathcal{B}\in\mathcal{M}$ *and* $\mathcal{P}\in\mathbb{B}(\mathcal{B}^b)$.

$K_t(\cdot,\mathcal{B})$ and $J_t(\cdot,\mathcal{B})$, respectively, have been shown to be absolutely continuous with respect to V and A; Axiom 8 reinforces this by requiring a Lipschitz-type continuity.

In Section 4 the First Law was used to show that $Q_t(\mathcal{S}) = -Q_t(-\mathcal{S})$ for any material surface $\mathcal{S}$. For J_t we shall prove the corresponding result: $J_t(\mathcal{S}) + J_t(-\mathcal{S}) \leq 0$; but we are able to do so only under certain additional smoothness assumptions. Moreover the result that $q_{\mathcal{S}}$ is a function only of the normal vector to $\mathcal{S}$ at a given point also does not carry over to $j_{\mathcal{S}}$; the corresponding result is again an inequality and again can be obtained only upon further hypotheses.

In analogy to the convention established in Section 4 we call $\underset{\sim}{x}$ a point of density of J_t on $\mathcal{S}$ if $\underset{\sim}{x}$ is a regular point of $\mathcal{S}$,

$$j_{\mathcal{S}}(\underset{\sim}{x},t) = \lim_{r \to 0} \frac{J_t(\mathcal{S}(r))}{A(\mathcal{S}(r))},$$

and, in addition,

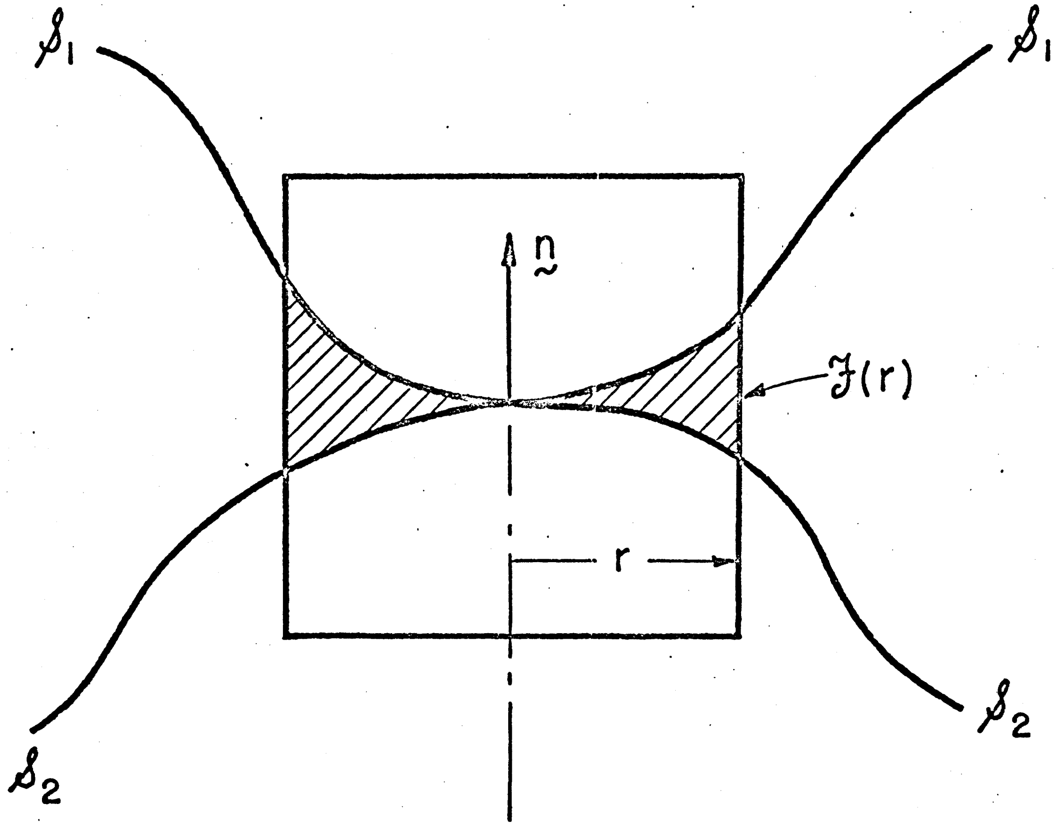
$$j_{\mathcal{S}}(\underset{\sim}{x},t) = \frac{q_{\mathcal{S}}(\underset{\sim}{x},t)}{\varphi_{\mathcal{S}}(\underset{\sim}{x},t)}$$

provided $\underset{\sim}{x}$ is a point of density of Q_t on $\mathcal{S}$. As before, we assume without loss in generality that if $\underset{\sim}{x}$ is a point of density of Q_t on $\mathcal{S}$, then $\underset{\sim}{x}$ is a point of density of J_t on $\mathcal{S}$ whenever the above limit exists.

Let $\mathcal{S}_1$ and $\mathcal{S}_2$ be two surfaces through a point $\underset{\sim}{x}$ such that $\underset{\sim}{x}$ is a regular point of each. Suppose further that $\mathcal{S}_1$ and $\mathcal{S}_2$ are tangent at $\underset{\sim}{x}$ and have opposite orientation in the sense that if $\underset{\sim}{n}$ is the positive unit normal to $\mathcal{S}_1$ at $\underset{\sim}{x}$, $-\underset{\sim}{n}$ is the positive unit normal to $\mathcal{S}_2$ at $\underset{\sim}{x}$. Then $\mathcal{S}_1$ and $\mathcal{S}_2$ are said to be compatible at $\underset{\sim}{x}$ if for r sufficiently small there exists a subbody $\mathcal{A}(r)$ such that

$$\partial\mathcal{A}(r) = \mathfrak{F}(r) + \mathcal{S}_1(r) + \mathcal{S}_2(r),$$

where $\mathfrak{F}(r)$ is a positive segment of $\partial C(\underset{\sim}{x},\underset{\sim}{n},r)$ and $\mathcal{S}_\alpha(r) = \mathcal{S}_\alpha \cap C(\underset{\sim}{x},\underset{\sim}{n},r)$ with orientation induced by $\mathcal{S}_\alpha$ (Figure 3). Here, as before, $C(\underset{\sim}{x},\underset{\sim}{n},r)$ is the cylinder centered at $\underset{\sim}{x}$ with axis $\underset{\sim}{n}$, radius r, and height $2r$. Thus, roughly speaking, two surfaces are compatible at $\underset{\sim}{x}$ if they are tangent at $\underset{\sim}{x}$ but do not "cross" in some neighborhood of $\underset{\sim}{x}$. Any material surface is compatible with a sphere of sufficiently small radius, but not



$\mathcal{S}_1$
$\mathcal{S}_1$
$\underset{\sim}{n}$
$\mathfrak{J}(r)$
r
$\mathcal{S}_2$
$\mathcal{S}_2$

Figure 3

every two tangent material surfaces are compatible. We may now state the following analog of Theorem 7.

Theorem 15: Let $\mathcal{S}_1$ and $\mathcal{S}_2$ be material surfaces compatible at $\underset{\sim}{x}$ and suppose $\underset{\sim}{x}$ is a point of density of both Q_t and J_t on both $\mathcal{S}_1$ and $\mathcal{S}_2$. Then

$$j_{\mathcal{S}_1}(\underset{\sim}{x},t) + j_{\mathcal{S}_2}(\underset{\sim}{x},t) \leq 0$$

and

$$q_{\mathcal{S}_1}(\underset{\sim}{x},t)\left[\frac{\varphi_{\mathcal{S}_1}(\underset{\sim}{x},t) - \varphi_{\mathcal{S}_2}(\underset{\sim}{x},t)}{\varphi_{\mathcal{S}_1}(\underset{\sim}{x},t)\varphi_{\mathcal{S}_2}(\underset{\sim}{x},t)}\right] \geq 0.$$

Proof: Let $\mathcal{Q}(r)$ be the subbody defined above. Then since $\partial\mathcal{Q}(r) = \mathfrak{F}(r) + \mathcal{S}_1(r) + \mathcal{S}_2(r)$ the Second Law implies

$$\dot{S}_t(\mathcal{Q}(r)) \geq K_t(\mathcal{Q}(r), \mathcal{Q}(r)^e) + J_t(\mathfrak{F}(r)) + J_t(\mathcal{S}_1(r)) + J_t(\mathcal{S}_2(r)).$$

It is not difficult to verify that as $r \to 0$

$$A(\mathcal{S}_\alpha(r)) = \pi r^2 + o(r^2), \quad \alpha = 1,2,$$

$$A(\mathfrak{F}(r)) = o(r^2),$$

$$V(\mathcal{Q}(r)) = o(r^2).$$

Thus, since S_t, K_t, and J_t obey Lipschitz conditions (Axioms 5 and 8), the above inequality implies

$$J_t(\mathcal{S}_1(r)) + J_t(\mathcal{S}_2(r)) \leq o(r^2)$$

as $r \to 0$. If we now divide by πr^2, take the limit as $r \to 0$, and use Theorem 12, we arrive at the desired results, for $\underset{\sim}{x}$ is a point of density for both J_t and Q_t and $q_{\mathcal{S}_1}(\underset{\sim}{x},t) = -q_{\mathcal{S}_2}(\underset{\sim}{x},t)$.

The second inequality of Theorem 15 is of the same form as the heat conduction inequality derived in Theorem 17; the discussion following Theorem 17 is therefore applicable also to the above inequality.

We now turn to the analog of the result $Q_t(\mathcal{S}) = -Q_t(-\mathcal{S})$. We shall show that under a certain continuity assumption

$J_t(\mathcal{S}) + J_t(-\mathcal{S}) \leq 0$. We phrase this assumption in terms of the set function J_t; continuity assumptions on $j_{\mathcal{S}}(\underset{\sim}{x},t)$ sufficient to guarantee this are easy to derive. Given a material surface $\mathcal{S}$, a sequence $\{\mathcal{A}_n\}$ of subbodies is said to *tend to* $\mathcal{S} + (-\mathcal{S})$ *in* J_t if

$$\lim_{n \to \infty} J_t(\partial \mathcal{A}_n) = J_t(\mathcal{S}) + J_t(-\mathcal{S}),$$

$$\lim_{n \to \infty} V(\mathcal{A}_n) = 0.$$

Theorem 16: Let $\mathcal{S}$ be a material surface and suppose that there exists a sequence of subbodies which tends to $\mathcal{S} + (-\mathcal{S})$ in J_t. Then

$$J_t(\mathcal{S}) + J_t(-\mathcal{S}) \leq 0.$$

Proof: By the Second Law

$$\dot{S}_t(\mathcal{A}_n) \geq K_t(\mathcal{A}_n, \mathcal{A}_n^e) + J_t(\partial \mathcal{A}_n);$$

thus if $\{\mathcal{A}_n\}$ tends to $\mathcal{S} + (-\mathcal{S})$ in J_t the fact that

$$\dot{S}_t(\mathcal{A}_n) \to 0, \quad K_t(\mathcal{A}_n, \mathcal{A}_n^e) \to 0,$$

as $n \to \infty$ (see Axioms 5 and 8) implies the validity of Theorem 16.

We shall now establish a somewhat more enlightening version of the above result. Suppose $\underset{\sim}{x}$ is a regular point of a material surface $\mathcal{S}$ and $\underset{\sim}{n}$ is the positive unit normal to $\mathcal{S}$ at $\underset{\sim}{x}$. For r sufficiently small there exists a positive connected segment $\mathcal{S}(r)$ of $\mathcal{S}$ that contains $\underset{\sim}{x}$ and whose (relative) boundary is contained in the boundary of the cylinder $\mathcal{C}(\underset{\sim}{x},\underset{\sim}{n},r)$. Given $\varepsilon > 0$ let $-\mathcal{S}_\varepsilon(r)$ denote the surface

$$-\mathcal{S}_\varepsilon(r) = \{\underset{\sim}{y} \mid (\underset{\sim}{y} + \varepsilon\underset{\sim}{n}) \in \mathcal{S}(r)\}$$

with orientation corresponding to $-\underset{\sim}{n}$ at $\underset{\sim}{x} - \varepsilon\underset{\sim}{n}$. Then for ε and r small enough the set $\mathcal{A}_\varepsilon(r)$ enclosed by $\partial\mathcal{C}(\underset{\sim}{x},\underset{\sim}{n},r)$, $\mathcal{S}(r)$, and $-\mathcal{S}_\varepsilon(r)$ is (by Axiom 1) a subbody whenever $\mathcal{S}$ is interior to $\mathcal{B}$ (see Figure 4).

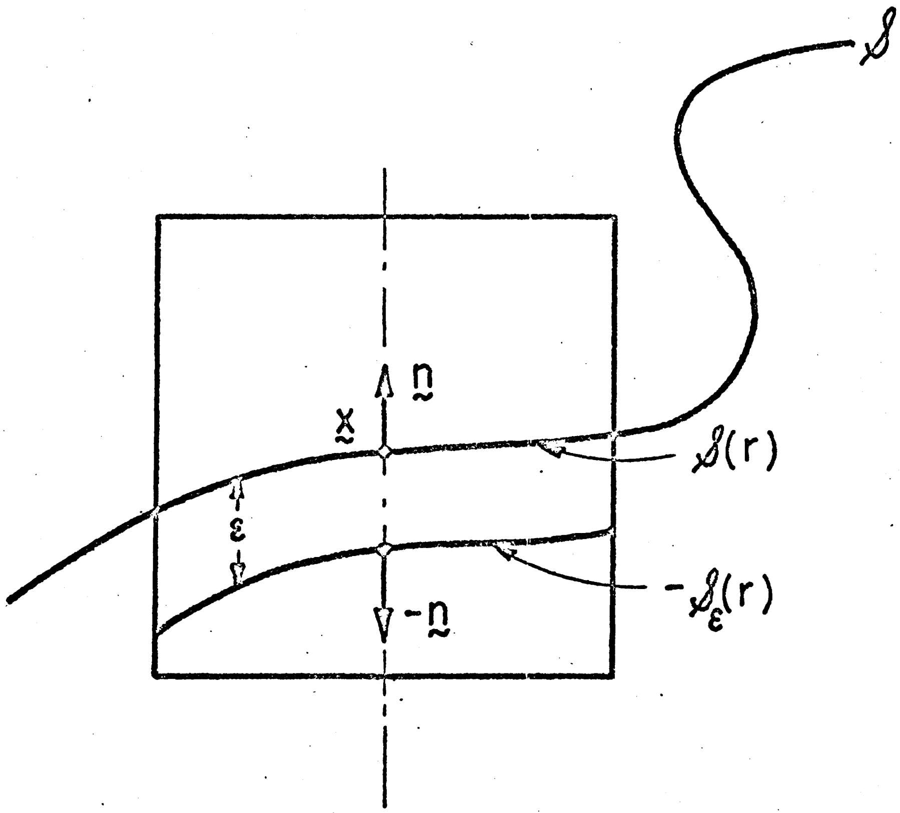

$\mathscr{S}$
$\underset{\sim}{n}$
$\underset{\sim}{x}$
$\mathscr{S}(r)$
ε
$-\mathscr{S}_{\varepsilon}(r)$
$-\underset{\sim}{n}$

Figure 4

Theorem 17: Let $\mathcal{S}$ be interior to $\mathcal{B}$ and let $\underset{\sim}{x}$ be a regular point of $\mathcal{S}$. Then if

$$\lim_{\epsilon \to 0} J_t(-\mathcal{S}_\epsilon(r)) = J_t(-\mathcal{S}(r))$$

it follows that

$$J_t(\mathcal{S}) + J_t(-\mathcal{S}) \leq 0.$$

If, in addition, $\underset{\sim}{x}$ is a point of density of J_t and Q_t on $\mathcal{S}$, then

$$j_{\mathcal{S}}(\underset{\sim}{x},t) + j_{-\mathcal{S}}(\underset{\sim}{x},t) \leq 0$$

which yields the *heat conduction inequality*

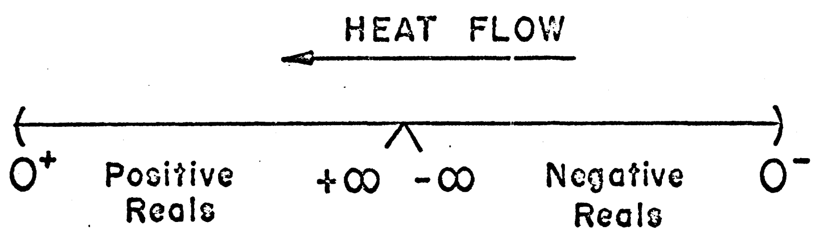
$$q_{\mathcal{S}}(\underset{\sim}{x},t)\left[\frac{\varphi_{\mathcal{S}}(\underset{\sim}{x},t) - \varphi_{-\mathcal{S}}(\underset{\sim}{x},t)}{\varphi_{\mathcal{S}}(\underset{\sim}{x},t)\,\varphi_{-\mathcal{S}}(\underset{\sim}{x},t)}\right] \geq 0.$$

Proof: Consider the subbody $\mathcal{a}_\epsilon(r)$ defined above. Since the area of the portion of $\partial\mathcal{a}_\epsilon(r)$ contained in $\partial C(\underset{\sim}{x},\underset{\sim}{n},r)$ tends to zero as $\epsilon \to 0$, we conclude from our hypothesis on J_t that

$$J_t(\partial\mathcal{a}_\epsilon(r)) \to J_t(\mathcal{S}(r)) + J_t(-\mathcal{S}(r))$$

as $\epsilon \to 0$. Therefore, since $\lim_{\epsilon \to 0} V(\mathcal{a}_\epsilon(r)) = 0$, $\mathcal{a}_\epsilon(r)$ tends to $\mathcal{S}(r) + (-\mathcal{S}(r))$ in J_t and Theorem 16 implies $J_t(\mathcal{S}(r)) + J_t(-\mathcal{S}(r)) \leq 0$. The remainder of the proof is obvious.

In order to discuss the heat conduction inequality we must distinguish two cases. If $\varphi_{\mathcal{S}}$ and $\varphi_{-\mathcal{S}}$ are of the same sign at $\underset{\sim}{x}$ with $\varphi_{\mathcal{S}} > \varphi_{-\mathcal{S}}$, then $q_{\mathcal{S}}(\underset{\sim}{x},t) \geq 0$, which means heat flows from the positive side of $\mathcal{S}$ to the negative side, and thus that heat flows from higher to lower temperatures. If on the other hand $\varphi_{\mathcal{S}}$ and $\varphi_{-\mathcal{S}}$ are of different sign, it follows that heat flows from negative to positive temperature; thus negative temperatures represent "hotter" states than positive temperatures. These conclusions are summarized on the temperature scale shown in Figure 5.



Temperature Scale

Figure 5

Notice that in a continuous transition from negative to positive temperatures one must pass through an infinite temperature; this is an unfortunate result of the choice of temperature as the <u>reciprocal</u> of the Radon-Nikodym derivative of the entropy flux with respect to heat flux. The heat conduction inequality given in the previous theorem is similar to the classical heat conduction inequality, which is the assertion that

$$\underset{\sim}{q}\cdot\mathrm{grad}\varphi \leq 0.$$

VIII. Reduction to the Clausius-Duhem Inequality

In the previous section we derived a general form for the Second Law (Theorem 14) as well as the following general restriction on the surface entropy flux:

$$J_t(\mathscr{S}) + J_t(-\mathscr{S}) \leq 0.$$

It is the purpose of this section to show that under certain additional hypotheses the Second Law reduces to the Clausius-Duhem inequality. To accomplish this we first prove that in the presence of sufficient smoothness the conductive temperature $\varphi_{\mathscr{S}}$ is independent of $\mathscr{S}$ provided: (i) $J_t(\mathscr{S}) = -J_t(-\mathscr{S})$ for every $\mathscr{S}$, and (ii) the conductive temperature at any point has the same sign for all surfaces through that point. We will then show that in the absence of internal radiation the radiative entropy transfer is determined by a single temperature field. These two results will then imply a slightly generalized version of the Clausius-Duhem inequality: one which involves both a conductive and a radiative temperature field.[1] Finally we will show that certain constitutive assumptions imply that these two fields are equal.

We shall say that the *surface entropy flux is balanced* if

$$J_t(\mathscr{S}) = -J_t(-\mathscr{S}).$$

To simplify the statement of the following theorem let us agree to write

$$j(\underset{\sim}{x},\underset{\sim}{n},t) = j_\pi(\underset{\sim}{x},t)$$

for any $\underset{\sim}{x} \in \mathring{\mathscr{B}}$, where π is a plane material surface through $\underset{\sim}{x}$ with positive normal $\underset{\sim}{n}$.[2]

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[1] This general form involving two temperatures was first proposed by Gurtin and Williams [1966-2].

[2] It is clear from the discussion following Theorem 11 that $j_\pi(\underset{\sim}{x},t)$ is the same for all plane material surfaces through $\underset{\sim}{x}$ with positive normal $\underset{\sim}{n}$.

Theorem 18: (Existence of a Single Conductive Temperature Field) Suppose that

(i) the surface entropy flux is balanced;

(ii) for each $\underset{\sim}{x} \in \mathring{\mathcal{B}}$, $\operatorname{sgn}\varphi_{\mathcal{S}}(\underset{\sim}{x},t)$ is independent of $\mathcal{S}$;

(iii) for each $\underset{\sim}{n}$ the functions $q(\cdot,\underset{\sim}{n},t)$ and $j(\cdot,\underset{\sim}{n},t)$ are continuous on $\mathring{\mathcal{B}}$.

Then there exists an extended non-zero-valued function $\varphi(\cdot,t)$ on $\mathring{\mathcal{B}}$ such that for any material surface $\mathcal{S}$ interior to $\mathcal{B}$

$$\varphi_{\mathcal{S}}(\underset{\sim}{x},t) = \varphi(\underset{\sim}{x},t)$$

for almost every $\underset{\sim}{x} \in \mathcal{S}$ (with respect to the measure Q_t). We call $\varphi(\underset{\sim}{x},t)$ the conductive temperature at $(\underset{\sim}{x},t)$.

Proof: The proof will proceed in a series of lemmas, each of which is of interest in itself. The first of these lemmas is an immediate consequence of hypothesis (i).

Lemma 1: For any material surface $\mathcal{S}$,

$$j_{\mathcal{S}}(\underset{\sim}{x},t) = -j_{-\mathcal{S}}(\underset{\sim}{x},t)$$

for almost every $\underset{\sim}{x} \in \mathcal{S}$.

Lemma 2: Let $\mathcal{S}$ be a material surface interior to $\mathcal{B}$. Then every regular point $\underset{\sim}{x} \in \mathcal{S}$ is a point of density of J_t on $\mathcal{S}$ and

$$j_{\mathcal{S}}(\underset{\sim}{x},t) = j(\underset{\sim}{x},\underset{\sim}{n},t),$$

where $\underset{\sim}{n}$ is the positive unit normal to $\mathcal{S}$ at $\underset{\sim}{x}$.

Proof: Let $\underset{\sim}{x}$ be a regular point of $\mathcal{S}$ and $\underset{\sim}{n}$ the positive unit normal to $\mathcal{S}$ at $\underset{\sim}{x}$. Further, let π_h denote the plane which passes through $\underset{\sim}{x} - h\underset{\sim}{n}$ and has positive unit normal $-\underset{\sim}{n}$. Consider the infinite cylinder $\hat{C}(\underset{\sim}{x},\underset{\sim}{n},r)$ centered at $\underset{\sim}{x}$, with axis parallel $\underset{\sim}{n}$ and radius r, let $\mathcal{S}(r)$ and $\pi_h(r)$ be defined as before (see Figure 6 and the discussion preceding Theorem 7), and let

$$h^*(r) = r^2 + \inf\{h > 0 \mid \pi_h(r) \cap \mathcal{S}(r) = \emptyset\},$$

$$\pi^*(r) = \pi_{h^*(r)}(r).$$

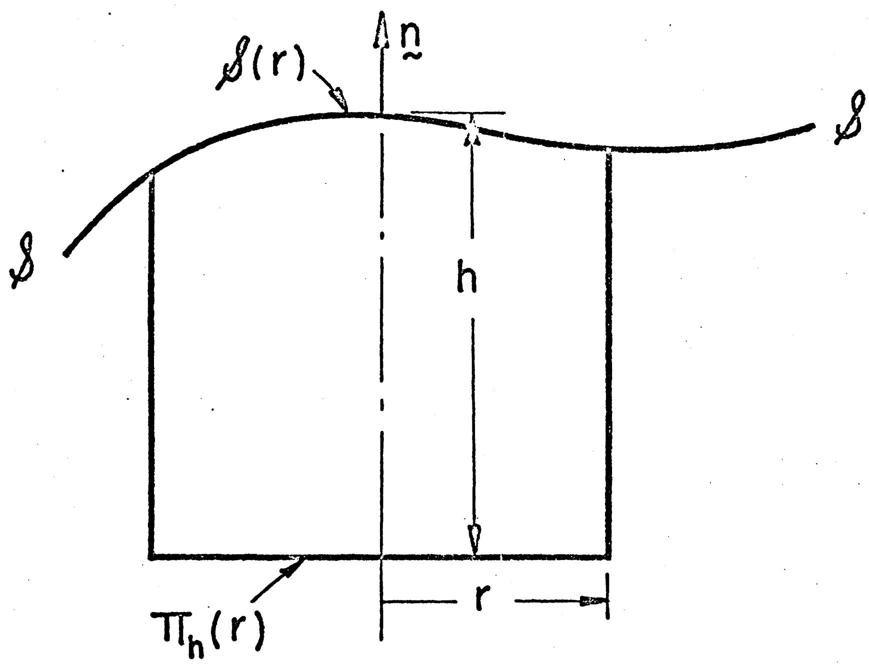

Figure 6

Then, since $\mathcal{S}$ is interior to $\mathcal{B}$, the following conditions must hold for all sufficiently small r: the set $\mathcal{Q}(r)$ enclosed by $\mathcal{S}(r)$ and $\pi^*(r)$ in $\hat{C}(\underset{\sim}{x},\underset{\sim}{n},r)$ is a subbody, and

$$\partial\mathcal{Q}(r) = \mathcal{S}(r) + \pi^*(r) + \mathcal{J}(r),$$

where $\mathcal{J}(r) \subset \partial\hat{C}(\underset{\sim}{x},\underset{\sim}{n},r)$. Since $\mathcal{S}$ is smooth in a neighborhood of $\underset{\sim}{x}$, we have the following estimates:

$$A(\mathcal{S}(r)) = \pi r^2 + o(r^2),$$
$$A(\pi^*(r)) = \pi r^2,$$
$$A(\mathcal{J}(r)) = o(r^2),$$
$$V(\mathcal{Q}(r)) = o(r^2),$$

as r tends to zero. Next the Second Law requires

$$\dot{S}_t(\mathcal{Q}(r)) \geq J_t(\partial\mathcal{Q}(r)) + K_t(\mathcal{Q}(r),\mathcal{Q}(r)^e).$$

But as r tends to zero $\dot{S}_t(\mathcal{Q}(r)) = o(r^2)$, $K_t(\mathcal{Q}(r),\mathcal{Q}(r)^e) = o(r^2)$, and

$$J_t(\partial\mathcal{Q}(r)) = J_t(\mathcal{S}(r)) + J_t(\pi^*(r)) + o(r^2);$$

hence

$$J_t(\mathcal{S}(r)) + J_t(\pi^*(r)) \leq o(r^2).$$

Now

$$J_t(\pi^*(r)) = \int_{\pi^*(r)} j(\underset{\sim}{y},-\underset{\sim}{n},t)\,dA(\underset{\sim}{y}) = \int_{\pi_o(r)} j(\underset{\sim}{y}-h^*(r)\underset{\sim}{n},-\underset{\sim}{n},t)\,dA(\underset{\sim}{y}),$$

and, since $j(\cdot,-\underset{\sim}{n},t)$ is continuous on $\mathring{\mathcal{B}}$ and $h^*(r) = o(1)$,

$$\int_{\pi_o(r)} j(\underset{\sim}{y}-h^*(r)\underset{\sim}{n},-\underset{\sim}{n},t)\,dA(\underset{\sim}{y}) = \int_{\pi_o(r)} j(\underset{\sim}{y},-\underset{\sim}{n},t)\,dA(\underset{\sim}{y}) + o(r^2);$$

thus we have

$$J_t(\pi^*(r)) = J_t(\pi_o(r)) + o(r^2)$$

and hence

$$J_t(\mathcal{S}(r)) + J_t(\pi_o(r)) \leq o(r^2).$$

The same argument clearly may be applied to $-\mathcal{S}$, yielding

$$J_t(-\mathcal{S}(r)) + J_t(-\pi_o(r)) \leq o(r^2).$$

But since the surface entropy flux is balanced the left-hand sides of the last two inequalities are equal in magnitude and opposite in sign; therefore

$$J_t(\mathscr{S}(r)) = J_t(-\pi_o(r)) + o(r^2).$$

If we divide by πr^2 and use the above area estimates we obtain

$$\frac{J_t(\mathscr{S}(r))}{A(\mathscr{S}(r))} = \frac{J_t(-\pi_o(r))}{A(\pi_o(r))} + o(1);$$

since the limit on the right exists so does that on the left and

$$j_{\mathscr{S}}(\underset{\sim}{x},t) = j(\underset{\sim}{x},\underset{\sim}{n},t).$$

Lemma 3: There exists a vector-valued function $\underset{\sim}{j}(\cdot,t)$ on $\mathring{\mathscr{B}}$ such that

$$j(\underset{\sim}{x},\underset{\sim}{n},t) = \underset{\sim}{j}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}$$

for all $\underset{\sim}{x}\in\mathring{\mathscr{B}}$ and any unit vector $\underset{\sim}{n}$.

Proof:[1] For any $x\in\mathring{\mathscr{B}}$ we extend the function $j(x,\cdot,t)$ to the entire vector space as follows:

$$j(\underset{\sim}{x},\underset{\sim}{w},t) = |\underset{\sim}{w}|\, j(\underset{\sim}{x},\frac{\underset{\sim}{w}}{|\underset{\sim}{w}|},t), \qquad \underset{\sim}{w} \neq \underset{\sim}{0},$$

$$j(\underset{\sim}{x},\underset{\sim}{0},t) = 0.$$

It suffices to show that the function $j(\underset{\sim}{x},\cdot,t)$ is linear, for we may then appeal to the familiar representation theorem for linear forms to deduce the existence of $\underset{\sim}{j}(\underset{\sim}{x},t)$. Clearly the extended function $j(\underset{\sim}{x},\cdot,t)$ is homogeneous; we have only to show that it is additive.

Trivially

$$j(\underset{\sim}{x},\underset{\sim}{u}+\underset{\sim}{v},t) = j(\underset{\sim}{x},\underset{\sim}{u},t) + j(\underset{\sim}{x},\underset{\sim}{v},t)$$

if $\underset{\sim}{u}$ and $\underset{\sim}{v}$ are linearly dependent. Suppose $\underset{\sim}{u}$ and $\underset{\sim}{v}$ are linearly independent. Let us fix $\delta > 0$ and consider $\pi_{\underset{\sim}{u}}$, the plane through $\underset{\sim}{x}$ with normal $\underset{\sim}{u}$; $\pi_{\underset{\sim}{v}}$, the plane through $\underset{\sim}{x}$ with normal $\underset{\sim}{v}$; and $\pi_{\underset{\sim}{u}+\underset{\sim}{v}}$, the plane through $\underset{\sim}{x} - \delta(\underset{\sim}{u} + \underset{\sim}{v})$ with normal $\underset{\sim}{u} + \underset{\sim}{v}$. Consider the solid $\mathscr{Q}(\delta)$ bounded by these three planes and two planes parallel to $\underset{\sim}{u}$ and $\underset{\sim}{v}$ and each a distance b from $\underset{\sim}{x}$

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[1] The improvement of the classical proof of Cauchy's Theorem of which this is a minor variation is due to W. Noll.

(see Figure 7), and let b and δ be sufficiently small that $\mathcal{A}(\delta)$ is a subbody. Then

$$\partial\mathcal{A}(\delta) = \mathcal{U} + \mathcal{V} + \mathcal{W} + \mathcal{F} + \mathcal{G},$$

where $\mathcal{U}, \mathcal{V}, \mathcal{W}$ are contained in $\pi_{\underset{\sim}{u}}, \pi_{\underset{\sim}{v}}, \pi_{\underset{\sim}{u}+\underset{\sim}{v}}$ respectively, and $\mathcal{F}$ and $\mathcal{G}$ are the parallel faces; then $\mathcal{U}$ is oriented by $\underset{\sim}{u}$, $\mathcal{V}$ by $\underset{\sim}{v}$, and $\mathcal{W}$ by $-\underset{\sim}{u}-\underset{\sim}{v}$. If $\epsilon = \epsilon(\delta)$ denotes the area of $\mathcal{W}$ it is a simple exercise to show that

$$A(\mathcal{U}) = \frac{|\underset{\sim}{u}|}{|\underset{\sim}{u} + \underset{\sim}{v}|}\,\epsilon,$$

$$A(\mathcal{V}) = \frac{|\underset{\sim}{v}|}{|\underset{\sim}{u} + \underset{\sim}{v}|}\,\epsilon,$$

$$V(\mathcal{A}(\delta)) = 2bA(\mathcal{F}) = 2bA(\mathcal{G}) = \frac{1}{2}\epsilon\delta|\underset{\sim}{u} + \underset{\sim}{v}|,$$

and of course $\epsilon(\delta) = O(\delta)$. By the Second Law

$$\dot{S}_t(\mathcal{A}(\delta)) \geq J_t(\partial\mathcal{A}(\delta)) + K_t(\mathcal{A}(\delta), \mathcal{A}(\delta)^e);$$

and, since $\dot{S}_t(\mathcal{A}(\delta))$, $K_t(\mathcal{A}(\delta), \mathcal{A}(\delta)^e)$, $J_t(\mathcal{F})$, and $J_t(\mathcal{G})$ are all $o(\delta)$ (see Axioms 5 and 8), this inequality implies

$$J_t(\mathcal{U}) + J_t(\mathcal{V}) + J_t(\mathcal{W}) \leq o(\delta).$$

Thus

$$\frac{|\underset{\sim}{u}|}{|\underset{\sim}{u} + \underset{\sim}{v}|}\;\frac{J_t(\mathcal{U})}{A(\mathcal{U})} + \frac{|\underset{\sim}{v}|}{|\underset{\sim}{u} + \underset{\sim}{v}|}\;\frac{J_t(\mathcal{V})}{A(\mathcal{V})} + \frac{J_t(\mathcal{W})}{A(\mathcal{W})} \leq o(1),$$

and taking the limit as $\delta \to 0$ we arrive at

$$\frac{|\underset{\sim}{u}|}{|\underset{\sim}{u} + \underset{\sim}{v}|}\, j(\underset{\sim}{x}, \frac{\underset{\sim}{u}}{|\underset{\sim}{u}|}, t) + \frac{|\underset{\sim}{v}|}{|\underset{\sim}{u} + \underset{\sim}{v}|}\, j(\underset{\sim}{x}, \frac{\underset{\sim}{v}}{|\underset{\sim}{v}|}, t) + j(\underset{\sim}{x}, \frac{-\underset{\sim}{u}-\underset{\sim}{v}}{|\underset{\sim}{u} + \underset{\sim}{v}|}, t) \leq 0;$$

or, as $j(\underset{\sim}{x}, \cdot, t)$ is homogeneous,

$$j(\underset{\sim}{x}, \underset{\sim}{u}, t) + j(\underset{\sim}{x}, \underset{\sim}{v}, t) + j(\underset{\sim}{x}, -\underset{\sim}{u}-\underset{\sim}{v}, t) \leq 0.$$

Since $\underset{\sim}{x} \notin \partial\mathcal{B}$ we can carry out the same construction for $-\underset{\sim}{u}$ and $-\underset{\sim}{v}$, which yields the same equation with reversed signs on $\underset{\sim}{u}$ and $\underset{\sim}{v}$. However, the definition of $j(\underset{\sim}{x}, \underset{\sim}{w}, t)$ and Lemma 1 imply that $j(\underset{\sim}{x}, \underset{\sim}{w}, t) = -j(\underset{\sim}{x}, -\underset{\sim}{w}, t)$, and hence

$$j(\underset{\sim}{x}, \underset{\sim}{u}, t) + j(\underset{\sim}{x}, \underset{\sim}{v}, t) + j(\underset{\sim}{x}, -\underset{\sim}{u}-\underset{\sim}{v}, t) \geq 0.$$

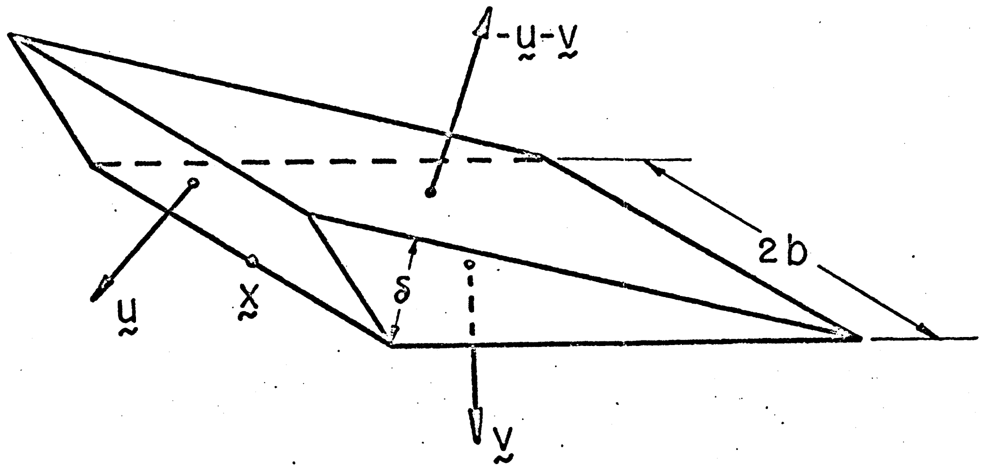

Figure 7

The last two inequalities imply that

$$j(\underset{\sim}{x},\underset{\sim}{u},t) + j(\underset{\sim}{x},\underset{\sim}{v},t) = -j(\underset{\sim}{x},-\underset{\sim}{u}-\underset{\sim}{v},t) = j(\underset{\sim}{x},\underset{\sim}{u}+\underset{\sim}{v},t);$$

and the proof is complete.

Lemma 4: For any $\underset{\sim}{x}\in\mathring{\mathcal{B}}$ the vectors $\underset{\sim}{j}(\underset{\sim}{x},t)$ and $\underset{\sim}{q}(\underset{\sim}{x},t)$ are linearly dependent.

Proof: Assume $\underset{\sim}{j}(\underset{\sim}{x},t)$ and $\underset{\sim}{q}(\underset{\sim}{x},t)$ are linearly independent. By hypothesis (ii) $\varphi_{\mathcal{S}}(\underset{\sim}{x},t)$ is either (a) positive for all $\mathcal{S}$ or (b) negative for all $\mathcal{S}$. Assume (a) holds. Then $\dfrac{\underset{\sim}{q}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}}{\underset{\sim}{j}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}} \geq 0$ for all $\underset{\sim}{n}$ not orthogonal to $\underset{\sim}{j}(\underset{\sim}{x},t)$.[1] But for any $\underset{\sim}{n}$ in the span of $\underset{\sim}{j}(\underset{\sim}{x},t)$ and $\underset{\sim}{q}(\underset{\sim}{x},t)$ that is normal to $\underset{\sim}{q}(\underset{\sim}{x},t) + \underset{\sim}{j}(\underset{\sim}{x},t)$ we must have $\dfrac{\underset{\sim}{q}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}}{\underset{\sim}{j}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}} < 0$, which is a contradiction. A similar argument applies to case (b). This completes the proof of Lemma 4.

The proof of Theorem 13 follows at once from Lemma 4. Indeed, Lemma 4 implies the existence of a non-zero (possibly infinite) function $\varphi(\cdot,t)$ on $\mathring{\mathcal{B}}$ such that

$$\underset{\sim}{j}(\underset{\sim}{x},t) = \frac{1}{\varphi(\underset{\sim}{x},t)}\,\underset{\sim}{q}(\underset{\sim}{x},t)$$

whenever $\underset{\sim}{q}(\underset{\sim}{x},t) \neq \underset{\sim}{0}$; and this function clearly satisfies $\varphi(\underset{\sim}{x},t) = \varphi_{\mathcal{S}}(\underset{\sim}{x},t)$ for almost every $\underset{\sim}{x}\in\mathcal{S}$ (with respect to Q_t).

Thus we have established conditions under which J_t assumes the classical form for entopy conduction. The fundamental assumption was that J_t is balanced. Unfortunately, assuming that the radiative entropy flux K_t is balanced does not suffice to reduce the radiative temperature to a single field. Indeed, if K_t is balanced we may apply the analog of Theorem 6 to show that $K_t(\mathcal{Q},\mathcal{Q}^e)$ is described by a single density $k(\cdot,t)$; but it does not follow that there is a single temperature field relating

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[1]Recall our agreement, in the discussion preceeding Theorem 15, that $j_{\mathcal{S}}(\underset{\sim}{x},t) = \dfrac{1}{\varphi_{\mathcal{S}}(\underset{\sim}{x},t)}\, q_{\mathcal{S}}(\underset{\sim}{x},t)$ at a point of density of J_t and Q_t.

$k(\cdot,t)$ and the corresponding density for R_t, $r(\cdot,t)$; this requires further assumptions. One such assumption is that there be no internal radiation. We prove below that this implies balance of radiative entropy transfer and guarantees the reduction to a single radiative temperature field.

Theorem 19: (*Existence of a Single Radiative Temperature Field*) *Assume there is no internal radiation. Then for every subbody* $\mathcal{A}$

$$K_t(\mathcal{A},\mathcal{A}^e) = \int_{\mathcal{A}} \frac{r(\underset{\sim}{x},t)}{\theta(\underset{\sim}{x},t)}\, dV(\underset{\sim}{x}),$$

where $r(\underset{\sim}{x},t) \equiv r_{\mathcal{B}^e}(\underset{\sim}{x},t)$ *and* $\theta(\underset{\sim}{x},t) \equiv \theta_{\mathcal{B}^e}(\underset{\sim}{x},t)$.

Proof: As we saw in Section 3 the absence of internal radiation implies

$$R_t(\mathcal{P},\mathcal{A}) = 0$$

for every subbody $\mathcal{A}$ and $\mathcal{P}\in\mathbb{B}(\mathcal{A}^b)$. Since $K_t(\cdot,\mathcal{A}) \ll R_t(\cdot,\mathcal{A})$ by Theorem 10, the above relation must also hold for $K_t(\cdot,\mathcal{A})$ and, of course, also for $K_t(\cdot,\mathcal{A}^b)$. Thus we may conclude from the identity

$$K_t(\mathcal{P},\mathcal{A}^e) = K_t(\mathcal{P},\mathcal{A}^b) + K_t(\mathcal{P},\mathcal{B}^e)$$

that

$$K_t(\mathcal{P},\mathcal{A}^e) = K_t(\mathcal{P},\mathcal{B}^e)$$

for every $\mathcal{P}\in\mathbb{B}(\mathcal{A})$. This result, when combined with Theorem 12, yields the desired result.

Of course there are more general conditions under which there is a single radiative temperature. Suppose K_t is balanced. Any condition which guarantees that the measure generated by the function $\mathcal{A}\to K_t(\mathcal{A},\mathcal{A}^e)$ (see the argument in the appendix) is absolutely continuous with respect to the measure similarly generated by $\mathcal{A}\to R_t(\mathcal{A},\mathcal{A}^e)$ will suffice to define a single radiative temperature.

As noted, lack of internal radiation implies that $K_t(\cdot,\mathcal{Q}) = 0$ for any subbody $\mathcal{Q}$ and hence trivially it implies that K_t is balanced. Thus if we also assume that J_t is balanced it follows that M_t is balanced and from Theorem 9 we obtain

Theorem 20: Assume that there is no internal radiation and that the surface entropy flux is balanced. Then the entropy production N_t is s-additive on $\mathcal{M}^{\mathcal{B}}$.

Theorems 18 and 19 now imply the main result of this section: the generalized Clausius-Duhem inequality.

Theorem 21: (The Generalized Clausius-Duhem Inequality) Let J_t obey the conditions of Theorem 18 and suppose that there is no internal radiation. Then for any subbody $\mathcal{Q}$

$$\int_{\mathcal{Q}} \dot{s}(\underset{\sim}{x},t)\,dV(\underset{\sim}{x}) \geq \int_{\partial\mathcal{Q}} \frac{\underset{\sim}{q}(\underset{\sim}{x},t)\cdot\underset{\sim}{n}}{\varphi(\underset{\sim}{x},t)}\,dA(\underset{\sim}{x}) + \int_{\mathcal{Q}} \frac{r(\underset{\sim}{x},t)}{\theta(\underset{\sim}{x},t)}\,dV(\underset{\sim}{x}).$$

Of course, under suitable smoothness assumptions this becomes

$$\dot{s} \geq \operatorname{div}\left(\frac{\underset{\sim}{q}}{\varphi}\right) + \frac{r}{\theta}.$$

The relation in Theorem 21 differs from the usual Clausius-Duhem inequality only by the presence of separate radiative and conductive temperatures. We believe the assumption that the two temperatures coincide should be regarded as a constitutive assumption, rather than as a general axiom. In fact it can be shown[1] that for a very general class of materials the modified Clausius-Duhem inequality requires the two temperatures be equal. As an illustration of the conditions which lead to this result let us consider the special case of a simple heat conductor (without memory). Such a material is defined by two constitutive assumptions. The first is that there is no internal radiation and that the conductive temperature $\varphi_{\mathcal{S}}$ is independent of $\mathcal{S}$ at

[1] Gurtin and Williams [1966-2].

each point; therefore, in the presence of sufficient smoothness, the relevant forms of the first two laws are

$$\dot{e} = \operatorname{div}\mathbf{q} + r,$$
$$\dot{s} \geq \operatorname{div}\left(\frac{\mathbf{q}}{\varphi}\right) + \frac{r}{\theta}.$$

The second constitutive assumption is that there exist four *response functions*, $\hat{\mathbf{q}}, \hat{e}, \hat{s}$, and $\hat{\theta}$, which give the heat flux vector $\mathbf{q}$, the specific internal energy e, the specific internal entropy s, and the radiative temperature θ at any $(\mathbf{x},t)$ whenever the conductive temperature φ and its gradient

$$\mathbf{g} = \operatorname{grad}\varphi$$

are known at $(\mathbf{x},t)$:

$$\mathbf{q}(\mathbf{x},t) = \hat{\mathbf{q}}(\varphi(\mathbf{x},t),\ \mathbf{g}(\mathbf{x},t),\mathbf{x}),$$
$$\mathbf{e}(\mathbf{x},t) = \hat{e}(\varphi(\mathbf{x},t),\ \mathbf{g}(\mathbf{x},t),\mathbf{x}),$$
$$s(\mathbf{x},t) = \hat{s}(\varphi(\mathbf{x},t),\ \mathbf{g}(\mathbf{x},t),\mathbf{x}),$$
$$\theta(\mathbf{x},t) = \hat{\theta}(\varphi(\mathbf{x},t),\ \mathbf{g}(\mathbf{x},t),\mathbf{x}).$$

We shall assume that the response functions are defined and of class C^1 on $\mathcal{R} \times \mathcal{V} \times \mathring{\mathcal{B}}$, where $\mathcal{R}$ is the extended real number system with zero deleted and $\mathcal{V}$ is the vector space associated with $\mathcal{E}$.

Given a class C^2 time-dependent conductive temperature field φ on $\mathring{\mathcal{B}}$ for all time we can compute the fields $\mathbf{q}, e, s$ and θ by means of the foregoing constitutive equations and r by means of the First Law; the ordered array $\{\varphi,\mathbf{q},e,s,\theta,r\}$ so defined will be called a *process*. The above constitutive assumption is *compatible with thermodynamics* if every process satisfies the Second Law.

We call the linear transformation $\mathbf{K}(\varphi,\mathbf{g},\mathbf{x})$ defined by

$$\mathbf{K}(\varphi,\mathbf{g},\mathbf{x}) = \partial_{\mathbf{g}}\hat{\mathbf{q}}(\varphi,\mathbf{g},\mathbf{x})$$

the *conductivity tensor* (corresponding to $(\varphi, \underset{\sim}{g}, \underset{\sim}{x})$). Of course $\partial_{\underset{\sim}{g}}$ denotes the gradient with respect to the vector $\underset{\sim}{g}$ computed holding φ and $\underset{\sim}{x}$ fixed.

Theorem 22: (Reduction to a Single Temperature) Let the simple heat conductor described above be compatible with thermodynamics and assume that the conductivity tensor is never skew. Then the radiative temperature equals the conductive temperature in every process, i.e.,

$$\varphi = \hat{\theta}(\varphi, \underset{\sim}{g}, \underset{\sim}{x})$$

for all $\varphi \in \mathcal{R}$, $\underset{\sim}{g} \in \mathcal{V}$, $\underset{\sim}{x} \in \mathring{\mathcal{B}}$.

Proof: We choose $(\varphi_o, \underset{\sim}{g}_o, \underset{\sim}{x}_o) \in \mathcal{R} \times \mathcal{V} \times \mathring{\mathcal{B}}$ arbitrarily. It is a trivial matter to exhibit a time-independent conductive temperature field φ such that

$$\varphi(\underset{\sim}{x}_o) = \varphi_o, \qquad \operatorname{grad}\varphi(\underset{\sim}{x}_o) = \underset{\sim}{g}_o,$$

and

$$\operatorname{grad}^2\varphi(\underset{\sim}{x}_o) = \underset{\sim}{A},$$

where $\underset{\sim}{A}$ is an arbitrary symmetric tensor (linear transformation). By hypothesis the (time-independent) process $\{\varphi, \underset{\sim}{q}, e, s, \theta, r\}$ generated by φ must obey the first two laws; thus

$$\operatorname{div}\underset{\sim}{q} + r = 0,$$

$$\operatorname{div}\left(\frac{\underset{\sim}{q}}{\varphi}\right) + \frac{r}{\theta} \leq 0,$$

and therefore, eliminating r and evaluating the resulting inequality at $\underset{\sim}{x}_o$,

$$\left(\frac{1}{\varphi_o} - \frac{1}{\theta(\underset{\sim}{x}_o)}\right)\operatorname{div}\underset{\sim}{q}(\underset{\sim}{x}_o) - \frac{1}{\varphi_o^2}\,\hat{\underset{\sim}{q}}(\varphi_o, \underset{\sim}{g}_o, \underset{\sim}{x}_o)\cdot\underset{\sim}{g}_o \leq 0,$$

where[1]

$$\operatorname{div}\underset{\sim}{q}(\underset{\sim}{x}_o) = \partial_\varphi \hat{\underset{\sim}{q}}(\varphi_o, \underset{\sim}{g}_o, \underset{\sim}{x}_o) + \operatorname{tr}\big(\underset{\sim}{K}(\varphi_o, \underset{\sim}{g}_o, \underset{\sim}{x}_o)\underset{\sim}{A}\big) + \operatorname{tr}\big(\partial_{\underset{\sim}{x}}\hat{\underset{\sim}{q}}(\varphi_o, \underset{\sim}{g}_o, \underset{\sim}{x}_o)\big)$$

and

$$\theta(\underset{\sim}{x}_o) = \hat{\theta}(\varphi_o, \underset{\sim}{g}_o, \underset{\sim}{x}_o).$$

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[1] Here tr denotes the trace operation.

Since $\underset{\sim}{K}(\varphi_o,\underset{\sim}{g}_o,\underset{\sim}{x}_o)$ is not skew, $\operatorname{div}\underset{\sim}{g}(\underset{\sim}{x}_o)$ can be made to take on any given value by proper choice of $\underset{\sim}{A}$; if φ_o were not equal to $\hat{\theta}(\varphi_o,\underset{\sim}{g}_o,\underset{\sim}{x}_o)$ we could choose $\underset{\sim}{A}$ so as to violate the above inequality. Therefore

$$\varphi_o = \hat{\theta}(\varphi_o,\underset{\sim}{g}_o,\underset{\sim}{x}_o)$$

and the proof is complete.

Appendix

In this appendix we shall prove the following

Theorem: *Let α be an s-additive set function on $\mathcal{M}^{\mathcal{B}}$ and suppose that*

$$|\alpha(\mathcal{Q})| \leq kV(\mathcal{Q})$$

for all $\mathcal{Q} \in \mathcal{M}^{\mathcal{B}}$ and some real number k. Then α is the restriction to $\mathcal{M}^{\mathcal{B}}$ of one and only one measure $\tilde{\alpha}$ on $\mathbb{B}(\mathcal{B})$ with

$$|\tilde{\alpha}(\mathcal{P})| \leq kV(\mathcal{P})$$

for all $\mathcal{P} \in \mathbb{B}(\mathcal{B})$.

Proof: Given any set A, let $\bar{\bar{A}}$ denote the closure of its interior:

$$\bar{\bar{A}} = \overline{\mathring{A}}.$$

Further, let $\mathbb{P}$ denote the set of all finite unions of half-open rectangular prisms of the form

$$\{\underset{\sim}{x} | \; a^i < x^i \leq b^i, \quad i = 1,2,3\},$$

and let

$$\mathbb{R} = \{A | \; A = B \cap \mathcal{B}, \quad B \in \mathbb{P}\}.$$

Clearly $\mathbb{R}$ is a ring. Moreover, by Axiom 1,

$$A \in \mathbb{R} \Rightarrow \bar{\bar{A}} \in \mathcal{M}^{\mathcal{B}}.$$

Next, we define the set function $\hat{\alpha}$ on $\mathbb{R}$ by

$$\hat{\alpha}(A) = \alpha(\bar{\bar{A}}),$$

and we let $|\hat{\alpha}|$, $\hat{\alpha}^+$, and $\hat{\alpha}^-$ denote, respectively, the total, positive, and negative variation of $\hat{\alpha}$ (see Dunford and Schwartz [1958], pp. 95-99). The function $\hat{\underset{\sim}{\alpha}}$ and (hence) the functions $|\hat{\underset{\sim}{\alpha}}|$, $\hat{\alpha}^+$, and $\hat{\alpha}^-$ are finitely additive; indeed, if $A, B \in \mathbb{R}$ are disjoint, then $\bar{\bar{A}}$ and $\bar{\bar{B}}$ are separate and

$$\hat{\alpha}(A \cup B) = \alpha(\overline{\overline{A \cup B}}) = \alpha(\bar{\bar{A}} \cup \bar{\bar{B}}) = \alpha(\bar{\bar{A}}) + \alpha(\bar{\bar{B}}) = \hat{\alpha}(A) + \hat{\alpha}(B).$$

Further, if $A_i \in \mathbb{R}$, $i = 1,2,\ldots,N$, is any finite collection of disjoint subsets of $A \in \mathbb{R}$, then

$$\sum_{i=1}^{N} |\hat{\alpha}(A_i)| = \sum_{i=1}^{N} |\alpha(\overline{\overline{A}}_i)| \leq \sum_{i=1}^{N} kV(\overline{\overline{A}}_i) = \sum_{i=1}^{N} kV(A_i) = kV(\bigcup_{i=1}^{N} A_i) \leq kV(A);$$

thus

$$|\hat{\alpha}|(A) \leq kV(A), \quad \hat{\alpha}^+(A) \leq kV(A), \quad \hat{\alpha}^-(A) \leq kV(A),$$

for all $A \in \mathbb{R}$. Consequently, given any monotone decreasing sequence $\{A_n\}$ in $\mathbb{R}$ with $\bigcap_{n=1}^{\infty} A_n = \emptyset$ we have

$$\lim_{n\to\infty} |\hat{\alpha}|(A_n) = \lim_{n\to\infty} \hat{\alpha}^+(A_n) = \lim_{n\to\infty} \hat{\alpha}^-(A_n) = 0;$$

and this in turn implies (Halmos [1950], p. 39) that $|\hat{\alpha}|$, $\hat{\alpha}^+$, $\hat{\alpha}^-$, and (hence) $\hat{\alpha}$ are countably additive and bounded on $\mathbb{R}$. Next, since the σ-ring generated by $\mathbb{R}$ is $\mathbb{B}(\mathcal{B})$, we may conclude from a well-known theorem (Dunford and Schwartz [1958], pp. 134-136) that $\hat{\alpha}$, $\hat{\alpha}^+$, and $\hat{\alpha}^-$ have unique countably additive extensions $\tilde{\alpha}$, $\tilde{\alpha}^+$, and $\tilde{\alpha}^-$ to $\mathbb{B}(\mathcal{B})$. Moreover $\tilde{\alpha} = \tilde{\alpha}^+ - \tilde{\alpha}^-$ and

$$\tilde{\alpha}^+(A) = \inf \sum_{n=1}^{\infty} \hat{\alpha}^+(A_n), \qquad \tilde{\alpha}^-(A) = \inf \sum_{n=1}^{\infty} \hat{\alpha}^-(A_n)$$

where each infimum is taken over all sequences $\{A_n\}$ of sets in $\mathbb{R}$ whose union contains A. Then, since

$$\sum_{n=1}^{\infty} \hat{\alpha}^+(A_n) \leq k \sum_{n=1}^{\infty} V(A_n),$$

we must have

$$\inf \sum_{n=1}^{\infty} \hat{\alpha}^+(A_n) \leq k \inf \sum_{n=1}^{\infty} V(A_n) = kV(A);$$

thus $\tilde{\alpha}^+(A) \leq kV(A)$. Similarly $\tilde{\alpha}^-(A) \leq kV(A)$, and hence

$$|\tilde{\alpha}(A)| \leq kV(A).$$

To complete the proof we have only to show that

$$\tilde{\alpha}(\mathcal{A}) = \alpha(\mathcal{A})$$

for any $\mathcal{A} \in \mathcal{M}^{\mathcal{B}}$. Given any $\mathcal{A} \in \mathcal{M}^{\mathcal{B}}$ we have the inequality

$$|\tilde{\alpha}(\mathcal{A}) - \alpha(\mathcal{A})| \leq |\tilde{\alpha}(\mathcal{A}) - \tilde{\alpha}(A)| + |\alpha(\overline{\overline{A}}) - \alpha(\mathcal{A})|$$

which must hold for <u>every</u> $A \in \mathbb{R}$. Now it is a consequence of a well-known result[1] that given any $\epsilon > 0$ we can always find an $A \in \mathbb{R}$ such that

$$|\tilde{\alpha}(\mathcal{A}) - \tilde{\alpha}(A)| \leq \epsilon, \quad V(\mathcal{A} \triangle A) \leq \epsilon;$$

and this implies

$$|\tilde{\alpha}(\mathcal{A}) - \alpha(\mathcal{A})| \leq \epsilon + |\alpha(\bar{\bar{A}}) - \alpha(\mathcal{A})|.$$

Next, if we denote the operation of relative complementation (subtraction) in the Boolean algebra $\mathcal{M}^{\mathcal{B}}$ by "$\setminus$" (i.e. $\mathcal{A} \setminus \mathcal{H} = \mathcal{A} \wedge \mathcal{H}^b$) then, since

$$\alpha(\bar{\bar{A}}) - \alpha(\mathcal{A}) = \alpha(\bar{\bar{A}} \setminus \mathcal{A}) - \alpha(\mathcal{A} \setminus \bar{\bar{A}}),$$

it follows that

$$|\alpha(\bar{\bar{A}}) - \alpha(\mathcal{A})| \leq k\big(V(\bar{\bar{A}} \setminus \mathcal{A}) + V(\mathcal{A} \setminus \bar{\bar{A}})\big).$$

It is not difficult to show that

$$V(\bar{\bar{A}} \setminus \mathcal{A}) + V(\mathcal{A} \setminus \bar{\bar{A}}) = V(\mathcal{A} \triangle A).$$

Thus

$$|\hat{\alpha}(\mathcal{A}) - \alpha(\mathcal{A})| \leq \epsilon + 2k\epsilon$$

which implies the desired result.

To establish the uniqueness of this extension, suppose $\tilde{\alpha}_1, \tilde{\alpha}_2$ both satisfy the conditions of the theorem. Then, since they are both volume-continuous, $A \in \mathbb{R}$ implies

$$\tilde{\alpha}_1(A) = \tilde{\alpha}_1(\bar{\bar{A}}) = \alpha(\bar{\bar{A}}) = \tilde{\alpha}_2(\bar{\bar{A}}) = \tilde{\alpha}_2(A).$$

Hence they agree on $\mathbb{R}$, and it is a classical result[2] that they must then agree on $\mathbb{B}(\mathcal{B})$, which is the σ-ring generated by $\mathbb{R}$. This completes the proof.

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[1] See Halmos [1950], p. 56.

[2] See Halmos [1950], p. 54.

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In this report we present a complete set of axioms, based upon physically acceptable gross forms of the laws of thermodynamics, which yield appropriate forms of these laws for continuum physics. We then find conditions under which these reduce to the classical forms.

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