On Thermodynamics and Intrinsically Equilibrated Materials (*) (**).

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Dedicated to DARIO GRAFFI on his 70th Birthday

Summary. – *The existence and uniqueness of free energy functions is demonstrated for a class of materials broad enough to contain as special cases those of the theory of finite elasticity, the theory of hypo-elasticity, and the theory of internal state variables for which the path of evolution is invariant under rescalings of time.*

1. – Introduction.

We have recently proposed and explored a mathematical theory of thermodynamics in which the existence of certain caloric functions of state, such as entropy and free energy, is deduced from «cyclic» inequalities for a class of generalized integrals called «actions» [1], [2]. Here, after summarizing the basic definitions and listing some of the main theorems of our mathematical theory, we apply the theory to a class of systems called «intrinsically equilibrated elements». This class of systems, which is closely related to a class studied by OWEN and WILLIAMS [3] from another point of view, is broad enough to contain as special cases material elements obeying the constitutive equations of the following theories from continuum mechanics: the classical theory of isothermal finite elastic deformations, NOLL's recently proposed generalization [4] of TRUESDELL's theory of hypo-elasticity [5], and certain theories of materials with internal state variables whose path of evolution is invariant under temporal rescalings. We show that if an intrinsically equilibrated element is compatible with thermodynamics, then it has a Helmholtz free energy function ψ which is unique (to within an additive constant), and ψ enters into a relation which generalizes the classical «stress relation» of elasticity theory. For simplicity of exposition, we confine the present discussion to isothermal cases, i.e. to cases in which the temperature gradient vanishes and the temperature remains constant in time at the material element under consideration.

(*) Entrata in Redazione il 24 giugno 1975.

(**) This research was supported by the U. S. National Science Foundation under Grant GP-32951X2.

2. – On the general theory of systems and actions.

Let (Σ, Π) be an ordered pair in which Σ is a topological space and Π a set of objects such that each P in Π determines a continuous mapping ϱ_P of a non-empty open subset $\mathfrak{D}(P)$ of Σ onto a subset $\mathfrak{R}(P)$ of Σ . If **(I)** for each σ in Σ , the set

$$(2.1) \quad \Pi\sigma \triangleq \{\varrho_P\sigma | P \in \Pi, \sigma \in \mathfrak{D}(P)\}$$

is dense in Σ , and **(II)** on the set

$$(2.2) \quad \mathfrak{F} = \{(P'', P') \in \Pi \times \Pi | \mathfrak{D}(P'') \cap \mathfrak{R}(P') \neq \emptyset\}$$

there is defined a Π -valued function $(P'', P') \mapsto P''P'$ such that

$$(2.3) \quad \mathfrak{D}(P''P') = \varrho_{P'}^{-1}(\mathfrak{D}(P'') \cap \mathfrak{R}(P')) ,$$

and, for each σ in $\mathfrak{D}(P''P')$,

$$(2.4) \quad \varrho_{P''P'}\sigma = \varrho_{P'}\varrho_{P''}\sigma ,$$

then (Σ, Π) is called a *system*, the elements σ of Σ are called *states*, and the elements P of Π are called *processes*; for a process P , the function ϱ_P is referred to as the *transformation induced by P* ; for a state σ , $\Pi\sigma$ is called the *set of states accessible from σ* ; each element (P'', P') of $\mathfrak{F}$ is called an *ordered pair of successively applicable processes*, and the value $P''P'$ of the function $(P'', P') \mapsto P''P'$ of (2.3) and (2.4) is referred to as the *process resulting from the successive application of P' and P''* ; for the set of all ordered pairs (P, σ) with P in Π and σ in $\mathfrak{D}(P)$, one writes $\Pi \diamond \Sigma$, i.e.,

$$(2.5) \quad \Pi \diamond \Sigma \triangleq \{(P, \sigma) \in \Pi \times \Sigma | \sigma \in \mathfrak{D}(P)\} .$$

An *action* α for a system (Σ, Π) is a function from $\Pi \diamond \Sigma$ into $\mathbb{R}$ obeying the following two conditions:

Additivity: if (P'', P') is in $\mathfrak{F} \subset \Pi \times \Pi$ and σ is in $\mathfrak{D}(P''P')$, then

$$(2.6) \quad \alpha(P''P', \sigma) = \alpha(P', \sigma) + \alpha(P'', \varrho_{P'}\sigma);$$

Continuity: for each P in Π , the function $\alpha(P, \cdot): \mathfrak{D}(P) \rightarrow \mathbb{R}$ is continuous.

When α is an action we refer to $\alpha(P, \sigma)$ [with, of course, (P, σ) in $\Pi \diamond \Sigma$] as the *supply of α on going from σ to $\varrho_P\sigma$ via the process P* .

There are systems for which two processes P', P'' can induce the same transformation $\varrho_{P''} = \varrho_{P'}$ but can give different values to an action α . Hence, one must bear in mind the distinction between processes and their induced transformations.

However, because the theory of systems and actions is more concisely described if one does not continually render this distinction explicit, we usually simplify our notation and write $P\sigma$ for $\varrho_P\sigma$. For a pair (P'', P') in $\mathfrak{F}$, we often write $P''P'\sigma$ for $\varrho_{P''P'}\sigma$, which, by (2.4), is the same as $\varrho_{P''}\varrho_{P'}\sigma$. In accord with these conventions, (2.6) can be written

$$\alpha(P''P', \sigma) = \alpha(P', \sigma) + \alpha(P'', P'\sigma).$$

When discussing an action α , if we write the expressions $\alpha(P, \sigma)$ or $P\sigma$ ($= \varrho_P\sigma$), we automatically assume that σ is in $\mathfrak{D}(P)$, i.e. that (P, σ) is in $\Pi \diamond \Sigma$, and if we write $P''P'$ we automatically assume that $\mathfrak{D}(P'') \cap \mathfrak{R}(P')$ is not empty, i.e. that (P'', P') is in $\mathfrak{F}$; for it is only under these circumstances that the expressions $\alpha(P, \sigma)$, $P\sigma$, and $P''P'$ can have meaning in the present theory.

If $\mathfrak{z}$ is an action for (Σ, Π) , and σ^0 is in Σ , we say that $\mathfrak{z}$ has the *dissipation property* at σ^0 if and only if for each $\varepsilon > 0$ there is a neighborhood ⁽¹⁾ $\mathcal{O}$ of σ^0 such that whenever $P\sigma^0$ is in $\mathcal{O}$ there holds

$$(2.7) \quad \mathfrak{z}(P, \sigma^0) > -\varepsilon.$$

In terms not quite precise, an action $\mathfrak{z}$ has the dissipation property at a state σ^0 if the supply of $\mathfrak{z}$ on going from σ^0 to any state in a small neighborhood $\mathcal{O}$ of σ^0 is approximately positive for all processes which effect such a transition. If $\mathfrak{z}$ has the dissipation property at σ^0 , then, for each process P such that $P\sigma^0 = \sigma^0$ (of course, there may not exist even one such process), there holds $\mathfrak{z}(P, \sigma^0) \geq 0$.

A real-valued function Z on a dense subset $\mathfrak{J}$ of Σ is called a *lower potential* for a given action $\mathfrak{z}$ if whenever σ_1 and σ_2 are in $\mathfrak{J}$ there is, for each $\varepsilon > 0$, a neighborhood $\mathcal{O}$ of σ_2 such that, for every process P with $P\sigma_1$ in $\mathcal{O}$, there holds

$$(2.8) \quad Z(\sigma_2) - Z(\sigma_1) < \mathfrak{z}(P, \sigma_1) + \varepsilon.$$

It is easily seen that if Z is a lower potential for $\mathfrak{z}$ and if σ and $P\sigma$ are in the domain of Z , then,

$$(2.9) \quad Z(P\sigma) - Z(\sigma) \leq \mathfrak{z}(P, \sigma).$$

The main general theorems about the dissipation property and lower potentials are stated below; in each of these theorems it is assumed that $\mathfrak{z}$ is an action for a given system (Σ, Π) .

THEOREM 1 ⁽²⁾. — If $\mathfrak{z}$ has the dissipation property at a state σ^0 , then $\mathfrak{z}$ has that property at all states accessible from σ^0 .

⁽¹⁾ Here, as in [1] and [2], by a « neighborhood » of a state σ^0 we mean an open subset of Σ containing σ^0 .

⁽²⁾ [2], Thm. 3.1; see also [1], Remark 3.1.

THEOREM 2 ⁽³⁾. — If $\mathfrak{z}$ has a lower potential Z , then $\mathfrak{z}$ has the dissipation property at every state in the domain of Z .

Less trivially, there holds

THEOREM 3 ⁽⁴⁾. — If there is a state σ^0 at which $\mathfrak{z}$ has the dissipation property, then $\mathfrak{z}$ has a lower semicontinuous lower potential whose domain contains all states accessible from σ^0 .

3. — Intrinsically equilibrated elements.

Let $\mathfrak{L}$ be the set of all (second-order) tensors on the translation space $\mathfrak{U}$ of the usual three-dimensional Euclidean point space, let $\mathfrak{S}$ be the set of symmetric tensors in $\mathfrak{L}$, and let $\mathfrak{B}$ be an open connected subset of a given (not necessarily finite-dimensional) Banach space $\mathfrak{U}$ with norm $\|\cdot\|$. We assume that there is given a function K on $\mathfrak{B}$ whose value is, for each σ in $\mathfrak{B}$, a linear transformation $K(\sigma)[\cdot]$ of $\mathfrak{L}$ such that the function $(\sigma, L) \mapsto K(\sigma)[L]$ is a locally Lipschitz continuous mapping of $\mathfrak{B} \times \mathfrak{L}$ into $\mathfrak{U}$. We also assume that there is given a (distinguished) element σ^0 in $\mathfrak{B}$, which we shall later refer to as «the standard state». We say that an $\mathfrak{L}$ -valued function L_t on $[0, t]$, with $0 < t < \infty$, is piecewise continuous if $L_t(\tau+) \stackrel{\Delta}{=} \lim_{\xi \rightarrow \tau+} L_t(\xi)$ exists and equals $L_t(\tau)$ for each τ in $[0, t]$, $L_t(\tau-) \stackrel{\Delta}{=} \lim_{\xi \rightarrow \tau-} L_t(\xi)$ exists for each τ in $(0, t]$, and $L_t(\tau-) = L_t(\tau+)$ at all but a finite number of points in $(0, t)$. For each element σ^* of $\mathfrak{B}$ we write $\Psi(\sigma^*)$ for the set of all piecewise continuous functions $L_t: [0, t] \rightarrow \mathfrak{L}$, with $0 < t < \infty$, which are such that the differential equation

$$(3.1) \quad \dot{\sigma}(\tau) = K(\sigma(\tau))[L_t(\tau)]$$

has a (classical) solution on $[0, t]$ obeying the initial condition

$$(3.2) \quad \sigma(0) = \sigma^*$$

and lying in $\mathfrak{B}$. (Using the Lipschitz theory of ordinary differential equations, one can easily show that if a solution $\sigma(\cdot): [0, t] \rightarrow \mathfrak{B}$ of (3.1) with $\sigma(0) = \sigma^*$ exists, it is unique.)

Now, let Σ be the set of all elements σ of $\mathfrak{B}$ which occur as values $\sigma(\tau)$ of solutions of (3.1) with $\sigma(0) = \sigma^0$ and with L_t in $\Psi(\sigma^0)$; let Σ have the metric (and hence the topology) induced by the norm $\|\cdot\|$; and put

$$(3.3) \quad \Pi \stackrel{\Delta}{=} \bigcup_{\sigma \in \Sigma} \Psi(\sigma).$$

⁽³⁾ [3], Thm. 3.2; see also [1], Thm. 3.2.

⁽⁴⁾ [2], Thm. 3.3; see also [1], Thm. 3.3.

For each L_t in Π , let $\mathcal{D}(L_t)$ be the set of all σ in Σ for which L_t is in $\Psi(\sigma)$, and for each such σ let $L_t\sigma$ (i.e. $\varrho_{L_t}\sigma$) be the value at time t of the (unique) solution of (3.1) with $\sigma(0) = \sigma$. Let $\mathcal{R}(L_t)$ be the range of $\varrho_{L_t}: \mathcal{D}(L_t) \rightarrow \Sigma$. [It is not difficult to show that $\mathcal{D}(L_t)$ is open in $\mathfrak{B}$, and hence open in Σ , and that ϱ_{L_t} is a continuous mapping of $\mathcal{D}(L_t)$ onto $\mathcal{R}(L_t)$.] For each pair (L_{t_2}, L_{t_1}) of elements of Π for which $\mathcal{D}(L_{t_2})$ intersects $\mathcal{R}(L_{t_1})$, let $L_{t_2}L_{t_1}$ be the function $L_{t_1+t_2}: [0, t_1+t_2] \rightarrow \mathfrak{L}$ defined by

$$(3.4) \quad L_{t_1+t_2}(\tau) \stackrel{\Delta}{=} \begin{cases} L_{t_1}(\tau) & \text{for } \tau \in [0, t_1], \\ L_{t_2}(\tau - t_1) & \text{for } \tau \in [t_1, t_1 + t_2]. \end{cases}$$

The following remark is easily verified.

REMARK 1. — A pair (Σ, Π) constructed from $\mathbf{K}$ and σ^0 as described above is a *system*, in the sense of the general theory of Section 2, with the elements σ of Σ the *states* and the elements L_t of Π the *processes*. Such a system is called an *intrinsically equilibrated element*, $\mathbf{K}$ is called the *rate function* for the element, and σ^0 is called the *standard state*. For an intrinsically equilibrated element (Σ, Π) , the set of states accessible from an arbitrary state σ in Σ is equal to all of Σ , i.e.

$$(3.5) \quad \Pi\sigma \stackrel{\Delta}{=} \{L_t\sigma \mid L_t \in \Pi, \sigma \in \mathcal{D}(L_t)\} = \Sigma,$$

and the process $L_{t_2}L_{t_1}$ resulting from the successive application of two processes L_{t_2} and L_{t_1} , with $\mathcal{D}(L_{t_2}) \cap \mathcal{R}(L_{t_1}) \neq \emptyset$, is just the function $L_{t_1+t_2}$ defined in (3.4).

We assume that with each intrinsically equilibrated element there is associated a locally Lipschitz continuous function $T: \Sigma \rightarrow \mathfrak{S}$ called the *stress function*. The value $T(\sigma)$ of T is interpreted as the Cauchy stress divided by the mass density.

REMARK 2. — A familiar example of an intrinsically equilibrated element is given by TRUESDELL's theory of hypo-elastic materials [5], [6]. For an element of such a material each state σ is an ordered pair (F, S) with F an invertible tensor, interpreted as the deformation gradient, and S a symmetric tensor (i.e. an element of $\mathfrak{S}$), interpreted as the Cauchy stress tensor. In that theory T reduces to the function

$$(3.6) \quad \sigma = (F, S) \mapsto v_r |\det F| S = T(\sigma)$$

with v_r a constant equal to the specific volume in the reference configuration, and the differential equation (3.1) takes the form

$$(3.7) \quad \begin{aligned} \dot{F}(\tau) &= L_t(\tau) F(\tau), \\ \dot{S}(\tau) &= \mathbf{H}(F(\tau), S(\tau)) [D_t(\tau)] + W_t(\tau) S(\tau) - S(\tau) W_t(\tau), \end{aligned}$$

with

$$(3.8) \quad \begin{aligned} 2D_t(\tau) &= L_t(\tau) + L_t(\tau)^T, \\ 2W_t(\tau) &= L_t(\tau) - L_t(\tau)^T, \end{aligned}$$

and with $\mathbf{H}$ a given continuously differentiable function whose value is, for each pair (F, S) , a linear transformation $\mathbf{H}(F, S)[\cdot]$ of $\mathfrak{S}$ into $\mathfrak{S}$. BERNSTEIN [7] was apparently the first to point out that the set Σ of states, (F, S) of a hypo-elastic material depends upon the choice of the standard state $\sigma^0 = (F^0, S^0)$ ⁽⁵⁾. Note that for a hypo-elastic element, $\mathfrak{B}$ and hence Σ is a subset of the finite dimensional Banach space $\mathfrak{L} \oplus \mathfrak{S}$. (In TRUESDELL's original presentation of hypo-elasticity [5], it was assumed that $\mathbf{H}$ is independent of its first variable F , i.e. that (3.7)₂ can be written

$$\dot{S}(\tau) = \mathbf{H}(S(\tau))[D_t(\tau)] + W_t(\tau)S(\tau) - S(\tau)W_t(\tau);$$

the formulation given here is essentially equivalent to that recently proposed by NOLL [4].)

REMARK 3. - A very general type of intrinsically equilibrated element is obtained by assuming that each state σ is an ordered pair (F, Ω) , with F again an invertible tensor interpreted as the deformation gradient, but with Ω now an element of some Banach space $\mathfrak{B}$, not necessarily isomorphic to $\mathfrak{S}$. Here $T(\sigma) = T(F, \Omega)$, and in place of (3.7) we have, for (3.1),

$$(3.9) \quad \begin{aligned} \dot{F}(\tau) &= L_t(\tau)F(\tau) \\ \dot{\Omega}(\tau) &= \mathbf{B}(F(\tau), \Omega(\tau))[L_t(\tau)] \end{aligned}$$

with $\mathbf{B}(\cdot)[\cdot]$ a given locally Lipschitz continuous function such that, for each pair (F, Ω) , $\mathbf{B}(F, \Omega)[\cdot]$ is a linear mapping of $\mathfrak{L}$ into $\mathfrak{B}$. For such a material element, $\mathfrak{B} \subset \mathfrak{L} \oplus \mathfrak{B}$. When $\mathfrak{B}$ is finite-dimensional and $\Omega \neq S$, one may be tempted to call Ω the *vector of internal state variables*. For an *elastic element*, $\sigma = F$, and $\mathbf{B}$ can be taken to be zero.

For each pair (L_t, σ) in $\Pi \diamond \Sigma$, i.e. with L_t in Π and σ in $\mathfrak{D}(L_t)$, the number

$$(3.10) \quad w(L_t, \sigma) \stackrel{\Delta}{=} \int_0^t T(\sigma(\tau)) \cdot L_t(\tau) d\tau$$

is called the *work done by the stress on going from σ to $L_t\sigma$ via the process L_t* . Of course, $\sigma(\tau)$ is here the value at time τ of the solution of (3.1) with initial state σ , i.e. with $\sigma(0) = \sigma$. (For the inner product $A \cdot B$ of two elements, A and B of $\mathfrak{L}$, we take $\text{trace}(AB^T)$ with T the transposition operator.) Since the inner product of a sym-

⁽⁵⁾ See also the more recent discussions of TRUESDELL & NOLL [6] and NOLL [4].

metric tensor (in $\mathfrak{L}$) with a skew tensor (in $\mathfrak{L}$) is zero, (3.10) can be written

$$(3.11) \quad \mathfrak{w}(L_t, \sigma) = \int_0^t T(\sigma(\tau)) \cdot D_t(\tau) d\tau$$

with $D_t(\tau)$, called the «stretching tensor», equal to the symmetric part of L_t , i.e. defined as in (3.8)₁.

It is a straightforward exercise to verify

REMARK 4. – For each intrinsically equilibrated element (Σ, Π) , the function $\mathfrak{w}: \Pi \diamond \Sigma \rightarrow \mathbb{R}$, defined in (3.10), is an *action* in the sense of Section 2.

We call $\mathfrak{w}$ the *work action* for (Σ, Π) .

To each process L_t of an intrinsically equilibrated element there corresponds a process ${}_R L_t: [0, t] \rightarrow \mathfrak{L}$ which is called the *reversal* of L_t and is defined as follows:

$$(3.12) \quad {}_R L_t(\tau) = \lim_{\alpha \rightarrow \tau+} L_t(t - \alpha), \quad \tau \in [0, t].$$

(Thus, ${}_R L_t(\tau) = L_t(t - \tau)$, except at the finite number of points at which L_t is discontinuous and at those points ${}_R L_t(\tau) = {}_R L_t(\tau +)$.)⁽⁶⁾ One may easily verify that for every intrinsically equilibrated element (Σ, Π) there holds

REMARK 5. – If L_t is in Π , then (i) ${}_R L_t$ is in Π , (ii) $\mathfrak{D}({}_R L_t) = \mathfrak{R}(L_t)$, (iii) $\mathfrak{R}({}_R L_t) = \mathfrak{D}(L_t)$, (iv) ${}_R L_t \sigma_2 = \sigma_1$ if and only if $L_t \sigma_1 = \sigma_2$, (v) ${}_{RR} L_t = L_t$, and (vi)

$$(3.13) \quad \mathfrak{w}({}_R L_t, \sigma_2) = -\mathfrak{w}(L_t, \sigma_1)$$

whenever $\sigma_2 = \bar{L}_t \sigma_1$.

We say that an intrinsically equilibrated element is *compatible with thermodynamics* if its work action $\mathfrak{w}$ has the dissipation property at the standard state σ^0 .

In view of (3.5) and Theorems 1 and 3, we make the following observation.

REMARK 6. – If an intrinsically equilibrated element (Σ, Π) is compatible with thermodynamics, its work action $\mathfrak{w}$ has the dissipation property at every state σ in Σ , and there exists a lower semicontinuous function $\psi: \Sigma \rightarrow \mathbb{R}$ which is a lower potential for $\mathfrak{w}$.

A lower potential for $\mathfrak{w}$ which has all of Σ for its domain is called a *free energy function* (or a «Helmholtz free energy function»).

The following theorem shows that a general intrinsically equilibrated material shares with its special prototype, the elastic material, the property of having at most one Helmholtz free energy function ψ which is «normalized» to vanish at a standard state. Moreover, here, as for an elastic material, ψ serves, in a certain sense, as a «potential» for the work.

⁽⁶⁾ A related concept of «reversed process» was employed by NOLL [4].

THEOREM 4. — Each intrinsically equilibrated element compatible with thermodynamics has precisely one free energy function ψ which vanishes at the standard state σ^0 ; this function ψ is lower semicontinuous and obeys the equation

$$(3.14) \quad \psi(\sigma_2) - \psi(\sigma_1) = \mathfrak{w}(L_t, \sigma_1)$$

for every pair of states σ_1, σ_2 and process L_t with $L_t\sigma_1 = \sigma_2$.

In another notation, (3.14) takes the form

$$(3.15) \quad \psi(\sigma(t)) - \psi(\sigma(0)) = \int_0^t T(\sigma(\tau)) \cdot L_t(\tau) d\tau = \int_0^t T(\sigma(\tau)) \cdot D_t(\tau) d\tau.$$

We refer to the function ψ determined by $\mathfrak{w}$ in accord with Theorem 4 as «the free energy function» of the intrinsically equilibrated element.

PROOF OF THEOREM 4. — By (2.9), every free energy function for the action $\mathfrak{w}$ obeys the relation

$$(3.16) \quad \psi(\sigma_2) - \psi(\sigma_1) \leq \mathfrak{w}(L_t, \sigma_1)$$

whenever $\sigma_2 = L_t\sigma_1$. Let ${}_RL_t$ be the reversal of L_t , and note that, by Remark 5, whenever $\sigma_2 = L_t\sigma_1$ there holds $\sigma_1 = {}_RL_t\sigma_2$, and hence, by (2.9) and (3.13),

$$(3.17) \quad \psi(\sigma_1) - \psi(\sigma_2) \leq \mathfrak{w}({}_RL_t, \sigma_2) = -\mathfrak{w}(L_t, \sigma_1),$$

i.e.

$$(3.18) \quad \psi(\sigma_2) - \psi(\sigma_1) \geq \mathfrak{w}(L_t, \sigma_1).$$

The relations (3.16) and (3.18) obviously yield (3.14), and hence every free energy function for an intrinsically equilibrated element (Σ, II) obeys (3.14). Since a free energy function remains a free energy function after addition of a constant, Remark 6 tells us that if (Σ, II) is compatible with thermodynamics, (Σ, II) does have a free energy function with $\psi(\sigma^0) = 0$. By (3.14), such a free energy function must obey

$$(3.19) \quad \psi(\sigma) = \mathfrak{w}(L_t, \sigma^0)$$

whenever $\sigma = L_t\sigma^0$. However, by (3.5), for every state σ in Σ there holds $\sigma = L_t\sigma^0$ for some L_t in II , and therefore there can be at most one function ψ on Σ obeying (3.19). Thus, if (Σ, II) is compatible with thermodynamics, (Σ, II) has exactly one free energy function ψ with $\psi(\sigma^0) = 0$; moreover, by Remark 6, this function ψ is lower semicontinuous; q.e.d.

As an immediate corollary to Theorem 4, we have

THEOREM 5. – The work action $\mathfrak{w}$ of an intrinsically equilibrated element (Σ, II) which is compatible with thermodynamics, has the following special properties:

(1) it vanishes on every «closed path» in the sense that

$$(3.20) \quad \sigma_1 = L_t \sigma_1 \Rightarrow \mathfrak{w}(L_t, \sigma_1) = 0;$$

(2) it is «path independent» in the sense that if L_t and $M_{t'}$ are two processes which have a given state σ_1 in their domains $\mathfrak{D}(L_t)$ and $\mathfrak{D}(M_{t'})$, then

$$(3.21) \quad L_t \sigma_1 = M_{t'} \sigma_1 \Rightarrow \mathfrak{w}(L_t, \sigma_1) = \mathfrak{w}(M_{t'}, \sigma_1).$$

Let $L_t: [0, t] \rightarrow \mathfrak{L}$ be in II ; for each τ in $(0, t]$, let L_τ be the restriction of L_t to $[0, \tau]$; and note that L_τ is then in II with $\mathfrak{D}(L_\tau) \supset \mathfrak{D}(L_t)$. For each state σ in $\mathfrak{D}(L_t)$ and for each τ in $(0, t]$, there holds, by (3.15),

$$(3.22) \quad \psi(L_\tau \sigma) - \psi(\sigma) = \int_0^\tau T(L_\zeta \sigma) \cdot L_t(\zeta) d\zeta,$$

and this implies that

$$(3.23) \quad \delta\psi(\sigma; L_t) \triangleq \lim_{\tau \rightarrow 0} \frac{1}{\tau} [\psi(L_\tau(\sigma)) - \psi(\sigma)]$$

exists and obeys

$$(3.24) \quad \delta\psi(\sigma; L_t) = T(\sigma) \cdot L_t(0).$$

This last equation tells us, moreover, that $\delta\psi(\sigma, L_t)$ depends on the function L_t only through its initial value $L_t(0)$; i.e. if L_t and $M_{t'}$ in II are such that σ is in both $\mathfrak{D}(L_t)$ and $\mathfrak{D}(M_{t'})$, then

$$(3.25) \quad L_t(0) = M_{t'}(0) \Rightarrow \delta\psi(\sigma; L_t) = \delta\psi(\sigma; M_{t'}).$$

In other words, if, for each A in $\mathfrak{L}$, we use the symbol A_* for an unspecified process L_t with $A_*(0) = A$ and σ in $\mathfrak{D}(A_*)$, then (3.24) can be written

$$(3.26) \quad \delta\psi(\sigma; A_*) = T(\sigma) \cdot A.$$

It follows from the (local) existence theory for differential equations of the type (3.1) that, for each pair (σ, A) with σ in Σ and A in $\mathfrak{L}$, there is at least one process A_* such that σ is in $\mathfrak{D}(A_*)$ and $A_*(0) = A$. Since $\delta\psi(\sigma, A_*)$ is, by (3.26), *linear* in A , and is defined for *every* A in $\mathfrak{L}$, there is, for each σ in Σ , a tensor $\nabla\psi(\sigma)$ in $\mathfrak{L}$ (in

fact, in $\mathcal{S}$) which obeys the equation $\nabla\psi(\sigma) \cdot A = \delta\psi(\sigma; A_*)$ for each A in $\mathcal{L}$. For this tensor $\nabla\psi(\sigma)$ we have, again by (3.26),

$$(3.27) \quad \nabla\psi(\sigma) \cdot A = T(\sigma) \cdot A ,$$

and as this holds for every A in $\mathcal{L}$, there follows

$$(3.28) \quad T(\sigma) = \nabla\psi(\sigma) ,$$

which proves

THEOREM 6. – Let (Σ, II) be an intrinsically equilibrated element compatible with thermodynamics. The free energy function ψ for (Σ, II) has a «gradient» $\nabla\psi: \Sigma \rightarrow \mathcal{S}$ defined by the formula

$$(3.29) \quad \nabla\psi(\sigma) \cdot A = \delta\psi(\sigma; A_*)$$

which holds for all A in $\mathcal{L}$ and σ in Σ . In (3.29), A_* is an arbitrary process with $A_*(0) = A$ and σ in $\mathcal{D}(A_*)$, and $\delta\psi(\cdot; \cdot)$ is the function defined in (3.23). This «gradient» $\nabla\psi$ obeys the «stress relation»

$$(3.30) \quad T = \nabla\psi .$$

Theorems 4-6 may be regarded as broad generalization of some theorems obtained by CAPRIOLI [8] for elastic material elements. In the theory of hypo-elasticity (as described in Remark 2) Theorems 4 and 5 have the following corollary, which generalizes certain results of BERNSTEIN and ERICKSEN [9].

REMARK 7. – Suppose (Σ, II) is a hypo-elastic element and is compatible with thermodynamics. Then (Σ, II) has precisely one free energy function ψ with $\psi(\sigma^0) = 0$; this function ψ is lower-semicontinuous on $\Sigma \subset \mathcal{L} \oplus \mathcal{S}$ and obeys the equation

$$(3.31) \quad \psi(F(t), S(t)) - \psi(F(0), S(0)) = v_r \int_0^t |\det F(\tau)| S(\tau) \cdot D_t(\tau) d\tau .$$

Moreover, ψ has a «gradient» $\nabla\psi$ as explained in Theorem 6, and the «stress relation» (3.30), which here takes the form

$$(3.32) \quad S = \frac{1}{v_r |\det F|} \nabla\psi(\sigma) ,$$

actually asserts that the stress S and deformation gradient F corresponding to a given state $\sigma = (F, S)$ are related by the implicit (tensorial) equation

$$(3.33) \quad G(F, S) = 0 ,$$

where $G: \Sigma \rightarrow \mathbb{S}$ is determined by $\psi: \Sigma \rightarrow \mathbb{R}$ through the equation

$$(3.34) \quad G(F, S) \stackrel{\Delta}{=} v_r |\det F| S - \nabla \psi(F, S) .$$

REFERENCES

- [1] B. D. COLEMAN - D. R. OWEN, *A mathematical foundation for thermodynamics*, Archive for Rational Mechanics and Analysis, **54** (1974), pp. 1-104.
 - [2] B. D. COLEMAN - D. R. OWEN, *On thermodynamics and elastic-plastic materials*, Archive for Rational Mechanics and Analysis, **59** (1975), pp. 25-51.
 - [3] D. R. OWEN - W. O. WILLIAMS, *On the time derivatives of equilibrated response functions*, Archive for Rational Mechanics and Analysis, **33** (1969), pp. 288-306.
 - [4] W. NOLL, *A new mathematical theory of simple materials*, Archive for Rational Mechanics and Analysis, **48** (1972), pp. 1-50, particularly p. 46 (§ 20).
 - [5] C. TRUESDELL, *Hypo-elasticity*, Journal of Rational Mechanics and Analysis, **4** (1955), pp. 83-133.
 - [6] C. TRUESDELL - W. NOLL, *The non-linear field theories of mechanics*, Handbuch der Physik, vol. III/3, ed. S. Flugge, Berlin-Heidelberg-New York: Springer-Verlag (1965), §§ 99-103 pp. 401-426.
 - [7] B. BERNSTEIN, *Hypo-elasticity and elasticity*, Archive for Rational Mechanics and Analysis, **6** (1960), pp. 89-104.
 - [8] L. CAPRIOLI, *Su un criterio per l'esistenza dell'energia di deformazione*, Bollettino della Unione Matematica Italiana (III), **10** (1955), pp. 481-483.
 - [9] B. BERNSTEIN - J. L. ERICKSEN, *Work functions in hypo-elasticity*, Archive for Rational Mechanics and Analysis, **5** (1958), pp. 396-409.
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