

Giuseppe Grioli (Ed.)

# Proprietà di media e teoremi di confronto in fisica matematica

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FONDAZIONE  
**CIME**  
ROBERTO CONTI

Giuseppe Grioli (Ed.)

# Proprietà di media e teoremi di confronto in fisica matematica

Lectures given at the  
Centro Internazionale Matematico Estivo (C.I.M.E.),  
held in Bressanone (Bolzano), Italy,  
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 Springer

  
**FONDAZIONE**  
**CIME**  
**ROBERTO CONTI**

C.I.M.E. Foundation  
c/o Dipartimento di Matematica “U. Dini”  
Viale Morgagni n. 67/a  
50134 Firenze  
Italy  
**cime@math.unifi.it**

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PRIOPRIETÀ DI MEDIA E TEOREMI DI CONFRONTO  
IN FISICA MATEMATICA

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**CENTRO INTERNAZIONALE MATEMATICO ESTIVO**  
**(C. I. M. E.)**

**B. D. COLEMAN**

**ON GLOBAL AND LOCAL FORMS**  
**OF THE SECOND LAW OF THERMODYNAMICS**

**ROMA - Istituto Matematico dell'Università**

## Preface

The mathematical methods used here were set forth in the following two articles :

- (1) "Thermodynamics of elastic materials with heat conduction and viscosity", B.D. Coleman and W. Noll, *Archive for Rational Mechanics and Analysis* 13, 167-178 (1963).
- (2) "Thermodynamics and departures from Fourier's Law of heat conduction", B.D. Coleman and V. J. Mizel, *Archive for Rational Mechanics and Analysis* 13, 245-261 (1963).

Parts of the present text have been taken, with alterations and elaborations, from (1). These lectures are concerned, however, mainly with some new research to be published shortly by B.D. Coleman and V. J. Mizel in an article entitled "Existence of caloric equations of state in thermodynamics".

Lecture I

§ 1. Introduction

The basic physical concepts of classical continuum mechanics are body, configuration of a body, and force system acting on a body. In a formal rational development of the subject, one first tries to state precisely what mathematical entities represent these physical concepts. In rough language, a body is regarded to be smooth manifold whose elements are the material points; a configuration is defined as a mapping of the body into a three-dimensional Euclidean space, and a force system is defined to be a vector-valued function defined for pairs of bodies.\* Once these concepts are made precise one can proceed to the statement of general principles, such as the principle of objectivity or the law of balance of linear momentum, and to the statement of specific constitutive assumptions, such as the assertion that a force system can be resolved into body forces with a mass density and contact forces with a surface density, or the assertion that the contact forces at a material point depend on certain local properties of the configuration at the point. While the general principles are the same for all work in classical continuum mechanics, the constitutive assumptions vary with the application in mind and serve to define the material under consideration. When one has stated the mathematical nature of bodies, configurations and forces, and has laid down the ways in which these concepts occur in the general principles and the constitutive assumptions, then the properties of these concepts are fixed, and one can present rigorous arguments without recourse to "operational definitions" and other metaphysical paraphernalia, which may be of some use in deciding

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\* For more extensive discussions of the foundations of continuum mechanics see references [1] - [4] .

on the applicability of a theory to a specific physical situation but seem to have no place in its mathematical development.

Albeit the problem of the formulation of a detailed list of axioms for mechanics still has, even for the experts, some troublesome open questions, we can still assume in these lectures that we have sufficient familiarity with continuum mechanics to use the basic concepts and principles of the subject without continual reference to such a list.

To discuss the thermodynamics of continua, it appears that to the concepts of continuum mechanics one must add five new basic concepts: these are temperature, specific internal energy<sup>\*</sup>, specific entropy<sup>\*\*</sup>, heat flux, and heat supply<sup>\*\*\*</sup> (due to radiation). Once mechanics is axiomatized, it is easy to give the mathematical entities representing the thermodynamic concepts: temperature, specific internal energy, specific entropy and heat supply are scalar fields defined over the body, while heat flux is a vector field over the body. I believe that in presenting thermodynamics one should retain all the general principles of mechanics but add to them two new principles: the first law of thermodynamics, i. e. the law of balance of energy<sup>\*\*\*\*</sup>, and the second law, which for continua takes the form of the Clausius-Duhem inequality<sup>\*\*\*\*\*</sup>. Of course in thermodynamics one must make constitutive assumptions which involve some of the new variables which the subject introduces. The main

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\* Sometimes called "internal energy density".

\*\* Sometimes called "entropy density".

\*\*\* Sometimes called "density of absorbed radiation".

\*\*\*\* Cf. §§ 241 and 242 of [4] .

\*\*\*\*\* Cf. § 257 of [4] .



purpose of these lectures will be to examine the restrictions which the second law places on constitutive assumptions.\*

Generalizing some earlier work of Truesdell [6], Truesdell and Toupin [4] have formulated the following principle of equipresence: "a variable present as an independent variable in one constitutive equation should be so present in all". In other words, one should start a theory by assuming that all causes contribute to all effects. If one suspects a certain separation of effects one should not assume it a priori but should rather prove that general physical principles or assumed material symmetries require the separation. In their qualitative explanation of their original formulation of this principle, Truesdell and Toupin emphasized the separation of effects due to the invariance requirements of material objectivity and symmetry. I at first found myself unable to believe in the usefulness of equipresence, but a study of the consequences of thermodynamics restrictions [7] on constitutive equations has changed my viewpoint.

Here we shall use equipresence and assume that an independent variable present in one constitutive equation is so present in all, unless its presence is in direct contradiction with the assumed symmetry of the material, the principle of material objectivity or the laws of thermodynamics.

One of the things which we shall do here is to show that it is possible to use equipresence to motivate the classical linear theory of viscous fluids with heat conduction, although a cursory examination of the constitutive equations of that theory can yield the specious conclusion that the theory does not allow every cause to contribute to every effect.

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\* This concept of the structure of thermodynamics is explained in more detail in [5].

### On Notation

We shall use the direct, as distinguished from the component, tensor notation, denoting vectors and points in Euclidean space by boldface Latin minuscules and tensors by lightface Latin majuscules. Tensors of order higher than two will not occur. We shall denote the transpose of a tensor  $F$  by  $F^T$ . The tensor  $Q$  will be said to be orthogonal if  $QQ^T = Q^TQ = I$ , where  $I$  is a unit tensor. The symbol  $\underline{0}$  will always denote the zero vector, but  $0$  may denote either the scalar zero or the zero tensor.

## § 2. Thermodynamic Processes

Consider a body consisting of material points  $X$ . A thermodynamic process for this body is described by eight functions of  $X$  and the time  $t$ , with physical interpretations as follows:

- (1) The spatial position  $\underline{x} = \underline{\chi}(X, t)$ ; here the function  $\underline{\chi}$ , called the deformation function, describes a motion of the body.
- (2) The symmetric stress tensor  $T = T(X, t)$ .
- (3) The body force  $\underline{b} = \underline{b}(X, t)$  per unit mass (exerted on the body by the external world).
- (4) The specific internal energy  $\mathcal{E} = \mathcal{E}(X, t)$ .
- (5) The heat flux vector  $\underline{q} = \underline{q}(X, t)$ .
- (6) The heat supply  $r = r(X, t)$  per unit mass and unit time (absorbed by the material and furnished by radiation from the external world).
- (7) The specific entropy  $\eta = \eta(X, t)$ .
- (8) The local temperature  $\theta = \theta(X, t)$ , which is assumed to be always positive,  $\theta > 0$ .

We say that such a set of eight functions is a thermodynamic process [5] if the following two conservation laws\* are satisfied not only for the body but for each of its parts  $\mathcal{B}$ :

(A) The law of balance of linear momentum:

$$(2.1) \quad \int_{\mathcal{B}} \ddot{\underline{x}} \, dm = \int_{\mathcal{B}} \underline{b} \, dm + \int_{\partial \mathcal{B}} T \underline{n} \, ds .$$

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\* A thorough discussion of these conservation laws is given in [4], §§ 196-205, 240, 241.

(B) The law of balance of energy

$$(2.2) \quad \frac{1}{2} \frac{d}{dt} \int_{\mathcal{B}} \dot{\underline{x}} \cdot \ddot{\underline{x}} \, dm + \int_{\mathcal{B}} \dot{\underline{\epsilon}} \, dm = \int_{\mathcal{B}} (\dot{\underline{x}} \cdot \underline{b} + r) dm + \int_{\partial \mathcal{B}} (\dot{\underline{x}} \cdot \underline{T} \underline{n} - \underline{q} \cdot \underline{n}) ds.$$

In (2.1) and (2.2),  $dm$  denotes the element of mass in the body,  $\partial \mathcal{B}$  the surface of  $\mathcal{B}$ ,  $ds$  the element of surface area in the configuration at time  $t$ , and  $\underline{n}$  the exterior unit normal vector to  $\partial \mathcal{B}$  in the configuration at time  $t$ ; a superimposed dot denotes the material time derivative, i. e. the derivative with respect to  $t$  keeping  $\underline{X}$  fixed.  $\mathcal{B}$  and  $\underline{\chi}$  are assumed to be such that the region,  $\underline{\chi}(\mathcal{B}, t)$ , occupied by  $\mathcal{B}$  is, for each  $t$ , the closure of a bounded open connected set possessing a piecewise smooth surface.

The assumed symmetry of the stress tensor  $\underline{T}$  insures that the moment of momentum is automatically balanced. Couple stresses, body couples and other mechanical interactions not included in  $\underline{T}$  or  $\underline{b}$  are assumed to be absent.

Under suitable smoothness assumptions the balance equations (2.1) and (2.2) in integral form are equivalent to the following two balance equations in differential form<sup>\*</sup>:

$$(2.3) \quad \text{div } \underline{T} - \rho \ddot{\underline{x}} = -\rho \underline{b},$$

$$(2.4) \quad \text{tr} \{ \underline{T} \underline{L} \} - \text{div } \underline{q} - \rho \dot{\underline{\epsilon}} = -\rho r.$$

Here  $\rho$  denotes the mass density;  $\underline{L}$  is the velocity gradient, i. e.

$\underline{L} = \text{grad } \dot{\underline{x}}$ ;  $\text{tr}$  is the trace operator; and the operators  $\text{grad}$  and  $\text{div}$  refer

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\* See the sections of [4] cited above.

to spatial derivatives, i. e. the gradient and divergence with respect to  $\underline{x}$  keeping  $t$  fixed.

We note that in order to define a thermodynamic process it suffices to prescribe the six functions  $\underline{\chi}$ ,  $T$ ,  $\epsilon$ ,  $q$ ,  $\eta$ , and  $\theta$ . The remaining functions  $\underline{b}$  and  $r$  are then determined by (2.3) and (2.4).

It is often convenient to identify the material point  $X$  with its position  $\underline{X}$  in a fixed reference configuration  $R$  and to write

$$(2.5a) \quad \underline{x} = \underline{\chi}(\underline{X}, t).$$

The gradient  $F$  of  $\underline{\chi}(\underline{X}, t)$  with respect to  $\underline{X}$ , i. e.

$$(2.5b) \quad F = F(\underline{X}, t) = \nabla \underline{\chi}(\underline{X}, t),$$

is called the deformation gradient at  $\underline{X}$  (i. e. at  $X$ ) relative to the configuration  $R$ . It is well known that

$$(2.6) \quad \dot{F} = LF, \quad \text{i. e.} \quad L = \dot{F}F^{-1}.$$

We assume that  $\underline{\chi}(\underline{X}, t)$  is always smoothly invertible in its first variable, i. e. that the  $\tilde{\text{inverse}}$   $F^{-1}$  of  $F$  exists, or, equivalently, that  $\det F \neq 0$ . We consistently use the symbol  $\nabla$  to indicate a gradient in the reference configuration  $R$ , i. e. a gradient computed taking  $\underline{X}$  as the independent variable, whereas  $\text{grad}$  is used when the position  $\underline{x}$  in the present configuration is taken as the independent variable. For a scalar field over  $\mathcal{B}$ , such as  $\theta$ , it is easily shown that

$$(2.7) \quad \nabla \theta = F^T \text{grad } \theta.$$

Since  $\text{grad } \theta$  occurs often in our subject, it is convenient to have a single symbol for this vector. Let us use the abbreviation

$$(2.8) \quad \underline{g} \equiv \text{grad } \theta .$$

The mass density  $\rho$  is determined by  $F$  through the equation

$$(2.9) \quad \rho = \frac{1}{|\det F|} \rho_r$$

where  $\rho_r$  is a positive number, constant in time and equal to the mass density in the reference configuration  $R$ , and  $|\det F|$  is the absolute value of the determinant of  $F$ .

$$(3.5) \quad \mathcal{U} = \int \rho u \, dV \quad ,$$

where  $\mathcal{U}$  denotes the specific intrinsic energy, dependent on the mechanical state of the element, i. e., on its deformation, and on the temperature. The influx of heat into the volume  $V$  is

$$(3.6) \quad \dot{\mathcal{Z}}^{(\mathcal{U})} = - \int q_k \nu_k \, dS \quad ,$$

where the vector  $q_k$  denotes the heat flux. Starting from (1.2) and observing that, in a continuum, the energy of an element is composed of its kinetic and intrinsic energies, we state the first fundamental theorem for the volume  $V$  in the following form :

The material rate of increase of the sum of the kinetic and intrinsic energies is equal to the rate of work of the exterior forces plus the heat influx.

The analytical form of this statement is

$$(3.7) \quad \int \rho (\mathbf{v}_k \dot{\mathbf{v}}_k + \dot{u}) \, dV = \int \rho \mathbf{f}_k \mathbf{v}_k \, dV + \int (\sigma_{kl} \nu_k - q_l) \nu_l \, dS$$

$$= \int (\rho \mathbf{f}_k \mathbf{v}_k + \sigma_{kl} \mathbf{v}_{k,l} + \sigma_{kl,l} \mathbf{v}_k - q_{l,l}) \, dV$$

On account of (3.4) and the symmetry of  $\sigma_{kl}$  (3.7) reduces to

$$(3.8) \quad \int \rho \dot{u} \, dV = \int (\sigma_{kl} \mathbf{v}_{kl} - q_{k,k}) \, dV \quad ,$$

where

$$(3.9) \quad \mathbf{v}_{kl} = \frac{1}{2} (\mathbf{v}_{k,l} + \mathbf{v}_{l,k})$$

Lecture II

§ 3. Admissible Processes and Constitutive Assumptions

We assume that the material at the point  $X$  is characterized by four functions  $\hat{\epsilon}_{(X)}, \hat{\eta}_{(X)}, \hat{T}_{(X)}, \hat{q}_{(X)}$  which we call response functions and which give  $\epsilon, \eta, T, q$  at  $X$  when  $\theta, \underline{g}, F, \dot{F}$  are known at  $X$ :

$$(3.1) \quad \epsilon = \hat{\epsilon}_{(X)}(\theta, \underline{g}, F, \dot{F}) ,$$

$$(3.2) \quad \eta = \hat{\eta}_{(X)}(\theta, \underline{g}, F, \dot{F}) ,$$

$$(3.3) \quad T = \hat{T}_{(X)}(\theta, \underline{g}, F, \dot{F}) ,$$

$$(3.4) \quad q = \hat{q}_{(X)}(\theta, \underline{g}, F, \dot{F}) .$$

We say that a thermodynamic process in  $\mathcal{B}$  is an admissible thermodynamic process [5] if it is compatible with the constitutive equations (3.1)-(3.4) .

In dealing with response functions it is often important to distinguish between them and their values. Here a symbol with a superimposed  $\wedge, \sim, -,$  or  $=$  always denotes a function. Since, for a given process, the values of  $F$  and  $\dot{F}$  must depend on the choice of the reference configuration  $R$  , the response functions  $\hat{\epsilon}_{(X)}, \hat{\eta}_{(X)}, \hat{T}_{(X)}, \hat{q}_{(X)}$  will depend on  $R$  . As the notation of (3.1)-(3.4) indicates, in general, these functions can also de-



pend on the material point  $X$ . If there exists a reference configuration  $R^*$  of  $\mathcal{B}$  which makes  $\hat{\epsilon}_{(X)}, \hat{\eta}_{(X)}, \hat{T}_{(X)}, \hat{q}_{(X)}$  independent of  $X$  for all  $X$  in  $\mathcal{B}$ , then we say that  $\mathcal{B}$  is materially homogeneous and that  $R^*$  is a homogeneous configuration of  $\mathcal{B}$ ; if there is no such configuration  $R^*$  of  $\mathcal{B}$ , then  $\mathcal{B}$  is materially inhomogeneous. For ease in writing, we shall drop the subscript  $(X)$  on response functions; however, all the arguments we shall give here are valid equally for materially homogeneous and materially inhomogeneous bodies.

In an admissible thermodynamic process, the arguments  $\theta, g, F, \dot{F}$  and the values  $\epsilon, \eta, T, q$  of the response functions  $\hat{\epsilon}, \hat{\eta}, \hat{T}, \hat{q}$  will, of course, depend on the time  $t$ . We assume that the functions  $\hat{\epsilon}, \hat{\eta}, \hat{T}, \hat{q}$  are themselves independent of  $t$ .

The constitutive equations considered here are not the most general imaginable; for example, they do not allow for all the long range memory effects covered in the purely mechanical theory of simple materials<sup>\*</sup>. Our assumptions are, however, sufficiently general to cover many applications; in particular, they include as special cases the constitutive equations of the classical theories of thermoelastic phenomena and the hydrodynamics of viscous fluids with heat conduction. In contradistinction to the usual presentations of these classical theories, we here, in Eqs. (3.1)-(3.4), start with constitutive assumptions that are compatible with the principle of equipresence.

We do not lay down constitutive equations for body force density  $\underline{b}$  and the heat supply  $r$  due to absorbed radiation. The quantities  $\underline{b}$  and  $r$  are regarded as assignable; they can be assigned any values compatible with the balance equations (2.3) and (2.4). Let us elaborate on the physical

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\* Cf. [2] & [8].

significance of this assumption. Let  $X$  be a material point in  $\mathcal{B}$ . In the present theory we are following standard procedure and are ignoring mutual body forces and self-radiation within  $\mathcal{B}$ . Here  $\underline{b}$  and  $r$  at  $X$  depend not only on the "local state"  $(\theta, \underline{g}, F, \dot{F})$  at  $X$  but also on the "external world", i. e. on the state of regions outside of  $\mathcal{B}$ . Our mathematical assumption that  $\underline{b}$  and  $r$  are assignable has the physical meaning that we suppose that for each local state at  $X$  one can adjust the conditions outside of  $\mathcal{B}$  so that  $r$  and  $\underline{b}$  take on arbitrary values compatible with balance of momentum and energy. That an experimenter might prefer to fix the outside conditions and thus lose freedom in assigning thermodynamic fields should not affect our proofs: the theorist can consider processes which the experimenter finds difficult to realize, provided only that they are not impossible to realize.

We assume that for any fixed set of values of  $\underline{g}, F, \dot{F}$  the function  $\hat{\Sigma}$  is smoothly invertible in its first variable  $\theta$ ; i. e.,

$$(3.5) \quad \frac{\partial \hat{\Sigma}}{\partial \theta}(\theta, \underline{g}, F, \dot{F}) \neq 0.$$

This implies that there exist functions  $\tilde{\theta}, \tilde{\eta}, \tilde{T}, \tilde{q}$ , also called response functions, which can be used to rewrite (3.1)-(3.4) in the forms

$$(3.6) \quad \theta = \tilde{\theta}(\underline{\epsilon}, \underline{g}, F, \dot{F})$$

$$(3.7) \quad \eta = \tilde{\eta}(\underline{\epsilon}, \underline{g}, F, \dot{F})$$

$$(3.8) \quad T = \tilde{T}(\underline{\epsilon}, \underline{g}, F, \dot{F})$$

$$(3.9) \quad \underline{q} = \tilde{q}(\underline{\epsilon}, \underline{g}, F, \dot{F})$$

For each set of the quantities  $\underline{g}, F, \dot{F}$ , the function  $\tilde{\theta}(\bullet, \underline{g}, F, \dot{F})$  is the inverse function of  $\hat{\mathcal{E}}(\bullet, \underline{g}, F, \dot{F})$ , and  $\tilde{\eta}$  is defined by

$$(3.10) \quad \tilde{\eta}(\underline{\varepsilon}, \underline{g}, F, \dot{F}) \equiv \hat{\eta}(\tilde{\theta}(\underline{\varepsilon}, \underline{g}, F, \dot{F}), \underline{g}, F, \dot{F}) .$$

$\tilde{T}$  and  $\tilde{q}$  are defined by formulae analogous to (3.10).

To every choice of the deformation function  $\underline{\chi}$  and the temperature distribution  $\theta$ , as functions of  $X$  and  $t$ , there corresponds a unique admissible thermodynamic process in  $\mathcal{A}$ . For, when  $\underline{\chi}(X, t)$  and  $\theta(X, t)$  are known for all  $X$  and  $t$ , clearly  $F, \dot{F}$ , and  $\tilde{\theta}$  are determined throughout  $\mathcal{B}$ . The constitutive equations (3.1)-(3.4) then determine  $\underline{\varepsilon}, \eta, T$ , and  $\underline{q}$  throughout  $\mathcal{B}$ . Once the fields  $\underline{\chi}, T, \underline{\varepsilon}, \underline{q}$ , and  $\theta$  are known,  $\underline{r}$  and  $\underline{b}$  are determined by the balance laws (2.3) and (2.4).

Let  $\underline{q}(t)$  be any time-dependent positive scalar;  $\underline{a}(t)$  any time-dependent vector;  $A(t)$  any time-dependent invertible tensor; and  $\underline{Y}$  any material point of  $\mathcal{B}$  whose spatial position in the reference configuration  $R$  is  $\underline{Y}$ . We can always construct at least one admissible thermodynamic process in  $\mathcal{B}$  such that  $\theta(\underline{X}, t), \underline{g}(\underline{X}, t), F(\underline{X}, t)$  have, respectively, the values  $\underline{q}(t), \underline{a}(t), A(t)$  at  $\underline{X} = \underline{Y}$ . An example of such a process is the one determined by the following deformation function and temperature distribution:

$$(3.11a) \quad \underline{x} = \underline{\chi}(X, t) = \underline{Y} + A(t) [\underline{X} - \underline{Y}] ,$$

$$(3.11b) \quad \theta = \theta(\underline{X}, t) = \underline{q}(t) + [A^T(t)\underline{a}(t)] \cdot [\underline{X} - \underline{Y}] ,$$

i. e. ,

$$(3.11b') \quad \theta = \theta(\underline{x}, t) = \alpha(t) + \underline{a}(t) \cdot [\underline{x} - \underline{y}]$$

where  $\underline{y} = \underline{\chi}(\underline{Y}, t) = \underline{Y}$ . Thus, at a given time  $t$ , we can arbitrarily specify only  $\tilde{\theta}, \underline{g}$  and  $F$  but also their time derivatives  $\dot{\tilde{\theta}}, \dot{\underline{g}}, \dot{F}, \ddot{F}$ , etc. at a point  $\underline{Y}$  and be sure that there exists at least one admissible thermodynamic process corresponding to this choice. Furthermore, it follows from this, (3.1) and (3.5) that  $\underline{\varepsilon}, \underline{g}, F$  and the time-derivatives  $\dot{\underline{\varepsilon}}, \dot{\underline{g}}, \dot{F}, \ddot{F}$  also form a set of quantities which can be chosen independently at one fixed point and time.

Lecture III

§ 4. The Clausius-Duhem Inequality and Its Consequences

We regard  $\underline{q}/\theta$  to be the vectorial flux of entropy due to heat flow and  $r/\theta$  to be a scalar supply of entropy from radiation. In other words, for each process we define the rate of production of entropy in the part  $\mathcal{B}$  to be

$$(4.1) \quad \Gamma = \frac{d}{dt} \int_{\mathcal{B}} \eta \, dm - \int_{\mathcal{B}} \frac{r}{\theta} dm + \int_{\partial \mathcal{B}} \frac{1}{\theta} \underline{q} \cdot \underline{n} ds$$

where  $dm$  is the element of mass in  $\mathcal{B}$ ,  $\underline{n}$  the exterior unit normal to the surface  $\partial \mathcal{B}$  of  $\mathcal{B}$ , and  $ds$  the element of surface area in the configuration at time  $t$ . Under appropriate smoothness assumptions we can write

$$(4.2) \quad \Gamma = \int_{\mathcal{B}} \gamma \, dm$$

where

$$(4.3) \quad \begin{aligned} \gamma &= \dot{\eta} - r/\theta + \rho^{-1} \operatorname{div} \underline{q}/\theta \\ &= \dot{\eta} - \frac{r}{\theta} + \frac{1}{\rho\theta} \operatorname{div} \underline{q} - \frac{1}{\rho\theta^2} \underline{q} \cdot \underline{g} \end{aligned}$$

is the specific rate of production of entropy.

One way [5] of giving the Second Law of Thermodynamics a precise mathematical meaning is to lay down the following postulate.

Postulate: For every admissible thermodynamic process in a body, the following inequality must hold for all  $t$  and all parts  $\mathcal{B}$  of the body:

$$(4.4) \quad \dot{\mathcal{I}} \geq 0.$$

The inequality (4.4) is called the Clausius-Duhem inequality. Our postulate places restrictions on constitutive equations of the type (3.1)-(3.4), [or (3.6)-(3.9)]. We now attempt to find necessary and sufficient set of such restrictions.

In order that (4.4) holds for all parts  $\mathcal{B}$  of a body, it is necessary and sufficient that

$$(4.5) \quad \delta \geq 0$$

at all material points  $X$  of the body.

For each thermodynamic process, the energy balance equation (2.2) permits us to rewrite (4.3) as follows

$$(4.6) \quad \delta = \dot{\eta} - \frac{\dot{\epsilon}}{\theta} + \frac{1}{\rho\theta} \operatorname{tr} \{TL\} - \frac{1}{\rho\theta^2} \mathbf{q} \cdot \mathbf{g}$$

In an admissible process  $\mathbf{q}$  and  $T$  must be given by (3.8) and (3.9), and  $\dot{\eta}$  must be given by

$$(4.7) \quad \dot{\eta} = \eta_{\epsilon} \dot{\epsilon} + \eta_{\mathbf{g}} \cdot \mathbf{g} + \operatorname{tr} \{ \eta_{\mathbf{F}} \dot{\mathbf{F}} \} + \operatorname{tr} \{ \eta_{\mathbf{F}} \ddot{\mathbf{F}} \},$$

where  $\eta_{\epsilon}$  is the (scalar) value of  $\frac{\partial \tilde{\eta}}{\partial \epsilon}$ ;  $\eta_{\mathbf{g}}$  is the (vector) value of the gradient of the function  $\tilde{\eta}$  with respect to its second variable  $\mathbf{g}$ ; while  $\eta_{\mathbf{F}}$  and  $\dot{\eta}_{\mathbf{F}}$  are, respectively, the (tensor) values of gradients of

$\tilde{\eta}$  with respect to its third variable  $F$  and its fourth variable  $\dot{F}$ . It follows from (4.6), (4.7), and (2.5) that

$$(4.8) \quad \gamma = \eta_{\dot{g}} \cdot \dot{g} + \text{tr} \{ \eta_{\dot{F}\dot{F}} \} + \left( \eta_{\dot{\epsilon}} - \frac{1}{\theta} \right) \dot{\epsilon} + \text{tr} \{ \eta_{F\dot{F}} \} + \\ + \text{tr} \left\{ \frac{1}{\theta} T F F^{-1} \right\} - \frac{1}{\theta^2} g \cdot g \quad .$$

On looking at (4.8), (3.6)-(3.9), and (2.7) we see that  $\gamma$  depends on only the values of the seven quantities,  $\epsilon, g, F, \dot{\epsilon}, \dot{g}, \dot{F}, \ddot{F}$  at  $X$  and  $t$ . According to the remarks made at the end of Section 3, these seven quantities can be independently and arbitrarily chosen at  $X$  and  $t$ , and there will always exist an admissible thermodynamic process corresponding to the choice. Our postulate (4.4) is equivalent to the assertion that  $\gamma$  be  $\geq 0$  for all such choices.

To find the necessary conditions for the validity of our postulate first observe that (4.8) can be written in the form

$$(4.9) \quad \gamma = \tilde{\eta}_{\dot{g}} (\epsilon, g, F, \dot{F}) \cdot \dot{g} + f(\epsilon, g, F, \dot{\epsilon}, \dot{F}, \ddot{F}) \quad .$$

If we assign  $\epsilon, g, F, \dot{\epsilon}, \dot{F}, \ddot{F}$  any fixed values,  $f(\epsilon, g, F, \dot{\epsilon}, \dot{F}, \ddot{F})$  will be fixed at some finite value, say  $\underline{a}$ , and the postulate will require that

$$(4.10) \quad \tilde{\eta}_{\dot{g}} (\epsilon, g, F, \dot{F}) \cdot \dot{g} + \underline{a} \geq 0$$

for all values of  $\dot{g}$ . But clearly this is possible only if

$$(4.11) \quad \tilde{\eta}_{\underline{g}}(\underline{\mathcal{E}}, \underline{g}, F, \dot{F}) = \underline{0} \quad .$$

Futhermore, this equation must hold for all values of  $\underline{\mathcal{E}}, \underline{g}, F, \dot{F}$  ; i. e.,  $\eta$  in (3.7) cannot depend on  $\underline{g}$  .

It follows from (4.11) that (4.8) can be written in the form

$$(4.12) \quad \gamma = \text{tr} \{ \tilde{\eta}_{\dot{F}}(\underline{\mathcal{E}}, F, \dot{F}) \ddot{F} \} + \ell(\underline{\mathcal{E}}, \underline{g}, F, \dot{\underline{\mathcal{E}}}, \dot{F})$$

Hence for any fixed values of  $\underline{\mathcal{E}}, \underline{g}, \dot{\underline{\mathcal{E}}}, F, \dot{F}$ , the postulate (4.4) requires that

$$(4.13) \quad \text{tr} \{ \tilde{\eta}_{\ddot{F}}(\underline{\mathcal{E}}, F, \dot{F}) \ddot{F} \} + b \geq 0$$

where  $b$  is a finite number. The inequality (4.13) can hold for all choices of  $\ddot{F}$  only if

$$(4.14) \quad \tilde{\eta}_{\ddot{F}}(\underline{\mathcal{E}}, F, \dot{F}) = 0$$

where  $0$  is the zero tensor. Since (4.14) must hold for all values of  $\underline{\mathcal{E}}, F$ , and  $\dot{F}$ , we have proved that our postulate requires that not only  $\underline{g}$ , but also  $\dot{F}$ , must drop out of (3.7), i. e. that  $\eta$  must be given by a function  $\tilde{\eta}$  of  $\underline{\mathcal{E}}$  and  $F$  alone :

$$(4.15) \quad \eta = \tilde{\eta}(\underline{\mathcal{E}}, F) \quad .$$

Of course, the function  $\tilde{\eta}$  depends on the point  $X$  under consideration.

It follows from what we have done so far that