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13. ABSTRACT

The manner in which the thermomechanics of materials with fading memory can be developed from the First and Second Laws of Thermodynamics, without using the Clausius-Duhem inequality, is outlined. It is shown how many of the results which are often claimed to be derivations from Coleman's formulation of the thermomechanics of "simple materials with fading memory" are, in fact, well-known classical results. Some of these results stem from the fact that the materials considered by Coleman possess instantaneous elasticity.

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Comments on Some Recent Researches in Thermomechanics

by

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1. Introduction

I feel that this paper requires an apology since almost the whole of it is, in fact, material which, with virtually no change of essential content, might well form part of an undergraduate course on thermodynamics. My justification for writing it is my concern regarding a phenomenon, which has been developing over the past fifteen years or so and which has, in my opinion, had the effect of confusing many workers. These are rarely, if ever, physicists, or engineers whose main area of specialization is thermodynamics. Many of them are engineers whose specialty lies rather in mechanics; others are workers whose background lies largely in mathematics.

The root of the confusion, it appears to me, lies in the point of view which has been advocated by a number of workers in the field of continuum mechanics, that theories in continuum mechanics and thermodynamics should properly be based on a set of axioms, whose relevance to the behavior of real systems is not a major responsibility of the theorist. In this connection, I may quote Professor Truesdell [1], who is a leading protagonist of this point of view: "As for 'physical meaning', I claim no physical applicability for anything I ever say. That is, the application of the theory is left to the appliers. The theorist attempts to get the theory clear and to prove the theorems. Whether a theory applies to a given piece of material at a given time is something very important, but something the theorist cannot be expected to tell, in thermodynamics or any other theory". To a limited extent, this statement is perhaps valid, in the sense that most theories that relate to the behavior of materials are based on idealizations. In application to particular real materials, deductions from such a theory are significant only to the extent that the idealizations on which the theory is based are valid for the particular material and the particular phenomenon with which the physicist is concerned. If the actual behavior of a physical system does not conform to that predicted, the theorist can always defend himself by maintaining that the axioms of the theory are not satisfied by the physical system considered. This, of course, makes it all the more necessary that it be reasonably evident, in formulating a theory, for what materials and under what conditions the axioms of the theory are likely to be valid. Certainly, if, following Professor Truesdell, one makes no claim that a theory has any physical applicability, and if indeed it has not, it would seem to leave the theory rather barren, unless perhaps it can claim standing as pure mathematics. If the latter is the case, it seems rather misleading to use the terminology of physics in the formulation of the theory and even more misleading, as has been done in certain cases, to claim for it a seminal position in some branch of physics.

In this paper, I shall be mainly concerned with a thermomechanical theory which was advanced by Coleman [2] in 1964. Since its publication, many papers have been written which, either ostensibly or in reality, stem from it. Furthermore, it has given rise to a secondary and even tertiary literature, substantial in volume. Most of this development is presented in an idiom which makes it opaque to the majority of physical scientists and obscures the fact that many of the results of the theory are, in fact, well-known results in thermomechanics, albeit derived from foundations which are less meaningful than those of conventional thermomechanics. In some cases, the apparent originality - and even surprising character - of the results stems from the use of common terms with an unconventional meaning. The fact that these results are usually presented and widely advertised as novel results of great depth serves further to confuse the issue.

The point of view on Coleman's thermomechanics advanced in the present paper has been briefly touched on previously in my review [3] of a book by Truesdell and Noll [4] and in [5]. A more general comment on the axiomatic approach advocated by Truesdell has been given by Woods [6].

2. The First Law of Thermodynamics

The First Law of Thermodynamics states that the rate at which energy enters a body is equal to the rate at which the energy of the body increases. The energy of the body is the sum of its internal energy $\mathcal{U}$ and kinetic energy $\mathcal{T}$. The rate at which energy enters the body is the sum of the power $\mathcal{P}$ of the external forces applied to the body and the rate $\mathcal{Q}$ at which heat enters the body. The First Law can then be expressed as

$$\dot{\mathcal{U}} + \dot{\mathcal{T}} = \mathcal{P} + \mathcal{Q} , \tag{2.1}$$

where the dot denotes differentiation with respect to time t.

We consider that the body undergoes a deformation, in which a particle with vector position $\underset{\sim}{X}$ in some reference configuration has vector position $\underset{\sim}{x}$ at time t. The deformation is then completely described if the dependence

$$\underset{\sim}{x} = \underset{\sim}{x}(\underset{\sim}{X},t) \tag{2.2}$$

is known.

We assume that, at time t, body forces $\underset{\sim}{\phi}$ per unit mass and surface forces $\underset{\sim}{F}$ per unit area, measured in the reference configuration, act on the body. Then, the power of these forces is given by

$$\mathcal{P} = \int_V \rho_0 \underset{\sim}{\phi} \cdot \dot{\underset{\sim}{x}} \, dV + \int_A \underset{\sim}{F} \cdot \dot{\underset{\sim}{x}} \, dA , \tag{2.3}$$

where V is the domain occupied by the body in the reference configuration, A is the boundary of this domain and ρ_0 is the material density in the reference configuration.

We assume also that heat enters the body throughout its volume at a rate R per unit mass and through its surface at a rate Q per unit area, measured in the reference configuration. Then, the rate at which heat enters the body is given by

$$\mathcal{Q} = \int_V \rho_0 R \, dV + \int_A Q \, dA . \tag{2.4}$$

In the present paper, we shall assume that the internal energy of the body is an extensive quantity, so that we may write

$$\mathcal{U} = \int_V \rho_0 U \, dV , \tag{2.5}$$

where U is the specific internal energy. Underlying this mathematical assumption is the physical assumption that the forces exerted on one part of the body by another are short-range forces.

The kinetic energy $\mathcal{T}$ of the body is given by

$$\mathcal{T} = \int_V \tfrac{1}{2}\rho_0 \dot{\underset{\sim}{x}} \cdot \dot{\underset{\sim}{x}} \, dV . \tag{2.6}$$

From (2.1), with (2.3), (2.4), (2.5) and (2.6), we can, by a method given by Green and Rivlin [7], derive the usual Piola-Kirchoff point equations of continuum mechanics.

Denoting the Piola-Kirchoff stress by $\underset{\sim}{\Pi}$ and the flux vector by $\underset{\sim}{Q}$, we obtain the point equation of motion

$$\underset{\sim}{\nabla}\cdot\underset{\sim}{\Pi} + \rho_0\underset{\sim}{\phi} = \rho_0\underset{\sim}{\ddot{x}} , \tag{2.7}$$

the expressions for the surface force $\underset{\sim}{F}$ and heat flux Q, on a surface element with unit area and unit normal $\underset{\sim}{N}$ in the reference state,

$$\underset{\sim}{F} = \underset{\sim}{N}\cdot\underset{\sim}{\Pi} , \quad Q = \underset{\sim}{N}\cdot\underset{\sim}{Q} , \tag{2.8}$$

the symmetry condition

$$\underset{\sim}{G}\cdot\underset{\sim}{\Pi} = (\underset{\sim}{G}\cdot\underset{\sim}{\Pi})^{\dagger} \tag{2.9}$$

and the dissipation equation

$$\rho_0\dot{U} = \mathrm{tr}\ \underset{\sim}{\dot{G}}\cdot\underset{\sim}{\Pi} + \underset{\sim}{\nabla}\cdot\underset{\sim}{Q} + \rho_0 R . \tag{2.10}$$

In these equations, $\underset{\sim}{G}$ denotes the deformation gradient matrix $\underset{\sim}{\nabla}\underset{\sim}{x}$, $\underset{\sim}{\nabla}$ is the operator $\partial/\partial\underset{\sim}{X}$ and the superscript $\dagger$ denotes the transpose.

In a cartesian coordinate system, equations (2.7) - (2.10) take the forms, with obvious notation,

$$\begin{aligned}
&\Pi_{Ai,A} + \rho_0\phi_i = \rho_0\ddot{x}_i , \\
&F_i = \Pi_{Ai}N_A , \qquad Q = Q_A N_A , \\
&x_{i,A}\Pi_{Aj} = x_{j,A}\Pi_{Ai} , \\
&\rho_0\dot{U} = \dot{x}_{i,A}\Pi_{Ai} + Q_{A,A} + \rho_0 R ,
\end{aligned} \tag{2.11}$$

where $_{,A}$ denotes $\partial/\partial X_A$.

Equations (2.7), (2.8) and (2.10), were derived by Green and Rivlin [7] from the First Law by using the consideration that the internal energy, applied forces and rate at which heat enters the body are unaltered if a rigid translational motion with constant velocity is superposed on the assumed deformation (2.2). The derivation of (2.9) requires that U, $\underset{\sim}{\Pi}$, $\underset{\sim}{Q}$ and R be unchanged if a rigid angular velocity is superposed on the assumed deformation (2.2).

The more conventional method for deriving equations (2.7) - (2.10) employs, as its starting point, the laws of balance of linear and angular momentum, as well as the First Law of Thermodynamics, but does not employ any considerations of invariance. Such considerations are, however, necessary in the formulation of constitutive equations. It is therefore strange that the protagonists of the axiomatic approach to continuum mechanics should adopt, in their expository writings, the conventional approach to the derivation of the point equations of thermomechanics, rather than the approach of Green and Rivlin [7], which would involve fewer axioms.

The dissipation equation (2.10) may be written, in terms of increments of the specific internal energy and deformation gradient matrix and the heat entering the body, as

$$\rho_0 dU = \mathrm{tr}\, d\underset{\sim}{G}\cdot\underset{\sim}{\Pi} + \underset{\sim}{\nabla}\cdot d\underset{\sim}{H} + \rho_0 d\chi , \qquad (2.12)$$

where

$$\underset{\sim}{Q} = \frac{d\underset{\sim}{H}}{dt} \quad \text{and} \quad R = \frac{d\chi}{dt} . \qquad (2.13)$$

In this form it may be applied in the idealized limiting cases when the deformation is carried out quasistatically or infinitely rapidly. If the dissipation equation is used in the form (2.12), we require equation $(2.8)_2$ in the correspondingly different form

$$dH = \underset{\sim}{N}\cdot d\underset{\sim}{H} , \qquad (2.14)$$

where

$$Q = \frac{dH}{dt} . \qquad (2.15)$$

The dissipation equation (2.10) and the heat flux equation $(2.8)_2$ may also be applied in these limiting cases, by taking t to be an appropriate time-like parameter, rather than real time, and regarding $\underset{\sim}{Q}$ and R as rates measured with respect to this time-like parameter.

3. Empirical temperature

The concept of empirical temperature is fundamental to the discussion of the Second Law of Thermodynamics. It is usually introduced in the context of systems in thermo-mechanical equilibrium. For an elastic material undergoing a quasistatic process, the state of the material at any point of the process is characterized by values $\underset{\sim}{G}$ and U, at that point, of the deformation gradient matrix and specific internal energy. The empirical temperature θ, at the point of the process considered, is then some function of $\underset{\sim}{G}$ and U, thus

$$\theta = \theta(\underset{\sim}{G},U) , \qquad (3.1)$$

which depends on the particular material considered and on the scale on which the empirical temperature is measured. It has the property that, if two bodies having the same values of θ, on the same scale, are in thermal contact, no heat flows from one to the other. If the values of θ for the two bodies are different, then heat flows from the body for which θ is greater to that for which θ is less.

It is also necessary to broaden the definition of empirical temperature to enable us to use it in discussing systems which undergo non-quasistatic processes.

We consider materials with memory, for which the Piola-Kirchoff stress $\underset{\sim}{\Pi}$ at any instant t depends on the histories $\underset{\sim}{G}(\tau)$ and $U(\tau)$ of the deformation gradient matrix and specific internal energy up to time t^{+}; i.e. $\underset{\sim}{\Pi}$ is a functional of

$\underset{\sim}{G}(\tau)$ and $U(\tau)$ with support $-\infty < \tau \leq t^+$, thus[*]

$$\underset{\sim}{\Pi} = \underset{\sim}{\Pi}[\underset{\sim}{G}(\tau), U(\tau)] \ . \tag{3.2}$$

Let θ be the value at time t of some scalar functional of $\underset{\sim}{G}(\tau)$ and $U(\tau)$ with support $-\infty < \tau \leq t^+$

$$\theta = \theta[\underset{\sim}{G}(\tau), U(\tau)] \ . \tag{3.3}$$

Now suppose two bodies, of which the materials are not necessarily the same[**] and which are undergoing thermomechanical processes which may be different, are in thermal contact. If there is no heat exchange at time t , whenever θ is the same for the two bodies, then θ may be regarded as the empirical temperature of the bodies at time t .

According to this definition, if at the instant t the heat flux vector $\underset{\sim}{Q}$ is zero everywhere in the body, the temperature is constant throughout the body. Now suppose we put this body in contact with another body, in which the temperature is also constant. If one or both of the bodies is not in thermomechanical equilibrium, it may be that the instantaneous

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[*] We take the support to be $-\infty<\tau\leq t^+$, rather than $-\infty<\tau<t$, in order to accommodate materials for which $\underset{\sim}{\Pi}$ may be a function of the instantaneous values at time t of the velocity gradients, acceleration gradients, etc. (see, for example, [8,9]).

[**] The functional dependence of θ on $U(\tau)$ and $\underset{\sim}{G}(\tau)$ expressed by (3.3) may, accordingly be different for the two bodies.

rate of exchange of heat between the bodies at time t is zero when the contact is made over certain parts of the surfaces and non-zero when the contact is made over other parts. If this is the case, the concept of temperature, as a single scalar quantity characterizing the ability of the body to exchange heat with another body in contact with it, breaks down and we cannot assign a single scalar empirical temperature to the body. This is likely to occur when the thermomechanical processes are rapid on a scale measured by the characteristic times associated with molecular motions. Accordingly, the use of the concept of empirical temperature is restricted to situations which are slow on this time scale.

It is implicit in the definition of an ideal, or perfectly, elastic material that the characteristic times associated with molecular motions are zero. Accordingly, for such materials we may employ the same relation (3.1) to define the empirical temperature at points of quasistatic and non-quasistatic processes equally.

Finally, we remark that provided the definition of empirical temperature given in this section is valid for the non-quasistatic processes in materials with memory considered, then instead of describing a process by the functions $\underset{\sim}{G}(\tau)$ and $U(\tau)$ and regarding $\underset{\sim}{\Pi}$ and θ as functionals of these, as we have done in (3.2) and (3.3), we may describe it by $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$. Then $\underset{\sim}{\Pi}$ and U are functionals of $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$, with support $-\infty < \tau \leq t^+$, thus

$$\underset{\sim}{\Pi} = \underset{\sim}{\Pi}[\underset{\sim}{G}(\tau),\ \theta(\tau)] \ ,$$

$$U = U[\underset{\sim}{G}(\tau),\ \theta(\tau)] \ . \qquad (3.4)$$

4. The Second Law of Thermodynamics for quasistatic processes.

For many materials for which constitutive equations of the form (3.4) are valid, the memory implied by the functional dependence is of the fading memory type; i.e. the differences in $\underset{\sim}{\Pi}$ and U, measured at time t, for two deformation-temperature histories which differ only up to time $t - \bar{\tau}$, decreases to zero as $\bar{\tau}$ increases to infinity. This behavior of the material considered can be expressed in mathematical terms in a variety of ways by placing appropriate continuity restrictions on the functionals in (3.4). Whatever the details of the mathematical description of fading memory, it is apparent that materials with fading memory behave as elastic materials with respect to quasistatic processes, so that, for such processes, we may write

$$\underset{\sim}{\Pi} = \underset{\sim}{\Pi}(\underset{\sim}{G},\theta) \ , \quad U = U(\underset{\sim}{G},\theta) \ , \tag{4.1}$$

or, alternatively,

$$\underset{\sim}{\Pi} = \underset{\sim}{\Pi}(\underset{\sim}{G},U) \ , \quad \theta = \theta(\underset{\sim}{G},U) \ . \tag{4.2}$$

The tensor functions in $(4.1)_1$ and $(4.2)_1$ are, of course, not the same.

We consider a mass ρ_0 of the material to be taken from an equilibrium state 1 to an equilibrium state 2 by a quasi-static homothermal* process. Let $\underset{\sim}{G}_1$, θ_1 and $\underset{\sim}{G}_2$, θ_2 be the

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* A homothermal process is a process in which, at each instant of time, the empirical temperature is uniform throughout the material and consequently the heat flux vector $\underset{\sim}{Q}$ is zero.

values of $\underset{\sim}{G}$ and θ in states 1 and 2 respectively. Let $\underset{\sim}{G},\theta$ and $\underset{\sim}{G} + d\underset{\sim}{G},\theta + d\theta$ characterize neighboring equilibrium states on the path followed by the quasistatic process. Let $\rho_0 d\chi$ be the amount of heat introduced into the material in passing from the first of these states to the second. From (2.12), we have

$$\rho_0 d\chi = \rho_0 dU - \mathrm{tr}\, d\underset{\sim}{G}\cdot\underset{\sim}{\Pi} \ . \tag{4.3}$$

The amount of heat which is introduced into the material in taking it from state 1 to state 2 is then given by $\rho_0 \oint d\chi$. This integral is not independent of the quasistatic process (i.e. the path in $\underset{\sim}{G},\theta$ space)by which the material is taken from state 1 to state 2 . However, it follows from the Second Law of Thermodynamics that there exists a monotonic function T of the empirical temperature θ , thus

$$T = T(\theta) \ , \tag{4.4}$$

which is unique apart from an arbitrary multiplying constant, such that $\oint d\chi/T$ is independent of the quasistatic process by which the material is taken from the equilibrium state 1 to the equilibrium state 2 . T is called the <u>absolute</u> <u>temperature</u> of the material. It may, without loss of generality be taken to be positive. Since the integral $\oint d\chi/T$ is independent of the quasistatic process connecting states 1 and 2, it must be expressible in the form

$$\oint \frac{d\chi}{T} = S_2 - S_1 , \tag{4.5}$$

where $S_2 = S(\underset{\sim}{G}_2,\theta_2)$ and $S_1 = S(\underset{\sim}{G}_1,\theta_1)$ are determined apart from equal constants. S_2 is called the <u>specific entropy</u> of the material in state 2 and S_1 is its specific entropy in state 1. We note that we have defined the absolute temperature only when the material is in thermomechanical equilibrium and $\underset{\sim}{Q} = 0$. Accordingly, in (4.5), S_2 can be regarded as a function of $\underset{\sim}{G}_2, T_2$ and S_1 can be regarded as a function of $\underset{\sim}{G}_1, T_1$, where T_1 and T_2 are the absolute temperatures corresponding to empirical temperatures θ_1 and θ_2 .

We now consider a non-quasistatic homothermal process in which the material is taken from equilibrium state 1 to equilibrium state 2. Let $\rho_0 d\bar{\chi}$ be the amount of heat introduced into the material in passing from values $\underset{\sim}{G}$ and θ of the deformation gradient matrix and empirical temperature to values $\underset{\sim}{G} + d\underset{\sim}{G}$ and $\theta + d\theta$, in this non-quasistatic process. Then, it follows from the Second Law of Thermodynamics that

$$S_2 - S_1 > \oint \frac{d\bar{\chi}}{T} , \tag{4.6}$$

where the integration is carried out over the path followed by the non-quasistatic process connecting equilibrium states 1 and 2, T is the same function of θ as obtains when the material is subjected to a quasistatic process and $S_2 - S_1$ is defined by (4.5). The integrals in (4.5) and (4.6) are the <u>Clausius</u> integrals for the quasistatic and non-quasistatic processes respectively. Otherwise expressed, the relation (4.6), with (4.5), tells us that the Clausius integral, for a non-quasistatic homothermal process connecting two quilibrium states is less than that for a quasistatic homothermal process connecting the same two states. Combining the relations (4.6) and (4.5), we have, for any homothermal process connecting the two equilibrium states 1 and 2 ,

$$S_2 - S_1 \geq \oint \frac{d\chi}{T} , \tag{4.7}$$

where the equality sign applies for quasistatic processes, and $\rho_0 d\chi$ denotes the amount of heat introduced into the body in an elementary step of the process. The relation (4.7) is usually called the *Clausius inequality*, or the *Clausius-Planck inequality*.

For an elastic material, the constitutive equations (3.4) take the form (4.1), whether or not the process considered is quasistatic. We consider quasistatic and non-quasistatic homothermal processes, which follow the same path in $\underset{\sim}{G}, \theta$ space and connect points where the deformation gradient matrix and empirical temperature take the values $\underset{\sim}{G}_1, \theta_1$ and $\underset{\sim}{G}_2, \theta_2$ respectively. Then, it follows from (4.2) and (4.3), that the amounts of heat $\rho_0 d\chi$ and $\rho_0 \overline{d\chi}$ fed into the material in these processes, in the step between $\underset{\sim}{G}, \theta$ and $\underset{\sim}{G} + d\underset{\sim}{G}, \theta + d\theta$, are equal. Consequently, for an elastic material, in which $\underset{\sim}{Q} = 0$, the equality sign in (4.7) applies, whether or not the process considered is quasistatic and whether or not the material is in equilibrium at the end-points of the process considered.

5. Instantaneous elasticity

For materials with memory, the basic constitutive assumptions are usually made in the forms (3.4). We now envisage processes for which $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ change relatively slowly, except in a neighborhood $(t-\varepsilon,t]$ of t, where they may change very rapidly. For a material which exhibits instantaneous elasticity, the response to these rapid changes is similar to that for an elastic material. Consequently, provided that the histories $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ remain unchanged for $\tau < t-\varepsilon$, the stress $\underset{\sim}{\Pi}$ and internal energy U at time t are substantially independent of the manner in which the process is continued in the interval $(t-\varepsilon,t]$ and depends only on $\underset{\sim}{G}(t)$ and $\theta(t)$. We idealize this behavior in constitutive assumptions of the form (cf.[10])

$$\begin{aligned} \underset{\sim}{\Pi} &= \underset{\sim}{\Pi}[\underset{\sim}{G}(\tau),\ \theta(\tau)\ ;\ \underset{\sim}{G},\theta]\ , \\ U &= U[\underset{\sim}{G}(\tau),\ \theta(\tau)\ ;\ \underset{\sim}{G},\theta]\ , \end{aligned} \tag{5.1}$$

where $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ are considered to be continuous functions of time τ, with support $-\infty < \tau < t$, and $\underset{\sim}{G}$ and θ are the instantaneous values of the deformation gradient matrix and empirical temperature at time t. $\underset{\sim}{\Pi}$ is a tensor-valued functional of $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ and a tensor-valued function of $\underset{\sim}{G}$ and θ. Analogously, U is a scalar functional of $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ and an ordinary function of $\underset{\sim}{G}$ and θ.

Now, we consider processes for which $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ in (5.1) are specified functions of τ, for $-\infty < \tau < t$ and $\underset{\sim}{G}$ and θ may take any values. The constitutive equations (5.1) are then relations between $\underset{\sim}{\Pi}$, U and $\underset{\sim}{G}$, θ. We now suppose that these constitutive equations describe the behavior of some fictitious material, $\underset{\sim}{G}$ and θ being the values at time t of the deformation gradient matrix and empirical temperature for an arbitrary process, with zero temperature gradient. Such a material would, of course, be an elastic material precisely of the type already discussed at the end of §4. Accordingly, for it we can define the absolute temperature T and specific entropy change dS in an infinitesimal process, whether quasistatic or not, by the formula

$$dS = d\chi/T , \tag{5.2}$$

where $d\chi$ is the amount of heat fed into the material per unit mass in the infinitesimal process. The end-points of the infinitesimal process are characterized by values $\underset{\sim}{G}, \theta$ and $\underset{\sim}{G} + d\underset{\sim}{G}$, $\theta + d\theta$ of the deformation gradient matrix and empirical temperature. Since $d\chi$ and T are independent of the rate at which the process is carried out, the formula (5.2) is applicable to processes carried out instantaneously at time t in a material having instantaneous elasticity, for which the constitutive equations (5.1) are valid and the process prior to time t is fixed. This is the case, notwithstanding the fact that $\underset{\sim}{G}$ and θ cannot be varied quasistatically, while keeping the histories $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ fixed, as they could be in the hypothetical elastic material considered.

In (5.2), S is, of course, a function of the instantaneous values $\underset{\sim}{G}$ and θ (or T) of the deformation gradient matrix and temperature, the actual form of this function depending on the fixed histories $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ (or $T(\tau)$) prior to time t. We may accordingly write S in the form

$$S = S[\underset{\sim}{G}(\tau),\ \theta(\tau)\ ;\ \underset{\sim}{G},\theta]\ , \tag{5.3}$$

or in the form

$$S = S[\underset{\sim}{G}(\tau),\ T(\tau)\ ;\ \underset{\sim}{G},T]\ . \tag{5.4}$$

However, in writing S in these forms, we must bear in mind that they can only be used in the discussion of processes carried out at fixed histories $\underset{\sim}{G}(\tau)$ and $\theta(\tau)$ (equivalently of $T(\tau)$). We note also, that the absolute temperature may be used as an independent variable in the expressions for $\underset{\sim}{\Pi}$ and U, instead of the empirical temperature, thus

$$\underset{\sim}{\Pi} = \underset{\sim}{\Pi}[\underset{\sim}{G}(\tau),\ T(\tau)\ ;\ \underset{\sim}{G},T]\ ,\quad U = U[\underset{\sim}{G}(\tau),\ T(\tau);\ \underset{\sim}{G},T]\ . \tag{5.5}$$

For a process taking place at time t, between points characterized by the values $\underset{\sim}{G}_1$, θ_1 and $\underset{\sim}{G}_2$, θ_2 of $\underset{\sim}{G}$, θ, we see from (5.2) that the change in the specific entropy is given, as it is for an elastic material, or for quasistatic processes in a material with fading memory, by

$$S_2 - S_1 = \oint \frac{d\chi}{T} \qquad (5.6)$$

6. Application of the Clausius inequality to a body

We consider the body described in §2 to undergo a thermomechanical process in which the deformation is described by (2.1) and the absolute temperature T is also a function of position and time, thus:

$$\underset{\sim}{x} = \underset{\sim}{x}(\underset{\sim}{X},t) \quad \text{and} \quad T = T(\underset{\sim}{X},t) \; . \tag{6.1}$$

The body is considered to consist of a material with fading memory for which constitutive equations of the type (3.4) are valid. Using the fact, which follows from the Second Law of Thermodynamics, that entropy is an additive quantity, the Clausius inequality (4.7) can be written for the body as

$$\begin{aligned} S_2 - S_1 &= \int_V \rho_0 (S_2 - S_1) dV \\ &\geq \int_V \oint \frac{\rho_0 d\chi}{T} \, dV + \int_A \oint \frac{dH}{T} \, dA \; . \end{aligned} \tag{6.2}$$

S_2 and S_1 are the entropies of the body in the states 2 and 1. Using (2.14) and the divergence theorem, we can rewrite (6.2) as

$$\int_V \rho_0 (S_2 - S_1) dV \geq \int_V \oint \left[\frac{1}{T} (\rho_0 d\chi + \underset{\sim}{\nabla} \cdot \underset{\sim}{H}) - \frac{1}{T^2} \, d\underset{\sim}{H} \cdot \underset{\sim}{\nabla} T \right] dV \; . \tag{6.3}$$

This result may be applied to any infinitesimal element of the body, since such an element may itself be regarded as a body.

We accordingly obtain

$$\rho_0(S_2-S_1) \geq \oint \left[\frac{1}{T}(\rho_0 dx + \underset{\sim}{\nabla}\cdot d\underset{\sim}{H}) - \frac{1}{T^2}\, d\underset{\sim}{H}\cdot\underset{\sim}{\nabla}T\right] . \qquad (6.4)$$

With (2.12), this relation yields

$$\rho_0(S_2-S_1) \geq \oint \left[\frac{1}{T}(\rho_0 dV - \mathrm{tr}\, d\underset{\sim}{G}\cdot\underset{\sim}{\Pi}) - \frac{1}{T^2}\, d\underset{\sim}{H}\cdot\underset{\sim}{\nabla}T\right] . \qquad (6.5)$$

Parenthetically, we note that if the process considered is isothermal, homothermal and cyclic, so that T is constant throughout the process, $\underset{\sim}{\nabla}T = 0$, and the equilibrium states 1 and 2 are the same, and we assume that the temperature gradient is zero, we obtain from (6.5),

$$\oint \mathrm{tr}\, d\underset{\sim}{G}\cdot\underset{\sim}{\Pi} \geq 0 \quad ; \qquad (6.6)$$

i.e. the stress work round a closed isothermal, homothermal path is non-negative. This well-known classical result appears in the book by Truesdell and Noll [4 §96b] as "Coleman's theorem on isothermal cyclic processes"!

Returning to equation (6.5), we see that, for an <u>infinitesimal</u> process connecting equilibrium states (i.e. for a process connecting equilibrium states for which the state variables are infinitesimally different), we have

$$\rho_0(dU-TdS) \leq \mathrm{tr}\, d\underset{\sim}{G}\cdot\underset{\sim}{\Pi} + \frac{1}{T}\, d\underset{\sim}{H}\cdot\underset{\sim}{\nabla}T . \qquad (6.7)$$

The equality sign will, of course, apply if the process is quasistatic and $\nabla T = 0$ or $d\underset{\sim}{H} = 0$.

We now consider the material of the body to be elastic. We define the specific Helmholtz free energy W by

$$W = U - TS \ . \tag{6.8}$$

Then, (6.7) may be written as

$$\rho_0 (dW + SdT) \leq \mathrm{tr}\, d\underset{\sim}{G} \cdot \underset{\sim}{\Pi} + \frac{1}{T}\, d\underset{\sim}{H} \cdot \underset{\sim}{\nabla} T \ . \tag{6.9}$$

Since U and S are functions of $\underset{\sim}{G}$ and T only, so also is W. Thus*,

$$dW = \mathrm{tr}\,\left\{ d\underset{\sim}{G} \cdot \left(\frac{\partial W}{\partial \underset{\sim}{G}}\right)_T^{\dagger} \right\} + dT \left(\frac{\partial W}{\partial T}\right)_{\underset{\sim}{G}} \ . \tag{6.10}$$

Introducing (6.10) into (6.9), and bearing in mind that the relation obtained is valid for arbitrary values of $d\underset{\sim}{G}$ and dT, we obtain

$$\underset{\sim}{\Pi} = \left(\frac{\partial W}{\partial \underset{\sim}{G}}\right)_T^{\dagger} , \quad S = -\left(\frac{\partial W}{\partial T}\right)_{\underset{\sim}{G}} \quad \text{and} \quad d\underset{\sim}{H} \cdot \underset{\sim}{\nabla} T \geq 0 \ . \tag{6.11}$$

We note, in deriving these results, that $d\underset{\sim}{H}$ may be varied

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* In cartesian notation $\partial W/\partial \underset{\sim}{G}$ may be written as $\partial W/\partial x_{i,A}$. The superscript † denotes the transpose of this quantity.

independently of $d\underset{\sim}{G}$ and dT and that $\underset{\sim}{\Pi}$ and S are independent of these quantities. The relations (6.11) are called the <u>Gibbs relations</u>.

From (6.10) and (6.11), it follows that if $\underset{\sim}{\nabla}T = 0$, i.e. if there is no temperature gradient in the material, the equality sign in (6.9) necessarily applies. Alternatively, if $d\underset{\sim}{H} = 0$ the equality sign in (6.9) applies. This means that the equality sign may apply in a perfect thermal insulator, even if there is a temperature gradient in the material. If $\underset{\sim}{\nabla}T \cdot d\underset{\sim}{H} \neq 0$, then the inequality sign must apply. Physically, this implies that if a temperature gradient exists in a thermally conducting elastic material, the inequality in (6.9) must apply.

For processes carried out instantaneously at time t in a material possessing instantaneous elasticity, $\underset{\sim}{\Pi}$, U and S have the forms (5.4) and (5.5). Accordingly W also has the form

$$W = W[\underset{\sim}{G}(\tau) \; , \; T(\tau) \; ; \; \underset{\sim}{G}, T] \; . \qquad (6.12)$$

By considering arbitrary processes at time t , at fixed histories $\underset{\sim}{G}(\tau)$, $T(\tau)$, it is seen that the Gibbs relations (6.11) are still valid, where the differentiations are carried out at fixed $\underset{\sim}{G}(\tau)$ and $T(\tau)$, as well as at fixed T in the first relation and at fixed $\underset{\sim}{G}$ in the second relation.

For a process carried out in the interval $-\infty < \tau \leq t$, for which there is no discontinuity at time t , we may calculate the values of $\underset{\sim}{\Pi}$ and S at time t from the expression for the specific Helmholtz free energy W by using the Gibbs relations in the manner just described and taking $\underset{\sim}{G} = \underset{\sim}{G}(t)$ and $T = T(t)$ in the expressions obtained.

7. The Clausius-Duhem inequality

We have seen that the specific entropy S of an element of material which has fading memory, in a specified state, is defined by considering a quasistatic homothermal process in which the element is taken to that state from some base state. For an arbitrary process connecting two equilibrium states 1 and 2, the Clausius integral is not greater than the difference in the specific entropies for the two states. Thus, (cf. equation (4.7))

$$S_2 - S_1 \geq \oint \frac{d\chi}{T} , \qquad (7.1)$$

where T is the absolute temperature of the element and it is assumed that no temperature gradient exists in the element. The equality sign applies for a quasistatic process connecting the states. For an elastic material the equality sign applies for all homothermal processes, and whether or not the material is in equilibrium at the end-points of the process. We may call such processes reversible processes. For them, we can differentiate the equation (7.1) with respect to time to obtain the result

$$\dot{S} = \dot{\chi}/T , \qquad (7.2)$$

at each point of the reversible process.

It is tempting to consider the possibility that at each point of an arbitrary process, in an elastic material or in a material with fading memory, the relation

$$\dot{S} \geq \dot{\chi}/T \ , \qquad (7.3)$$

is satisfied. This relation is called the Clausius-Duhem inequality. However, before the relation (7.3) can be given meaning, it is necessary to give a definition of S at an arbitrary point of an irreversible process. Most thermodynamicists do this by means of the so-called local state assumption. If the path in the $\underset{\sim}{G}$, T space, which is followed in the irreversible process, can also be followed by a reversible quasistatic process*, then we can, of course, define the specific entropy S at each point for the latter process. According to the local state assumption this is the meaning to be attached to S in the Clausius-Duhem inequality (7.3).

The essential physical difference between the Clausius-Duhem and Clausius inequalities is particularly evident if we consider a material with fading memory to be taken from an equilibrium state 1 to an equilibrium state 2 by irreversible and quasistatic reversible processes following the same paths in $\underset{\sim}{G},\theta$ (or $\underset{\sim}{G},T$) space. The Clausius inequality states that less heat is fed into the system for the irreversible process than for the quasistatic reversible process. The

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* Such a reversible quasistatic process can certainly take place in a material with fading memory.

Clausius-Duhem inequality, on the other hand, asserts that the amount of heat fed into the system, *in each infinitesimal step* of the irreversible process, is no greater than that for the corresponding step of the quasistatic process.

With the local state interpretation, the Clausius-Duhem inequality cannot be valid for all materials and all processes. This is evidently true for the plastic deformation of a metal, say, for which a corresponding reversible quasistatic process cannot generally be defined. Even where this objection is not valid, it is doubtful that the relation (7.3) is always satisfied. In the opinion of some thermodynamicists, its validity is restricted to irreversible processes for which the departure from reversible conditions is not too great.

Coleman [2] has proposed a different approach to the interpretation of the Clausius-Duhem inequality for materials with fading memory. He calls $\dot{S}$ in (7.3), the rate of change of specific entropy for the *irreversible* process and assumes that it is a functional of the histories $\underset{\sim}{G}(\tau)$ and $T(\tau)$ of the deformation gradient matrix and absolute temperature. No prescription is, however, given for determining the actual form of this functional dependence, either by experiment or by calculation from a physical model. Coleman and his followers prefer to regard it as a primitive quantity. For example, Truesdell [11, p.324) states "What is entropy? Heads have split for a century trying to define entropy in terms of other things. I tell you, entropy, like force, is an undefined onject..." or, again, [1, p.374] "As I have said for many years, disregarding the scoffs of those endowed with physical intuition, temperature and entropy join mass and place and time as primitive, undefined variables, described only by such properties as are laid down for them in mathematical terms".

Now, despite the eloquent confidence of these statements, the point of view adopted by Coleman and his followers, with regard to the definition of entropy at a point of an irreversible process, leaves us in a very different situation from that which obtains in the definition of mass, length and time. This would not, of course, be the case if Professor Truesdell had deposited in Paris, or elsewhere, a standard of entropy and had provided us with a prescription by means of which we could compare with it the entropy of a system undergoing an arbitrary irreversible process.

These comments do not, of course, imply that a relation of the form (7.3) may not, in fact, be valid, with an appropriate definition of the quantity $\dot{S}$, other than that implied by the local state assumption. Only, that in the absence of such a definition, the statement (7.3) is devoid of physical meaning.

We note, however, that by integrating (7.3) along a path connecting the equilibrium states 1 and 2, we can arrive at the Clausius inequality (7.1). It is, therefore, not surprising that meaningful results can be obtained from the

Coleman version version of the Clausius-Duhem inequality. However, these are, in effect, obtained either by way of the Clausius inequality, or they are results for processes for which the material behaves essentially elastically.

8. Coleman's thermodynamics of materials with memory

In 1964, Coleman [2] formulated a thermomechanical theory for materials with fading memory. The class of materials with which he was concerned in this theory were essentially materials for which the constitutive equations of the form (5.5) are valid, with the instantaneous value of the temperature gradient $\underset{\sim}{\nabla} T$ added as an independent variable. Also, the argument function $\underset{\sim}{G}(\tau)$ is replaced by $\underset{\sim}{G}(\tau)\underset{\sim}{G}^{-1}$, i.e. by the deformation gradient matrix at time τ, measured with respect to the configuration at time t as reference configuration*. In addition to constitutive equations for the stress and specific internal energy, Coleman adopts constitutive equations for the specific entropy S and the heat flux vector $\underset{\sim}{Q}$, in which they depend on the same variables. Thus,

$$\begin{aligned}
\underset{\sim}{\Pi} &= \underset{\sim}{\Pi}[\underset{\sim}{G}(\tau)\underset{\sim}{G}^{-1}, T(\tau);\ \ \underset{\sim}{G}, T, \underset{\sim}{\nabla} T] ,\\
U &= U[\underset{\sim}{G}(\tau)\underset{\sim}{G}^{-1}, T(\tau);\ \ \underset{\sim}{G}, T, \underset{\sim}{\nabla} T] ,\\
S &= S[\underset{\sim}{G}(\tau)\underset{\sim}{G}^{-1}, T(\tau);\ \ \underset{\sim}{G}, T, \underset{\sim}{\nabla} T] ,\\
\underset{\sim}{Q} &= \underset{\sim}{Q}[\underset{\sim}{G}(\tau)\underset{\sim}{G}^{-1}, T(\tau);\ \ \underset{\sim}{G}, T, \underset{\sim}{\nabla} T] .
\end{aligned} \tag{8.1}$$

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* In cartesion notation, $[\underset{\sim}{G}(\tau)]_{iA} = G_{iA}(\tau) = \partial x_i(\tau)/\partial X_A$,

$\underset{\sim}{G} = \partial x_i/\partial X_A$ and $(\underset{\sim}{G}^{-1})_{Aj} = \partial X_A/\partial x_j$, so that

$(\underset{\sim}{G}(\tau)\underset{\sim}{G}^{-1})_{ij} = \partial x_i(\tau)/\partial x_j$.

Coleman also makes certain continuity assumptions regarding the manner in which $\underset{\sim}{\Pi}$, U, S and $\underset{\sim}{Q}$ depend on the argument functions $\underset{\sim}{G}(\tau)\underset{\sim}{G}^{-1}$ and $T(\tau)$. These assumptions* imply that the material has fading memory, in the sense described in §4. While the constitutive equations (8.1), together with the continuity assumptions made by Coleman, imply that the material, whose behavior they describe, has fading memory in the usual sense, they also imply that the material possesses instantaneous elasticity**. While this point appears to have been appreciated by Coleman [12] and, in fine print, by Truesdell and Noll [4, §96b], it does not appear to have been appreciated that this invalidates many of the extravagant claims that have been made on helalf of Coleman's theory. For example, Truesdell and Noll state [4, §96b] "While this treatise was in press, Coleman constructed the thermodynamics of irreversible deformation processes at a level of generality of the simple material obeying the principle*** of fading memory". An incautious reader might

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* It may be mentioned that the continuity assumptions made by Coleman are only marginally different from those made earlier by Green and Rivlin [10] in a purely mechanical theory for materials which possess instantaneous elasticity. The continuity assumptions of Green and Rivlin [10] also imply that the material considered has fading memory [9], as do most of the possible continuity assumptions which readily come to mind. The continuity assumptions of Coleman, in fact, restrict the applicability of his constitutive equations to a narrower class of materials than do those of Green and Rivlin.

** This was pointed out in the review by Rivlin [3] of the book by Truesdell and Noll [4] and in [5].

*** Here we note the device often employed by Truesdell and certain of his protegés of lending dignity to assumptions by calling them principles.

be led to believe that the theory applies to such materials as Newtonian fluids or Kelvin solids, which would normally be considered to be pre-eminent.examples of materials with fading memory. Again, in [4, §96b] we read, after a presentation of the Gibbs relations (6.11) as a deduction from Coleman's theory, "This capital (<u>sic</u>.) result generalizes the classical stress relation and temperature relation of thermo-elasticity to simple materials with memory". Of course, it does nothing of the kind. It is merely the well-known result that the Gibbs relations are valid for an elastic material, whether or not it is in mechanical equilibrium.

In developing the implications of the constitutive assumptions (8.1), Coleman omits the dependence of $\underset{\sim}{\Pi}$, U and S on $\underset{\sim}{\nabla} T$. His original inclusion of $\underset{\sim}{\nabla} T$ as an argument in the constitutive equations for $\underset{\sim}{\Pi}$, U and S was motivated by an appeal to the Principle of Equipresence, which was advanced by Truesdell and Toupin [12] and has been criticized by Rivlin [5,14]. A justification for the omission was given by Coleman [2]. We shall not here discuss the validity of Coleman's argument, beyond noting that it is based on the Clausius-Duhem inequality, as interpreted by Coleman. We note, however, that the omission of $\underset{\sim}{\nabla} T$ as an argument in the first three equations (8.1) brings Coleman's expressions for $\underset{\sim}{\Pi}$ and U into line with those given in (5.5) for a material with memory possessing instantaneous elasticity. Although it formally brings Coleman's expression for the specific entropy into line with that given by (5.4), the interpretation of the expressions is quite different. While equation (5.4) is interpreted as being valid only for fixed histories and arbitrary instantaneous changes, at time t, of the deformation gradient matrix and absolute temperature, Coleman's expression $(8.1)_3$, with $\underset{\sim}{\nabla} T = 0$, is allegedly valid for arbitrary histories and arbitrary instantaneous changes, at time t, of these.

9. Waves in materials possessing instantaneous elasticity

In §8 attention has been drawn to the confusion that has arisen from the presentation of well-known results in thermodynamics as highly significant new results obtained from the Clausius-Duhem inequality, unconventionally and inexplicitly interpreted, and from the largely irrelevant assumption of fading memory. Further evidence of this confusion is provided by claims which have been made with respect to a considerable body of work on the propagation of surfaces of discontinuity, which - at any rate formally - stems from it.

In 1965, Coleman, Gurtin and Herrera [15] showed that surfaces of second-order discontinuity can propagate in materials governed by constitutive equations of the type considered by Coleman. They further showed that such discontinuities can develop into shock waves, which can then propagate in the material.

Similar conclusions to those of Coleman, Gurtin and Herrera were reached independently by Varley [16]* . In many respects the paper by Varley, while far simpler than that of Coleman, Gurtin and Herrera, goes far beyond it. While the paper of Coleman,

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* Both the papers of Coleman, Gurtin and Herrera and of Varley were published in the Archive for Rational Mechanics and Analysis, the published dates of submission being October 22, 1964, and January 28, 1965 respectively. From the standpoint of essential content, both papers were anticipated by Whitham [17], who, in a magnetohydrodynamic context, discussed the propagation of surfaces of discontinuity in a system in which instantaneous elastic response is followed by dissipative after-effects.

Gurtin and Herrera considers only the propagation of plane singular surfaces, that of Varley considers singular surfaces of arbitrary shape.

In both of the papers, the materials considered are materials with fading memory, in the sense of Coleman, i.e., in the usual terminology, they possess instantaneous elasticity. In this respect, the propaganda by Truesdell on behalf of the paper by Coleman, Gurtin and Herrera has been highly misleading. In [4, §96t] Truesdell remarks "In 1901 the kinds of singular surfaces that may exist and propagate in a linearly viscous fluid were proved by Duhem to be extremely limited. Acceleration waves are altogether impossible and shock waves can occur only in pecular combinations of circumstances connected with the presence or absence of heat conduction of suitable kind and amount". In the next paragraph, Truesdell states "In a monumental study now going to press, Coleman and Gurtin, partly in collaboration with Herrera, have constructed a <u>general theory of wave propagation in materials with memory</u>. Not only mechanical but also thermal effects are included, in the full generality of Coleman's thermodynamics of simple materials". An incautious reader might be led to conclude that, contrary to current opinion, singular surfaces can be propagated in viscous materials. This is, of course, not the case. The confusion disappears when we realize that the simple materials considered in Coleman's thermodynamics possess instantaneous elasticity. Plainly, in such materials, singular surfaces, both of first and second order, may propagate. The dissipative character of the material tends to weaken the singularity, while the non-linearity of the instantaneous elastic response tends to reinforce it. Notwithstanding that the possibility of propagating surfaces of discontinuity in materials of the type considered is in no way surprising, the actual working out of the conditions under which they propagate, under which second-order discontinuities can develop into shocks, and so on, represents an interesting advance. This advance, however, has extremely little thermodynamic content and what little it has, is, as far as I can tell, based in conventional thermodynamics. Rather, the theory of the propagation of singular surfaces in materials possessing instantaneous elasticity forms an integral part of an extensive development on non-linear wave propagation, which has taken place in the last several years. In this development, Gurtin and his collaborators and Varley and his collaborators have played significant roles* . It seems to me that relative to the Varley contribution, that of Gurtin suffers substantially from his adoption of the so-called axiomatic style which surrounds relatively simple matters in the idiom of modern pure mathematics and obscures their physical content. The work of Varley, on the other hand, is in a much more traditional vein and is much closer to physics.

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* I may remark that the early work of Gurtin in this area, as well as that of his students, was supported by an Office of Naval Research contract on which I was Senior Investigator. Likewise, much of the more recent work of Varley and his students and collaborators has been supported by government contracts and grants on which I was Senior Investigator.

He is, therefore, able to handle problems of much greater complexity which bear much more directly on physical phenomena.

10. Coda

In this paper, I have pointed out that the thermomechanical theory advanced by Coleman in 1964 is, in the main, devoid of physical meaning. I have further pointed out that certain of the results, which have been widely propagandized as being triumphs of the theory, are, in fact, well-known results in classical thermodynamics. Similar comments could be made about many other results which have allegedly been derived by Coleman and his followers from the theory, but it would be tedious to do so.

Despite the extensive propaganda, it appears that there is some doubt in the minds of even the most dedicated protagonists of the Coleman point of view, as to the validity of his theory. For example, Truesdell [18, p. 58], while berating those who do not join in his adulation of Coleman's theory, and while attributing to them unworthy motives, remarks "Obviously, a mathematical thermodynamics of irreversible processes is possible. We have only to find it, and already we are far along the road to it. Equally obviously, the Clausius-Duhem inequality may not be the final basis, and those who are capable of using it may be capable also of modifying it or replacing it". Now, it may, in fact, be that a theory relating to strongly irreversible processes, which may reasonably be called thermodynamics, is possible, but I fail to see why this is so obvious. It may be that a satisfactory theory of strongly irreversible processes can only be constructed in terms of kinetic theory, or in terms of statistical mechanics, or indeed in a form not so far envisaged. Or, again, it may, if and when it arrives, involve a combination of these characteristics as well as those of a continuum thermodynamics. As we have seen, in my present remarks, and indeed in the quotation from Truesdell as well, the Clausius-Duhem inequality, which is a central feature of Coleman's formulation of thermodynamics, is open to serious question, with respect to its interpretation, its validity, and the significance of the results derived from it. With regard to the last statement in my quotation from Truesdell, I feel that it is rash to predict who - if anyone - will formulate a satisfactory and fruitful theory of the thermodynamics of strongly irreversible processes and when - if ever - this will be done.

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