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PARADOXES IN THE APPLICATION OF THERMODYNAMICS TO STRAINED SOLIDS

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This paper identifies the difficulties encountered in extending thermostatics to the description of irreversible processes in solid materials, and compares the resolutions proposed for them. The difficulties stem from the requirement of a continuum formulation of the theory in view of the nonuniform fields accompanying processes, and also from the paradoxes which arise in a casual adaption of the theoretical framework to the description of state for inelastic behavior such as plasticity, creep, and relaxation. The discussion is in terms of the classical theory of irreversible processes. Basic concepts and results are compared with the more recent nonlinear field theory, employing memory functional representations. Finally, the role of internal variables is examined in bringing inelastic behavior within the framework of the classical theory. One noteworthy result, for a wide class of rate-dependent materials, is the existence of a potential function of stress, at each set of internal variables, from which the inelastic strain rate may be derived.

1. INTRODUCTION

At the present time, there exists no generally acceptable formalism for the extension of thermostatics to the description of irreversible processes in solid continua. Difficulties begin at the foundations of the subject, and stem from two largely unrelated sources. First, processes in solid continua generally involve nonuniform fields, so that systems must be regarded as continuous as they transverse a sequence of nonequilibrium states. Thus, it becomes necessary to formulate a postulate for the description of the state of a continuous system as well as local, continuum forms for the laws of thermodynamics. The second group of difficulties arises even for uniform systems when inelastic deformations are imposed on them. These include the phenomena of plasticity, creep, and relaxation. A casual application of the theoretical framework to such processes may lead to paradoxes [1] which must be resolved; otherwise, the theory may appear to fail for important classes of materials.

The purpose of this paper is to identify these difficulties, first by confronting two formalisms: The classical theory of irreversible processes [2, 3, 4], or classical formalism (CF) for short, and the nonlinear theories

of continuum mechanics, or field-theory formalism (FF) [5, 6]. Realizing that many eminent thermodynamicists and applied mathematicians, notably G. R. Kirchhoff, W. Schottky, J. Hadamard, P. Duhem, as well as others, made parenthetic remarks about the inadequacy of thermostatics for the rigorous handling of irreversible processes, but did not supply us with a resolution of this problem, we shall omit all historical remarks and refrain from assigning priorities. It will be argued that the comparison of CF and FF must involve a discussion of the concept of state, of the appropriate form of the First Part of the Second Law, of the concepts of entropy and temperature and, finally, of the expression for entropy production.

The emphasis is laid on adapting the concepts of thermostatics to irreversible processes including the problems posed by the existence of nonuniform fields, and on a careful interpretation of experimental results related to inelastic deformations.

As a natural extension of CF [2], the present paper discusses the part that internal variables can play in the theory, and, in particular, in the description of the state of an elementary subsystem. This leads to the presentation of a theory which is broad enough to include plastic as well as nonlinear viscoelastic straining of solids. One noteworthy result consists in showing that there exists a scalar potential function of stress for a class of solid materials at each internal state from which the inelastic strain rate may be derived.

2. SIMPLIFYING EXCLUSIONS

In order to concentrate on essentials, we exclude the consideration of interactions at a distance through physical fields or radiation as well as the presence of diffusion. Furthermore, we adopt the elementary theory of infinitesimal strain ϵ_{ij}, and assume that the specific work per unit volume is $\sigma_{ij}\,d\epsilon_{ji}$, with σ_{ij} denoting the stress tensor.

With the preceding reservations, all interactions between systems and subsystems can be reduced to two: the performance of work and the exchange of heat. Finally, to simplify expression, we shall consider only systems which are homogeneous, at least on the average.

3. THERMOSTATICS

3.1. *State*

The first primitive concept in thermostatics is that of the equilibrium state of a uniform system. This is described by n independent, measurable properties ϕ_i, the characteristic number n for each system being determined experimentally. Any other thermodynamic parameter ψ_k is evaluated from

the preceding ones by an empirical, single-valued equation of state

$$\psi_k = \psi_k(\phi_1, \cdots, \phi_n). \tag{1}$$

The primary list of thermodynamic variables specifically excludes thermodynamic temperature T, energy E, and entropy S; their existence and operational definitions follow from the postulated laws of thermodynamics.

3.2. *The Laws*

Paraphrasing Callen [7], it is recognized that the laws of thermostatics are formulated with the following basic process in mind: We consider a system enclosed by a rigid adiabatic envelope (isolated system) in an initial equilibrium state 1. This state is maintained by a specified set of internal constraints. An irreversible process is released by manipulating the constraints; the system becomes continuous and ceases to be in equilibrium. Ultimately, the system reaches a final equilibrium state 2 within the new set of constraints.

The *First Law* asserts that the work, W_{ad}, performed between states 1 and 2 is independent of the details of the process. It follows that all states 2 for which W_{ad} has a fixed value lie on a potential hypersurface in the space of n dimensions ϕ_i. This proves the existence of a thermodynamic energy

$$E = E(\phi_i, \cdots, \phi_n) \tag{2}$$

for all equilibrium states of any system.

If the external boundary of the system is neither rigid nor adiabatic, we may write

$$dE = dQ - dW, \tag{3}$$

and show that only E has the properties of a potential.

The *First Part* of the *Second Law* is formulated expressly with respect to a reversible process (a parametric family of equilibria). In such circumstances, the heat $Q°$, and work $W°$, are evaluated as line integrals, the integrand for the latter being of the form

$$dW° = Y_i \, dX_i \qquad \text{(sum over } i\text{)}.* \tag{4}$$

The symbol Y_i denotes one of α intensive, and X_i denotes one of α extensive thermodynamic parameters (deformation variables). It is postulated that the linear differential form for reversible heat,

$$dQ° = dE + Y_i \, dX_i, \tag{5}$$

* Here and later the summation convention will be followed.

is integrable. The integrating denominator

$$T = T(E, X_1, \cdots, X_\alpha) \tag{6}$$

is the thermodynamic temperature, and the associated potential

$$S = S(E, X_1, \cdots, X_\alpha) \tag{7}$$

is the entropy.

Thus, for any two equilibrium states, regardless of how one arose from the other in an actual process, we have

$$S_2 - S_1 = \int_R \frac{dQ^\circ}{T} = \int_R \frac{dE + Y_i \, dX_i}{T} \; ; \tag{8}$$

here, R indicates that the line integral must be evaluated along a curve (any curve) in the space of the n independent properties ϕ_i. Hence

$$n = \alpha + 1. \tag{9}$$

Equation (8) assigns a well-defined temperature and entropy exclusively to equilibrium states, and entropy differences are defined only for such pairs of states 1 and 2 as *can* be linked by a reversible path. It is, however, assumed that this is always so for physically viable systems. More precisely, this implies that experimental results can always be so interpreted as to lead to a definition of entropy for all states of equilibrium.

It can be shown that the relation in Eq. (7), called a fundamental equation of state, contains a complete description of the physical properties of the equilibrium states of the system.

The *Second Part* of the *Second Law* reverts to the isolated system and postulates that the entropy difference

$$S_2 - S_1 = \Sigma, \tag{10}$$

defined as the entropy produced during the irreversible process, must be positive (or zero for reversible processes):

$$\Sigma \geq 0. \tag{11}$$

If the surface of the system is crossed by heat and exchanges it with β ideal sources, each of constant temperature T_k (real systems in the limit of zero thermal relaxation time or of infinite thermal conductivity and infinite energy), Eq. (10) becomes

$$S_2 - S_1 - (Q_k/T_k) = \Sigma. \tag{12}$$

3.3. *Solid Continua*

The methodology of thermostatics is capable of describing elastic continua only. In the classical theory of elasticity, it is postulated that an

equilibrium state is described by a field of strains ϵ_{ij}, together with a single value of temperature T, for the whole system. It is possible to ascribe a local internal energy density per unit mass $u(x_k)$, and a local entropy density per unit mass $s(x_k)$, to each point in the continuum, and to establish a local fundamental equation

$$u = u(s, \epsilon_{ij}). \tag{13}$$

Thus, it becomes possible to consider in detail only reversible processes which are also isothermal and to make more general statements about irreversible processes on condition that the initial and the final state are each characterized by a uniform temperature T_1 or T_2.

Evidently, for the whole system, we put

$$U = \int_V \rho u \, dV \qquad \text{and} \qquad S = \int_V \rho s \, dV. \tag{14a,b}$$

4. THE PROBLEM OF GENERALIZING TO NONEQUILIBRIUM STATES

The absence of equilibrium is characterized by spatial gradients and temporal variations of every thermodynamic property at every point in the continuum and by the appearance of a velocity field $v_i(x_k)$ as well as of local fluxes of heat and work. In contrast with equilibrium, every elementary subsystem which we may define in the continuum now interacts with those surrounding it. This makes it necessary to generalize thermostatics, and the only sure guide is the requirement that the new formalism must go over to that of thermostatics when all rates and gradients vanish identically.

5. THE CLASSICAL FORMALISM (CF)

The continuous thermodynamic system is subdivided into elementary subsystems of volume $\Delta V \to 0$, and it is postulated that the latter constitute systems that obey the laws of thermodynamics. The subsystems undergo irreversible processes and change from one nonequilibrium state to a neighboring nonequilibrium state.

5.1. *State. Principle of Local State*

The state is defined by the adoption of the principle of local state which asserts that the state of an elementary subsystem is determined by the same thermodynamic properties as would be used if the subsystem were uniform instantaneously. The rates and gradients are specifically excluded from this description and the mathematical properties of being thermodynamic variables are not postulated for them.

In other words, the state is described by n fields $\phi_i(x_j)$ and a velocity field $v_i(x_j)$. Among the n fields $\phi_i(x_j)$, we are free to include an energy density field $e(x_i)$, a temperature field $T(x_i)$, and an entropy density field $s(x_i)$. Here, e includes all forms of energy: the internal energy density u, and the kinetic energy density $\frac{1}{2}v_iv_i$; if necessary, potential (or any additional form of) energy may also be included.

The adoption of the principle of local state signifies that the fundamental equation of state and all equations of state derivable from it are valid locally and instantaneously.

The absence of equilibrium is accounted for by the introduction of the rates

$$d/dt \int_V \rho\phi_i \, dV \quad \text{etc.,} \quad \dot{Q} \text{ and } \dot{W},$$

together with the velocity field. The rate of heat exchange $\dot{Q}$ is described in terms of the interaction vector of heat flux $q_i(x_j)$. The rate of performance of work $\dot{W}$ is characterized by the work flux density vector

$$w_j(x_i) = -\sigma_{ji}v_i, \tag{15}$$

The preceding constitute the simplest (and certainly *not* the most general) assumptions that can be made in the circumstances.

5.2. The First Law

This no longer serves to define energy, but to establish an energy balance. In local form, we may write

$$\rho \, de/dt + \partial q_i/\partial x_i + \partial w_i/\partial x_i = 0. \tag{16}$$

The equation of thermostatics, like Eq. (3) from which Eq. (16) is derived, presupposes closed systems (conservation of mass in subsystem). Thus, we must add an equation of mass conservation to the list of fundamental equations. The laws of mechanics (conservation of linear momentum, conservation of angular momentum) are said to be valid regardless of the thermodynamic state of the system and must also be woven into the theory. Assuming that the equations of thermodynamics must be Galilei-invariant, we can prove the additivity of internal, kinetic, and potential energy,* and transform Eq. (16) to read

$$\rho\dot{u} + \partial q_i/\partial x_i - \sigma_{ij}\dot{\epsilon}_{ij} = 0. \tag{17}$$

(A dot above a symbol denotes a derivative with respect to time.) Strictly

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* By inverting the argument, Green and Rivlin [8] derived Cauchy's equations of motion from the energy balance equation and the assumed addivity of internal and kinetic energy.

speaking, $\dot{\epsilon}_{ij}$ is the rate-of-stretching tensor, but may be interpreted as the time derivative of the infinitesimal strain tensor for the small deformation theory considered here.

5.3. *The First Part of the Second Law—Reversible Work and Entropy*

The central difficulty in extending thermostatics to the study of irreversible processes turns on the existence of an entropy in terms of which the Second Part of the Second Law could acquire a physical meaning. A simple resolution of this difficulty is contained in the principle of local state in cases when the state variables of subsystems differ negligibly from those of an equilibrium state. This assigns to entropy the equilibrium value itself. The usual procedure followed, for example, in thermoelasticity is based on the preceding remark. While not immediately apparent, the same procedure may be adopted for a wide class of systems undergoing inelastic deformations, as will be shown later.

More generally, the classical formalism asserts that a reversible work increment per unit mass dW° (in the form of a sum of terms involving products of appropriate forces and displacement increments), can be associated with every pair of neighboring states achieved by an elementary subsystem during a process. The prefix "reversible" is intended to mean that the corresponding reversible heat increment

$$dQ^\circ = du + dW^\circ$$

has the temperature of the subsystem as an integrating factor, the entropy being defined by $dQ^\circ = T\,ds$. Hence

$$\dot{s} = \dot{Q}^\circ/T = T^{-1}(\dot{u} + \dot{W}^\circ). \qquad (18)$$

Generally speaking, a distinction must be made between the reversible work and heat rates, $\dot{W}^\circ$ and $\dot{Q}^\circ$, and the actual rates in a process, $-\rho^{-1}\sigma_{ij}\dot{\epsilon}_{ij}$ and $-\rho^{-1}\,\partial q_i/\partial x_i$, although both sets combine to give $\dot{u}$. Clearly, the applicability of CF hinges on our ability to interpret experimental results so as to associate a reversible work with every process. Each deformation variable entering u will have a force associated with it in dW°. The simplest form would be to write

$$dW^\circ = -\rho^{-1}\sigma^0{}_{ij}\,d\epsilon^0{}_{ij},$$

where $\sigma^0{}_{ij}$ and $\epsilon^0{}_{ij}$ are "reversible" stress and strain fields [1] associated with states in the process. One of these, or both for thermoelastic behavior, may be taken to have the actual value, but, in general, neither needs to be, and there is no requirement that they must satisfy the Cauchy equations of motion and the compatibility conditions. While convenient in some cases, the assumption that a strain $\epsilon^0{}_{ij}$ can characterize the state is too limited a

view, and we proceed with the general development in terms of dW°, leaving the discussion of the specific forms that it may take to Sections 7 and 8.

5.4. *The Second Part of the Second Law*

The transcription of the Second Part of the Second Law to continuous systems has given rise to many misunderstandings. On first impulse, it might be thought that the local form of Eq. (12) is

$$\rho\dot{s} + T^{-1}\,\partial q_i/\partial x_i = \dot{\sigma}_1, \tag{19}$$

where $\dot{\sigma}_1$ is the volume rate of entropy production. However, it must be remembered that the rigorous derivation of Eq. (12) from the principle of entropy increase in an isolated system explicitly identifies temperatures with those of the heat sources. Hence, it is the heat added over the temperatures on the boundaries of the subsystem that enters. It is as serious an error to consider boundary temperatures uniform as it would be, say, to consider the stress in each subsystem uniform and, hence, to conclude that equilibrium is satisfied no matter how the stress varies from subsystem to subsystem. Thus, the proper local form is

$$\rho\dot{s} + \partial(q_i/T)/\partial x_i = \dot{\sigma} > 0. \tag{20}$$

The volume rate of entropy production $\dot{\sigma}$ may be thought of as made up of the part $\dot{\sigma}_1$ given in Eq. (19) and another part, $\dot{\sigma}_2$, where evidently

$$\dot{\sigma}_2 = q_i\,\partial T^{-1}/\partial x_i. \tag{21}$$

Equation (20) is simply the local form of the so-called Clausius–Duhem inequality. This equation is a rigorous consequence of the Second Part of the Second Law in its most-general and least-biased form given in Eq. (10) and of the principle of local state.

5.5. *The Rate of Entropy Production*

We have expressed $\dot{s}$ in terms of $\dot{u}$ and the reversible work rate $\dot{W}^\circ$ in Eq. (18). On the other hand, $\dot{u}$ may be eliminated through the energy balance law, Eq. (17), and this leads to the following expression for the entropy production rate:

$$\dot{\sigma} = q_i\,\partial T^{-1}/\partial x_i + T^{-1}(\sigma_{ij}\dot{\epsilon}_{ij} + \rho\dot{W}^\circ). \tag{22}$$

The interpretation of the vector q_i/T in Eq. (20) is obviously that of a local entropy flux. The Second Part of the Second Law, extended to the present case, demands that

$$\dot{\sigma} > 0, \tag{23}$$

as already noted. The interpretation of the entropy production terms in

Eqs. (21) and (22) is now quite clear. This consists of a term $q_i \, \partial T^{-1}/\partial x_i$ imposed by the heat interactions. The second term, often represented in the form of an energy dissipation* and defined as

$$\dot{\delta} = T\dot{\sigma}_1 = \sigma_{ij}\dot{\epsilon}_{ij} + \rho\dot{W}^\circ, \tag{24}$$

brings into evidence the fact that the volumetric rate of entropy production due to work interaction is proportional to the difference between the ideal work done by the system $\rho\dot{W}^\circ$ per unit volume in a *reversible process* and that done, also by the system, $-\sigma_{ji} \, d\epsilon_{ji}$ per unit volume in a real process.

A priori there is no reason to suppose that the terms

$$\dot{\sigma}_2 = q_i \, \partial T^{-1}/\partial x_i \qquad \text{and} \qquad \dot{\sigma}_1 = \dot{\delta}/T \tag{25}$$

must be positive singly. Thus, in principle, q_i and $\partial T/\partial x_i$ may form an acute angle if $\dot{\sigma}_1 > |\dot{\sigma}_2|$.

The expression for the strength of the entropy source appears in a form which can be interpreted as consisting of products of generalized forces (intensive thermodynamic variables) and conjugate generalized fluxes (rates of extensive thermodynamic variables). The relations between them are not contained in the fundamental equation of state and must be postulated (or measured) in the form of (not necessarily linear) homogeneous phenomenological equations. When the linear assumption is made, it is accepted in the form of a new postulate that the Onsager–Casimir reciprocal relations apply.

5.6. *Constitutive Equations*

Equation (22) identifies the quantities which must depend upon each other in addition to the relations postulated by the principle of local state and transferred from thermostatics. This means that the relation between $\dot{q}_i$ and $\partial T/\partial x_i$ may contain any local properties chosen as independent, say entropy (or temperature) and strain, etc. However, the local energy or entropy must be independent of $\dot{q}_i$ or $\dot{\epsilon}_{ij}$, because they are functions of local thermodynamic parameters only.

A priori it is not possible to assign a general role to stress, strain, or rate of strain, each of which may play the part of an equilibrium property, a force or a flux, or may split into parts which are either one or the other. It follows that a constitutive equation (defined as a relation between stress,

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*It is easy to show that

$$\dot{\delta} = \sigma_{ji} \, d\epsilon_{ji}/dt - \rho s \, dT/dt - \rho \, df/dt$$
$$= \sigma_{ji} \, d\epsilon_{ji}/dt - \rho \, (du/dt - T \, ds/dt)$$
$$= \rho T \, ds/dt + \partial q_i/\partial x_i,$$

where $f = u - Ts$ is the local, specific Helmholtz potential.

strain, and rate of strain, etc.) must be pieced together from two statements: the equation of state and the phenomenological relations.

5.7. *Internal Variables*

The classical formalism adopts an additional concept from thermostatics, namely, the concept of constrained equilibrium. The divergent behavior of systems (including solids) depending upon whether the rate of change of external forces is very fast or very slow (as measured in relation to one or several characteristic relaxation times for the system) can be understood if it is accepted that a solid material can develop internal constraints. Thus, in certain circumstances, the elementary subsystems appear to be in a state of constrained equilibrium which is characterized by additional (internal) independent variables ξ_α. When the external actions are slow, the system is in unconstrained equilibrium, and the variables ξ_α assume predetermined values. They, therefore, cease to be independent. When the external actions are very fast, the system is in constrained equilibrium, the internal variables retain the values which they had in the original state. Thus, in the two extremes, the system behaves as if the internal variables had no effect on processes, but the fundamental equations are different, because the values assumed by the variables ξ_α are different.

When the system is allowed slowly to return to equilibrium from a constrained to an unconstrained state, the internal variables become independent.

As the theory is developed, it is implied that the internal forces (affinities) A_α can perform reversible work $A_\alpha \, d\xi_\alpha$ on the internal displacements $d\xi_\alpha$ which could be exchanged with the surroundings if the system traversed reversibly a sequence of constrained equilibrium states. Since, in natural processes, there exists no mechanism for the retrieval of this work, the terms $A_\alpha \, d\xi_\alpha$ appear in dW° but not in dW. Thus, the difference $dW^\circ - dW$ yields entropy production terms of the form

$$(A_\alpha/T)\xi_\alpha. \tag{26}$$

The presence of internal variables leads to the emergence of memory functions when the internal variables are eliminated from the equations of motion, etc. [12, 2, 3].

6. THE FF FORMALISM

The FF formalism, as developed by Coleman and Noll, does not accept the principle of local state, viewing it as too restrictive. The problem of defining energy, temperature, and entropy during processes is divorced from any considerations involving the laws of thermostatics. Instead, the existence of these quantities is simply *postulated*: "... temperature and

entropy join mass and place and time as primitive, undefined variables, described only by such properties as are laid down for them" [5], that is, by the consequences of the two laws as outlined below. The only property that is specifically assigned to energy and entropy at the outset is that they are extensive, so that for a continuous system

$$U = \int_V \rho u \, dV \qquad \text{and} \qquad S = \int_V \rho s \, dV. \qquad (27\text{a,b})$$

The acceptance of the preceding ideas breaks the link between the laws of thermostatics and the description of state, which makes it possible to treat the two problems separately.

Two general laws are postulated: the equation of balance of energy

$$d/dt \int_V \rho(u + \tfrac{1}{2} v_i v_i) \, dV + \int_A (q_i + w_i) n_i \, dA = 0, \qquad (28)$$

the global form of Eq. (16), and the Clausius–Duhem inequality

$$d/dt \int_V \rho s \, dV + \int_A (q_i/T) n_i \, dA \geq 0, \qquad (29)$$

where the n_i denotes an outwardly directed unit vector. This is the global form of Eq. (20) in which $\dot{\sigma} \geq 0$.

The description of the nonequilibrium state of a continuous system is governed by the principle of equipresence which states, essentially, that all quantities, such as the local temperature gradient etc. must be included in addition to the usual state parameters like energy, entropy etc. Moreover, and in order to secure maximum generality, the dependent fields are assumed to be functionals rather than functions of the independent fields. More specifically, for a solid continuum the constitutive equations lay down that

$$f, \, s, \, \sigma_{ij}, \, q_i \qquad \text{are functionals of} \qquad \epsilon_{ij}, \, T, \, \partial T/\partial x_i. \qquad (30)$$

This is tantamount to supposing that the local state at every point in the continuum depends upon the present, instantaneous values of the deformation tensor, the temperature and the temperature gradient as well as on their past values.

From this *precis* it is clear that the basic equations of CF and FF are formally identical, except for the trivial difference that additivity of internal and kinetic energy is assumed. Both lead to the same nonnegative entropy production rate

$$\dot{\sigma} = q_i \, \partial T^{-1}/\partial x_i + T^{-1}[\sigma_{ij}\dot{\epsilon}_{ij} - \rho(\dot{f} + s\dot{T})] > 0. \qquad (31)$$

The real differences are in the interpretation of the terms. CF views f and s

as known in terms of state variables entering a reversible work expression, and hence leads to an *explicit* expression for the entropy production rate. As in Eq. (22), and the subsequent Eq. (64) for an internal variable formulation, it thereby restricts the relations between "forces" and "fluxes" in a process. FF, on the other hand, takes a more general viewpoint, as necessitated in part by the rejection of the principle of local state. In particular, it regards the inequality as a restriction on the form of constitutive functionals for free energy and entropy, as well as for stress and heat flux.

The approach appears thus far to have been successful in significantly restricting the constitutive functionals for materials of the fading-memory type, specifically in connection with abrupt variations of ϵ_{ij}, T, and $\partial T/\partial x_i$ from values in a *given* prior history. The response is termed *quasi-elastic* by Bowen and Wang [9], in the sense that the idealization requires that for a fixed prior history, path-independent equations result for relating the functionals in Eq. (30) to current values:

$$f = f(\mathbf{\varepsilon}, T, \partial T/\partial \mathbf{x}; t), \qquad \sigma_{ij} = \sigma_{ij}(\mathbf{\varepsilon}, T, \partial T/\partial \mathbf{x}; t), \qquad \text{etc.} \qquad (32)$$

Here, t denotes the time in the given history at which abrupt variations are considered, and $\mathbf{\varepsilon}$, T, $\partial T/\partial \mathbf{x}$ denote the current values. Thus, the inequality becomes

$$\dot{\sigma} = q_i\, \partial T^{-1}/\partial x_i - (\rho/T)\, \partial f/\partial t + T^{-1}[\sigma_{ij} - \rho\, \partial f/\partial \epsilon_{ij}]\dot{\epsilon}_{ij}$$

$$+ (\rho/T)[s + \partial f/\partial T]\,\dot{T} - (\rho/T)[\partial f/\partial(\partial T/\partial x_i)](\partial T/\partial x_i)^{\cdot} \geq 0. \qquad (33)$$

Since the rates may be varied arbitrarily, all bracketed terms must vanish for the inequality to be valid, and it follows that

$$\sigma_{ij} = \rho\, \partial f/\partial \epsilon_{ij}, \qquad s = -\partial f/\partial T, \qquad \partial f/\partial(\partial T/\partial x_i) = 0. \qquad (34)$$

This proves that the quasi-elastic response is unaffected by the temperature gradient, validating the principle of local state in this case, and stress and entropy follow from the Helmholtz potential as in the usual thermoelastic relations. The remaining part of Eq. (34) is

$$\dot{\sigma} = q_i\, \partial T^{-1}/\partial x_i - (\rho/T)\, \partial f/\partial t \geq 0. \qquad (35)$$

The term $\partial f/\partial t$, interpreted as the rate of variation of free energy with strain and temperature held fixed, does not vary with the temperature gradient for a material exhibiting quasi-elastic response. But, the inequality must hold for any $\partial T/\partial x_i$, and thus $\partial f/\partial t$ must be negative. The bracketed term in Eq. (31) is, evidently, equal to $-(\rho/T)\, \partial f/\partial t$, and thus positive. It is noteworthy that the same conclusion follows from CF, for the principle of local state rules out the dependence of the bracketed term upon the temperature gradient.

The present authors are unable to resolve the following problem which seems to be important for future developments. Given that the basic equation and the basic inequality are identical in FF and CF, does it necessarily follow that the assumptions which led to their derivation in CF are wholly or partly implied in FF, at least for a class of constitutive equations? In any case, it is clear that CF is imbedded in FF as a special case, and this leads to another unresolved question. Does the field of possible constitutive equations, which is admitted by FF but excluded from CF, contain descriptions of physically realistic materials?

7. PARADOXES IN THE INTERPRETATION OF EXPERIMENTAL RESULTS

The second set of difficulties mentioned in the Introduction is best discussed in terms of the simplest possible system. Accordingly, we center attention on a rod in tension ($\sigma > 0$) or compression ($\sigma < 0$), disregarding such complicating phenomena as necking or buckling. Assuming a uniform stress and temperature, we are thus dealing with a uniform system and apply the laws of thermostatics to it. All material coefficients will be treated as constants.

The phenomena we want to consider comprise: (a) elasticity, (b) ideal plasticity, (c) strain hardening and the Bauschinger effect, (e) viscoelasticity, (f) creep, and (g) stress relaxation. In each case, our task will consist in determining the appropriate thermodynamic variables and the form of a fundamental equation. The classical formalism permits us in each case to write down the proper differential field equations—a task we shall refrain from performing here. In order to identify thermodynamic variables, we shall frequently call on Eq. (5), valid for reversible processes only, in which X_i is a deformation variable and $Y_i = -(\partial U/\partial X_i)_S$ is the conjugate intensive variable.

7.1. *Elasticity*

Assuming that the thermal equation of state is of the form

$$f(\sigma, \epsilon, T) = 0, \tag{36}$$

it is a trivial task to show that

$$u = u(s, \epsilon) \tag{37}$$

is a fundamental equation. This has been derived in [1] for a uniform, as well as a continuous system in terms of specific quantities per unit volume.

7.2. *Ideal Plasticity*

The assumption that Eq. (36) continues to represent the thermal equation of state of the system leads to a paradox of long standing (see Ref.

[10]): the relation is not single-valued, and a pair of specific values σ_1, T_1 does not determine a unique value of ϵ.

A possible resolution of the paradox follows from the observation that, during plastic deformation, the work per unit mass is

$$dW = -\rho^{-1}\sigma_y \, d\epsilon^p, \qquad (\sigma_y - \text{yield stress}) \qquad (38)$$

whereas, during elastic loading or unloading, regardless of the value of ϵ^p, we have

$$dW^\circ = -\rho^{-1}\sigma \, d\epsilon^e. \qquad (39)$$

As indicated by the superscript $^\circ$, the latter process is considered to be reversible, which identifies ϵ^e as a proper local parameter in ideal plastic deformation. Guided by the results of cruder experiments, we further assume that, in isothermal ideal plastic deformation, the rate of the performance of work is exactly balanced by the exchange of heat. The First Law would then indicate that the energy remains constant during the process of plastic deformation and ϵ^e constitutes the only proper deformation variable. Thus, the total strain

$$\epsilon = \epsilon^e + \epsilon^p \qquad (40)$$

is composed of an elastic and a plastic part, the latter giving rise to the flux $\dot{\epsilon}^p$. The fundamental equation (37) retains its validity, and can be used to analyze, e.g., adiabatic processes from a knowledge of the isothermal behavior of a given material.

In this simplified theory, σ_y is independent of $d\dot{\epsilon}^p/dt$, because σ_y is treated as a constant characteristic of the material.

7.3. Creep and Relaxation

The assumption that Eq. (36) represents the thermal equation of state of the system again leads to a paradox. In creep, ϵ varies with σ and T kept constant, whereas in stress relaxation, σ varies when ϵ and T are kept constant. This paradox can be resolved if it is admitted that the material is capable of developing internal constraints. This reduces the treatment of creep and relaxation to the theory mentioned in Section 5.7. For example, in the simplest case of one internal variable, the dynamic equation

$$\sigma + \tau_\epsilon \dot{\sigma} = E(\epsilon + \tau_\sigma \dot{\epsilon}) \qquad (41)$$

naturally follows in the framework of a linearized theory in which

$$f(\sigma, \epsilon, \xi, T) = 0 \qquad (41a)$$

is the form of the thermal equation of state.

7.4. *Viscoelasticity*

The natural tendency is to assume that the thermal equation of state contains strain as well as the rate of strain,

$$f(\sigma, \epsilon, \dot{\epsilon}, T) = 0. \tag{42}$$

On the other hand, experiments seem to indicate that only processes with $\dot{\epsilon} = 0$ can be treated as reversible. This is paradoxical, because Eq. (42) implies that there must exist an equilibrium set of states along $\dot{\epsilon} = \text{const} \neq 0$ in the space of three independent parameters. In other words, a reversible process at constant strain rate should be possible.

The paradox is resolved by removing the strain rate from the list of possible thermodynamic variables. Since at $\dot{\epsilon} = 0$, we have

$$dW^\circ = -\rho^{-1}\sigma^e \, d\epsilon, \tag{43}$$

and since for $\dot{\epsilon} > 0$ we have $\sigma \neq \sigma^e$ as well as

$$dW = -\rho^{-1}\sigma \, d\epsilon,$$

it appears that

$$\sigma = \sigma^e + \sigma^v \tag{44}$$

must be split into an elastic and a viscous part, the latter playing the role of a generalized force in the entropy production term

$$\sigma^v \dot{\epsilon}/T.$$

Thus $\sigma > \sigma^e$ if $\dot{\epsilon} > 0$, and $\sigma < \sigma^e$ if $\dot{\epsilon} < 0$.

These observations permit us to establish a formalism for this process. However, experiments indicate that viscoelastic materials also exhibit relaxation effects and their behavior can be described by suitable memory functions. On the other hand, Eq. (41a) of the theory of internal variables reduces to the above simple viscoelastic behavior for very slow rates of strain. It appears, therefore, that a more satisfactory theory of viscoelasticity can be formulated by assuming the existence of internal variables. In this manner, viscoelasticity, creep, and stress relaxation presumably can be treated by a single unified theory.

7.5. *Strain Hardening and Bauschinger Effect*

It seems to be impossible to fit the phenomena of strain hardening and the occurrence of a Bauschinger effect into a theory in which the system is considered to be uniform [1, 3]. Recognizing this, the simplest assumption seems to be to regard the system as a collection of elastic-plastic domains and to suppose that each such domain deforms ideally plastically under the action of a sufficiently large shearing stress.

Such a simple theory was sketched in Refs. [1, 3]. By applying purely mechanical considerations, it is easy to show that a collection of elastic-plastic domains exhibits both strain hardening and a Bauschinger effect. The consideration of thermodynamic relations leads to the conclusion that a complete stress cycle leaves the system with an unchanged volume, an increased internal energy but unchanged entropy. The energy is stored in the system elastically, by virtue of its having developed a field of locked-in microstresses.

A closer examination of this theory by Rubin [11] revealed that a simple model of this kind fails in two respects. First, the Bauschinger effect which results from it predicts that the absolute sum of the yield stresses in extension and compression for a given process of unloading is largest when there are no microstresses. In actual fact, for most materials, this sum increases with the amount of strain hardening. Secondly, the application of the so-called shake-down theorem of ideal plasticity leads to the conclusion that a large number of appropriately restricted stress cycles should restore the microstress-free state. This is also contrary to experimental results.

These two failures of the theory can be attributed to the fact that the assumed properties of a domain are too simple. A more detailed consideration of the mechanics of dislocations, which are known to be responsible for the phenomena under consideration, suggests that the passage, multiplication and crossing of dislocations is associated with the creation of intense elastic fields. These, in turn, change the internal energy and the entropy of the domain, rather than leaving them constant, as assumed. In short, a changing dislocation pattern produces a change in state which must be accounted for if the theory is to be brought into closer accord with experimental facts. The next section shows that this can be achieved by the introduction of a set of internal variables endowed with specific mathematical properties.

8. INTERNAL VARIABLES IN THE DESCRIPTION OF INELASTIC PROCESSES

8.1. *Prefatory Remarks*

Within limits, a given extension of a metallic specimen may be accomplished through elastic deformation under an applied load. The same extension may also be produced with one of an enormous variety of suitable slip processes resulting from the generation and motion of dislocations. Two substantially different dislocation arrangements, both resulting in the same extension of the specimen, lead to different subsequent responses to applied loads. We must conclude that a specification of the current values of stress or strain and temperature is insufficient to describe the state. In other

words, stress and strain, whose relation to each other we seek to understand, are not the *only* relevant thermodynamic variables. The current internal arrangement produced by slip in a metal, or by related microstructural mechanisms, must be included through a set of internal variables.

As far as solid continua are concerned, internal variables appear first to have been introduced by Meixner [2, 12] in the linear theory of visco-elasticity, and also by Biot [13]. The present section will attempt to show that the same formalism can also account for the phenomena of plasticity and nonlinear creep, relaxation, etc., in metals and polymers. The central assumption is that all internal arrangements achieved during a process can be regarded as constrained *equilibrium* states, corresponding to current values of the internal variables.

We consider only the case of a solid subjected to macroscopically homogeneous stress and small strain fields, σ_{ij} and ϵ_{ij}, and at a spatially uniform temperature. In accord with experimental evidence in the small strain range, it is postulated that processes which occur at fixed values of the internal variables are governed by the equations of linear thermoelasticity with moduli and expansion coefficients which are independent of the deformation history. In this manner, the formalism will lead to a fixed modulus in elastic loading or unloading from a yielded state in plasticity, as well as a fixed modulus for an instantaneous elastic response in visco-elasticity. Nevertheless, substantial nonlinearities in the inelastic range are not ruled out.

It may still be difficult to find a way to characterize the internal variables in a reasonable finite form for a particular material and to relate them to a macroscopic deformation history, short of specifying all dislocation positions in a metal. Nevertheless, some important conclusions can be arrived at even before this detailed problem has been resolved. One noteworthy conclusion reached here for a wide class of linear and nonlinear processes is that the inelastic (or permanent) strain rate is derivable, at each stage in the process, from a potential function of stress. The reasoning also shows that the most obvious generalization of the linear theory [14]—namely, that the strain-rate vector should be normal to the surface of constant entropy production rate—fails.

8.2. *Specification of State and Reversible Work*

The state is characterized by a stress tensor σ_{ij}, by the temperature T, and a discrete set of internal displacements ξ_α whose number is left unspecified. The values of ϵ_{ij} and ξ_α are assumed to vanish at a reference state at temperature T_0.

The infinitesimal strain ϵ_{ij} may be regarded as a function of σ_{ij}, T, and ξ_α. We assume that the thermal expansion coefficients α_{ij}, as well as the elastic

moduli C_{ijkl}, are constants. Thus

$$\partial\epsilon_{ij}(\mathfrak{d},\, T,\, \xi)/\partial T = \alpha_{ij} \tag{45}$$

and

$$\partial\epsilon_{ij}(\mathfrak{d},\, T,\, \xi)/\partial\sigma_{kl} = C_{ijkl}{}^{-1}. \tag{46}$$

These definitions may be integrated at once to yield

$$\epsilon_{ij}(\mathfrak{d},\, T,\, \xi) = \epsilon_{ij}{}^{e}(\mathfrak{d},\, T) + \epsilon_{ij}{}^{p}(\xi), \tag{47}$$

where

$$\epsilon_{ij}{}^{e} = \alpha_{ij}(T - T_0) + C_{ijkl}{}^{-1}\sigma_{kl}. \tag{48}$$

We call $\epsilon_{ij}{}^{e}$ the recoverable or elastic strain. Similarly, the unspecified function of the ξ_α's is called the permanent or inelastic strain, since it would remain in the system if it were returned to the reference values of σ_{ij} and T at constant values of ξ_α. For the time being, the form of $\epsilon_{ij}{}^{p}(\xi)$ is left open.

In order to derive the fundamental equation of state, it is necessary to introduce a specific heat, and we choose $c_0(T)$, the specific heat at zero strain and zero values of the internal variables for this purpose.

The set of affinities conjugate to the ξ_α's is denoted by P_α, so that $P_\alpha\, d\xi_\alpha$ represents the reversible work per unit volume done by local forces on the internal displacements. (The sign convention for P_α is opposite to that of σ_{ij}.) This work could be retrieved if it were possible to connect the site of the displacement with the surroundings of the system. Hence, the total reversible work per unit volume is

$$\rho\, dW^\circ = -\sigma_{ij}\, d\epsilon_{ij} + P_\alpha\, d\xi_\alpha. \tag{49}$$

Here, consistently with the infinitesimal-strain assumption, ρ denotes the density of the solid in the reference state.

8.3. *Fundamental Equation*

In view of Eq. (49), the fundamental equation is implied in the differential of the Helmholtz free energy

$$\rho\, df = \sigma_{ij}\, d\epsilon_{ij} - P_\alpha\, d\xi_\alpha - \rho s\, dT. \tag{50}$$

Making use of Eq. (47), which separates strain into an elastic and a permanent part, we can equally well write

$$\rho\, df(\varepsilon^e,\, T,\, \xi) = \sigma_{ij}\, d\epsilon_{ij}{}^{e} + \left[\sigma_{ij}(\partial\epsilon_{ij}{}^{p}/\partial\xi_\alpha) - P_\alpha\right]d\xi_\alpha - \rho s\, dT. \tag{51}$$

We shall let state functions denoted by the superscript e be those associated with thermoelastic behavior with the ξ_α's at their reference values, so that

$$\rho\, df^e(\varepsilon^e,\, T) = \sigma_{ij}\, d\epsilon_{ij}{}^{e} - \rho s^e\, dT \tag{52}$$

and

$$\rho f^e(\mathbf{\varepsilon}^e,\ T) = \tfrac{1}{2} C_{ijkl}\epsilon_{ij}{}^e[\epsilon_{kl}{}^e - 2\alpha_{kl}(T - T_0)] - \rho \int_{T_0}^{T} \frac{T-\theta}{\theta}\, c_0(\theta)\, d\theta, \quad (53)$$

with

$$s^e = -\partial f^e/\partial T \qquad \text{and} \qquad u^e = f^e - T\, \partial f^e/\partial T. \qquad (54a,b)$$

Here, the usual symmetry of elastic moduli is implied, and the specific heat at constant strain (but with the ξ_α's at their reference state) does not depend upon strain because the moduli and expansion coefficients have been assumed independent of temperature.

Subtracting Eq. (52) from (51) we find that

$$\rho\, d[\,f(\mathbf{\varepsilon}^e,\ T,\ \xi) - f^e(\mathbf{\varepsilon}^e,\ T)\,] = [\sigma_{ij}(\partial\epsilon_{ij}{}^p/\partial\xi_\alpha) - P_\alpha]\, d\xi_\alpha - \rho(s - s^e)\, dT,$$

$$(55)$$

and conclude that $f - f^e$ is independent of $\mathbf{\varepsilon}^e$. This allows us to write the Helmholtz function as the sum of an elastic and an inelastic part:

$$f(\mathbf{\varepsilon}^e,\ T,\ \xi) = f^e(\mathbf{\varepsilon}^e,\ T) + f^p(\xi,\ T), \qquad (56)$$

with

$$f^p(0,\ T) = 0. \qquad (57)$$

Similarly, we may write

$$s = s^e + s^p, \qquad \text{etc,}$$

where, in each case, the inelastic (or permanent) contribution vanishes when $\xi_\alpha = 0$. With this notation, Eq. (55) becomes

$$\rho\, df^p(\xi,\ T) = [\sigma_{ij}(\partial\epsilon_{ij}{}^p/\partial\xi_\alpha) - P_\alpha]\, d\xi_\alpha - \rho s^p\, dT. \qquad (58)$$

Equating the coefficients of dT, we see that the entropy, and thus also the internal energy, contributions from inelastic behavior are related to f^p in the standard way:

$$s^p(\xi,\ T) = -\partial f^p(\xi,\ T)/\partial T \qquad (59a)$$

$$u^p(\xi,\ T) = f^p(\xi,\ T) - T[\partial f^p(\xi,\ T)/\partial T]. \qquad (59b)$$

The most useful result follows from equating the coefficients of each $d\xi_\alpha$. Thus, if P_α is now thought of as a function of stress, temperature, and the internal variables ξ_α, we find that

$$P_\alpha(\mathbf{\sigma},\ T,\ \xi) = \sigma_{ij}[\partial\epsilon_{ij}{}^p(\xi)/\partial\xi_\alpha] - \rho[\partial f^p(\xi,\ T)/\partial\xi_\alpha]. \qquad (60a)$$

This proves that the internal forces must depend linearly upon stress, and that

$$\partial P_\alpha(\mathbf{\sigma},\ T,\ \xi)/\partial\sigma_{ij} = \partial\epsilon_{ij}{}^p(\xi)/\partial\xi_\alpha. \qquad (61)$$

Thus, if the variation of the internal forces with stress can be predicted in any particular case, the relation between the permanent strain and the internal variables can be determined, and conversely.

Considering the derivative

$$\partial P_\alpha(\mathfrak{d}, T, \xi)/\partial T = -\rho[\partial^2 f^p(\xi, T)/\partial \xi_\alpha\, \partial T] = \rho[\partial s^p(\xi, T)/\partial \xi_\alpha], \quad (62)$$

we see that the permanent strain and entropy due to permanent deformation play somewhat analogous roles, as respective conjugates to stress and temperature. Differentiating once more, we obtain

$$\partial^2 P_\alpha(\mathfrak{d}, T, \xi)/\partial T^2 = \rho[\partial^2 s^p(\xi, T)/\partial \xi_\alpha\, \partial T]$$

$$= \rho[\partial^2 s(\varepsilon^e, T, \xi)/\partial \xi_\alpha\, \partial T] = (\rho/T)[\partial c(\varepsilon^e, \xi, T)/\partial \xi_\alpha],$$

$$(63)$$

where $c(\varepsilon^e, \xi, T)$ is the specific heat at constant elastic strain and internal variables. Thus, if the specific heat does not vary with the amount of permanent deformation (i.e., with the ξ_α's), we have

$$\partial^2 P_\alpha/\partial T^2 = 0,$$

and the internal forces turn out to be linear in temperature as well as stress. In this case, f^p is also linear in temperature, and we may conclude from Eqs. (57), (59), and (60) that s^p and u^p depend only upon the internal variables. This means that the thermoelastic and inelastic contributions to entropy and energy are additive in the same sense as strain.

8.4. *Entropy Production and Restrictions Imposed by Second Part of the Second Law*

From Eq. (22) in Section 5.5, it is immediately apparent that the rate of entropy production is

$$\dot{\sigma} = T^{-1} P_\alpha \dot{\xi}_\alpha \geq 0, \quad (64)$$

so that the work rate of the internal forces on the internal displacements must be non-negative. The macroscopic form follows from Eq. (60) and is

$$\dot{\sigma} = T^{-1}[\sigma_{ij}(\partial \epsilon_{ij}{}^p/\partial \xi_\alpha) - \rho(\partial f^p/\partial \xi_\alpha)]\dot{\xi}_\alpha$$

$$= T^{-1}[\sigma_{ij}\dot{\epsilon}_{ij}{}^p - \rho(\dot{f}^p + s^p \dot{T})] \geq 0. \quad (64a)$$

This shows that, for isothermal deformation, the rate of inelastic working must exceed the rate of storage of permanent Helmholtz free energy,

$$\sigma_{ij}\dot{\epsilon}_{ij}{}^p \geq \rho \dot{f}^p.$$

In the absence of stress, the Helmholtz function can only decrease. Bau-

schinger effects in plasticity* or strain recovery in viscoelasticity must involve negative inelastic work if they set in before the complete removal of an applied stress. This is done at the expense of the Helmholtz free energy, which must decrease at a faster absolute rate.

8.5. *Local Dependence and a Potential Function for the Inelastic Strain Rate*

We suppose here that the equations governing the evolution of internal variables are rate-dependent, and assume that it is possible to choose internal variables exhibiting the following property of *local dependence*: For a given set of ξ_α's and temperature, the current rate of change $\dot{\xi}_\alpha$ in any particular variable is a function *only* of the force P_α associated with that variable. The structure of the functional relationship may vary markedly as changes occur in the ξ_α's, but the local dependence, with force in the working direction governing the rate, is essential to the following development.

While seemingly restrictive, this assumption is consistent with the conventional picture of the motion of a segment of dislocation line being governed by the local stresses in its vicinity, and in particular by the shear-stress component in the direction of its Burgers vector (i.e., in the working direction). This case is also one for which the form of the functional relationship would vary markedly with the ξ_α's or, equivalently, with the current pattern of dislocations. At a grosser level of description, the internal variables may be identified as crystalline slip displacements or shear strains within, say, individual grains of a polycrystal, with the same local dependence constituting an adequate idealization of experimental results. The rate-dependent view of plastic deformation has been popularized by Johnston, Gilman, and co-workers in recent years [15].

In order to investigate the consequences of local dependence, we consider a particular set of internal variables representing the current state of the solid. These, together with the stress and temperature, determine the internal forces [Eq. (60)] and, therefore, $\dot{\xi}_\alpha$ and also $\dot{\epsilon}_{ij}{}^p$, since the latter depends only upon the ξ_α's:

$$\dot{\epsilon}_{ij}{}^p(\mathbf{\sigma}; \xi, T) = [\partial \epsilon_{ij}{}^p(\xi)/\partial \xi_\alpha] \dot{\xi}_\alpha(\mathbf{P}; \xi, T). \tag{64b}$$

Here the notation $\dot{\epsilon}_{ij}{}^p(\mathbf{\sigma}; \xi, T)$ indicates that we are interested in the dependence of inelastic strain rate upon stress, with temperature and current internal variables as parameters. Similarly, $\dot{\xi}_\alpha(\mathbf{P}; \xi, T)$ indicates that the dependence is upon P, with other variables as parameters. Now

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* Since a change in the values of the internal displacements ξ_α in a region causes it to deform, it is clear that the system under consideration will exhibit a Bauschinger effect due to requirements of contiguity, in the same way as in the theory of elastic-plastic domains.

let us use Eq. (61) to write this as

$$\dot{\epsilon}_{ij}{}^{p}(\mathfrak{d};\,\xi,\,T) \,=\, \dot{\xi}_{\alpha}(\mathbf{P};\,\xi,\,T)[\partial P_{\alpha}(\mathfrak{d},\,T,\,\xi)/\partial\sigma_{ij}]. \qquad (65)$$

But, for the local dependence assumed, $\dot{\xi}_{\alpha}(\mathbf{P};\,\xi,\,T)\,dP_{\alpha}$ is trivially an exact differential, since each term in the sum is a differential involving only one variable, and we may write

$$\int \dot{\xi}_{\alpha}(\mathbf{P};\,\xi,\,T)\,dP_{\alpha} \,=\, \omega(\mathbf{P};\,\xi,\,T) \,=\, \Omega(\mathfrak{d};\,\xi,\,T). \qquad (66)$$

With ξ_{α} and T as parameters, the dependence upon P_{β} may be thought of as a dependence upon σ_{ij}, permitting us to define the potential $\Omega(\mathfrak{d};\,\xi,\,T)$. Thus, Eq. (65) becomes

$$\dot{\epsilon}_{ij}{}^{p}(\mathfrak{d};\,\xi,\,T) \,=\, \partial\Omega(\mathfrak{d};\,\xi,\,T)/\partial\sigma_{ij}, \qquad (67)$$

and we see that the inelastic strain rate at any time in the deformation history is derivable from a potential function of stress.

While the form of the potential function may be worked out in principle from Eqs. (66) and (60), not enough information is available to set up the relevant equations, and the details are far too complicated. Thus, it is primarily a matter for experiment to determine appropriate functional forms. In this connection, we note that the parametric dependence upon ξ_{α} may be viewed equally well as a dependence upon the previous macroscopic history of the deformation.

The potential function representation of the nonlinear inelastic strain rate is reminiscent of Onsager's reciprocal relations for linear phenomenological assumptions. Guided by the entropy production expression, Eq. (64), the usual procedure is to write the most general linear force–flux relation as

$$\dot{\xi}_{\alpha} \,=\, L_{\alpha\beta}P_{\beta}, \qquad (68)$$

and to conclude that the coefficients are symmetric, $L_{\alpha\beta} = L_{\beta\alpha}$. There is, however, a fine distinction in points of view. The Onsager extension of the classical theory, as presented earlier, deals with small deviations of a system from a definite equilibrium state, toward which it would proceed if given enough time, whereas internal variable formulations (at least in the elementary forms discussed thus far) consider every state of a system as a state of constrained equilibrium.

We now turn to an alternative interpretation of the symmetry in $L_{\alpha\beta}$ for the linear case. First, we note that this is the condition needed for $\dot{\xi}_{\alpha}\,dP_{\alpha}$ to be an exact differential in Eq. (66). Now, there is no need for any special choice of internal variables. Given one set ξ_{α}, other sets may be

defined by choosing an equal number of suitably independent functions of ξ_α, say $\eta_\beta = \eta_\beta(\xi)$. The forces Q_β associated with the fluxes η_β are determined by the invariance of the expression for work, $Q_\alpha\, d\eta_\alpha = P_\alpha\, d\xi_\alpha$. In particular, let us suppose that $L_1, L_2, \cdots$, and $k_\alpha^{(1)}, \cdots$ are the eigenvalues and normalized eigenvectors for the matrix of coefficients. We may, then, choose the η_β's as the normal coordinates:

$$\xi_\alpha = k_\alpha^{(\beta)}\eta_\beta \qquad \text{and thus} \qquad Q_\beta = k_\alpha^{(\beta)}P_\alpha. \tag{69}$$

Multiplying the linear rate equation by an eigenvector, and noting that symmetry implies orthogonality, we find that

$$\dot\eta_1 = L_1 Q_1, \qquad \dot\eta_2 = L_2 Q_2, \qquad \text{etc.} \tag{70}$$

Thus, another interpretation of symmetry is to say that a set of internal variables can be found exhibiting the local dependence property assumed at the start of this section. Indeed, for linear or nonlinear behavior, the local dependence property will not be immediately apparent in rate equations for arbitrarily chosen coordinates but instead, if at all, for some judicious choices.

Determining the strain rate potential function for the linear case and comparing it with the entropy production rate, Eq. (64),

$$\Omega = \omega = \tfrac{1}{2}L_{\alpha\beta}P_\alpha P_\beta = \tfrac{1}{2}\dot\xi_\alpha P_\alpha = \tfrac{1}{2}T\dot\sigma. \tag{71}$$

Thus, surfaces of constant potential in stress space are surfaces of a constant rate of entropy production at the current temperature T, and the strain rate, being normal to the former, is normal to the latter. It is easy to see that these statements are not true in general for nonlinear behavior, so that the suggestion in Ref. [14], namely that the strain rate should be normal to surfaces of $\dot\sigma = \text{const}$, is not a correct generalization of the linear rate theory. Since the entropy production rate is proportional to $P_\alpha\dot\xi_\alpha = P_\alpha\,\partial\omega/\partial P_\alpha$, the condition for the surfaces of $\dot\sigma$ and Ω to coincide is that $P_\alpha\,\partial\omega/\partial P_\alpha$ must depend upon the P_β's only through being a function of ω. This will be true, in general, only if all surfaces of constant ω in the P_β space are geometrically similar or, equivalently, if ω is a function of a homogeneous function of the P_β's. For local rate dependence, this means that each $\dot\xi_\alpha$ must be proportional to a power of the corresponding P_α, the same power for each internal variable. Thus, conditions for the coincidence of surfaces are rather special.

The failure of the idea that the strain rate should be normal to surfaces $\dot\sigma = \text{const}$ in the nonlinear range has already been pointed out by Drucker [16] when he examined a simple combination of viscoelastic elements.

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