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Thermodynamics with Internal
State Variables

by

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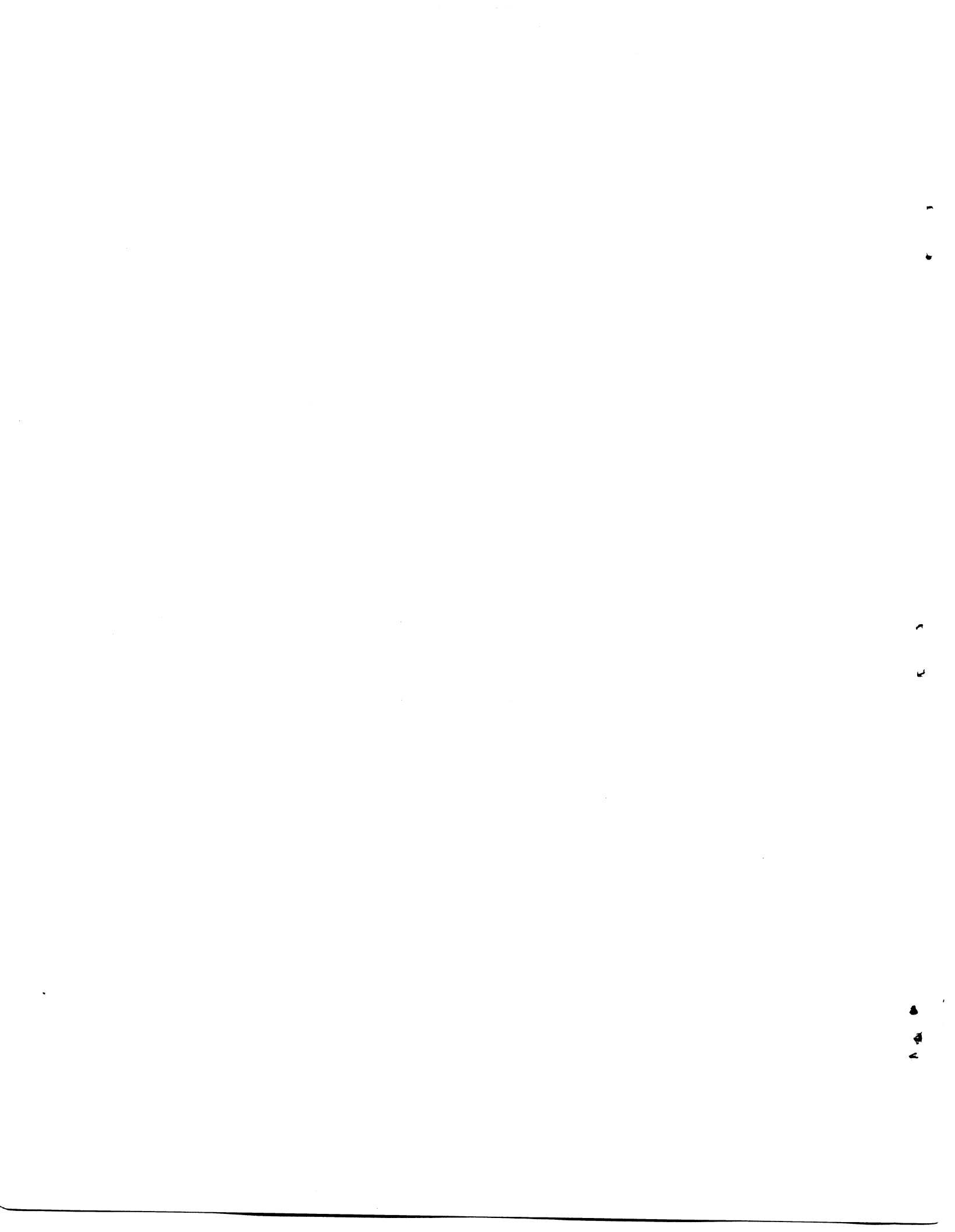
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Thermodynamics with Internal State Variables

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Abstract

This is a study of the thermodynamics of nonlinear materials with internal state variables whose temporal evolution is governed by ordinary differential equations. After employing a method developed by Coleman and Noll to find the general restrictions which the Clausius-Duhem inequality places on response functions, we analyze various types of dynamical stability that can be exhibited by solutions of the internal evolution equations. We also discuss integral dissipation inequalities, conditions under which temperatures can be associated with internal states, and the forms taken by response functions when the material is a fluid.

1. INTRODUCTION

In phenomenological theories of the dynamical behavior of continua there are several ways of accounting for the dissipative effects which, in addition to heat conduction, accompany deformation. The oldest and simplest way is to introduce a viscous stress which depends on the rate of strain, as is done in the Navier-Stokes theory of linearly viscous fluids. Another description of dissipation assumes that the entire past history of the strain influences the stress in a manner compatible with a principle of fading memory.¹ A third approach is to postulate the

¹We here have in mind the fading memory postulate introduced by Coleman and Noll^{2,3} and recently developed from a set of elementary axioms by Coleman and Mizel⁴.

²B. D. Coleman and W. Noll, Arch. Rational Mech. Anal. 6, 355 (1960).

³B. D. Coleman and W. Noll, Reviews Mod. Phys. 33, 239 (1961); Erratum, *ibid.* 36, 1103 (1964).

⁴B. D. Coleman and V. J. Mizel, Arch. Rational Mech. Anal. 23, 87 (1966).

existence of internal state variables which influence the free energy and whose rate of change is governed by differential equations in which the strain appears.

No one approach to dissipation is so general as to completely include all the others, and each of the three classes of theories has

its domain of usefulness. It has, for example, long appeared that the Navier-Stokes equations can successfully describe the mechanical behavior of water under ordinary conditions. On the other hand, when certain polyatomic gases such as carbon dioxide are studied in shock tubes^{5,6,7,8}

⁵H. A. Bethe and E. Teller, Aberdeen Proving Ground Rep. No. X-117 (1941).

⁶E. F. Greene, G. R. Cowan, and D. F. Hornig, J. Chem. Phys. 19, 427 (1951);
ibid. 21, 617 (1953).

⁷F. J. Smiley, E. H. Winkler, and T. K. Slawsky, J. Chem. Phys. 20, 923 (1952).

⁸W. Griffith, D. Brickl and V. Blackman, Phys. Rev. 102, 1209 (1956).

and in sonic absorption experiments,^{9,10,11} it is found that, in an

⁹G. W. Pierce, Proc. Acad. Sci. Amst. 60, 271 (1925).

¹⁰K. F. Herzfeld and F. O. Rice, Phys. Rev. 31, 691 (1928).

¹¹A survey is given by K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic Press, New York, 1959).

appropriate range of density and temperature, attenuation effects occur which can be well described, not by the introduction of a single and constant bulk viscosity, but rather by assuming that the ideal gas law $pV = R\theta$ holds, with θ the translational (or "active-mode") temperature, while accounting, in the constitutive equations governing the heat capacity, for the time required for the transfer of molecular motion from the translational mode to one, two, or several internal modes. This is a

classical example of a theory of dissipation involving a finite number of internal state variables; the internal variables being the amounts of energy associated with the various modes of molecular motion. At elevated temperatures the ideal gas law may fail due to chemical dissociation or ionization; the finite rates of the reactions of decomposition and reassociation can then also give rise to pressure-volume relaxation phenomena.¹²

¹²See, for example, the discussion of M. J. Lighthill, *J. Fluid Mech.* 2, 1 (1957).

Recent experience in high-polymer physics shows that the mechanical behavior of many materials, including polymer melts and solutions, is more easily described within the general theory of materials with fading memory than by theories of the viscous-stress type, which do not account at all for gradual stress relaxation, or by theories which rest on a finite number of internal state variables and which, therefore, give rise to discrete relaxation spectra when linearized.

Using an approach to the thermodynamics of continua proposed by Coleman and Noll¹³, Coleman and Mizel¹⁴ have found the restrictions the

¹³B. D. Coleman and W. Noll, *Arch. Rational Mech. Anal.* 13, 167 (1963).

¹⁴B. D. Coleman and V. J. Mizel, *J. Chem. Phys.* 40, 1116 (1964).

second law places on a class of theories of the viscous-stress type. Later, Coleman¹⁵ developed a general theory of the thermodynamics of

¹⁵B. D. Coleman, *Arch. Rational Mech. Anal.* 17, 1 (1964); *ibid.* 17, 230 (1964).

materials with fading memory. Here we discuss phenomenological theories of dissipation which rest upon evolution equations for internal state variables; we attempt to unify such theories by using the methods developed in references 13 and 14 together with techniques from the stability theory of nonlinear differential equations. We consider materials for which the basic local mechanical and thermal variables, such as the stress tensor \underline{T} , the heat flux vector \underline{q} , the specific Helmholtz free energy ψ , and the specific entropy η , are determined through constitutive equations when the following "state variables" are known: the temperature θ , the deformation gradient \underline{F} (or the "strain"), the temperature gradient $\text{grad } \theta$, and a set of N internal or "hidden" state variables $(\alpha_1, \dots, \alpha_N)$. We allow the rate of change of each of the α_i to be governed by a (generally nonlinear) function f_i of θ , \underline{F} , $\text{grad } \theta$, and the complete internal state $(\alpha_1, \dots, \alpha_N)$:

$$\dot{\alpha}_i = f_i(\theta, \underline{F}, \text{grad } \theta, \alpha_1, \dots, \alpha_N), \quad i = 1, \dots, N. \quad (1.1)$$

We first seek the general restrictions placed on theories of this type by the second law, in the form of the Clausius-Duhem inequality. We then give conditions, in terms of the thermodynamical functions, for dynamical stability of equilibrium solutions of the evolution equations (1.1). After finding logical relations between the various types of stability which can occur, we discuss special aspects of the theory, such as integral dissipation inequalities, the assignment of temperatures to internal states, and the requirements of invariance. We conclude our study by illustrating the general theory with its simplest nontrivial special case: ideal gases with a single internal mode of molecular motion.

2. THERMODYNAMIC PROCESSES

We consider a body \mathcal{B} with material points X and assume that the mechanical forces acting on \mathcal{B} can always be resolved into a body force field and a symmetric stress field. In particular, body couples, couple stresses, and multipolar interactions of higher order are assumed absent. We also assume there is no diffusion of mass in \mathcal{B} , but \mathcal{B} may deform and conduct heat. Thus, a thermodynamic process for \mathcal{B} is described by nine functions, of X and the time t , whose values have the following physical interpretations:

- (1) The spatial position $\underline{x} = \underline{\chi}(X, t)$ in the motion $\underline{\chi}$.
- (2) The symmetric Cauchy stress tensor $\underline{T} = \underline{T}(X, t)$.
- (3) The specific body force $\underline{b} = \underline{b}(X, t)$ per unit mass (exerted on \mathcal{B} at X by the external world, i.e. by other bodies which do not intersect \mathcal{B}).
- (4) The specific internal energy $\epsilon = \epsilon(X, t)$ per unit mass.
- (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 \mathcal{B} at X and furnished by radiation from the external world).
- (7) The specific entropy $\eta = \eta(X, t)$ per unit mass.

(8) The absolute temperature $\theta = \theta(X, t) > 0$.

(9) The internal state vector $\underline{\alpha} = \underline{\alpha}(X, t) = (\alpha_1, \alpha_2, \dots, \alpha_N)$;

the numbers $\alpha_i = \alpha_i(X, t)$ are the internal state variables.¹⁶

¹⁶Our present pair $(\underline{F}, \underline{\alpha})$ forms a vector which Truesdell and Toupin¹⁷, pp. 615-647, call the thermodynamic substate.

¹⁷C. Truesdell and R. A. Toupin, "The Classical Field Theories", in Encyclopedia of Physics, edited by S. Flügge (Springer-Verlag, Berlin & Heidelberg, 1960). Vol. III/1.

Such a set of nine functions, defined for all X in \mathcal{B} and all t , will here be called a thermodynamic process in \mathcal{B} if and only if it is compatible with the law of balance of linear momentum and the law of balance of energy. Under sufficient smoothness assumptions, the familiar integral forms of these laws are equivalent to the field equations,

$$\rho \dot{\underline{x}} - \text{div } \underline{T} = \rho \underline{b} \quad (2.1)$$

and

$$\rho \dot{\epsilon} - \underline{T} \cdot \underline{L} + \text{div } \underline{q} = \rho r. \quad (2.2)$$

Here ρ is the mass density, $\underline{L} = \text{grad } \dot{\underline{x}}$ is the velocity gradient, and $\underline{T} \cdot \underline{L}$ is the inner product of \underline{T} and \underline{L} ; i.e. $\underline{T} \cdot \underline{L} = \text{trace } \underline{T} \underline{L}^T$ with \underline{L}^T the transpose of \underline{L} . Since grad and div are the gradient and divergence with respect to \underline{x} keeping t fixed, these operators refer to spatial derivatives. A superposed dot denotes the material time derivative, i.e. the derivative with respect to t computed keeping X fixed.

To specify a thermodynamic process it suffices to prescribe the seven functions \underline{x} , \underline{T} , ϵ , \underline{q} , η , θ , and $\underline{\alpha}$. The remaining functions \underline{b} and r are then determined by (2.1) and (2.2).

In continuum physics one usually identifies each material point X with its position \underline{X} in a fixed reference configuration \mathcal{R} and writes $\underline{x} = \chi(\underline{X}, t)$. The gradient \underline{F} of $\chi(\underline{X}, t)$ with respect to \underline{X} ,

$$\underline{F} = \underline{F}(\underline{X}, t) = \text{GRAD } \chi(\underline{X}, t), \quad (2.3)$$

is called the deformation gradient at \underline{X} (or at X) relative to the configuration \mathcal{R} . We consistently use the notation GRAD for the gradient in \mathcal{R} , i.e. the gradient with respect to \underline{X} . For a scalar field over \mathcal{B} , such as θ , an elementary chain rule yields

$$\text{GRAD } \theta = \underline{F}^T \text{grad } \theta. \quad (2.4)$$

Since $\text{grad } \theta$ occurs frequently in thermodynamics it is convenient to have a single symbol for this vector. We use the abbreviation

$$\underline{g} = \text{grad } \theta. \quad (2.5)$$

Because we assume that $\chi(\underline{X}, t)$ is smoothly invertible in its first variable, the inverse \underline{F}^{-1} of \underline{F} exists, and the velocity gradient $\underline{L} = \text{grad } \dot{\underline{x}}$ is given by

$$\underline{L} = \dot{\underline{F}} \underline{F}^{-1}. \quad (2.6)$$

Let us call the tensor \underline{S} , defined by

$$\underline{S} = \frac{1}{\rho} \underline{T}(\underline{F}^T)^{-1}, \quad (2.7)$$

the Piola-Kirchoff stress tensor. Using this tensor we can write (2.2) in the form

$$\rho \dot{\epsilon} - \rho \underline{S} \cdot \underline{F} + \text{div } \underline{q} = \rho r. \quad (2.8)$$

3. THE CLAUSIUS-DUHEM INEQUALITY

When \underline{q}/θ is regarded to be a flux of entropy due to heat flow and \underline{r}/θ a supply of entropy from radiation, the specific rate γ of production of entropy is given by

$$\rho\gamma = \rho\dot{\eta} - \left(\frac{\rho\underline{r}}{\theta} - \text{div} \frac{\underline{q}}{\theta} \right). \quad (3.1)$$

The Clausius-Duhem inequality asserts that the rate of production of entropy is not negative:

$$\gamma \geq 0. \quad (3.2)$$

For each thermodynamic process the energy balance equation (2.8) permits us to write (3.1) in the form

$$\gamma = \dot{\eta} - \frac{\dot{\epsilon}}{\theta} + \frac{1}{\theta} \underline{s} \cdot \underline{\dot{F}} - \frac{1}{\rho\theta^2} \underline{q} \cdot \underline{g}. \quad (3.3)$$

From this equation and the inequality (3.2) we read off the following implications of the Clausius-Duhem inequality:

$$\dot{\eta} \geq 0 \quad \text{whenever} \quad \underline{\dot{F}} = \underline{0}, \quad \dot{\epsilon} = 0, \quad \text{and} \quad \underline{g} = \underline{0}; \quad (3.4)$$

$$\dot{\epsilon} \leq 0 \quad \text{whenever} \quad \underline{\dot{F}} = \underline{0}, \quad \dot{\eta} = 0, \quad \text{and} \quad \underline{g} = \underline{0}. \quad (3.5)$$

The specific free energy ψ (also called the "Helmholtz free energy per unit mass") is defined by

$$\psi = \epsilon - \theta\eta. \quad (3.6)$$

Since

$$\dot{\psi} = \dot{\epsilon} - \dot{\theta}\eta - \theta\dot{\eta}, \quad (3.7)$$

(3.3) can be written

$$\theta\gamma = -\dot{\psi} - \eta\dot{\theta} + \underline{s} \cdot \dot{\underline{F}} - \frac{1}{\rho\theta} \underline{q} \cdot \underline{g}, \quad (3.8)$$

and hence (3.2) yields also

$$\dot{\psi} \leq 0 \quad \text{whenever} \quad \dot{\underline{F}} = \underline{0}, \quad \dot{\theta} = 0, \quad \text{and} \quad \underline{g} = \underline{0}. \quad (3.9)$$

4. CONSTITUTIVE ASSUMPTIONS

In the present theory the material at the point X is characterized by five response functions, $\hat{\psi}$, $\hat{\eta}$, $\hat{\underline{S}}$, $\hat{\underline{q}}$, and \underline{f} , which give ψ , η , \underline{S} , \underline{q} , and $\dot{\underline{\alpha}}$ at X when \underline{F} , θ , \underline{g} , and $\underline{\alpha}$ are known at X:

$$\psi = \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), \quad (4.1)$$

$$\eta = \hat{\eta}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), \quad (4.2)$$

$$\underline{S} = \hat{\underline{S}}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), \quad (4.3)$$

$$\underline{q} = \hat{\underline{q}}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), \quad (4.4)$$

$$\dot{\underline{\alpha}} = \underline{f}(\underline{F}, \theta, \underline{g}, \underline{\alpha}). \quad (4.5)$$

The superposed $\hat{}$ in $\hat{\psi}$, $\hat{\eta}$, $\hat{\underline{S}}$, and $\hat{\underline{q}}$ serves to distinguish these functions for a given process from their values. Since the value of \underline{F} depends on not only X and t, but also on the choice of the reference configuration \mathcal{R} , the form of each of the response functions depends on \mathcal{R} . In a materially inhomogeneous body the functions $\hat{\psi}$, $\hat{\eta}$, $\hat{\underline{S}}$, $\hat{\underline{q}}$, and \underline{f} will also vary with the material point X; although we do not render explicit this possible dependence of response functions on X, all the arguments we give here are valid equally for materially homogeneous and materially inhomogeneous bodies.

We say that a thermodynamic process is admissible if it is compatible with the constitutive equations (4.1)-(4.5).

Of course, in assuming (4.1)-(4.5) we are using Truesdell's principle of equipresence which asserts that a quantity present as an independent variable in one constitutive equation of a material should be so present in all, unless its presence contradicts some general law of physics or the assumed symmetry of the material.^{18,19} In the following

¹⁸C. Truesdell, U. S. Naval Res. Lab. Rep. No. P-3553 (1947) = J. Math. Pures Appl. 30, 111 (1951).

¹⁹C. Truesdell, Appl. Mech. Rev. 12, 75 (1959), reprinted with additions in Applied Mechanics Surveys (Spartan, Washington, 1966), pp. 225-236; see also C. Truesdell and R. A. Toupin¹⁷, pp. 703-704.

section we shall follow the approach of Coleman and Mizel^{14,20} who

²⁰B. D. Coleman and V. J. Mizel, Arch. Rational Mech. Anal. 13, 245 (1963).

regarded the Clausius-Duhem inequality as included among the laws of physics which can cause a separation of effects, i.e. which can be used to show that certain response functions must be independent of certain variables. In fact, we shall show that the derivatives of $\hat{\psi}$, $\hat{\eta}$, and $\hat{\zeta}$ with respect to \underline{g} must be zero.²¹

²¹A similar result holds in the general theory of materials with fading memory; cf. Coleman¹⁵, Theorem 1, p. 19.

5. CONSEQUENCES OF THE SECOND LAW

Within our present framework the second law of thermodynamics is given a precise mathematical meaning by the following postulate of positive production of entropy:²²

²²Cf. Coleman and Noll².

Every admissible thermodynamic process in \mathcal{B} must obey the inequality (3.2) at each time t and for all material points X in \mathcal{B} .

We now seek the restrictions this postulate places on the response functions in our basic constitutive equations (4.1)-(4.5).

It follows from (4.1) that in each admissible process

$$\dot{\psi} = (\partial_{\underline{F}} \hat{\psi}) \cdot \dot{\underline{F}} + (\partial_{\theta} \hat{\psi}) \dot{\theta} + (\partial_{\underline{g}} \hat{\psi}) \cdot \dot{\underline{g}} + (\partial_{\underline{\alpha}} \hat{\psi}) \cdot \dot{\underline{\alpha}}, \quad (5.1)$$

where

$$\partial_{\theta} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) = \frac{\partial}{\partial \theta} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}); \quad (5.2)$$

the components of $\partial_{\underline{g}} \hat{\psi}$ and $\partial_{\underline{F}} \hat{\psi}$, relative to an orthonormal basis $\underline{e}_1, \underline{e}_2, \underline{e}_3$, are given by

$$\left. \begin{aligned} \left[\partial_{\underline{g}} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) \right]_i &= \frac{\partial}{\partial g_i} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), & i = 1, 2, 3 \\ \left[\partial_{\underline{F}} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) \right]_{ij} &= \frac{\partial}{\partial F_{ij}} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), & i, j = 1, 2, 3, \end{aligned} \right\} \quad (5.3)$$

with g_i and F_{ij} the components of \underline{g} and \underline{F} ; $\partial_{\underline{\alpha}} \hat{\psi}$ is the N-vector,

$$\partial_{\underline{\alpha}} \hat{\psi} = [\partial_{\alpha_1} \hat{\psi}, \partial_{\alpha_2} \hat{\psi}, \dots, \partial_{\alpha_N} \hat{\psi}], \quad (5.4)$$

and, of course,

$$\partial_{\underline{\alpha}} \hat{\psi} \cdot \dot{\underline{\alpha}} = \partial_{\alpha_1} \hat{\psi} \dot{\alpha}_1 + \partial_{\alpha_2} \hat{\psi} \dot{\alpha}_2 + \dots + \partial_{\alpha_N} \hat{\psi} \dot{\alpha}_N. \quad (5.5)$$

Substituting (5.1) into (3.8) we obtain the following expression for the specific rate of production of entropy in an admissible process:

$$\theta \gamma = (\underline{s} - \partial_{\underline{F}} \hat{\psi}) \cdot \dot{\underline{F}} - (\partial_{\theta} \hat{\psi} + \eta) \dot{\theta} - \partial_{\underline{g}} \hat{\psi} \cdot \dot{\underline{g}} - \partial_{\underline{\alpha}} \hat{\psi} \cdot \dot{\underline{\alpha}} - \frac{1}{\rho \theta} \underline{q} \cdot \underline{g}. \quad (5.6)$$

Suppose that we are given an initial time t_0 , an initial internal state vector $\underline{\alpha}_0(\underline{x})$ for each \underline{x} in \mathcal{R} , a motion $\underline{\chi}$ of \mathcal{B} , and a time-dependent temperature distribution θ over \mathcal{B} . Suppose further that $\underline{\alpha}_0$, $\underline{F} = \text{GRAD } \underline{\chi}$, θ , and $\underline{g} = \text{grad } \theta$, as functions of \underline{x} and t , are smooth enough to insure the existence of a unique solution $\underline{\alpha} = \underline{\alpha}(\underline{x}, t)$ of (4.5) for all t in some interval $[t_0, t_0 + \tau]$ with $\underline{\alpha}(\underline{x}, t_0) = \underline{\alpha}_0(\underline{x})$. Then, with the constitutive equations (4.1)-(4.4) we can compute ψ , η , $\epsilon = \psi + \theta \eta$, \underline{s} , and \underline{q} at each \underline{x} for all t in $[t_0, t_0 + \tau]$. Thus to each sufficiently smooth choice of $\underline{\alpha}_0$, $\underline{\chi}$, and θ there corresponds a unique admissible thermodynamic process in \mathcal{B} for some small time interval $[t_0, t_0 + \tau]$.

Now, let $(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0)$ be an arbitrary point in the domain of the response functions $\hat{\psi}$, $\hat{\eta}$, $\hat{\underline{s}}$, $\hat{\underline{q}}$, and $\hat{\underline{f}}$ for that material point X' of \mathcal{B}

which occupies the place \underline{x}' in \mathcal{R} . Choosing arbitrarily a time t_0 , a tensor \underline{A} , a vector \underline{a} , and a scalar \underline{a} , we consider the motion $\underline{\chi}$, and the time-dependent temperature distribution θ defined by

$$\underline{\chi}(\underline{x}, t) = \underline{x}' + [\underline{F}_0 + (t-t_0)\underline{A}][\underline{x}-\underline{x}'], \quad (5.7)$$

$$\theta(\underline{x}, t) = \theta_0 + (t-t_0)\underline{a} + [\underline{g}_0 + (t-t_0)\underline{a}] \cdot \underline{F}_0 [\underline{x}-\underline{x}']$$

for all \underline{x} in \mathcal{R} and all $t \geq t_0$ sufficiently close to t_0 . It follows from the observation made in the previous paragraph that the fields shown in (5.7) and the initial condition $\underline{\alpha}(\underline{x}, t_0) = \underline{\alpha}_0$ determine an admissible thermodynamic process in \mathcal{B} for t in some time interval $[t_0, t_0 + \tau]$.

Furthermore, this process has the following properties:

$$\underline{F}(\underline{x}', t_0) = \underline{F}_0, \quad \theta(\underline{x}', t_0) = \theta_0, \quad \underline{g}(\underline{x}', t_0) = \underline{g}_0, \quad \underline{\alpha}(\underline{x}', t_0) = \underline{\alpha}_0, \quad (5.8)$$

and

$$\dot{\underline{F}}(\underline{x}', t_0) = \underline{A}, \quad \dot{\theta}(\underline{x}', t_0) = \underline{a}, \quad \dot{\underline{g}}(\underline{x}', t_0) = \underline{a}. \quad (5.9)$$

Hence, by (4.1)-(4.5), for this process at the point \underline{x}' and the time t_0 the equation (5.6) becomes

$$\begin{aligned} \theta_0 \gamma = & \left[\hat{\underline{S}}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) - \partial_{\underline{F}} \hat{\underline{\psi}}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) \right] \cdot \underline{A} - \left[\partial_{\theta} \hat{\underline{\psi}}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) + \hat{\eta}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) \right] \underline{a} \\ & + \partial_{\underline{g}} \hat{\underline{\psi}}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) \cdot \underline{a} - \partial_{\underline{\alpha}} \hat{\underline{\psi}}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) \cdot \underline{f}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) - \frac{1}{\rho_0 \theta_0} \hat{\underline{q}}(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0) \cdot \underline{g}_0, \quad (5.10) \end{aligned}$$

where ρ_0 is the mass density at X' corresponding to the deformation gradient \underline{F}_0 . It clearly follows from (5.10) that in order to have $\gamma \geq 0$ at X' and t_0 for every choice of \underline{A} , \underline{a} , and \underline{a} , we must have

$$\hat{\underline{S}}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) = \partial_{\underline{F}} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), \quad (5.11)$$

$$\hat{\eta}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) = -\partial_{\theta} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), \quad (5.12)$$

$$\partial_{\underline{g}} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) = 0, \quad (5.13)$$

$$\partial_{\underline{\alpha}} \hat{\psi}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) \cdot \underline{f}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) + \frac{1}{\rho\theta} \hat{q}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) \cdot \underline{g} \leq 0, \quad (5.14)$$

where, for convenience, we have dropped the subscript 0 in $(\underline{F}_0, \theta_0, \underline{g}_0, \underline{\alpha}_0)$. Since this point was arbitrarily chosen in the domain of our response functions, we have the following four consequences of our postulate of positive entropy production:

(I) The response functions $\hat{\psi}$, $\hat{\eta}$, and $\hat{\underline{S}}$ are independent of \underline{g} ; i.e. ψ , η , and \underline{S} are given by functions of \underline{F} , θ , and $\underline{\alpha}$ alone,

$$\psi = \hat{\psi}(\underline{F}, \theta, \underline{\alpha}), \quad \eta = \hat{\eta}(\underline{F}, \theta, \underline{\alpha}), \quad \underline{S} = \hat{\underline{S}}(\underline{F}, \theta, \underline{\alpha}). \quad (5.15)$$

(II) $\hat{\psi}$ determines $\hat{\eta}$ through the entropy relation (5.12); i.e.

$$\eta = -\partial_{\theta} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}). \quad (5.16)$$

(III) $\hat{\psi}$ determines \hat{S} through the stress relation (5.13); i.e.

$$\hat{S} = \partial_{\underline{F}} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}). \quad (5.17)$$

(IV) $\hat{\psi}$, \hat{f} , and \hat{q} obey the general dissipation inequality (5.14).

Conversely, using (5.6) it is easily verified that when the conditions (I)-(IV) hold every admissible process in \mathcal{B} obeys (3.2).

It follows from (2.7) and (5.17) that the symmetric Cauchy stress tensor \underline{T} is given by the equation

$$\underline{T} = \rho \partial_{\underline{F}} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}) \underline{F}^T \quad (5.18)$$

and hence is a function of \underline{F} , θ , and $\underline{\alpha}$.

The general dissipation inequality (5.14) implies that when $\underline{g} = \underline{0}$ the internal dissipation inequality,

$$\partial_{\underline{\alpha}} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}) \cdot \hat{f}(\underline{F}, \theta, \underline{0}, \underline{\alpha}) \leq 0, \quad (5.19)$$

holds, and when $\partial_{\underline{\alpha}} \hat{\psi} \cdot \hat{f} = \underline{0}$ the heat-conduction inequality,

$$\hat{q}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) \cdot \underline{g} \leq 0, \quad (5.20)$$

holds.

If we define the internal dissipation σ by

$$\sigma = \hat{\sigma}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) = -\frac{1}{\theta} \partial_{\underline{\alpha}} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}) \cdot \hat{f}(\underline{F}, \theta, \underline{g}, \underline{\alpha}), \quad (5.21)$$

we can write the internal dissipation inequality (5.19) in the form

$$\hat{\sigma}(\underline{F}, \theta, \underline{Q}, \underline{\alpha}) \geq 0. \quad (5.22)$$

Further, we may conclude from (4.5), (5.1), and (5.13) that

$$\sigma = -\frac{1}{\theta} \dot{\psi} \quad \text{whenever} \quad \dot{\underline{F}} = \underline{0} \quad \text{and} \quad \dot{\theta} = 0, \quad (5.23)$$

and this result when combined with (3.8) yields

$$\sigma = \gamma \quad \text{whenever} \quad \dot{\underline{F}} = \underline{0}, \quad \dot{\theta} = 0, \quad \text{and} \quad \underline{g} = \underline{0}. \quad (5.24)$$

One cannot generally resolve the inequality $\gamma \geq 0$ into an internal dissipation inequality $\partial_{\underline{\alpha}} \hat{\psi} \cdot \dot{\underline{\alpha}} \leq 0$ holding for nonzero \underline{g} and a heat conduction inequality $\underline{q} \cdot \underline{g} \leq 0$ holding for nonzero $\dot{\underline{\alpha}}$. Such a resolution is valid, however, when the following conditions are met: that $\underline{f}(\underline{F}, \theta, \underline{g}, \underline{\alpha})$ be independent of \underline{g} and $\hat{q}(\underline{F}, \theta, \underline{g}, \underline{\alpha})$ be independent of $\underline{\alpha}$. These conditions do not follow from our general assumptions. Yet, the first condition does often follow from special assumptions of linearity and material symmetry; therefore, it is worth noting that

$$\partial_{\underline{g}} \underline{f}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) \equiv 0 \implies \hat{\sigma}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) \geq 0 \quad \text{for all } \underline{F}, \theta, \underline{g}, \text{ and } \underline{\alpha}. \quad (5.25)$$

It will be observed that the role played by σ in our present theory is nearly identical to that played by the quantity which Coleman in his articles on materials with fading memory¹⁵ also denotes by σ and calls the internal dissipation. For example, our equations (5.21) and

(5.15)-(5.17) here yield the equation

$$\dot{\psi} = \underline{\underline{g}} \cdot \underline{\underline{\dot{F}}} - \eta \dot{\theta} - \theta \sigma, \quad (5.26)$$

which has the same form as Eq. (8.1) on page 22 of reference 15. However, in our present theory, if $\frac{\partial}{\partial \underline{\underline{g}}} \underline{\underline{f}}$ is not identically zero, σ may be negative for certain values of $\underline{\underline{g}}$, albeit (5.22) tells us that $\sigma \geq 0$ whenever $\underline{\underline{g}} = 0$.

Using (3.6) we can write (5.26) in the form

$$\dot{\epsilon} = \underline{\underline{g}} \cdot \underline{\underline{\dot{F}}} + \theta \dot{\eta} - \theta \sigma; \quad (5.27)$$

therefore,

$$\sigma = -\frac{\dot{\epsilon}}{\theta} \quad \text{whenever} \quad \underline{\underline{\dot{F}}} = \underline{\underline{0}} \quad \text{and} \quad \dot{\eta} = 0, \quad (5.28)$$

and

$$\sigma = \dot{\eta} \quad \text{whenever} \quad \underline{\underline{\dot{F}}} = \underline{\underline{0}} \quad \text{and} \quad \dot{\epsilon} = 0. \quad (5.29)$$

Since (2.8) and (5.27) imply

$$\sigma = \dot{\eta} - \frac{1}{\theta} \left[r - \frac{1}{\rho} \text{div } \underline{\underline{q}} \right], \quad (5.30)$$

we also have

$$\sigma = \dot{\eta} \quad \text{whenever} \quad \rho r - \text{div } \underline{\underline{q}} = 0. \quad (5.31)$$

Thus, we can assert that in general σ measures the rate $\dot{\eta}$ at which the entropy of a material point would change if the total rate $\rho r - \text{div } \underline{\underline{q}}$ of addition of heat were set equal to zero. In particular, $\sigma = \dot{\eta}$ whenever the strain and energy are held constant momentarily.

6. STABILITY OF EQUILIBRIUM STATES

Throughout this section we focus our attention on one arbitrary material point X in \mathcal{B} . A triplet $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ with

$$\underline{f}(\underline{F}^*, \theta^*, \underline{0}, \underline{\alpha}^*) = \underline{0} \quad (6.1)$$

is called

an equilibrium state for the material at X . The domain of attraction at constant strain and temperature of an equilibrium state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is the set $\mathcal{D}(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ of all $\underline{\alpha}_0$ such that the solution $\underline{\alpha} = \underline{\alpha}(t)$ of the initial value problem,

$$\dot{\underline{\alpha}} = \underline{f}(\underline{F}^*, \theta^*, \underline{0}, \underline{\alpha}) \quad (6.2)$$

with

$$\underline{\alpha}(0) = \underline{\alpha}_0, \quad (6.3)$$

exists for all $t \geq 0$ and tends to $\underline{\alpha}^*$:

$$\underline{\alpha}(t) \rightarrow \underline{\alpha}^* \quad \text{as } t \rightarrow \infty. \quad (6.4)$$

An equilibrium state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is said to be (locally) asymptotically stable at constant strain and temperature if $\mathcal{D}(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ contains a neighborhood of $\underline{\alpha}^*$, i.e. if there exists a $\zeta > 0$ such that every internal state vector $\underline{\alpha}_0$ with $|\underline{\alpha}_0 - \underline{\alpha}^*| < \zeta$ is in $\mathcal{D}(\underline{F}^*, \theta^*, \underline{\alpha}^*)$.

Let $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ be an equilibrium state for the material at X, and let $\underline{\alpha}_0$ be in $\mathcal{D}(\underline{F}^*, \theta^*, \underline{\alpha}^*)$. It follows from the argument containing Eqs. (5.7) that there exists at least one admissible thermodynamic process with the property that at X

$$\underline{\alpha}(0) = \underline{\alpha}_0, \quad \text{while for all } t \geq 0, \quad \underline{F}(t) = \underline{F}^*, \quad \theta(t) = \theta^*, \quad \text{and} \quad \underline{g}(t) = \underline{0}. \quad (6.5)$$

It follows from (3.9) that for this process $\psi(t) \leq \psi(0)$, or by (5.15)₁,

$$\hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}(t)) \leq \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}_0). \quad (6.6)$$

But, since $\underline{\alpha}_0$ is assumed to be in $\mathcal{D}(\underline{F}^*, \theta^*, \underline{\alpha}^*)$, it follows from (6.4) and the continuity of $\hat{\psi}$ that

$$\lim_{t \rightarrow \infty} \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}(t)) = \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}^*). \quad (6.7)$$

Combining (6.6) and (6.7) we obtain

$$\hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}^*) \leq \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}_0). \quad (6.8)$$

In words: If the internal state vector $\underline{\alpha}$ is in the domain of attraction of the equilibrium state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ at constant strain and temperature, then the free energy corresponding to $(\underline{F}^*, \theta^*, \underline{\alpha})$ cannot be less than that corresponding to $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$.

The following theorem follows at once from (6.8) and the definition of asymptotic stability: If $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is an equilibrium state that is asymptotically stable at constant strain and temperature, then

$$\hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}) \geq \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}^*) \quad (6.9)$$

for all internal state vectors $\underline{\alpha}$ in some neighborhood of $\underline{\alpha}^*$, and, consequently,

$$\left. \frac{\partial \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha})}{\partial \underline{\alpha}} \right|_{\underline{\alpha}=\underline{\alpha}^*} = \underline{0}. \quad (6.10)$$

The equation (6.10) may be called the equation of internal equilibrium. In deriving this equation we have, of course, assumed that the variables $\alpha_1, \dots, \alpha_N$ have been chosen so as to be free from constraints of the type $h(\underline{\alpha}) = 0$. Thus, when changes in the internal state are due to chemical reactions, α_i is not a concentration but rather the degree of advancement of the i'th reaction, in the sense in which the term is used by De Donder²³. In this case $-\partial_{\alpha_i} \psi$ is the affinity of the i'th reaction,

²³Th. De Donder, Leçons de Thermodynamique et de Chimie Physique (Edited by F. H. van den Dungen and G. van Lerberghe, Paris, 1920) p. 117.

and the relation $\partial_{\alpha_i} \psi = 0$, is just De Donder's form of the equation of

chemical equilibrium for that reaction.^{24,25}

²⁴Th. De Donder, Bull. Ac. Roy. Belg. (Cl. Sc.) (5) 7, 197, 205 (1922).

²⁵See, for example, I. Prigogine and R. Defay, Chemical Thermodynamics (Translated by D. H. Everett; Longmans, London, 1954) Chapters I-IV, particularly Eq. (3.29) on p. 40 and Eq. (4.29) on p. 52.

We say that an equilibrium state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is Lyapunov stable at constant strain and temperature if for each arbitrary $\epsilon > 0$ there exists a $\delta_\epsilon > 0$ such that every solution $\underline{\alpha}(t)$ of the differential equation (6.2) with

$$|\underline{\alpha}(0) - \underline{\alpha}^*| < \delta_\epsilon \quad (6.11)$$

has the property that

$$|\underline{\alpha}(t) - \underline{\alpha}^*| < \epsilon \quad (6.12)$$

for all $t \geq 0$.

Roughly speaking, $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is Lyapunov stable at constant strain and temperature if holding \underline{F} and θ fixed for all t and initially setting the internal state vector $\underline{\alpha}$ sufficiently near to $\underline{\alpha}^*$ guarantees that $\underline{\alpha}$ will remain near to $\underline{\alpha}^*$ for all t .

Since it follows from (5.19) that for all $\underline{\alpha}$

$$\partial_{\underline{\alpha}} \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}) \cdot \underline{f}(\underline{F}^*, \theta^*, \underline{\alpha}) \leq 0, \quad (6.13)$$

$\hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha})$, as a function of $\underline{\alpha}$, can serve as a Lyapunov function²⁶ for the

²⁶J. Wei, J. Chem. Phys. 36, 1578 (1962), has pointed out that thermodynamic quantities, such as the free-energy, can yield Lyapunov functions for investigation of stability properties of chemical reactions.

equation (6.2), and familiar results in the theory of ordinary differential equations²⁷ yield the following theorem: Let $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ be an equilibrium

²⁷See, for example, P. Hartman, Ordinary Differential Equations (John Wiley, New York, 1964), pp. 37-40. Particularly Theorem 8.1.

state and suppose that, in some neighborhood of $\underline{\alpha}^*$, the following strengthened form of (6.9) holds:

$$\hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}) > \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}^*) \quad \text{if } \underline{\alpha} \neq \underline{\alpha}^*. \quad (6.14)$$

Then $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is Lyapunov stable at constant strain and temperature.

If

$$\gamma > 0 \quad \text{whenever } \dot{\underline{F}} = \underline{0}, \quad \dot{\theta} = 0, \quad \dot{\underline{g}} = \underline{0}, \quad \text{but } \dot{\underline{\alpha}} \neq \underline{0}, \quad (6.15)$$

then we say that the material under consideration is strictly dissipative.

It is not difficult to show that (4.5), (5.21), and (5.24) imply the following proposition: A material is strictly dissipative if and only if the internal dissipation inequality (5.19) is strict in the sense that

$$\partial_{\underline{\alpha}} \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}) \cdot \underline{\xi}(\underline{F}^*, \theta^*, \underline{0}, \underline{\alpha}) < 0 \quad (6.16)$$

for every triplet $(\underline{F}^*, \theta^*, \underline{\alpha})$ that is not an equilibrium state.

Suppose that $(\underline{F}^*, \theta^*, \underline{Q}^*)$ is an equilibrium state and that (6.16) holds for all $\underline{Q} \neq \underline{Q}^*$ in some neighborhood $\mathcal{N}(\underline{Q}^*)$ of \underline{Q}^* ; if $(\underline{F}^*, \theta^*, \underline{Q}^*)$ is asymptotically stable at constant strain and temperature then the argument which gave us (6.8) also gives us the stronger result (6.14) for all \underline{Q} in $\mathcal{N}(\underline{Q}^*)$. On the other hand, it follows from Lyapunov's theorem on asymptotic stability²⁸ that if (6.14) and (6.16) hold for all $\underline{Q} \neq \underline{Q}^*$ in a neighborhood

²⁸See ref. 27, Theorem 8.2.

of \underline{Q}^* , then $(\underline{F}^*, \theta^*, \underline{Q}^*)$ is asymptotically stable. Combining these observations with the remark containing (6.14), we obtain the following theorem: Let $(\underline{F}^*, \theta^*, \underline{Q}^*)$ be an equilibrium state with the property that (6.16) holds for all $\underline{Q} \neq \underline{Q}^*$ in some neighborhood of \underline{Q}^* . Then:

(i) $(\underline{F}^*, \theta^*, \underline{Q}^*)$ is asymptotically stable at constant strain and temperature if and only if (6.14) holds in some neighborhood of \underline{Q}^* .

(ii) If $(\underline{F}^*, \theta^*, \underline{Q}^*)$ is asymptotically stable at constant strain and temperature then $(\underline{F}^*, \theta^*, \underline{Q}^*)$ is also Lyapunov stable under the same conditions.²⁹

²⁹Usually when one defines asymptotic stability one presupposes that the singular point under consideration is Lyapunov stable. Here, however, we have been considering a concept of asymptotic stability that is separate from Lyapunov stability. Thus it is worthwhile for us to observe that Lyapunov stability is actually implied by our weak concept of asymptotic stability when (6.16) holds.

If $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is asymptotically stable, then, throughout some neighborhood of $\underline{\alpha}^*$, the only triplet of the type $(\underline{F}^*, \theta^*, \underline{\alpha})$ that is an state is the one for which $\underline{\alpha} = \underline{\alpha}^*$. [If this were not the case, then in each neighborhood of $\underline{\alpha}^*$ we could find an $\underline{\alpha}_0$ such that $\underline{\alpha}(t) \equiv \underline{\alpha}_0$ satisfies (6.2) and (6.3) but not (6.4).] Thus we have the following corollary of the preceding theorem: Suppose that the material under consideration is strictly dissipative and let $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ be an equilibrium state that is asymptotically stable at constant strain and temperature. Then:

- (i) The inequality (6.14) holds in a neighborhood of $\underline{\alpha}^*$.
- (ii) $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is Lyapunov stable at constant strain and temperature.

For the remainder of this section we assume that corresponding to each strain-temperature pair $(\underline{F}^*, \theta^*)$ there is exactly one internal state vector $\underline{\alpha}^*$ such that (6.1) holds, i.e. such that the triplet $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ forms an equilibrium state for the material at X. The function

$$\underline{\alpha}^* = \hat{\underline{\alpha}}^*(\underline{F}^*, \theta^*) \quad (6.17)$$

determined by this correspondence may be called the equilibrium response function for $\underline{\alpha}$. Using (5.15) and (4.4) we may construct equilibrium response functions $\hat{\psi}^*$, $\hat{\eta}^*$, $\hat{\underline{S}}^*$, and $\hat{\underline{q}}^*$. These functions give the equilibrium free energy ψ^* , entropy η^* , stress \underline{S}^* , and heat flux \underline{q}^* as functions of

only \underline{F}^* and θ^* :

$$\begin{aligned}
 \psi^* &= \hat{\psi}^*(\underline{F}^*, \theta^*) \stackrel{\text{def}}{=} \hat{\psi}(\underline{F}^*, \theta^*, \hat{\alpha}^*(\underline{F}^*, \theta^*)), \\
 \eta^* &= \hat{\eta}^*(\underline{F}^*, \theta^*) \stackrel{\text{def}}{=} \hat{\eta}(\underline{F}^*, \theta^*, \hat{\alpha}^*(\underline{F}^*, \theta^*)), \\
 \underline{s}^* &= \hat{\underline{s}}^*(\underline{F}^*, \theta^*) \stackrel{\text{def}}{=} \hat{\underline{s}}(\underline{F}^*, \theta^*, \hat{\alpha}^*(\underline{F}^*, \theta^*)), \\
 \underline{q}_0 &= \hat{\underline{q}}^*(\underline{F}^*, \theta^*) \stackrel{\text{def}}{=} \hat{\underline{q}}(\underline{F}^*, \theta^*, 0, \hat{\alpha}^*(\underline{F}^*, \theta^*)).
 \end{aligned} \tag{6.18}$$

Now,

$$\partial_{\theta} \hat{\psi}^*(\underline{F}, \theta) = \partial_{\theta} \hat{\psi}(\underline{F}, \theta, \alpha) + \partial_{\alpha} \hat{\psi}(\underline{F}, \theta, \alpha) \cdot \partial_{\theta} \hat{\alpha}(\underline{F}, \theta), \tag{6.19}$$

and a similar formula holds for $\partial_{\underline{F}} \hat{\psi}$. Therefore, the general entropy relation (5.16) and stress relation (5.17), when combined with the equation of internal equilibrium (6.10), yield the equations,

$$\eta^* = -\partial_{\theta^*} \hat{\psi}^*(\underline{F}^*, \theta^*), \tag{6.20}$$

$$\underline{s}^* = \partial_{\underline{F}^*} \hat{\psi}^*(\underline{F}^*, \theta^*), \tag{6.21}$$

and since (6.10) holds at every asymptotically stable equilibrium state we can assert the following proposition: If the equilibrium state corresponding to $(\underline{F}^*, \theta^*)$ is asymptotically stable, then $\hat{\eta}^*(\underline{F}^*, \theta^*)$ is given by the equilibrium entropy relation (6.20) and $\hat{\underline{s}}^*(\underline{F}^*, \theta^*)$ is given by the equilibrium stress relation (6.21).

It follows from the sentence containing (5.20) that whenever (6.10) holds we have, for all \underline{g} ,

$$\hat{\underline{q}}(\underline{F}^*, \theta^*, \underline{g}, \underline{\alpha}^*) \cdot \underline{g} \leq 0. \quad (6.22)$$

Hence this inequality holds for all \underline{g} whenever $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is asymptotically stable. The tensor

$$\underline{\underline{K}}(\underline{F}^*, \theta^*) = -\partial_{\underline{g}} \hat{\underline{q}}(\underline{F}^*, \theta^*, \underline{g}, \underline{\alpha}^*) \Big|_{\underline{g}=\underline{0}} \quad (6.23)$$

may be called the equilibrium thermal conductivity tensor corresponding $(\underline{F}^*, \theta^*)$. Since (6.18)₄ and (6.23) yield

$$\underline{g} \cdot \hat{\underline{q}}(\underline{F}^*, \theta^*, \underline{g}, \underline{\alpha}^*) = \underline{g} \cdot \hat{\underline{q}}^*(\underline{F}^*, \theta^*) - \underline{g} \cdot \underline{\underline{K}}(\underline{F}^*, \theta^*) \underline{g} + o(|\underline{g}|^2), \quad (6.24)$$

(6.22) holds for all \underline{g} only if

$$\hat{\underline{q}}^*(\underline{F}^*, \theta^*) = \underline{0} \quad (6.25)^{30}$$

³⁰This equation can also be obtained using either an argument given by Pipkin and Rivlin³¹ or one given by Coleman and Noll¹³ (pp. 175 and 176).

³¹A. C. Pipkin and R. S. Rivlin, Tech. Rep. No. DA 4531/4, from Brown University to the U. S. Army Ordnance Corps (1958).

and

$$\underline{g} \cdot \underline{\underline{K}}(\underline{F}^*, \theta^*) \underline{g} \geq 0 \quad (6.26)$$

for all \underline{g} . This proves the following theorem: At an asymptotically stable equilibrium state the equilibrium heat flux vanishes and the thermal conductivity tensor is positive-semi-definite.

It is a corollary to this theorem that

$$\underline{q} = \hat{\underline{q}}(\underline{F}^*, \theta^*, \underline{g}, \underline{\alpha}^*) = \underline{K}(\underline{F}^*, \theta^*) \underline{g} + o(|\underline{g}|). \quad (6.27)$$

Thus, at an asymptotically stable equilibrium state Fourier's Law holds to within an error $o(|\underline{g}|)$.

7. ENTROPY AS AN INDEPENDENT VARIABLE

The heat capacity c is defined by³²

³²Since both \underline{F} and $\underline{\alpha}$ are held fixed in computing the derivative in (7.1), the number c may also be called the instantaneous specific heat at constant strain (and per unit mass).

$$c = \partial_{\theta} \hat{\epsilon}(\underline{F}, \theta, \underline{\alpha}), \quad (7.1)$$

where $\hat{\epsilon}$ is a response function giving internal energy:

$$\hat{\epsilon}(\underline{F}, \theta, \underline{\alpha}) = \hat{\psi}(\underline{F}, \theta, \underline{\alpha}) + \theta \hat{\eta}(\underline{F}, \theta, \underline{\alpha}). \quad (7.2)$$

It follows from the entropy relation (5.16) that

$$c = \theta \partial_{\theta} \hat{\eta}(\underline{F}, \theta, \underline{\alpha}). \quad (7.3)$$

Henceforth we shall assume that c is > 0 for all $(\underline{F}, \theta, \underline{\alpha})$. Since θ is > 0 , this implies that $\hat{\eta}(\underline{F}, \theta, \underline{\alpha})$ is smoothly invertible in θ for each choice of \underline{F} and $\underline{\alpha}$, and we may rewrite our basic constitutive equations (4.1)-(4.5) in the forms,

$$\epsilon = \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}), \quad (7.4)$$

$$\theta = \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}), \quad (7.5)$$

$$\underline{s} = \tilde{\underline{s}}(\underline{F}, \eta, \underline{\alpha}), \quad (7.6)$$

$$\underline{g} = \tilde{\underline{g}}(\underline{F}, \eta, \underline{g}, \underline{\alpha}), \quad (7.7)$$

$$\dot{\underline{\alpha}} = \tilde{\underline{f}}(\underline{F}, \eta, \underline{g}, \underline{\alpha}). \quad (7.8)$$

The function $\tilde{\theta}(\underline{F}, \cdot, \underline{\alpha})$ in (7.3) is just the inverse of the function $\hat{\eta}(\underline{F}, \cdot, \underline{\alpha})$ in (5.15)₂; the functions $\tilde{\epsilon}$, $\tilde{\xi}$, \tilde{q} , and \tilde{f} are given by

$$\left. \begin{aligned} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) &= \hat{\epsilon}(\underline{F}, \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}), \underline{\alpha}) = \hat{\psi}(\underline{F}, \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}), \underline{\alpha}) + \eta \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}) \\ \tilde{\xi}(\underline{F}, \eta, \underline{\alpha}) &= \hat{\xi}(\underline{F}, \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}), \underline{\alpha}), \\ \tilde{q}(\underline{F}, \eta, \underline{\alpha}) &= \hat{q}(\underline{F}, \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}), \underline{\alpha}), \\ \tilde{f}(\underline{F}, \eta, \underline{g}, \underline{\alpha}) &= \hat{f}(\underline{F}, \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}), \underline{g}, \underline{\alpha}). \end{aligned} \right\} \quad (7.9)$$

It follows from (7.9)₁ and familiar chain rules that

$$\left. \begin{aligned} \partial_{\eta} \tilde{\epsilon} &= (\partial_{\theta} \hat{\psi})(\partial_{\eta} \tilde{\theta}) + \tilde{\theta} + \eta \partial_{\eta} \tilde{\theta}, \\ \partial_{\underline{F}} \tilde{\epsilon} &= \partial_{\underline{F}} \hat{\psi} + (\partial_{\theta} \hat{\psi})(\partial_{\underline{F}} \tilde{\theta}) + \eta \partial_{\underline{F}} \tilde{\theta}, \\ \partial_{\underline{\alpha}} \tilde{\epsilon} &= (\partial_{\theta} \hat{\psi})(\partial_{\underline{\alpha}} \tilde{\theta}) + \partial_{\underline{\alpha}} \psi + \eta \partial_{\underline{\alpha}} \tilde{\theta}. \end{aligned} \right\} \quad (7.10)$$

Hence, the entropy relation (5.16) implies that

$$\left. \begin{aligned} \partial_{\eta} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) &= \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}), \\ \partial_{\underline{F}} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) &= \partial_{\underline{F}} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}), \\ \partial_{\underline{\alpha}} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) &= \partial_{\underline{\alpha}} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}). \end{aligned} \right\} \quad (7.11)$$

Of course, the number θ in (7.11)_{2&3} is just the temperature $\tilde{\theta}(\underline{F}, \eta, \underline{\alpha})$ corresponding to \underline{F} , η , and $\underline{\alpha}$.

Equation (7.11)₁ is the expected temperature relation,

$$\theta = \partial_{\eta} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}), \quad (7.12)$$

while (7.11)₂ may be combined with (5.17) to obtain the following form of the stress relation,

$$\underline{s} = \partial_{\underline{F}} \hat{\epsilon}(\underline{F}, \theta, \underline{\alpha}). \quad (7.13)$$

It follows from (7.11)₃ and (7.9)_{3&4} that the general dissipation inequality (5.14) may be written in the form

$$\rho \tilde{\theta}(\underline{F}, \eta, \underline{\alpha}) \partial_{\underline{\alpha}} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) \cdot \tilde{f}(\underline{F}, \eta, \underline{g}, \underline{\alpha}) + \tilde{q}(\underline{F}, \eta, \underline{g}, \underline{\alpha}) \cdot \underline{g} \leq 0, \quad (7.14)$$

and, in particular, we have the implication

$$\tilde{q} = 0 \implies \partial_{\underline{\alpha}} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) \cdot \tilde{f}(\underline{F}, \eta, \underline{g}, \underline{\alpha}) \leq 0 \quad (7.15)$$

which is useful for materials which do not conduct heat. Of course we also have the following counterpart of (5.19):

$$\partial_{\underline{\alpha}} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) \cdot \tilde{f}(\underline{F}, \eta, \underline{0}, \underline{\alpha}) \leq 0. \quad (7.16)$$

According to the definition laid down in Section 6, a triplet $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ is called an equilibrium state of the material at X if and only if it obeys (6.1) at X. It follows, however, from (7.9)₄ that this definition is equivalent to asserting that the triplet $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ with

$$\eta^* = \hat{\eta}(\underline{F}^*, \theta^*, \underline{\alpha}^*), \quad \theta^* = \tilde{\theta}(\underline{F}^*, \eta^*, \underline{\alpha}^*), \quad (7.17)$$

characterizes an equilibrium state if and only if

$$\tilde{f}(\underline{F}^*, \eta^*, \underline{0}, \underline{\alpha}^*) = \underline{0}. \quad (7.18)$$

When (7.18) holds we define the domain of attraction of $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ at constant strain and entropy to be the set $\tilde{D}(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ of internal state vectors $\underline{\alpha}_0$ such that the solution $\underline{\alpha} = \underline{\alpha}(t)$ of the initial value problem

$$\underline{\alpha} = \tilde{f}(\underline{F}^*, \eta^*, \underline{0}, \underline{\alpha}), \quad \underline{\alpha}(0) = \underline{\alpha}_0 \quad (7.19)$$

exists for all $t \geq 0$ and approaches $\underline{\alpha}^*$ as $t \rightarrow \infty$. We say that $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ is asymptotically stable at constant strain and entropy if $\tilde{D}(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ contains a neighborhood of $\underline{\alpha}^*$.

Since it follows from (7.16) that $\tilde{e}(\underline{F}^*, \eta^*, \underline{\alpha}(t))$ is a decreasing function of t along all solutions of (7.19), the argument which gave us (6.8) here tells us that for each $\underline{\alpha}$ in $\tilde{D}(\underline{F}^*, \eta^*, \underline{\alpha}^*)$

$$\tilde{e}(\underline{F}^*, \eta^*, \underline{\alpha}) \geq \tilde{e}(\underline{F}^*, \eta^*, \underline{\alpha}^*). \quad (7.20)$$

In particular, if $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ characterizes an equilibrium state that is asymptotically at constant strain and entropy, then (7.20) holds for all $\underline{\alpha}$ in some neighborhood of $\underline{\alpha}^*$, and

$$\left. \frac{\partial}{\partial \underline{\alpha}} \tilde{e}(\underline{F}^*, \eta^*, \underline{\alpha}^*) \right|_{\underline{\alpha} = \underline{\alpha}^*} = \underline{0}. \quad (7.21)$$

It of course follows from (7.11)₃ that (7.21) and (6.10) are equivalent, i.e. are just different forms of the same equation for $\underline{\alpha}^*$. This does not, however, imply that the concepts of stability at constant strain and temperature and stability at constant strain and entropy are logically equivalent: The equation (7.21), or (6.10), is a necessary, but not a sufficient, condition for these two types of stability.

We say that a triplet $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ obeying (7.18) characterizes a state that is Lyapunov stable at constant strain and entropy if for each $\epsilon > 0$ there exists a $\delta_\epsilon > 0$ such that every solution $\underline{\alpha} = \underline{\alpha}(t)$ of (7.19)₁ having $|\underline{\alpha}(0) - \underline{\alpha}^*| < \delta_\epsilon$ also has $|\underline{\alpha}(t) - \underline{\alpha}^*| < \epsilon$ for all $t \geq 0$. The following proposition is an immediate consequence of (7.16) and the theory²⁷ of Lyapunov functions: If $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ obeys (7.18) and has the property that for all $\underline{\alpha}$ in some neighborhood of $\underline{\alpha}^*$

$$\tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}) > \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}^*) \quad \text{whenever } \underline{\alpha} \neq \underline{\alpha}^*, \quad (7.22)$$

then $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ characterizes a state that is Lyapunov stable at constant strain and entropy.

It follows from (7.11)₃, (7.9)₄, and the proposition containing (6.16) that a material is strictly dissipative if and only if

$$\partial_{\underline{\alpha}} \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}) \cdot \tilde{f}(\underline{F}^*, \eta^*, \underline{\alpha}) < 0 \quad (7.23)$$

whenever $(\underline{F}^*, \eta^*, \underline{\alpha})$ does not characterize an equilibrium state.

The last proposition of this section follows from arguments completely analogous to arguments used in Section 6: If $(\tilde{F}^*, \eta^*, \alpha^*)$ obeys (7.18) and if (7.23) holds for all $\alpha \neq \alpha^*$ in some neighborhood of α^* , then the inequality (7.22) is a necessary and sufficient condition for the state characterized by $(\tilde{F}^*, \eta^*, \alpha^*)$ to be asymptotically stable at constant strain and entropy.

8. INTERNAL ENERGY AS AN INDEPENDENT VARIABLE

The temperature relation (7.12) and our assumption that θ is strictly positive imply that the function $\tilde{\epsilon}$ in (7.4) is smoothly invertible in its second variable η . Hence there exists a function $\bar{\eta}$ such that

$$\eta = \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}), \quad (8.1)$$

and putting

$$\left. \begin{aligned} \bar{\theta}(\underline{F}, \epsilon, \underline{\alpha}) &= \tilde{\theta}(\underline{F}, \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}), \underline{\alpha}), \\ \bar{\underline{S}}(\underline{F}, \epsilon, \underline{\alpha}) &= \tilde{\underline{S}}(\underline{F}, \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}), \underline{\alpha}), \\ \bar{\underline{q}}(\underline{F}, \epsilon, \underline{\alpha}) &= \tilde{\underline{q}}(\underline{F}, \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}), \underline{\alpha}), \\ \bar{\underline{f}}(\underline{F}, \epsilon, \underline{\alpha}) &= \tilde{\underline{f}}(\underline{F}, \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}), \underline{\alpha}), \end{aligned} \right\} \quad (8.2)$$

we can write the constitutive equations (7.5)-(7.8) as follows:

$$\theta = \bar{\theta}(\underline{F}, \epsilon, \underline{\alpha}), \quad (8.3)$$

$$\underline{S} = \bar{\underline{S}}(\underline{F}, \epsilon, \underline{\alpha}), \quad (8.4)$$

$$\underline{q} = \bar{\underline{q}}(\underline{F}, \epsilon, \underline{g}, \underline{\alpha}), \quad (8.5)$$

$$\underline{\dot{\alpha}} = \bar{\underline{f}}(\underline{F}, \epsilon, \underline{g}, \underline{\alpha}). \quad (8.6)$$

The equations (7.4) and (8.1) imply that

$$\left. \begin{aligned} \partial_{\epsilon} \bar{\eta} &= (\partial_{\eta} \tilde{\epsilon})^{-1}, \\ \partial_{\tilde{F}} \bar{\eta} + (\partial_{\epsilon} \bar{\eta}) (\partial_{\tilde{F}} \tilde{\epsilon}) &= 0, \\ (\partial_{\epsilon} \bar{\eta}) (\partial_{\tilde{\alpha}} \tilde{\epsilon}) + \partial_{\tilde{\alpha}} \bar{\eta} &= 0. \end{aligned} \right\} \quad (8.7)$$

It follows from the first two of these relations that (7.12) and (7.13) can be written in the forms

$$\theta = [\partial_{\epsilon} \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha})]^{-1} \quad (8.8)$$

$$\xi = - \frac{\partial_{\tilde{F}} \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha})}{\partial_{\epsilon} \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha})} = -\theta \partial_{\tilde{F}} \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}), \quad (8.9)$$

From (8.7)₃, (8.9), and (7.11)₃ we obtain

$$\partial_{\tilde{\alpha}} \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}) = -\frac{1}{\theta} \partial_{\tilde{\alpha}} \tilde{\epsilon}(\underline{F}, \eta, \underline{\alpha}) = -\frac{1}{\theta} \partial_{\tilde{\alpha}} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}), \quad (8.10)$$

and hence (7.16) becomes

$$\partial_{\tilde{\alpha}} \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}) \cdot \tilde{f}(\underline{F}, \epsilon, 0, \underline{\alpha}) \geq 0. \quad (8.11)$$

It follows from (8.2)₄ that a triplet $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$ characterizes an equilibrium state, i.e. obeys (7.18), if and only if the triplet $(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ with

$$\epsilon^* = \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}^*), \quad \eta^* = \bar{\eta}(\underline{F}^*, \epsilon^*, \underline{\alpha}^*), \quad (8.12)$$

obeys the relation

$$\bar{f}(\underline{F}^*, \epsilon^*, 0, \underline{\alpha}^*) = 0. \quad (8.13)$$

When such is the case, the domain of attraction of $(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ at constant strain and energy is the set $\bar{D}(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ of all internal state vectors $\underline{\alpha}_0$ with the property that the solution $\underline{\alpha} = \underline{\alpha}(t)$ of the initial value problem

$$\dot{\underline{\alpha}} = \bar{f}(\underline{F}^*, \epsilon^*, 0, \underline{\alpha}), \quad \underline{\alpha}(0) = \underline{\alpha}_0 \quad (8.14)$$

exists for all $t \geq 0$ and converges to $\underline{\alpha}^*$ as $t \rightarrow \infty$. We say that $(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ is asymptotically stable at constant strain and energy if $\bar{D}(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ contains a neighborhood of $\underline{\alpha}^*$. If for each $\epsilon > 0$ there exists a $\delta_\epsilon > 0$ such that $|\underline{\alpha}(0) - \underline{\alpha}^*| < \delta_\epsilon$ implies $|\underline{\alpha}(t) - \underline{\alpha}^*| < \epsilon$ for all $t \geq 0$, then we say that $(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ is Lyapunov stable at constant strain and entropy.

The next two theorems follow from (8.11).

If $\underline{\alpha}$ is in the domain of attraction of $(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ then

$$\bar{\eta}(\underline{F}^*, \epsilon^*, \underline{\alpha}) \leq \bar{\eta}(\underline{F}^*, \epsilon^*, \underline{\alpha}^*). \quad (8.15)$$

Hence, if $(\underline{F}^*, \epsilon^*, \underline{\alpha}^*)$ is asymptotically stable at constant strain and energy, (8.15) must hold throughout some neighborhood of $\underline{\alpha}^*$ and

$$\left. \frac{\partial}{\partial \underline{\alpha}} \bar{\eta}(\underline{F}^*, \epsilon^*, \underline{\alpha}) \right|_{\underline{\alpha}=\underline{\alpha}^*} = 0. \quad (8.16)$$

[It follows from (8.10) that the equations (6.10), (7.21), and (8.16), giving necessary conditions for three distinct types of stability that an equilibrium state may manifest, are equivalent.]

If $(\tilde{F}^*, \epsilon^*, \tilde{\alpha}^*)$ obeys (8.13) and if for all α in some neighborhood of $\tilde{\alpha}^*$

$$\bar{\eta}(\tilde{F}^*, \epsilon^*, \alpha) < \bar{\eta}(\tilde{F}^*, \epsilon^*, \tilde{\alpha}^*) \quad \text{whenever } \alpha \neq \tilde{\alpha}^*, \quad (8.17)$$

then $(\tilde{F}^*, \epsilon^*, \tilde{\alpha}^*)$ is Lyapunov stable at constant strain and energy.

We may conclude from (8.10), (8.2)₄, and the remark containing (7.23) that the material under consideration is strictly dissipative if and only if

$$\partial_{\tilde{\alpha}} \bar{\eta}(\tilde{F}^*, \epsilon^*, \alpha) \cdot \bar{f}(\tilde{F}^*, \epsilon^*, \alpha) > 0 \quad (8.18)$$

whenever $\bar{f}(\tilde{F}^*, \epsilon^*, \alpha) \neq 0$.

Using arguments given in Section 6 one can easily prove the following proposition which is similar to the last assertion of Section 7: If $(\tilde{F}^*, \epsilon^*, \tilde{\alpha}^*)$ obeys (8.13) and if (8.18) holds for all $\alpha \neq \tilde{\alpha}^*$ in a neighborhood of $\tilde{\alpha}^*$, then (8.17) supplies a necessary and sufficient condition for $(\tilde{F}^*, \epsilon^*, \tilde{\alpha}^*)$ to be asymptotically stable at constant strain and energy.

9. RELATION OF ISOTHERMAL TO ISENTROPIC AND ISOENERGETIC STABILITY

Let $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ be an equilibrium state for the material at X, and let

$$\eta^* = \hat{\eta}(\underline{F}^*, \theta^*, \underline{\alpha}^*), \quad (9.1)$$

$$\epsilon^* = \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}^*). \quad (9.2)$$

Assuming that the strong forms (6.16), (7.23), and (8.18) of the internal dissipation inequality hold, we here show that asymptotic stability of the state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ at constant strain and temperature implies asymptotic stability of the same state at constant strain and entropy, and that this latter type of stability is equivalent to stability at constant strain and energy. To prove the first implication we make use of our assumption that the heat capacity c of Eqs. (7.1) and (7.3) is positive, i.e. that

$$\partial_{\theta} \hat{\eta}(\underline{F}, \theta, \underline{\alpha}) > 0 \quad (9.3)$$

for all \underline{F} , θ , and $\underline{\alpha}$. Using the entropy relation (5.16), we can write (9.3) in the form

$$\partial_{\theta}^2 \hat{\psi}(\underline{F}, \theta, \underline{\alpha}) < 0, \quad (9.4)$$

which implies that for each pair $(\underline{F}, \underline{\alpha})$, $\hat{\psi}(\underline{F}, \theta, \underline{\alpha})$ must be a concave function of θ :

$$\hat{\psi}(\underline{F}, \theta, \underline{\alpha}) - \hat{\psi}(\underline{F}, \theta', \underline{\alpha}) - (\theta - \theta') \partial_{\theta} \hat{\psi}(\underline{F}, \theta', \underline{\alpha}) \leq 0, \quad (9.5)$$

or, equivalently,

$$\hat{\psi}(\underline{F}, \theta', \alpha) \geq \hat{\psi}(\underline{F}, \theta, \alpha) + (\theta - \theta') \hat{\eta}(\underline{F}, \theta', \alpha). \quad (9.6)$$

Using (9.6) we now prove the following lemma: If η^* is given by (9.1) then

$$\tilde{\epsilon}(\underline{F}^*, \eta^*, \alpha) - \tilde{\epsilon}(\underline{F}^*, \eta^*, \alpha^*) \geq \hat{\psi}(\underline{F}^*, \theta^*, \alpha) - \hat{\psi}(\underline{F}^*, \theta^*, \alpha^*). \quad (9.7)$$

It follows from (7.9)₁ that

$$\tilde{\epsilon}(\underline{F}^*, \eta^*, \alpha) - \tilde{\epsilon}(\underline{F}^*, \eta^*, \alpha^*) = \hat{\psi}(\underline{F}^*, \tilde{\theta}(\underline{F}^*, \eta^*, \alpha), \alpha) - \hat{\psi}(\underline{F}^*, \theta^*, \alpha^*) + [\tilde{\theta}(\underline{F}^*, \eta^*, \alpha) - \theta^*] \eta^*. \quad (9.8)$$

By (9.6),

$$\hat{\psi}(\underline{F}^*, \tilde{\theta}(\underline{F}^*, \eta^*, \alpha), \alpha) \geq \hat{\psi}(\underline{F}^*, \theta^*, \alpha) + [\theta^* - \tilde{\theta}(\underline{F}^*, \eta^*, \alpha)] \eta^*. \quad (9.9)$$

But

$$\hat{\eta}(\underline{F}^*, \tilde{\theta}(\underline{F}^*, \eta^*, \alpha), \alpha) = \eta^*, \quad (9.10)$$

and, therefore, when (9.9) is added to (9.8) the resulting inequality reduces to (9.7).

Using (9.7) we ^{now} establish the following theorem: Let $(\underline{F}^*, \theta^*, \alpha^*)$ be an equilibrium state, let η^* be given by (9.1), and assume that the strong forms (6.16) and (7.23) of the internal dissipation inequality hold for all $\alpha \neq \alpha^*$ in some neighborhood of α^* . If the state $(\underline{F}^*, \theta^*, \alpha^*)$ is asymptotically stable at constant strain and temperature, then this state is asymptotically stable at constant strain and entropy.

Proof: Let $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ be asymptotically stable at constant strain and temperature. Since we here assume that (6.16) holds for all $\underline{\alpha} \neq \underline{\alpha}^*$ in a neighborhood of $\underline{\alpha}$, it follows from conclusion (i) of the theorem on page 29 (Section 6) that for $\underline{\alpha}$ in a neighborhood $\mathcal{N}(\underline{\alpha}^*)$ of $\underline{\alpha}^*$

$$\underline{\alpha} \neq \underline{\alpha}^* \implies \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}) > \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}^*). \quad (9.11)$$

It is clear from our lemma (9.7), that (9.11) has the consequence that for $\underline{\alpha}$ in $\mathcal{N}(\underline{\alpha}^*)$

$$\underline{\alpha} \neq \underline{\alpha}^* \implies \hat{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}) > \hat{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}^*). \quad (9.12)$$

But, since we here also assume (7.23), we may observe that the last sentence of Section 7 tells us that (9.12) is a sufficient condition for asymptotic stability at constant strain and entropy of the state characterized by $(\underline{F}^*, \eta^*, \underline{\alpha}^*)$, i.e. the state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$, and this completes the proof.

To show the equivalence of isentropic and isoenergetic stability we first show that if $\epsilon^* = \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}^*)$, then

$$\epsilon^* < \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}) \iff \bar{\eta}(\underline{F}^*, \epsilon^*, \underline{\alpha}) < \eta^*. \quad (9.13)$$

Indeed, it follows from (8.1) and the positivity of θ that $\bar{\eta}(\underline{F}, \epsilon, \underline{\alpha})$ is a strictly increasing function of ϵ and hence

$$\epsilon^* < \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}) \iff \bar{\eta}(\underline{F}^*, \epsilon^*, \underline{\alpha}) < \bar{\eta}(\underline{F}^*, \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}), \underline{\alpha}). \quad (9.14)$$

But since the function $\bar{\eta}(\underline{F}, \cdot, \underline{\alpha})$ is the inverse of the function $\tilde{\epsilon}(\underline{F}, \cdot, \underline{\alpha})$, we have, for each value of $\underline{\alpha}$,

$$\bar{\eta}(\underline{F}^*, \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}), \underline{\alpha}) = \eta^*, \quad (9.15)$$

and therefore (9.14) implies (9.13).

Our desired result is now an immediate consequence of (9.13) and the concluding sentences of Sections 7 and 8: When the strong forms (7.23) and (8.18) of the internal dissipation inequality hold for all $\underline{\alpha} \neq \underline{\alpha}^*$ in a neighborhood of $\underline{\alpha}^*$, an equilibrium state is asymptotically stable at constant strain and entropy if and only if it is asymptotically stable at constant strain and energy.

10. INTEGRAL DISSIPATION INEQUALITIES

In a body undergoing an arbitrary thermodynamic process, we may consider, at a given material point, the following general dissipation integrals,³³ defined for any two times $t_0 < t_1$:

³³Our present \mathcal{H} , \mathcal{I} , and \mathcal{J} differ only in the terms containing q from the functionals which Coleman (on pp. 27, 35, & 39 of ref. 15) calls "dissipation integrals".

$$\mathcal{I}(t_1, t_0) = \int_{t_0}^{t_1} \left\{ \underline{\underline{S}} \cdot \underline{\underline{\dot{F}}} - \eta \dot{\theta} - \frac{1}{\rho \theta} \underline{\underline{q}} \cdot \underline{\underline{g}} \right\} dt, \quad (10.1)$$

$$\mathcal{J}(t_1, t_0) = \int_{t_0}^{t_1} \left\{ \underline{\underline{S}} \cdot \underline{\underline{\dot{F}}} + \theta \dot{\eta} - \frac{1}{\rho \theta} \underline{\underline{q}} \cdot \underline{\underline{g}} \right\} dt, \quad (10.2)$$

$$\mathcal{H}(t_1, t_0) = \int_{t_0}^{t_1} \left\{ \frac{1}{\theta} \underline{\underline{S}} \cdot \underline{\underline{\dot{F}}} - \dot{\epsilon} - \frac{1}{\rho \theta} \underline{\underline{q}} \cdot \underline{\underline{g}} \right\} dt; \quad (10.3)$$

It follows immediately from the law (3.2) of positive production of entropy and the expressions (3.3) and (3.8) for γ that

$$\begin{aligned} \mathcal{I}(t_1, t_0) &\geq \psi(t_1) - \psi(t_0), \\ \mathcal{J}(t_1, t_0) &\geq \epsilon(t_1) - \epsilon(t_0), \\ \mathcal{H}(t_1, t_0) &\geq \eta(t_0) - \eta(t_1). \end{aligned} \quad (10.4)$$

The theory we have been developing here can be brought closer to the theory of materials with fading memory^{2-4,15} by adding assumptions about the stability of solutions of the differential equation governing the evolution of the internal state vector $\underline{\alpha}$. For the remainder of this section we shall assume the following stability postulate:

Corresponding to each pair $(\underline{F}^*, \theta^*)$ there is an internal state vector $\underline{\alpha}^*$ which makes $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ an equilibrium state that is asymptotically stable in the large at constant strain and temperature.

In other words, we assume that given $(\underline{F}^*, \theta^*)$ there exists at least one $\underline{\alpha}^*$ such that $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ obeys (6.1) and also such that every solution of (6.2) obeys (6.4).

This postulate has the following consequences:

(i) Corresponding to each pair $(\underline{F}^*, \theta^*)$ there is exactly one equilibrium state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$.

(ii) At each equilibrium state $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$, the inequalities (6.9), (7.20), and (8.15) hold for all $\underline{\alpha}$ with η^* and ϵ^* given by (9.1) and (9.2).

To demonstrate conclusion (i) we need merely note that if to a given pair $(\underline{F}^*, \theta^*)$ there corresponded two equilibrium states $(\underline{F}^*, \theta^*, \underline{\alpha}^*)$ and $(\underline{F}^*, \theta^*, \underline{\alpha}^\dagger)$, both obeying (6.1) with $\underline{\alpha}^* \neq \underline{\alpha}^\dagger$, then $\underline{\alpha}(t) \equiv \underline{\alpha}^\dagger$ would be a solution of (6.2), and, by our stability postulate,

we would have $\underline{\alpha}(t) \rightarrow \underline{\alpha}^*$, which is impossible since $\underline{\alpha}(t) \equiv \text{const.} \neq \underline{\alpha}^*$. Conclusion (ii) is an immediate consequence of (9.7), (9.13), and the sentence following (6.8).

The stability postulate is not a consequence of the Clausius-Duhem inequality but is rather an independent hypothesis expected to hold for some materials but not all. Under this new postulate a single-valued function $\hat{\underline{\alpha}}^*$ relates $(\underline{F}^*, \theta^*)$ to $\underline{\alpha}^*$, as in (6.17), and equilibrium response functions $\hat{\psi}^*$, $\hat{\eta}^*$, etc., may be defined as in (6.18). Of course (6.20)-(6.27) hold, and the remark following (6.8) here yields

$$\hat{\psi}(\underline{F}, \theta, \underline{\alpha}) \geq \hat{\psi}^*(\underline{F}, \theta) \quad (10.5)$$

for all $\underline{\alpha}$.

Consider now a material point X and a time t_0 , and suppose that at X the triplet $(\underline{F}, \theta, \underline{g})$ has the following sort of time-dependence:

$$(\underline{F}(t), \theta(t), \underline{g}(t)) = \begin{cases} \text{arbitrary values for } t < t_0, \\ (\underline{F}_0, \theta_0, \underline{g}_0) \text{ for } t \geq t_0. \end{cases} \quad (10.6)$$

At the time t_0 , the internal state vector $\underline{\alpha}$ will have a value $\underline{\alpha}_0$, determined, through the differential equation (4.5), by the histories of \underline{F} , θ , and \underline{g} up to time t_0 and some initial data for $\underline{\alpha}$. Although we may not know the value of $\underline{\alpha}_0$, we do know that for $t > t_0$, $\underline{\alpha}(t)$ will be the solution of (6.2) corresponding to the initial condition $\underline{\alpha}(t_0) = \underline{\alpha}_0$. Since, by our present stability hypothesis, all solutions of (6.2) must

approach $\underline{\alpha}^* = \hat{\underline{\alpha}}^*(\underline{F}_0, \theta_0)$ we have

$$\lim_{t \rightarrow \infty} \underline{\alpha}(t) = \hat{\underline{\alpha}}^*(\underline{F}_0, \theta_0). \quad (10.7)$$

Therefore, it follows from the (tacitly assumed) continuity of $\hat{\psi}$, $\hat{\eta}$, \hat{T} , \hat{q} , and the equations (6.19) and (6.25), that at the point X

$$\begin{aligned} \lim_{t \rightarrow \infty} \psi(t) &= \lim_{t \rightarrow \infty} \hat{\psi}(\underline{F}_0, \theta_0, \underline{\alpha}(t)) = \hat{\psi}^*(\underline{F}_0, \theta_0), \\ \lim_{t \rightarrow \infty} \eta(t) &= \lim_{t \rightarrow \infty} \hat{\eta}(\underline{F}_0, \theta_0, \underline{\alpha}(t)) = \hat{\eta}^*(\underline{F}_0, \theta_0), \\ \lim_{t \rightarrow \infty} T(t) &= \lim_{t \rightarrow \infty} \hat{T}(\underline{F}_0, \theta_0, \underline{\alpha}(t)) = \hat{T}^*(\underline{F}_0, \theta_0), \\ \lim_{t \rightarrow \infty} q(t) &= \lim_{t \rightarrow \infty} \hat{q}(\underline{F}_0, \theta_0, \underline{\alpha}(t)) = 0. \end{aligned} \quad (10.8)$$

When a history up to some time t_0 is extended beyond t_0 in the manner illustrated in (10.7), we call the resulting extended history the isothermal static continuation of the original history. Our proof of (10.8) shows, in effect, that in any isothermal static continuation of an arbitrary history, the free energy, entropy, stress, and heat flux all approach their equilibrium values as t increases without limit. Moreover, the first of these limits is approached monotonically, for (3.9) here yields

$$\dot{\psi}(t) \leq 0 \quad \text{for all } t > t_0. \quad (10.9)$$

The relations (10.5) and (10.8)₁ tell us that the theorem on minimum free energy, originally proven for materials with memory³⁴, has the following

³⁴Ref. 15, Theorem 3, p. 26.

form in the present theory, provided we assume that equilibrium solutions of (6.2) are stable in the large: Of all histories ending with given values of \underline{F} and θ , the constant history with g held fixed at zero and \underline{F} and θ held fixed at the given values gives rise to the least free energy.

Thus, our new stability postulate gives the present theory many, but not all, the qualitative properties of Coleman's¹⁵ theory of materials with memory.

Let us now return to the dissipation integrals defined in (10.1)-(10.3) and consider processes which start from an equilibrium state, i.e. processes for which we have at X ,

$$\underline{F}(t_0) = \underline{F}^*, \quad \theta(t_0) = \theta^*, \quad \underline{\alpha}(t_0) = \underline{\alpha}^* = \hat{\underline{\alpha}}^*(\underline{F}^*, \theta^*), \quad (10.10)$$

but for which \underline{F} , θ , and g at X are given by arbitrary functions $\underline{F}(t)$, $\theta(t)$, $g(t)$ for $t > t_0$. For each such process, at X

$$\psi(t_0) = \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}^*), \quad (10.11)$$

$$\psi(t) = \hat{\psi}(\underline{F}(t), \theta(t), \underline{\alpha}(t)) \quad \text{for } t > t_0, \quad (10.12)$$

where $\underline{\alpha}(t)$ is to be obtained by solving the differential equation (4.5) with the initial condition $\underline{\alpha}(t_0) = \underline{\alpha}^*$. If \underline{F} and θ return to their initial values \underline{F}^* and θ^* at some time $t_1 > t_0$, then for $\psi(t_1)$ we have

$$\psi(t_1) = \hat{\psi}(\underline{F}^*, \theta^*, \underline{\alpha}(t_1)), \quad (10.13)$$

and this equation, when set alongside of (10.11) and the consequence (ii) of our stability postulate, implies that $\psi(t_1)$ is greater than $\psi(t_0)$:

$$\underline{F}(t_1) = \underline{F}^*, \theta(t_1) = \theta^* \implies \psi(t_0) \leq \psi(t_1). \quad (10.14)$$

Of course, (10.10) implies that

$$\epsilon(t_0) = \hat{\epsilon}(\underline{F}^*, \theta^*, \underline{\alpha}^*) \stackrel{\text{def}}{=} \epsilon^* = \tilde{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}^*), \quad (10.15)$$

$$\eta(t_0) = \hat{\eta}(\underline{F}^*, \theta^*, \underline{\alpha}^*) \stackrel{\text{def}}{=} \eta^* = \bar{\eta}(\underline{F}^*, \epsilon^*, \underline{\alpha}^*). \quad (10.16)$$

If it should happen that $\underline{F}(t_1) = \underline{F}^*$ and $\eta(t_1) = \eta^*$, then

$$\epsilon(t_1) = \hat{\epsilon}(\underline{F}^*, \eta^*, \underline{\alpha}(t_1)), \quad (10.17)$$

and, therefore, by (10.15) and the consequence (ii) of the stability postulate,

$$\underline{F}(t_1) = \underline{F}^*, \eta(t_1) = \eta^* \implies \epsilon(t_0) \leq \epsilon(t_1). \quad (10.18)$$

Similarly,

$$\underline{F}(t_1) = \underline{F}^*, \epsilon(t_1) = \epsilon^* \implies \eta(t_0) \geq \eta(t_1). \quad (10.19)$$

Combining (10.13), (10.18), and (10.19) with the inequalities (10.4), we obtain the following theorem on dissipation integrals:³⁵

³⁵For the corresponding theorem for materials with fading memory see Remarks 17, 24, and 32 on pp. 27, 36, and 39 of ref. 15.

Under the stability postulate stated above each of the following implications holds for processes which start at t_0 from an equilibrium state of the type (10.10), but which are otherwise arbitrary:

$$\begin{aligned} \tilde{F}(t_1) = \tilde{F}(t_0), \quad \theta(t_0) = \theta(t_1) &\implies \mathcal{L}(t_1, t_0) \geq 0, \\ \tilde{F}(t_1) = \tilde{F}(t_0), \quad \eta(t_0) = \eta(t_1) &\implies \mathcal{J}(t_1, t_0) \geq 0, \quad (10.20) \\ \tilde{F}(t_1) = \tilde{F}(t_0), \quad \epsilon(t_0) = \epsilon(t_1) &\implies \mathcal{H}(t_1, t_0) \geq 0. \end{aligned}$$

We call a process isothermal at X if $\dot{\theta} \equiv 0$ at X, isentropic if $\dot{\eta} \equiv 0$ at X, and isoenergetic if $\dot{\epsilon} \equiv 0$ at X. It is clear from (10.1)-(10.3), that the theorem just proven has the following corollary yielding inequalities for integrals of the stress power in special cyclic processes:³⁶ Consider a process starting from an equilibrium state of

³⁶For materials with fading memory analogous results are given in Theorem 4, Remark 2.5, and Remark 3.3 of ref. 15.

the type (10.10) and for which the temperature gradient \tilde{g} is zero for

$t_0 \leq t \leq t_1$. If the process is either isothermal or isentropic, then

$$\tilde{F}(t_1) = \tilde{F}(t_0) \implies \int_{t_0}^{t_1} \tilde{S} \cdot \dot{\tilde{F}} dt \geq 0. \quad (10.21)$$

If the process is isoenergetic, then

$$\tilde{F}(t_1) = \tilde{F}(t_0) \implies \int_{t_0}^{t_1} \frac{1}{\theta} \tilde{S} \cdot \dot{\tilde{F}} dt \geq 0. \quad (10.22)$$

11. TEMPERATURES ASSOCIATED WITH INTERNAL STATES

We here suppose that the first M of the N internal state variables α_i have the same dimension as the specific internal energy ϵ .

Putting

$$\epsilon_A = \epsilon - \sum_{i=1}^M a_i, \quad (11.1)$$

and

$$\beta = \{\alpha_{M+1}, \alpha_{M+2}, \dots, \alpha_N\}, \quad (11.2)$$

we call ϵ_A the specific internal energy of the active mode and α_i , $i = 1, 2, \dots, M$, the specific internal energy of the i 'th internal (or "hidden") mode. Defining the function $\check{\eta}$ by

$$\check{\eta}(\mathcal{E}, \epsilon_A, \alpha_1, \dots, \alpha_M, \beta) = \bar{\eta}\left(\mathcal{E}, \epsilon_A + \sum_{i=1}^M \alpha_i, \alpha\right), \quad (11.3)$$

we put

$$\theta_A = \left[\partial_{\epsilon_A} \check{\eta}(\mathcal{E}, \epsilon_A, \alpha_1, \dots, \alpha_M, \beta) \right]^{-1}, \quad (11.4)$$

$$\theta_i = \left[\partial_{\alpha_i} \check{\eta}(\mathcal{E}, \epsilon_A, \alpha_1, \dots, \alpha_M, \beta) \right]^{-1}, \quad (11.5)$$

for $i = 1, 2, \dots, M$. We refer to θ_A as the translational temperature (or the temperature of the active mode) and to θ_i as the temperature of the

i 'th mode. We may observe that the "temperature of the i 'th mode" need not be positive. In fact, as there is at this point no reason to suppose that $\partial_{\alpha_i} \check{\eta} \neq 0$, we must not rule out the possibility of θ_i being infinite.

Since (11.3) yields

$$\partial_{\epsilon_A} \check{\eta} = \partial_{\epsilon} \bar{\eta}, \quad (11.6)$$

the temperature relation (8.8) implies that "the temperature" θ is equal to the translational temperature θ_A :

$$\theta = \theta_A. \quad (11.7)$$

Therefore, we shall henceforth use the same symbol, θ , for both θ and θ_A .

It also follows from (11.3) that for $i = 1, 2, \dots, M$,

$$\partial_{\alpha_i} \check{\eta} = \partial_{\epsilon} \bar{\eta} + \partial_{\alpha_i} \bar{\eta}, \quad (11.8)$$

and hence we have the following expression for each θ_i

$$\frac{1}{\theta_i} = \frac{1}{\theta} + \partial_{\alpha_i} \bar{\eta}(\underline{F}, \epsilon, \underline{\alpha}). \quad (11.9)$$

This formula when combined with (8.16) implies the following theorem:

At an asymptotically stable equilibrium state the temperature θ_i of each internal mode is equal to the translational temperature θ .³⁷

³⁷This result should be compared with Truesdell's theorem about the compatibility of total with partial caloric equations of state for mixtures: C. Truesdell, Rend. Lincei (8) 22, 33, 158 (1957), Theorem IV.

Since $\theta > 0$, we conclude from the foregoing proposition that each θ_i is strictly positive when the material is close to a state of stable equilibrium.

By (11.1),

$$\dot{\epsilon} = 0 \iff \dot{\epsilon}_A + \sum_{i=1}^M \dot{\alpha}_i = 0; \quad (11.10)$$

hence (8.6), (8.11), and (11.9) imply that

$$\frac{\dot{\epsilon}_A}{\theta} + \sum_{i=1}^M \frac{\dot{\alpha}_i}{\theta_i} \geq 0 \quad \text{whenever } \dot{\epsilon} = 0, \quad \dot{g} = 0, \quad \text{and } \dot{\beta} = 0. \quad (11.11)$$

The inequality (11.11) appears to be in accord with intuitive prejudices about properties to be expected of temperatures associated with internal modes.

Suppose now that the function $\check{\eta}$ defined in (11.3) has the special form

$$\check{\eta}(\underline{F}, \epsilon_A, \alpha_1, \dots, \alpha_M, \beta) = \eta_A(\underline{F}, \epsilon_A, \beta) + \sum_{i=1}^M \eta_i(\underline{F}, \alpha_i). \quad (11.12)$$

Then $\theta = \theta_A$ is given by a function $\check{\theta}$ of $(\underline{F}, \epsilon_A, \beta)$, while each θ_i is given by a function $\check{\theta}_i$ of only $(\underline{F}, \alpha_i)$; for (11.4), (11.5), and (11.12) yield

$$\theta = \check{\theta}(\underline{F}, \epsilon_A, \beta) = [\partial_{\epsilon_A} \eta_A(\underline{F}, \epsilon_A, \beta)]^{-1}, \quad (11.13)$$

$$\theta_i = \check{\theta}_i(\underline{F}, \alpha_i) = [\partial_{\alpha_i} \eta_i(\underline{F}, \alpha_i)]^{-1}. \quad (11.14)$$

Let us assume, in addition, that there exists a function $\hat{\alpha}^*$ that assigns to each pair $(\underline{F}^*, \theta^*)$ an α^* , as in (6.17), such that the triplet $(\underline{F}^*, \theta^*, \alpha^*)$ constitutes an equilibrium state for the material point under consideration.

As we saw in the conclusion (i) of the first theorem of Section 10, this assumption is a consequence of the stability hypothesis of Section 10.

If we write (6.17) in the form

$$\alpha_i^* = \hat{\alpha}_i^*(\underline{F}^*, \theta^*), \quad i = 1, 2, \dots, N, \quad (11.15)$$

then the fact that $\theta = \theta_i$ at states of stable equilibrium implies

$$\check{\theta}_i(\underline{F}^*, \hat{\alpha}_i^*(\underline{F}^*, \theta^*)) = \theta^*, \quad i = 1, 2, \dots, M. \quad (11.16)$$

Since (11.16) must hold for all $(\underline{F}^*, \theta^*)$, $\check{\theta}_i(\underline{F}^*, \cdot)$ is a left inverse of $\hat{\alpha}_i^*(\underline{F}^*, \cdot)$. If we assume, as we shall, that for every pair $(\underline{F}, \alpha_i)$ we can find a θ such that $\alpha_i = \hat{\alpha}_i^*(\underline{F}, \theta)$, then we have the following theorem: If the stability postulate of Section 10 holds and if the caloric equation of state (8.1) can be cast in the special form (11.12), then for each i , $i = 1, 2, \dots, M$, and for each fixed \underline{F} , the function $\check{\theta}_i(\underline{F}, \cdot)$ is the inverse of the function $\hat{\alpha}_i^*(\underline{F}, \cdot)$.

We may use the foregoing theorem to motivate an alternative definition of internal mode temperatures which is free from the assumption that the α_i 's have the same dimension as the specific internal energy. To do this let us drop the assumption that the function $\check{\eta}$ defined in

(11.3) has the special form (11.12), but suppose that the first M of the functions $\hat{\alpha}_i^*$ of (11.15) are such that, for each value of \mathbb{F} , $\hat{\alpha}_i^*(\mathbb{F}, \theta)$ is an invertible function of θ , i.e. that there exist M functions $\check{\phi}_i$ such that

$$\check{\phi}_i(\mathbb{F}, \hat{\alpha}_i^*(\mathbb{F}, \theta)) = \theta \quad (11.17)$$

for all $\theta > 0$. When this condition is fulfilled the function $\check{\phi}_i$ is uniquely determined by the function $\hat{\alpha}_i^*$ and hence by the function \underline{f} on the right side of the constitutive equation (4.5). We call the value

$$\phi_i = \check{\phi}_i(\mathbb{F}, \alpha_i) \quad (11.18)$$

of $\check{\phi}_i$ at an arbitrary pair (\mathbb{F}, α_i) the temperature of the i 'th mode corresponding to (\mathbb{F}, α_i) . We shall continue to refer to the number entering the constitutive equations (5.15), (4.4), and (4.5) as the translational temperature. As an immediate consequence of (11.17) we have the following proposition: Each ϕ_i shares with θ_i the property of being equal to the translational temperature θ in states of stable equilibrium.

Unfortunately, the function $\check{\phi}_i$ is not, in general, identical to the function $[\partial_{\alpha_i} \check{\eta}]^{-1}$: Although $\theta_i = \phi_i = \theta$ at equilibrium, we can expect to have $\theta_i \neq \phi_i$ away from equilibrium, except, of course, when $\check{\eta}$ has the special form (11.12). As a matter of fact if $\check{\phi}_i$ were equal to

$[\partial_{\alpha_1} \check{\eta}]^{-1}$, then we could conclude from (11.18) that $\partial_{\alpha_1} \check{\eta}$ must be independent of ϵ_A and $\alpha_2, \dots, \alpha_N$, and hence that

$$\check{\eta}(\mathbb{F}, \epsilon_A, \alpha_1, \dots, \alpha_N) = \eta_1(\mathbb{F}, \alpha_1) + \eta_2(\mathbb{F}, \epsilon_A, \alpha_2, \dots, \alpha_N). \quad (11.19)$$

Thus we have the following result: A necessary condition that

$$\check{\phi}_1 = [\partial_{\alpha_1} \check{\eta}]^{-1} \quad (11.20)$$

is that the function $\check{\eta}$ have the special form (11.19). A similar result holds for α_2, α_3 , etc.

In view of the fact that temperatures of internal states are often regarded as definable only in terms of statistical concepts, we think it worthwhile to make the following observation. The results of this section suggest that if we accept the general assumptions made here and in Sections 4 and 5, then the question of whether we can associate a temperature θ_i with a particular internal state variable α_i becomes one that can be settled on purely phenomenological grounds, namely by inspection of the caloric equation of state and the equation governing the evolution of α_i in a thermodynamic process.

12. OBJECTIVITY

In Section 5 we found the restrictions placed on the response functions $\hat{\psi}$, $\hat{\eta}$, $\hat{\xi}$, \hat{q} , and \hat{f} of (4.1)-(4.5) by the postulate of positive production of entropy. The principle of material frame indifference³⁸,

³⁸W. Noll, Arch. Rational Mech. Anal. 2, 197 (1958), who called it the principle of objectivity of material properties.

which states that an admissible process must remain admissible after a change of frame, imposes further restrictions on response functions.

In our present theory a change of frame is characterized by a time-dependent orthogonal tensor Q . The scalars θ , ϵ , η , and ψ are unaffected by a change of frame, but \underline{F} , \underline{g} , \underline{q} , and \underline{T} transform as follows:

$$\left. \begin{aligned} \underline{F} &\rightarrow \underline{QF}, \\ \underline{g} &\rightarrow \underline{Qg}, \\ \underline{q} &\rightarrow \underline{Qq}, \\ \underline{T} &\rightarrow \underline{QTQ}^T. \end{aligned} \right\} \quad (12.1)$$

The manner in which the internal state vector $\underline{\alpha} = (\alpha_1, \dots, \alpha_N)$ transforms under a change of frame depends, of course, on the physical interpretation given to the components α_i of $\underline{\alpha}$, and therefore varies with the application

in mind. For definiteness we shall here assume that $\underline{\alpha}$ is an ordered N-tuple of scalars, each of which remains invariant upon a change of frame; i.e. we assume that simultaneously with (12.1) we have

$$\underline{\alpha} \rightarrow \underline{\alpha}. \quad (12.2)$$

[This is the case, for example, when each α_i represents the degree of advancement of a chemical reaction, the fraction of the total energy in a certain internal mode of molecular motion, or the probability that an internal degree of freedom is in a particular quantum state.] It follows from (12.2) that the response functions of the present theory are compatible with material frame-indifference if and only if they obey, for each orthogonal tensor \underline{Q} , the following identities in \underline{F} , θ , $\underline{\alpha}$, and \underline{g} :

$$\left. \begin{aligned} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}) &= \hat{\psi}(\underline{QF}, \theta, \underline{\alpha}), \\ \hat{\eta}(\underline{F}, \theta, \underline{\alpha}) &= \hat{\eta}(\underline{QF}, \theta, \underline{\alpha}), \\ \underline{Q}\hat{\underline{T}}(\underline{F}, \theta, \underline{\alpha})\underline{Q}^T &= \hat{\underline{T}}(\underline{QF}, \theta, \underline{\alpha}), \\ \underline{Q}\hat{\underline{q}}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) &= \hat{\underline{q}}(\underline{QF}, \theta, \underline{Qg}, \underline{\alpha}), \\ \underline{f}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) &= \underline{f}(\underline{QF}, \theta, \underline{Qg}, \underline{\alpha}). \end{aligned} \right\} \quad (12.3)$$

These identities can be used to derive the following reduced forms of our

constitutive equations:

$$\begin{aligned}
 \psi &= \check{\psi}(\underline{\underline{C}}, \theta, \underline{\underline{\alpha}}), \\
 \eta &= \check{\eta}(\underline{\underline{C}}, \theta, \underline{\underline{\alpha}}), \\
 \underline{\underline{T}} &= \check{\underline{\underline{T}}}(\underline{\underline{C}}, \theta, \underline{\underline{\alpha}}) \underline{\underline{F}}^T, \\
 \underline{\underline{q}} &= \check{\underline{\underline{q}}}(\underline{\underline{C}}, \theta, \underline{\underline{F}}^T \underline{\underline{g}}, \underline{\underline{\alpha}}), \\
 \underline{\underline{\dot{\alpha}}} &= \check{\underline{\underline{f}}}(\underline{\underline{C}}, \theta, \underline{\underline{F}}^T \underline{\underline{g}}, \underline{\underline{\alpha}});
 \end{aligned}
 \tag{12.4}$$

where

$$\underline{\underline{C}} = \underline{\underline{F}}^T \underline{\underline{F}}
 \tag{12.5}$$

is the right Cauchy-Green tensor; of course, by (2.4) and (2.5), $\underline{\underline{F}}^T \underline{\underline{g}}$ is just $\text{GRAD } \theta$. In terms of the response functions introduced here, the entropy relation (5.16) may be written

$$\check{\eta} = -\partial_{\theta} \check{\psi}
 \tag{12.6}$$

and the stress relation (5.18) becomes

$$\check{\underline{\underline{T}}} = 2\rho \partial_{\underline{\underline{C}}} \check{\psi}.
 \tag{12.7}$$

One might imagine that in some applications $\underline{\underline{\alpha}}$ could represent a vector of dimension three transforming as a spatial position vector under a change of frame, but such an interpretation for $\underline{\underline{\alpha}}$ is not

compatible with our constitutive equation (4.5). For, if

$$\underline{\alpha} \rightarrow \underline{Q}\underline{\alpha} \quad (12.8)$$

then for each time dependent orthogonal tensor \underline{Q} , \underline{f} must obey the identity

$$\dot{\underline{Q}}\underline{\alpha} = \underline{f}(\underline{Q}\underline{F}, \theta, \underline{Q}\underline{g}, \underline{Q}\underline{\alpha}) \quad (12.9)$$

where $\dot{\underline{Q}}$ is given by (4.5). Since

$$\dot{\underline{Q}}\underline{\alpha} = \dot{\underline{Q}}\underline{\alpha} + \underline{Q}\dot{\underline{\alpha}} = \underline{Q}\underline{f}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) + \underline{Q}\dot{\underline{\alpha}}, \quad (12.10)$$

when $\underline{Q}(t) = \underline{1}$, (11.8) and (11.9) yield

$$\dot{\underline{Q}}\underline{\alpha} = \underline{0}, \quad (12.11)$$

which equation must hold for all choices of $\dot{\underline{Q}}$. But, when $\underline{Q}(t) = \underline{1}$, the only restriction on $\dot{\underline{Q}}(t)$ is that this tensor be skew. Hence (12.10) states that $\underline{W}\underline{\alpha} = \underline{0}$ for all skew tensors \underline{W} , which implies that $\underline{\alpha} = \underline{0}$. In other words, if $\underline{\alpha}$ behaves as a spatial three-vector under changes of frame, then (4.5) must be replaced by the trivial equations $\underline{f} \equiv \underline{0}$, $\underline{\alpha} \equiv \underline{0}$.

13. MATERIAL SYMMETRY, FLUIDS

The symmetry group \mathcal{S} of a material is the set of all non-singular changes of local reference configuration that leave the response functions of the material unaltered.³⁹

³⁹This is essentially a definition due to Noll³⁸ who defined the local isotropy group \underline{G} of a material to be the set of density-preserving changes of local reference configuration which leave the response unaltered. It has recently been shown⁴⁰ that our present \mathcal{S} must reduce to Noll's \underline{G} .]

⁴⁰M. E. Gurtin and W. O. Williams, Arch. Rational Mech. Anal. 23,

If we assume that the internal state variables α_i are quantities unaffected by the choice of reference configuration, then in our present theory the symmetry group \mathcal{S} may be identified with the group of all invertible tensors \underline{H} for which the identities

$$\left. \begin{aligned} \hat{\psi}(\underline{F}, \theta, \underline{\alpha}) &= \hat{\psi}(\underline{FH}, \theta, \underline{\alpha}), \\ \hat{\eta}(\underline{F}, \theta, \underline{\alpha}) &= \hat{\eta}(\underline{FH}, \theta, \underline{\alpha}), \\ \hat{\underline{T}}(\underline{F}, \theta, \underline{\alpha}) &= \hat{\underline{T}}(\underline{FH}, \theta, \underline{\alpha}), \\ \hat{\underline{q}}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) &= \hat{\underline{q}}(\underline{FH}, \theta, \underline{g}, \underline{\alpha}), \\ \hat{\underline{f}}(\underline{F}, \theta, \underline{g}, \underline{\alpha}) &= \hat{\underline{f}}(\underline{FH}, \theta, \underline{g}, \underline{\alpha}), \end{aligned} \right\} \quad (13.1)$$

hold for all \underline{F} , θ , $\underline{\alpha}$, and \underline{g} . This group \mathcal{S} depends on the choice of reference configuration, but the symmetry group corresponding to two different reference configurations of the same material are conjugate and hence isomorphic. A theorem of Gurtin and Williams⁴⁰ tells us that the postulate of positive production of entropy requires that \mathcal{S} must be a subgroup of the unimodular group; i.e. that each \underline{H} in \mathcal{S} must have $|\det \underline{H}| = 1$.

The similarity between the equations (13.1) and the identities used to define the symmetry group of an elastic material with heat conduction is striking,⁴¹ and one can immediately apply here many results

⁴¹See, for example, ref. 13, Eq. (3.2).

originally obtained within the framework of the theory of elastic materials. For example, using an argument given by Coleman and Noll¹³ one can easily show that if the inversion transformation $-\underline{1}$ is in \mathcal{S} then

$$\hat{\underline{q}}(\underline{F}, \theta, \underline{\alpha}, \underline{\alpha}) = \underline{0} \quad (13.2)$$

for all \underline{F} , θ , and $\underline{\alpha}$. Thus, even if $(\underline{F}, \theta, \underline{\alpha})$ is not an equilibrium state, the presence of $-\underline{1}$ in \mathcal{S} implies that the heat flux \underline{q} vanishes when $\text{grad } \theta$ vanishes.

We shall not discuss here the symmetry groups appropriate to the various types of solids. The interested reader will have little

difficulty in extending to our present subject the known theory of symmetry in finite elastic deformations.⁴² However, since the theory of

⁴²For some pertinent results in that theory see the articles of Smith and Rivlin⁴³ and Coleman and Noll⁴⁴.

⁴³G. F. Smith and R. S. Rivlin, Trans. Am. Math. Soc. 88, 175 (1958).

⁴⁴B. D. Coleman and W. Noll, Arch. Rational Mech. Anal. 15, 87 (1964).

gases with internal molecular relaxation forms an important special case of our present theory, we shall give the reduced forms taken by our general constitutive equations when the material under consideration is a fluid.

We say that a material is a fluid if its symmetry group \mathcal{S} is the group \mathcal{U} of all unimodular tensors. The property of being a fluid is intrinsic to the material in the sense that $\mathcal{S} = \mathcal{U}$ for one reference configuration only if $\mathcal{S} = \mathcal{U}$ for all reference configurations. Assuming that the internal state variables α_i obey the "scalar-transformation rule" (12.2) under changes of frame, and using arguments now familiar in continuum mechanics, one can easily show that for a fluid the following representation formulae must hold for the response functions occurring

in the identities (12.3) and (13.1):

$$\psi = \hat{\hat{\psi}}(v, \theta, \alpha), \quad (13.3)$$

$$\eta = \hat{\hat{\eta}}(v, \theta, \alpha), \quad (13.4)$$

$$\tilde{T} = -p\tilde{1}, \quad p = \hat{\hat{p}}(v, \theta, \alpha), \quad (13.5)$$

$$\tilde{q} = -\kappa g, \quad \kappa = \hat{\hat{\kappa}}(v, \theta, g, \alpha), \quad (13.6)$$

$$\tilde{\alpha} = \hat{\hat{f}}(v, \theta, g, \alpha). \quad (13.7)$$

Here $v = 1/\rho$ is the specific volume, $g = \sqrt{g \cdot g}$ is the magnitude of grad θ ; $\hat{\hat{\psi}}$, $\hat{\hat{\eta}}$, $\hat{\hat{p}}$, $\hat{\hat{\kappa}}$, and the components $\hat{\hat{f}}_i$ of $\hat{\hat{f}}$ are all scalar-valued response functions; p and κ are called, respectively, the pressure and the thermal conductivity. It follows from (13.3)-(13.5) that for fluids the entropy relation (5.16) and the stress relation (5.18) become

$$\left. \begin{aligned} \eta &= -\partial_{\theta} \hat{\hat{\psi}}(v, \theta, \alpha), \\ p &= -\partial_v \hat{\hat{\psi}}(v, \theta, \alpha). \end{aligned} \right\} \quad (13.8)$$

When it is more convenient to take specific entropy of the fluid, rather than the temperature, as an independent variable, we have

$$\left. \begin{aligned} \epsilon &= \tilde{\tilde{\epsilon}}(v, \eta, \alpha), \\ \theta &= \tilde{\tilde{\theta}}(v, \eta, \alpha) = \partial_{\eta} \tilde{\tilde{\epsilon}}(v, \eta, \alpha), \\ p &= \tilde{\tilde{p}}(v, \eta, \alpha) = -\partial_v \tilde{\tilde{\epsilon}}(v, \eta, \alpha), \end{aligned} \right\} \quad (13.9)$$

and when the specific internal energy is the preferred independent variable

$$\left. \begin{aligned} \eta &= \bar{\eta}(v, \epsilon, \alpha), \\ \theta &= \bar{\theta}(v, \epsilon, \alpha) = [\partial_{\epsilon} \bar{\eta}(v, \epsilon, \alpha)]^{-1}, \\ p &= \bar{p}(v, \epsilon, \alpha) = \theta \partial_v \bar{\eta}(v, \epsilon, \alpha). \end{aligned} \right\} \quad (13.10)$$

It is clear that for fluids all the remarks we made about stability in Sections 6-10, remain valid if the modifier "at constant strain" is replaced by "at constant volume"; i.e. if the condition that \underline{F} be constant is replaced by the weaker condition that v be constant.

Equation (13.5)₁ asserts that, under the assumption that each α_i transforms as ^a scalar upon changes of frame, for a fluid the stress is always a hydrostatic pressure. This observation, when combined with the comments made at the end of Section 12, suggests that the present theory lacks the breadth of applications enjoyed by the theory of the thermodynamics of materials with fading memory¹⁵. In that theory a fluid out of equilibrium can exhibit shearing stresses. It should not, however, be concluded that the present theory is a trivial special case of the theory of reference 15. Three reasons for this are the following: (a) The materials we consider here need not obey the principle of fading memory; in fact, that principle follows from our present assumptions only after the addition of very strong stability assumptions for the differential equation (4.5). (b) Since \underline{g}

appears in (4.5), for the materials we consider here the past history of \underline{g} may influence the stress. (c) Those special materials which are covered by both the present theory and the fading memory theory can be described in the present theory with a mathematical language that is somewhat simpler and which, at the present time, appears closer to kinetic theory interpretations; (a good example of such a special case is given in our concluding section).

It is clear that by adding $\dot{\underline{F}}$ to the set $(\underline{F}, \theta, \underline{g}, \underline{\alpha})$ of independent variables used in (4.1)-(4.5), one can generalize our present development so as to obtain a theory in which fluids exhibit shearing stresses and in which $\underline{\alpha}$ can be a string of tensors of arbitrary tensorial rank under changes of frame.⁴⁵ However, such a theory, since it would mix two

⁴⁵A simple and particularly elegant special case of a fluid of this type, with the internal state vector $\underline{\alpha}$ transforming as a spatial position vector, has been studied by J. L. Ericksen, *Kolloid-Zeitschrift* 173, 117 (1960).

distinct but specialized concepts of internal dissipation, would lack both ^{the} simplicity of the present theory and the breadth of the general theory of materials with fading memory.

14. IDEAL GASES WITH VIBRATIONAL RELAXATION

We here illustrate our theory with a simple special case: a dilute non-dissociating diatomic gas which, although it does not conduct heat and obeys the ideal gas law in the form

$$pv = R\theta, \quad (14.1)$$

with R a constant, can, nonetheless, exhibit dissipative phenomena due to the finite time required for the transfer of molecular motion from the translational mode, where it contributes to the pressure, to the vibrational mode, where it does not. To place this familiar theory in our present framework, we first assume that the entropy of the gas can be written in the form

$$\eta = \bar{\eta}_A(v, \epsilon_A) + \bar{\eta}_V(\alpha) = \bar{\eta}(v, \epsilon, \alpha) \quad (14.2)$$

with

$$\epsilon = \epsilon_A + \alpha; \quad (14.3)$$

α is called the vibrational energy, ϵ_A is called the active mode energy,⁴⁶ the value η_V of $\bar{\eta}_V$ is called the vibrational entropy, and the

⁴⁶Or, at length, "the specific internal energy of the active mode".

value η_A of $\bar{\eta}_A$ is called the active mode entropy. The number

$$\theta_A = \left[\partial_{\epsilon_A} \bar{\eta}_A(v, \epsilon_A) \right]^{-1} \quad (14.4)$$

is the translational (or active mode) temperature, while

$$\theta_V = [\partial_{\alpha} \bar{n}_V(\alpha)]^{-1} \stackrel{\text{def}}{=} \bar{\theta}_V(\alpha) \quad (14.5)$$

is the vibrational temperature. We now add the usual assumption that α obeys a scalar differential equation of the type (13.7) with \hat{f} independent of g and linear in α :⁴⁷

⁴⁷This hypothesis, which differs only slightly from a postulate studied by Herzfeld and Rice¹⁰ in 1928, has been discussed by Rutgers⁴⁸, Knesser⁴⁹, Landau and Teller⁵⁰, Bethe and Teller⁵, Rubin and Shuler⁵¹, Montroll and Shuler⁵², and others. The studies of Rubin and Shuler⁵¹ and Montroll and Shuler⁵² indicate that since (14.6) holds precisely for a harmonic oscillator model, it should hold near to equilibrium for more general models. Cf. Vincenti and Kruger⁵³.

⁴⁸A. J. Rutgers, Ann. Physik 16, 350 (1933).

⁴⁹H. O. Knesser, Ann. Physik 16, 360 (1933).

⁵⁰L. Landau and E. Teller, Physik. Z. Sowjetunion 10, 34 (1936).

⁵¹R. J. Rubin and K. E. Shuler, J. Chem. Phys. 25, 59 (1956).

⁵²E. W. Montroll and K. E. Shuler, J. Chem. Phys. 26, 454 (1956).

⁵³W. G. Vincenti and C. H. Kruger, Introduction to Classical Gas Dynamics (John Wiley, New York, 1965), Chapter VII.

$$\dot{\alpha} = A(v, \theta) - B(v, \theta)\alpha. \quad (14.6)$$

If we assume that the temperature θ obeys a constitutive equation of the form $\theta = \bar{\theta}(v, \epsilon, \alpha)$, then the present theory based on the constitutive relations (14.1), (14.2), (14.3), and (14.6) clearly falls as a special case of the theory of fluids obeying (13.3)-(13.10). [Of course, here the internal state vector α has just the one component α .] We may therefore conclude from (13.10)_{2&3}, (14.2), (14.3), and (14.4) that

$$p = \theta \partial_v \bar{\eta}_A(v, \epsilon_A), \quad (14.7)$$

$$\theta = \theta_A. \quad (14.8)$$

Thus in this theory "the temperature" θ must be identified with the translational temperature θ_A . This fact has already been established in a much more general context; indeed, (14.8) is an immediate consequence of the remark containing (11.7). We may conclude from the theorem following (11.9) that in a stable equilibrium state the vibrational temperature θ_v is equal to the translational temperature θ .

Noting that (14.1) and (14.7) imply the partial differential equation

$$v \partial_v \bar{\eta}_A(v, \epsilon_A) = R, \quad (14.9)$$

we see that $\bar{\eta}_A$ must have the special form

$$\eta_A = R \ln v + h(\epsilon_A). \quad (14.10)$$

Assuming that h is smoothly invertible, we can write (14.10) in the form

$$\epsilon_A = \omega_A(v e^{-\eta_A/R}) = \omega_A\left(v \exp\left\{\frac{[\eta - \bar{\eta}_V(\alpha)]}{R}\right\}\right) \stackrel{\text{def}}{=} \tilde{\epsilon}(v, \eta, \alpha) - \alpha. \quad (14.11)$$

It follows from (13.9)₂ and (14.11) that

$$\theta = -\frac{1}{R} \omega'_A(v e^{-\eta_A/R}) v e^{-\eta_A/R} \quad (14.12)$$

with the prime indicating the derivative; hence θ is a function of only $v e^{-\eta_A/R}$. Assuming that this function is invertible, we may solve (14.12) for $v e^{-\eta_A/R}$ in terms of θ and write (14.11) in the form

$$\epsilon_A = \hat{\epsilon}_A(\theta). \quad (14.13)$$

Thus, the active-mode energy is here a function of the translational temperature alone.

We now add the natural assumptions that α is always positive and that the differential equation (14.6) obeys the stability postulate discussed in Section 10. These assumptions imply that (14.6) can be written in the form

$$\dot{\alpha} = k(v, \theta)(l(v, \theta) - \alpha), \quad (14.14)$$

with the functions k and l positive. Furthermore, the function l in (14.14) here plays the role of the equilibrium response function \hat{Q}^* in (6.17): For each pair (v^*, θ^*) the vibrational energy α^* given by

$$\alpha^* = l(v^*, \theta^*) \quad (14.15)$$

makes $(v^*, \theta^*, \alpha^*)$ an equilibrium state.

Let us now assume that for each α and v we can find a θ such that $\alpha = l(v, \theta)$. It is then a direct consequence of the theorem following (11.16) that for each fixed v the function $\bar{\theta}_v$ defined in (14.5) is the inverse of the function $l(v, \cdot)$. Hence $l(v, \theta)$ must be independent of v ,

$$l(v, \theta) = l(\theta), \quad (14.16)$$

and

$$\theta_v = \bar{l}^{-1}(\alpha), \quad \text{i.e. } \bar{\theta}_v \equiv \bar{l}^{-1}, \quad (14.17)$$

with the function \bar{l}^{-1} the inverse of l .

Equations (14.3), (14.13), (14.15), and (14.16) imply that the value ϵ^* of the specific internal energy of the gas when it is in equilibrium with temperature θ^* and specific volume v^* is independent of v^* ; in fact,

$$\epsilon^* = \hat{\epsilon}_A(\theta^*) + l(\theta^*). \quad (14.18)^{54}$$

⁵⁴Since the equilibrium pressure p^* is just $R\theta^*/v^*$, to prove that ϵ^* is a function of θ^* alone we could have used an argument similar to that giving us (4.13). In this instance the proof would proceed exactly as it does for an ideal gas without relaxation effects, in which context the proof is spelled out in detail by R. Courant and K. O. Friedrichs, Supersonic Flow and Shock Waves (Interscience, New York, 1948) pp. 8 and 9.

In view of (14.16), we can write (14.14) in the form

$$\dot{\alpha} = k(v, \theta) (\ell(\theta) - \alpha), \quad (14.19)$$

where

$$k(v, \theta) > 0, \quad \ell(\theta) > 0. \quad (14.20)$$

Since there is a one-to-one relation between θ_V and α , the differential equation (14.19) may be regarded as an evolution equation for θ_V . In fact if we put

$$c_V(\theta_V) \stackrel{\text{def}}{=} \frac{d\ell(\theta_V)}{d\theta_V}, \quad (14.21)$$

then (14.17) and (14.19) yield

$$\dot{\theta}_V = \frac{k(v, \theta)}{c_V(\theta_V)} (\ell(\theta) - \ell(\theta_V)). \quad (14.22)$$

The value of the function c_V is called the vibrational heat capacity, for, by (14.17) and (4.21), $c_V(\theta_V)$ is the rate of change of the vibrational energy α with the vibrational temperature θ_V .

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13. ABSTRACT This is a study of the thermodynamics of nonlinear materials with internal state variables whose temporal evolution is governed by ordinary differential equations. After employing a method developed by Coleman and Noll to find the general restrictions which the Clausius-Duhem inequality places on response functions, we analyze various types of dynamical stability that can be exhibited by solutions of the internal evolution equations. We also discuss integral dissipation inequalities, conditions under which temperatures can be associated with internal states, and the forms taken by response functions when the material is a fluid.		

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