

CONSIDER THE GOVERNING EQUATIONS OF THERMOMECHANICS (EULERIAN)

$$1) \quad \frac{\partial \rho}{\partial t} + (\rho v_i)_{,i} = 0 \quad \text{CONSERVATION OF MASS (CONTINUITY)}$$

$$2) \quad \sigma_{ji,j} + \rho b_i = \rho \dot{v}_i \quad \text{CONSERVATION OF LINEAR MOMENTUM}$$

$$3) \quad \rho \dot{u} = \sigma_{ij} D_{ij} + \rho r - q_{i,i} \quad \text{CONSERVATION OF ENERGY (1ST LAW OF THERMODYNAMICS)}$$

$$4) \quad \rho \dot{\theta} - \frac{\rho r}{\theta} + \left(\frac{q_i}{\theta}\right)_{,i} \geq 0 \quad \text{CLAUSIUS-DUHEM INEQUALITY (2ND LAW OF THERMODYNAMICS)}$$

PLUS

$$5) \quad \sigma_{ij} = \sigma_{ji} \quad \text{CONSERVATION OF ANGULAR MOMENTUM}$$

$$6) \quad D_{ij} = \frac{1}{2} (v_{i,j} + v_{j,i}) \quad \text{RATE OF DEFORMATION TENSOR (OR STRAIN DISPLACEMENT RELATIONS)}$$

IMPORTANT: ASSUMING THAT THE BODY FORCE (b_i) AND SPECIFIC HEAT SUPPLY (r) ARE KNOWN, THE FIRST THREE CONSERVATION LAWS REPRESENT FIVE EQUATIONS IN 14 UNKNOWNNS ($\overset{1}{\rho}, \overset{3}{v_i}, \overset{6}{\sigma_{ij}}, \overset{1}{u}, \overset{3}{q_i}$). CONSIDERATION OF THE C-D INEQUALITY INTRODUCES TWO MORE UNKNOWNNS (θ, θ), BUT THE 2ND LAW OF THERMODYNAMICS MAY ONLY BE USED TO SOLVE FOR UNKNOWNNS FOR REVERSIBLE (NON-DISSIPATING) PROCESSES (i.e., WHEN THE EQUALITY HOLDS)

HENCE, THERE ARE A TOTAL OF 16 UNKNOWNNS BUT ONLY FIVE EQUATIONS (1) - (3)

⇒ NEED 11 MORE EQUATIONS

⇒ THESE ARE THE CONSTITUTIVE EQUATIONS.

FUNDAMENTAL RESTRICTIONS ON THE FORMULATIONS OF CONSTITUTIVE LAWS

1) PHYSICAL ADMISSIBILITY: ALL CONSTITUTIVE EQUATIONS MUST BE CONSISTENT WITH:

- i) CONSERVATION OF MASS
- ii) CONSERVATION OF LINEAR AND ANGULAR MOMENTUM
- iii) CONSERVATION OF ENERGY
- iv) 2ND LAW OF THERMODYNAMICS
- v) EXPERIMENTAL OBSERVATIONS \Rightarrow MOST IMPORTANT

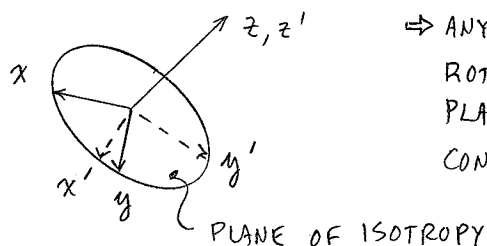
2) PRINCIPLE OF LOCAL ACTION: ONLY THE DEFORMATION WITHIN AN INFINITESIMAL NEIGHBORHOOD OF THE POINT \underline{x} AFFECTS THE MATERIAL BEHAVIOR AT \underline{x} .

3) PRINCIPLE OF EQUIPRESENCE: A STATE VARIABLE ASSUMED TO BE PRESENT IN ONE CONSTITUTIVE EQUATION OF A MATERIAL SHOULD BE SO PRESENT IN ALL, UNLESS ITS PRESENCE IS IN DIRECT CONTRADICTION WITH THE ASSUMED SYMMETRY OF THE MATERIAL, THE PRINCIPLE OF MATERIAL OBJECTIVITY, OR THE LAWS OF THERMODYNAMICS.

\Rightarrow WEAK RESTRICTION, OFTEN VIOLATED

4) MATERIAL SYMMETRY: THE CONSTITUTIVE EQUATIONS MUST BE FORM-INVARIANT WITH RESPECT TO COORDINATE TRANSFORMATIONS COMPRISING THE SYMMETRY (GROUP OR CLASS OF THE MATERIAL) (VERY IMPORTANT)

EXAMPLE: TRANSVERSELY ISOTROPIC MATERIAL



\Rightarrow ANY CHANGE OF COORDINATES THAT CONSISTS OF A ROTATION ABOUT THE AXIS PERPENDICULAR TO THE PLANE OF ISOTROPY, RESULTS IN NO CHANGE IN CONSTITUTIVE EQUATIONS.

The surface integral on the right-hand side can be converted into a volume integral by using the divergence theorem to give

$$\frac{d}{dt} \int_v \rho s \, dv \geq \int_v \left[\frac{\rho r}{\theta} - \nabla_x \cdot \left(\frac{\mathbf{q}}{\theta} \right) \right] dv \quad (3.64)$$

Since the choice of the volume v is arbitrary, we derive the following differential version of the Clausius-Duhem inequality

$$\frac{ds}{dt} \geq \frac{r}{\theta} - \frac{1}{\rho} \nabla_x \cdot \left(\frac{\mathbf{q}}{\theta} \right) \quad (3.65)$$

or

$$\frac{ds}{dt} - \frac{r}{\theta} + \frac{1}{\rho\theta} \nabla_x \cdot \mathbf{q} - \frac{\mathbf{q}}{\rho\theta^2} \cdot \text{grad } \theta \geq 0 \quad (3.66)$$

In terms of components, we have

$$\frac{ds}{dt} - \frac{r}{\theta} + \frac{1}{\rho\theta} q_{i,i} - \frac{1}{\rho\theta^2} q_i \theta_{,i} \geq 0 \quad (3.67)$$

or, elimination of r by using Eq. (3.58) gives

$$\rho\theta\dot{s} - \rho\dot{u} + \sigma_{ij} D_{ji} - \frac{1}{\theta} q_i \theta_{,i} \geq 0 \quad (3.68)$$

Again, the inequality implies an irreversible process and the equality represents a reversible process. By distinguishing the irreversible and reversible processes, the directional characteristics of the energy transformation can be clearly described by the second law of thermodynamics.

In thermodynamics the internal energy u , entropy s , heat flux \mathbf{q} , and the Cauchy stress $\boldsymbol{\sigma}$ are all considered state functions that can be determined by the state variables. The formulas that relate the state functions to the state variables are called *state equations* or *constitutive equations*. From a purely mechanical consideration, the only constitutive equation is that for the Cauchy stress $\boldsymbol{\sigma}$ or Piola-Kirchhoff stress $\boldsymbol{\Sigma}$.

For thermoelasticity one can expect that the state variables would be the deformation gradient \mathbf{F} and the temperature θ since here u , s , \mathbf{q} , and $\boldsymbol{\sigma}$ are determined completely by their current values. Thus, for an ideal thermoelastic behavior,

$$\begin{aligned} u &= u(\mathbf{F}, \theta), & s &= s(\mathbf{F}, \theta) \\ \mathbf{q} &= \mathbf{q}(\mathbf{F}, \theta), & \boldsymbol{\sigma} &= \boldsymbol{\sigma}(\mathbf{F}, \theta) \end{aligned} \quad (3.69)$$

The situation becomes much more complex if the deformation is inelastic. For example, the stress of a plastically deformed solid cannot be determined by the current value of deformation \mathbf{F} only. The history of the deformation is also necessary. Simple state equations or constitutive equations, such as Eq. (3.69), cannot describe correctly the plastic deformation of solids. If u , s , \mathbf{q} , and $\boldsymbol{\sigma}$ are assumed to be state functions, we face two fundamental problems. First, we have to find or specify the set of all state variables. For example, it is necessary to know for a plastically deformed solid what other variables are needed to uniquely describe the current state. As pointed out previously, knowing only \mathbf{F} and θ will be insufficient to characterize a state in the case of plastic deformation of solids, although they are adequate for thermoelastic materials. It is very hard to enumerate all the relevant state variables from macroscopic observations alone; microscopic deformation considerations and some assumptions have to be made to use certain macroscopic observable variable(s) as the representative(s) of the microscopic phenomena. Second the mathematical forms of the constitutive equations should be determined after the state variables are chosen. This involves the experimental evaluation and mathematical formalization. At times severe experimental or mathematical difficulties may arise during this process. In recent years great efforts have been made to study the constitutive equation for various materials under different loading conditions, as described in this book.

To solve the problem of specifying state variables, two different methods are usually adopted. The first method ignores the problem of state variables and assumes that u , s , \mathbf{q} , and $\boldsymbol{\sigma}$ are determined by the histories of \mathbf{F} and θ , and not by their current values only (Coleman 1964). Therefore these quantities should be expressed as the functional, not functions, of \mathbf{F} and θ . The second method introduces the concept of internal (or hidden) variables. In this method it is postulated that the current state of an inelastically deformed solid can be determined by the current values of \mathbf{F} , θ as well as a set of internal variables. The history of the deformation is indirectly included in the evolution of these internal variables. The material response will be different if the values of the internal variables are different even though \mathbf{F} , θ are the same. We state this mathematically as

$$\begin{aligned} u &= u(\mathbf{F}, \theta, \alpha_i) \\ s &= s(\mathbf{F}, \theta, \alpha_i) \\ \mathbf{q} &= \mathbf{q}(\mathbf{F}, \theta, \alpha_i) \\ \boldsymbol{\sigma} &= \boldsymbol{\sigma}(\mathbf{F}, \theta, \alpha_i) \end{aligned} \tag{3.70}$$

where α_i , $i = 1, 2, \dots, n$, are a set of n internal variables including mechanical, or thermal, or even electrical state variables. These variables can be scalars, vectors, or tensors, although they are all denoted by scalar symbols

here. The specific physical meaning for each internal variable and the actual number n need to be chosen and identified for different materials and different conditions. Different choices result in different models, which will be discussed in the subsequent chapters. It should be pointed out here that, instead of using θ as the state variable and s as the state function, it is quite common in the literature to find s used as the state variable and θ as the state function. For example,

$$u = u(\mathbf{F}, s, \alpha_i) \quad (3.71)$$

Similarly one can write θ , \mathbf{q} , and $\boldsymbol{\alpha}$ as functions of \mathbf{F} , s , and α_i .

In closing this section, we introduce another thermodynamic potential ψ called Helmholtz free energy:

$$\psi = u - s\theta \quad (3.72)$$

Note that $\dot{u} = \dot{\psi} + \dot{s}\theta + s\dot{\theta}$; thus Eq. (3.68) is rewritten as

$$-\rho\dot{\psi} - \rho\eta\dot{\theta} + \sigma_{ij}D_{ji} + \frac{1}{\theta}q_i\theta_{,i} \geq 0 \quad (3.73)$$

3.6 PRINCIPLE OF MATERIAL OBJECTIVITY OR FRAME INDIFFERENCE

Truesdell and Noll (1965) postulated three fundamental principles for a purely mechanical constitutive equation. These are (1) principle of determination for stress, (2) principle of local action, and (3) principle of material frame indifference. The first principle simply states that the stress in a body is determined by the history of the motion of that body. The principle of local action is that in determining the stress at a given particle, the motion outside an arbitrarily small neighborhood of it may be disregarded. These two principles are self-explanatory. We are more interested in the third principle, since it introduces the concept of objectivity that is significant when we consider the finite plasticity theory.

The detailed and rigorous treatment of the frame indifference principle can be found in any advance continuum mechanics book. Here we only present this principle and discuss various quantities under the change of frame of reference.

According to the principle of material frame indifference constitutive equations must be invariant under changes of reference frame. The change of a time-space reference is given by

$$x^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{x} \quad (3.74)$$

Internal variables

For dissipative phenomena, the current state also depends on the past history which is represented, in the method of local state, by the values at each instant of other variables called internal variables.

Plasticity and viscoplasticity require the introduction of the plastic (or viscoplastic) strain as a variable. For small strains, the plastic strain ϵ^p is the permanent strain associated with the relaxed configuration. This configuration is obtained by 'elastic unloading', leading to the additive strain decomposition:

$$\epsilon = \epsilon^p + \epsilon^e.$$

The two internal variables related to the above decomposition may formally be defined as: the plastic strain ϵ^p , and the thermoelastic strain ϵ^e (including, as well, the possibility of thermal dilatation).

Other phenomena such as hardening, damage, fracture, require the introduction of other internal variables of a less obvious nature. These represent the internal state of matter (density of dislocations, crystalline microstructure, configuration of microcracks and cavities, etc.) and there are no means of measuring them by direct observation. They do not appear explicitly either in the conservation laws or in the statement of the second principle of thermodynamics. They are called internal variables, but in fact, they are state variables which will be treated as observable ones.

There is no objective way of choosing the nature of the internal variables best suited to the study of a phenomenon. The choice is dictated by experience, physical feeling and very often by the type of application. They will be defined in the different chapters as the need arises. For their general study, they will be denoted by $V_1, V_2, \dots, V_k, \dots$; V_k representing either a scalar or a tensorial variable.

2.4.2 *Thermodynamic potential, state laws*

Once the state variables have been defined, we postulate the existence of a thermodynamic potential from which the state laws can be derived. Without entering into the details, let us say that the specification of a function with a scalar value, concave with respect to T , and convex with respect to other variables, allows us to satisfy *a priori* the conditions of thermodynamic stability imposed by the inequalities that can be derived from the second principle. It is possible to work in an equivalent way with different potentials. Here we choose the free specific energy potential Ψ ,

which depends on observable state variables and internal variables:

$$\Psi = \Psi(\epsilon, T, \epsilon^e, \epsilon^p, V_k).$$

In elastoplasticity (or viscoplasticity) the strains appear only in the form of their additive decomposition $\epsilon - \epsilon^p = \epsilon^e$, so that:

$$\Psi = \Psi((\epsilon - \epsilon^p), T, V_k) = \Psi(\epsilon^e, T, V_k)$$

which shows that:

$$\partial\Psi/\partial\epsilon^e = \partial\Psi/\partial\epsilon = -\partial\Psi/\partial\epsilon^p.$$

We now use the Clausius–Duhem inequality with:

$$\dot{\Psi} = \frac{\partial\Psi}{\partial\epsilon^e} : \dot{\epsilon}^e + \frac{\partial\Psi}{\partial T} \dot{T} + \frac{\partial\Psi}{\partial V_k} \dot{V}_k.$$

to obtain:

$$\left(\sigma - \rho \frac{\partial\Psi}{\partial\epsilon^e} \right) : \dot{\epsilon}^e + \sigma : \dot{\epsilon}^p - \rho \left(s + \frac{\partial\Psi}{\partial T} \right) \dot{T} - \rho \frac{\partial\Psi}{\partial V_k} \dot{V}_k - \frac{\bar{q}}{T} \cdot \overrightarrow{\text{grad}} T \geq 0.$$

A classical hypothesis permits us to cancel some terms in this inequality independently. We may imagine, first of all, an elastic deformation taking place at constant ($\dot{T} = 0$) and uniform ($\overrightarrow{\text{grad}} T = 0$) temperature which alters neither the plastic strain ($\dot{\epsilon}^p = 0$) nor the internal variables ($\dot{V}_k = 0$). For this to happen, it is necessary to consider that the elastic deformations can occur at a time scale higher than those which would question the validity of the hypothesis of local state, and lower than those of dissipative phenomena. Since the Clausius–Duhem inequality holds regardless of any particular $\dot{\epsilon}^e$, it necessarily follows that:

$$\sigma - \rho(\partial\Psi/\partial\epsilon^e) = 0.$$

Assuming this equality to hold, we now imagine a thermal deformation in which $\dot{\epsilon}^p = 0$, $\dot{V}_k = 0$, $\overrightarrow{\text{grad}} T = 0$. Then, since T is arbitrary, it follows that:

$$s + \partial\Psi/\partial T = 0.$$

These expressions define the thermoelastic laws:

- $\sigma = \rho(\partial\Psi/\partial\epsilon^e),$
- $s = -\partial\Psi/\partial T.$

We note that:

$$\sigma = \rho(\partial\Psi/\partial\epsilon^e) = \rho(\partial\Psi/\partial\epsilon) = -\rho(\partial\Psi/\partial\epsilon^p)$$

which shows that the stress is a variable associated with the elastic strain, with the total strain, and with the plastic strain (with a minus sign).

In an analogous manner, we define the thermodynamic forces associated with the internal variables by:

$$A_k = \rho(\partial\Psi/\partial V_k).$$

These relations constitute the state laws:

the entropy s and the stress tensor σ having been defined elsewhere, the specification of the thermodynamic potential $\Psi(\varepsilon^e, T, V_k)$ furnishes the coupled or uncoupled theories of thermo-elasticity;

in contrast, the variables A_k associated with the internal variables, which have not yet been introduced, are defined by the specification of the thermodynamic potential $\Psi(\dots, V_k)$;

s, σ and A_1, A_2, \dots, A_k constitute the associated variables. The vector formed by these variables is the gradient of the function Ψ in the space of the variables T, ε^e, V_k . This vector is normal to the surface $\Psi = \text{constant}$.

The associated variables form a set of normal variables in duality with the observable and internal state variables. Table 2.2 summarizes the set of variables introduced in this way.

2.4.3 Dissipation, complementary laws

As we have seen, the thermodynamic potential allows us to write relations between observable state variables and associated variables. However, for internal variables it allows only the definition of their associated variables. In order to describe the dissipation process, mainly the evolution of the internal variables, a complementary formalism is needed. This is precisely the objective of the dissipation potentials.

Intrinsic dissipation, thermal dissipation

Taking into account the state laws and putting $\vec{g} = \overrightarrow{\text{grad}} T$, the Clausius-Duhem inequality can be reduced to express the fact that dissipation is necessarily positive:

$$\bullet \quad \Phi = \sigma : \dot{\varepsilon}^p - A_k \dot{V}_k - \vec{g} \cdot \vec{q} / T \geq 0.$$

We note that Φ is a sum of the products of the force variables or dual

Method of local state

Table 2.2. Thermodynamic variables

State variables		
Observable	Internal	Associated variables
ε		σ
T		s
	ε^e	σ
	ε^p	$-\sigma$
	V_k	A_k

variables σ, A_k, \vec{g} with the respective flux variables $\dot{\varepsilon}^p, -\dot{V}_k, -\vec{q}/T$. The sum of the first two terms:

$$\Phi_1 = \sigma : \dot{\varepsilon}^p - A_k \dot{V}_k$$

is called the intrinsic dissipation (or mechanical dissipation). It consists of plastic dissipation plus the dissipation associated with the evolution of the other internal variables; it is generally dissipated by the volume element in the form of heat. The last term:

$$\Phi_2 = -\vec{g} \cdot \vec{q} / T = -\frac{\vec{q}}{T} \cdot \overrightarrow{\text{grad}} T$$

is the thermal dissipation due to the conduction of heat.

Dissipation potential

In order to define the complementary laws related to the dissipation process, we postulate the existence of a dissipation potential (or pseudo-potential) expressed as a continuous and convex scalar valued function of the flux variables, wherein the state variables may appear as parameters:

$$\varphi(\dot{\varepsilon}^p, \dot{V}_k, \vec{q}/T).$$

This potential is a positive convex function with a zero value at the origin of the space of the flux variables, $\dot{\varepsilon}^p, \dot{V}_k, \vec{q}/T$. The complementary laws are then expressed by the normality property (or normal dissipativity):

$$\sigma = \frac{\partial \varphi}{\partial \dot{\varepsilon}^p} \quad A_k = -\frac{\partial \varphi}{\partial \dot{V}_k} \quad \vec{g} = -\frac{\partial \varphi}{\partial (\vec{q}/T)}.$$

The thermodynamic forces are the components of the vector $\overrightarrow{\text{grad}} \varphi$ normal to the $\varphi = \text{constant}$ surfaces in the space of the flux variables.

STATE FUNCTIONS, STATE VARIABLES, AND EQUATIONS OF STATE

THE ENERGY EQUATION (1ST LAW OF THERMODYNAMICS) INVOLVES THE RATE OF CHANGE OF THE SPECIFIC INTERNAL ENERGY, u

$$\rho \dot{u} = \underline{\sigma} : \underline{D} + \rho \tau - \underline{\nabla} \cdot \underline{q} \quad \text{ENERGY EQUATION}$$

HENCE, SPECIFICATION OF THE INTERNAL ENERGY DEFINES THE THERMODYNAMIC STATE AT A POINT IN A CONTINUUM.

$\Rightarrow u$ IS A STATE FUNCTION

e.g., THE SPECIFIC INTERNAL ENERGY CAN BE EXPRESSED AS A FUNCTION OF SPECIFIC ENTROPY (η) AS WELL AS A NUMBER OF SUBSTATE VARIABLES (v_i), i.e.,

$$u = \hat{u}(\eta, v_1, v_2, \dots) = \hat{u}(\eta, v_i) \quad \begin{array}{l} \text{CALORIC EQUATION} \\ \text{OF STATE} \end{array}$$

\Rightarrow SPECIFICATION OF η AND SUBSTATE VARIABLES (v_i) UNIQUELY CHARACTERIZES THE THERMODYNAMIC STATE AT A POINT IN THE CONTINUUM

\Rightarrow SPECIFICATION OF THE FUNCTION $\hat{u}(\eta, v_i)$ DEFINES AN EQUATION OF STATE

$\hat{(\)}$ DENOTES FUNCTION OF ARGUMENTS

HERE,

v_i = SUBSTATE VARIABLES ($i = 1, \dots, n$). n = TOTAL NUMBER
= THERMODYNAMIC "DISPLACEMENT" (GENERALIZED)

\Rightarrow SUBSTATE VARIABLES CAN BE SCALARS, VECTORS, OR HIGHER RANK TENSORS

\Rightarrow IDEALLY SUBSTATE VARIABLES WILL BE OBSERVABLE

- EXAMPLES: KINEMATIC VARIABLES, $\underline{\epsilon}$, \underline{E} , \underline{e} , \underline{F} , \underline{D} , etc.

- NOT ALWAYS POSSIBLE \Rightarrow "INTERNAL STATE VARIABLES"

IMPORTANT: AS THE SPECIFIC ENTROPY INCREASES, THE CHANGE IN SPECIFIC INTERNAL ENERGY MANIFESTS ITSELF AS TEMPERATURE.

DEFINE:

$$\theta \equiv \left. \frac{\partial u}{\partial \eta} \right|_{v_i}$$

THERMODYNAMIC TEMPERATURE

$\Rightarrow \theta, \eta$ ARE THERMODYNAMIC CONJUGATE VARIABLES

- PRODUCT $\theta \eta$ HAS UNITS OF ENERGY (PER UNIT MASS)

ANALOGOUSLY, ONE MAY DEFINE A SET OF THERMODYNAMIC VARIABLES CONJUGATE TO THE SUBSTATE VARIABLES, v_i , I.E.,

$$\gamma_i \equiv \left. \frac{\partial u}{\partial v_i} \right|_{\eta}$$

THERMODYNAMIC "TENSIONS" ($i=1, \dots, n$)

(THERMODYNAMIC "FORCES" CONJUGATE TO THE GENERALIZED DISPLACEMENTS, v_i)

$\Rightarrow \gamma_i, v_i$ ARE THERMODYNAMIC CONJUGATE (WORK CONJUGATE) VARIABLES

- SCALAR PRODUCT: $\gamma_i v_i \dots$ (OR $\underline{\gamma} : \underline{v}$) HAS UNITS OF WORK/ENERGY (PER UNIT MASS); γ_i, v_j ARE OF SAME RANK.

SINCE $u = \hat{u}(\eta, v_i)$, THEN $\theta = \hat{\theta}(\eta, v_i)$ AND $\gamma_i = \hat{\gamma}_i(\eta, v_j)$

WE MAY EXPRESS THE DIFFERENTIAL SPECIFIC INTERNAL ENERGY AS

$$du = \left. \frac{\partial u}{\partial \eta} \right|_{v_i} d\eta + \sum_{i=1}^n \left. \frac{\partial u}{\partial v_i} \right|_{\eta} dv_i \quad (\text{SCALAR})$$

$$= \theta d\eta + \sum_{i=1}^n \gamma_i dv_i = \theta d\eta + \gamma_i dv_i$$

SUMMATION CONVENTION

IN GENERAL, THE RELATIONSHIP FOR THERMODYNAMIC TEMPERATURE $\theta = \tilde{\theta}(\eta, \nu_i)$ MAY BE INVERTED TO DEFINE THE ENTROPY, i.e.,

$$\eta = \hat{\eta}(\theta, \nu_i)$$

EQUATION OF STATE

THEN THE CALORIC EQUATION OF STATE MAY BE EXPRESSED AS

$$u = \hat{u}(\theta, \nu_i)$$

CALORIC EQUATION OF STATE (ALTERNATE FORM)

↳ GENERALIZED "DISPLACEMENTS" - PREFERABLY OBSERVABLE

θ = TEMPERATURE

ν_i = STATE VARIABLE

SIMILARLY, THE THERMODYNAMIC TENSIONS MAY BE EXPRESSED IN TERMS GENERALIZED DISPLACEMENTS θ AND ν_i .

$$\gamma_i = \hat{\gamma}_i(\theta, \nu_j)$$

THERMAL EQUATIONS OF STATE

INVERTING

$$\nu_i = \hat{\nu}_i(\theta, \gamma_j)$$

⇒ THERMAL EQUATIONS OF STATE RESEMBLE STRESS-STRAIN RELATIONS, BUT SOME CAUTION IS REQUIRED IN INTERPRETING THE THERMODYNAMIC TENSIONS (γ_i) AS STRESSES AND SUBSTATE PARAMETERS (ν_i) AS STRAINS.

⇒ EVEN IF THE ν_j CORRESPOND TO ELASTIC STRAINS, THE γ_i MAY DIFFER FROM THE USUAL COMPONENTS OF THE STRESS TENSOR.

IN ADDITION TO THE SPECIFIC INTERNAL ENERGY, OTHER POTENTIAL FUNCTIONS MAY BE USED TO EXPRESS THE PRINCIPLES OF THERMODYNAMICS. THESE INCLUDE:

1) SPECIFIC HELMHOLTZ FREE ENERGY, ψ

$$\psi = u - \eta \theta$$

SPECIFIC HELMHOLTZ FREE ENERGY

$\underbrace{\quad}_{\text{INTERNAL ENERGY}} \quad \underbrace{\quad}_{\text{NON-RECOVERABLE ENERGY}}$

⇒ THE HELMHOLTZ FREE ENERGY CORRESPONDS TO THAT PART OF THE INTERNAL ENERGY AVAILABLE TO DO WORK AT CONSTANT TEMPERATURE

⇒ ψ IS GOOD FOR THE ANALYSIS OF SOLIDS

NOTE: $\eta = - \frac{\partial \psi}{\partial \theta}$ SPECIFIC ENTROPY

2) SPECIFIC ENTHALPY, χ

$$\chi = u - \sum_{i=1}^n \gamma_i \nu_i$$

SPECIFIC ENTHALPY

$\underbrace{\quad}_{\text{SPECIFIC ENERGY ASSOCIATED WITH THERMODYNAMIC TENSIONS}}$

⇒ THE SPECIFIC ENTHALPY CORRESPONDS TO THAT PORTION OF THE INTERNAL ENERGY THAT CAN BE RELEASED AS HEAT WHEN THE THERMODYNAMIC TENSIONS ARE HELD FIXED.

3) GIBBS FREE ENERGY (FREE ENTHALPY)

$$\xi = \chi - \eta\theta = u - \eta\theta - \sum_{i=1}^n \gamma_i v_i$$

SPECIFIC GIBBS FREE ENTHALPY

NOTE: $u - \psi + \xi - \chi = 0$ RELATIONSHIP BETWEEN POTENTIALS

$\Rightarrow \xi$ IS GOOD FOR THE ANALYSIS OF FLUIDS OR OTHER PROCESSES

WHERE THE TEMPERATURE IS CONTROLLED AND THE HYDROSTATIC PRESSURE AND/OR DILATATION IS KNOWN

IN GENERAL, THE FOUR POTENTIALS MAY BE EXPRESSED IN TERMS OF ANY COMBINATION OF (TEMPERATURE OR ENTROPY) AND (SUBSTATE VARIABLES OR THERMODYNAMIC TENSIONS), i.e.,

COMMON FORMULATION

$$\begin{aligned} u &= \hat{u}(\eta, \gamma_i) = \hat{u}(\theta, \gamma_i) = \hat{u}(\theta, v_i) = \hat{u}(\eta, v_i) \\ \psi &= \hat{\psi}(\eta, \gamma_i) = \hat{\psi}(\theta, \gamma_i) = \hat{\psi}(\eta, v_i) = \hat{\psi}(\theta, v_i) \\ \chi &= \hat{\chi}(\theta, \gamma_i) = \hat{\chi}(\eta, v_i) = \hat{\chi}(\theta, v_i) = \hat{\chi}(\eta, \gamma_i) \\ \xi &= \hat{\xi}(\eta, v_i) = \hat{\xi}(\theta, v_i) = \hat{\xi}(\eta, \gamma_i) = \hat{\xi}(\theta, \gamma_i) \end{aligned}$$

ALTHOUGH THE LATTER FORMULATIONS LEAD TO PARTICULARLY CONVENIENT RESULTS.

THE RELATIONSHIPS BETWEEN THERMODYNAMIC POTENTIALS ARE SUMMARIZED BELOW

<u>POTENTIAL</u>	<u>RELATION TO u</u>	<u>INDEPENDENT VARIABLES</u>
INTERNAL ENERGY	u	η, v_i
HELMHOLTZ FREE ENERGY	$\psi = u - \eta\theta$	θ, v_i (SOLIDS)
ENTHALPY	$\chi = u - \gamma_i v_i$	η, γ_i
FREE ENTHALPY, OR GIBBS FUNCTION	$\xi = u - \eta\theta - \gamma_i v_i$ $= \chi - \eta\theta$	θ, γ_i (FLUIDS)

THE PRECEDING FOUR POTENTIALS CORRESPOND TO EQUATIONS OF STATE. THE DIFFERENTIAL INCREMENTS IN THE STATE FUNCTIONS (u, ψ, χ, ξ) MAY BE EXPRESSED AS

$$u = \hat{u}(\eta, \nu_j) \quad \Rightarrow \quad du = \theta d\eta + \gamma_j d\nu_j$$

$$\psi = \hat{\psi}(\theta, \nu_j) = u - \eta\theta \quad \Rightarrow \quad d\psi = -\eta d\theta + \gamma_j d\nu_j$$

$$\chi = \hat{\chi}(\eta, \gamma_j) = u - \gamma_j \nu_j \quad \Rightarrow \quad d\chi = \theta d\eta - \nu_j d\gamma_j$$

$$\begin{aligned} \xi = \hat{\xi}(\theta, \gamma_j) &= \chi - \eta\theta \quad \Rightarrow \quad d\xi = -\eta d\theta - \nu_j d\gamma_j \\ &= u - \eta\theta - \gamma_j \nu_j \end{aligned}$$

CLEARLY THE RELATIONSHIP BETWEEN THERMODYNAMIC "DISPLACEMENTS" (θ, ν_j) AND THERMODYNAMIC "FORCES" (η, γ_j) MAY BE EXPRESSED AS

$$\theta = \left. \frac{\partial u}{\partial \eta} \right|_{\nu_j} \quad \gamma_j = \left. \frac{\partial u}{\partial \nu_j} \right|_{\eta} \quad \text{FROM } du = \theta d\eta + \gamma_j d\nu_j$$

$$\eta = - \left. \frac{\partial \psi}{\partial \theta} \right|_{\nu_j} \quad \gamma_j = \left. \frac{\partial \psi}{\partial \nu_j} \right|_{\theta} \quad \text{FROM } d\psi = -\eta d\theta + \gamma_j d\nu_j$$

$$\theta = \left. \frac{\partial \chi}{\partial \eta} \right|_{\gamma_j} \quad \nu_j = - \left. \frac{\partial \chi}{\partial \gamma_j} \right|_{\eta} \quad \text{FROM } d\chi = \theta d\eta - \nu_j d\gamma_j$$

$$\eta = - \left. \frac{\partial \xi}{\partial \theta} \right|_{\gamma_j} \quad \nu_j = - \left. \frac{\partial \xi}{\partial \gamma_j} \right|_{\theta} \quad \text{FROM } d\xi = -\eta d\theta - \nu_j d\gamma_j$$

NOTE: THE SPECIFIC INTERNAL ENERGY, u , IS REQUIRED FOR THE ENERGY EQUATION. FOR SOLIDS SPECIFICATION OF THE HELMHOLTZ FREE ENERGY, ψ , AND SPECIFIC ENTROPY, η , LEADS TO THE SPECIFIC INTERNAL ENERGY $u = \psi + \theta\eta$.

⇒ WE MAY INTRODUCE ψ AS A STATE FUNCTION PROVIDED THAT THE CONSTITUTIVE LAW FOR η SATISFIES THE 2ND LAW OF THERMODYNAMICS

ONE MAY EXPRESS BOTH THE 1ST LAW OF THERMODYNAMICS (ENERGY EQUATION) AND 2ND LAW OF THERMODYNAMICS (C-D INEQUALITY) IN TERMS OF THE HELMHOLTZ FREE ENERGY.

RECALL

$$\rho \dot{u} = \underline{\underline{\sigma}} : \underline{\underline{D}} + \rho r - \underline{\underline{\nabla}} \cdot \underline{\underline{q}} \quad \text{ENERGY EQUATION}$$

OR
AND

$$\rho r - \underline{\underline{\nabla}} \cdot \underline{\underline{q}} = \rho \dot{u} - \underline{\underline{\sigma}} : \underline{\underline{D}}$$

$$\rho \theta \dot{\eta} - \rho r + \underline{\underline{\nabla}} \cdot \underline{\underline{q}} - \frac{1}{\theta} \underline{\underline{q}} \cdot \underline{\underline{\nabla}} \theta \geq 0 \quad \text{C-D INEQUALITY}$$

SUBSTITUTE THE ENERGY EQUATION INTO THE C-D INEQUALITY

$$\rho \theta \dot{\eta} - \rho \dot{u} + \underline{\underline{\sigma}} : \underline{\underline{D}} - \frac{1}{\theta} \underline{\underline{q}} \cdot \underline{\underline{\nabla}} \theta \geq 0$$

$$\text{BUT } \dot{\psi} = \dot{u} - \theta \dot{\eta} - \dot{\theta} \eta \Rightarrow \theta \dot{\eta} - \dot{u} = -\dot{\psi} - \dot{\theta} \eta$$

$$\therefore \boxed{-\rho \dot{\psi} - \rho \dot{\theta} \eta + \underline{\underline{\sigma}} : \underline{\underline{D}} - \frac{1}{\theta} \underline{\underline{q}} \cdot \underline{\underline{\nabla}} \theta \geq 0}$$

INTERNAL DISSIPATION

DISSIPATION DUE TO
HEAT CONDUCTION

LOCAL DISSIPATION

INEQUALITY (C-D INEQUALITY

CAST IN TERMS OF ψ)

* ERROR IN EQUATION
5.8-20 IN MASE

ANALOGOUSLY, FOR FLUIDS SPECIFICATION OF THE SPECIFIC ENTHALPY, $h = u + \gamma_i u_i$, OR SPECIFIC FREE ENTHALPY, $\xi = h - \theta$, LEADS TO THE SPECIFIC INTERNAL ENERGY, u .

ALTERNATIVELY, FOR MANY FLUIDS THERE IS A DIRECT RELATIONSHIP BETWEEN THE SPECIFIC INTERNAL ENERGY (u) AND ENTHALPY (h) INVOLVING THERMODYNAMIC PRESSURE (p), DENSITY (ρ), AND TEMPERATURE (θ). IT IS THEN POSSIBLE TO EXPRESS THE CALORIC EQUATION OF STATE IN TERMS OF TEMPERATURE AND DENSITY, I.E.,

$$u = \hat{u}(\theta, \nu_i) = \hat{u}(\theta, \rho) \quad \text{CALORIC EQUATION OF STATE}$$

IT IS THEN POSSIBLE TO DEFINE A THERMAL EQUATION OF STATE

$$\gamma_i = \hat{\gamma}_i(\theta, \nu_i) = \hat{\gamma}_i(\theta, \rho) \quad \text{THERMAL EQUATION OF STATE}$$

WHERE THE THERMODYNAMIC TENSION (γ_i) CORRESPONDS TO THE THERMODYNAMIC PRESSURE (p), I.E., $\gamma_i = p$. THIS LEADS TO AN EQUATION OF STATE OF THE FORM

$$f(p, \theta, \rho) = 0 \quad \text{KINETIC EQUATION OF STATE}$$

FOR AN IDEAL (PERFECT) GAS

$$p = \rho R \theta$$

↳ THERMODYNAMIC PRESSURE

KINETIC EQUATION OF STATE
(IDEAL GAS LAW)

R = GAS CONSTANT FOR A PARTICULAR GAS

METHOD OF LOCAL STATE: THE THERMODYNAMIC STATE OF A MATERIAL MEDIUM AT A GIVEN POINT AND INSTANT IS COMPLETELY DEFINED BY THE VALUES OF A CERTAIN NUMBER OF STATE VARIABLES AT THAT INSTANT, WHICH DEPEND ONLY ON THE POINT CONSIDERED.

EXAMPLE:
$$u = \hat{u}(\theta, \nu_i) = \hat{u}(\theta, \underbrace{F}_{\text{OBSERVABLE}}, \underbrace{\rho_1, \rho_2}_{\text{INTERNAL STATE VARIABLES}})$$

IN GENERAL, SINCE TIME DERIVATIVES OF STATE VARIABLES ($\dot{\theta}, \dot{\nu}_i$) ARE NOT INVOLVED IN THE DEFINITION OF THE STATE, THIS HYPOTHESIS IMPLIES THAT ANY EVOLUTION CAN BE CONSIDERED AS A SUCCESSION OF EQUILIBRIUM STATES.

⇒ THE PROCESS MUST SATISFY THE C-D INEQUALITY AT EVERY INSTANT OF EVOLUTION

THE STATE VARIABLES CAN BE DIVIDED INTO TWO CLASSES:

1) OBSERVABLE STATE VARIABLES (STRAIN, TEMPERATURE, DENSITY, ETC.)

- MEASURABLE QUANTITIES

- FOR REVERSIBLE PROCESSES, THE THERMODYNAMIC STATE UNIQUELY DEPENDS ON THE OBSERVABLE VARIABLES ALONE

2) INTERNAL STATE VARIABLES (ISV'S)

- FOR DISSIPATIVE PHENOMENA, THE CURRENT STATE DEPENDS ON THE PAST HISTORY WHICH CAN BE DETERMINED BY A SET OF "HIDDEN" OR INTERNAL VARIABLES THAT REPRESENT THE INTERNAL STATE OF MATTER (DENSITY OF DISLOCATIONS, DENSITY AND DISTRIBUTION OF VOIDS AND MICROCRACKS) NOT AMENABLE TO DIRECT MEASUREMENT

- ISV'S DO NOT EXPLICITLY APPEAR IN THE CONSERVATION LAWS OR C-D INEQUALITY BUT MUST BE ACCOUNTED FOR WHEN DEVELOPING CONSTITUTIVE EQUATIONS.

according to Hörl,³ are 3.307 Å center to center, and in γ -O₂, which are 3.41 Å. The orientation of the molecules helps to explain the fact that the spacing of (010) planes in the C-cell (3.429 Å) is less than the spacing of the (001) planes (3.748 Å), even though the molecular centers are not directly above each other along a line normal to (001). From the figure, it can be seen that there are no O₄ groups; this absence of dimers is also true of the other phases of O₂, as well as of the known phases of N₂, CO, and F₂.

A discussion of the packing of molecules in α -O₂ and β -O₂, the α - β transformation, and possible faults and twins in α has been submitted for publication elsewhere.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation Grant GP 5859, the U. S. Army Research Office Grant DA-ARO(D)-31-124-G542, the Office of Naval Research Contract Nonr 2121 (11), and facilities provided by the Advanced Research Projects Agency. The assistance of David Schiferl in some of the computations is acknowledged with thanks; also helpful discussions with P. M. de Wolff and W. H. Zachariassen. We are grateful to the referee of this paper for suggesting that we give a detailed presentation of the experimental data and some of our computations which are now included in the table and figures.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 47, NUMBER 2

15 JULY 1967

Thermodynamics with Internal State Variables

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(Received 13 February 1967)

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 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 include completely 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 tubes²⁻⁶ and in sonic absorption experiments,⁷⁻¹¹ it is found that, in an appropriate range of density and temperature, attenuation effects occur which can be well described, not by the introduction of a single and constant bulk

¹ H. A. Bethe and E. Teller, Aberdeen Proving Ground Rept. No. X-117, 1941.

² E. F. Greene, G. R. Cowan, and D. F. Hornig, *J. Chem. Phys.* 19, 427 (1951); 21, 617 (1953).

³ F. J. Smiley, E. H. Winkler, and T. K. Slawsky, *J. Chem. Phys.* 20, 923 (1952).

⁴ W. Griffith, D. Brickl, and V. Blackman, *Phys. Rev.* 102, 1209 (1956).

⁵ G. W. Pierce, *Proc. Acad. Sci. Amsterdam* 60, 271 (1925).

⁶ K. F. Herzfeld and F. O. Rice, *Phys. Rev.* 31, 691 (1928).

⁷ A survey is given by K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press Inc., New York, 1959). See also the critique by C. Truesdell, *J. Rational Mech. Analysis*, 2, 643 (1953).

¹ Here we have in mind the fading-memory postulate introduced by Coleman and Noll² and recently developed from a set of elementary axioms by Coleman and Mizel.³

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

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

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

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viscosity, but rather by assuming that the ideal-gas law $p\nu=R\theta$ 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

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 Noll,¹³ Coleman and Mizel¹⁴ have found the restrictions the second law places on a class of theories of the viscous-stress type. Later, Coleman¹⁵ developed a general theory of the thermodynamics of 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 Refs. 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 \mathbf{T} , the heat flux vector \mathbf{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 \mathbf{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 ρ , \mathbf{F} , $\text{grad}\theta$, and the complete internal state $(\alpha_1, \dots, \alpha_N)$:

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

We first seek the general restrictions placed on theories

¹² See, for example, the discussion of M. J. Lighthill, *J. Fluid Mech.* 2, 1 (1957). Apparently, the first paper expressing this idea is that of A. Einstein, *Sitzber. Akad. Wiss. Berlin Math. Phys. Kl.* 380 (1920).

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

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

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

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 $\mathbf{x} = \mathbf{x}(X, t)$ in the motion χ .
- (2) The symmetric Cauchy stress tensor $\mathbf{T} = \mathbf{T}(X, t)$.
- (3) The specific body force $\mathbf{b} = \mathbf{b}(X, t)$ 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 $\mathbf{q} = \mathbf{q}(X, t)$.
- (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 $\alpha = \alpha(X, t) = (\alpha_1, \alpha_2, \dots, \alpha_N)$; the numbers $\alpha_i = \alpha_i(X, t)$ are the internal state variables.¹⁶

Such a set of nine functions, defined for all X in \mathcal{B} and all t , is called here 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

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

and

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

Here ρ is the mass density, $\mathbf{L} = \text{grad} \dot{\mathbf{x}}$ is the velocity

¹⁶ Our present pair (\mathbf{F}, α) forms a vector which Truesdell and Toupin,¹⁷ pp. 615-647, call the *thermodynamic substate*.

¹⁷ C. Truesdell and R. A. Toupin, "The Classical Field Theories," in *Encyclopedia of Physics*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1960), Vol. 3, Pt. 1.

gradient, and $\mathbf{T} \cdot \mathbf{L}$ is the inner product of \mathbf{T} and \mathbf{L} ; i.e., $\mathbf{T} \cdot \mathbf{L} = \text{Tr } \mathbf{T} \mathbf{L}^T$ with \mathbf{L}^T the transpose of \mathbf{L} . Since grad and div are the gradient and divergence with respect to \mathbf{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 χ , \mathbf{T} , ϵ , \mathbf{q} , η , θ , and α . The remaining functions \mathbf{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 \mathbf{X} in a fixed reference configuration \mathcal{R} and writes $\mathbf{x} = \chi(\mathbf{X}, t)$. The gradient \mathbf{F} of $\chi(\mathbf{X}, t)$ with respect to \mathbf{X} ,

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

is called the *deformation gradient* at \mathbf{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 \mathbf{X} . For a scalar field over \mathcal{R} , such as θ , an elementary chain rule yields

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

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

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

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

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

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

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

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

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

3. THE CLAUSIUS-DUHEM INEQUALITY

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

$$\rho \gamma = \rho \dot{\eta} - [(\rho r/\theta) - \text{div}(\mathbf{q}/\theta)]. \quad (3.1)$$

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

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

From this equation and the inequality (3.2) we read

off the following implications of the Clausius-Duhem inequality:

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

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

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

$$\theta \gamma = -\dot{\psi} - \dot{\theta} \eta + \mathbf{S} \cdot \dot{\mathbf{F}} - (\rho \theta)^{-1} \mathbf{q} \cdot \mathbf{g}, \quad (3.8)$$

and hence (3.2) yields also

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

4. CONSTITUTIVE ASSUMPTIONS

In the present theory the *material* at the point X is characterized by five *response functions*, ψ , η , \mathbf{S} , \mathbf{q} , and $\dot{\alpha}$ at X when \mathbf{F} , θ , \mathbf{g} , and α are known at X :

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

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

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

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

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

The superposed caret in $\hat{\psi}$, $\hat{\eta}$, $\hat{\mathbf{S}}$, and $\hat{\mathbf{q}}$ serves to distinguish these functions from their values. Since for a given process the value of \mathbf{F} depends not only on 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 $\hat{\psi}$, $\hat{\eta}$, $\hat{\mathbf{S}}$, $\hat{\mathbf{q}}$, and \hat{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 section we follow the ap-

¹⁸ C. Truesdell, *J. Pure Appl. Math.* 30, 111 (1951).

¹⁹ C. Truesdell, *Appl. Mech. Rev.* 12, 75 (1959), reprinted with additions in *Applied Mechanics Surveys* (Spartan, Washington, D.C., 1966), pp. 225-236; see also C. Truesdell and R. A. Toupin,²⁰ pp. 703-704.

is that the function η^* 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 Secs. 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 Sec. 5 we found the restrictions placed on the response functions ψ , η , \hat{S} , \hat{q} , and f of (4.1)–(4.5) by the postulate of positive production of entropy. The principle of material frame indifference,²⁸ 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 F , g , q , and T transform as follows:

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

The manner in which the internal state vector $\alpha = (\alpha_1, \dots, \alpha_N)$ transforms under a change of frame depends, of course, on the physical interpretation given to the components α_i of α and therefore varies with the application in mind. For definiteness we assume here that α 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

$$\alpha \rightarrow \alpha. \quad (12.2)$$

(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 Q , the following identities in F , θ , α , and g :

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

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

$$\begin{aligned} \psi &= \psi^*(C, \theta, \alpha), \\ \eta &= \eta^*(C, \theta, \alpha), \\ T &= FT^*(C, \theta, \alpha)F^T, \\ q &= Fq^*(C, \theta, F^Tg, \alpha), \\ \dot{\alpha} &= f^*(C, \theta, F^Tg, \alpha), \end{aligned} \quad (12.4)$$

where

$$C = F^T F \quad (12.5)$$

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

$$\eta^* = -\partial_\theta \psi^* \quad (12.6)$$

and the stress relation (5.17) becomes

$$T^* = 2\rho \partial_C \psi^*. \quad (12.7)$$

One might imagine that in some applications α could represent a vector of dimension three transforming as a spatial position vector under a change of frame, but such an interpretation for α is not compatible with our constitutive equation (4.5). For, if

$$\alpha \rightarrow Q\alpha, \quad (12.8)$$

then for each time-dependent orthogonal tensor Q , f must obey the identity

$$(Q\alpha)' = f(QF, \theta, Qg, Q\alpha), \quad (12.9)$$

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

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

when $Q(t) = 1$, (12.9) yields

$$Q\alpha = 0, \quad (12.11)$$

which equation must hold for all choices of \dot{Q} at time t . But, when $Q(t) = 1$, the only restriction on $\dot{Q}(t)$ is that this tensor be skew. Hence (12.11) states that $W\alpha = 0$ for all skew tensors W , which implies that $\alpha = 0$. In other words, if α behaves as a spatial three-vector under changes of frame, then (4.5) must be replaced by the trivial equations $f \equiv 0$, $\alpha \equiv 0$.

²⁸ W. Noll, Arch. Rational Mech. Analysis 2, 197 (1958), who called it the "principle of objectivity of material properties."