Thermodynamics of a unique material structure (*)

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THE OBJECT of this paper is to examine thermodynamic restrictions for a unique material structure. The concept of the method of preparation introduced helps in this investigation. In the first part, the results of the paper [31] have been generalized in the case of a thermodynamic process. A unique material structure in a particle X of a body $\mathscr{B}$ is defined, and a general principle of determinism for thermodynamic processes is presented. In the second part, the topology for the method of preparation space and some smoothness assumptions for processes and response functions (functionals) are postulated. As a basis of thermodynamic requirements the dissipation principle in the form of the Clausius-Duhem inequality is assumed. In the third part it is shown that the dissipation principle implies two fundamental criteria for a theory of materials, namely the criterion of the selection of the response functions (functionals) and the criterion of the accessibility of the intrinsic states. The principle of the increase of entropy has been also deduced as a result of the dissipation principle. The principle of the increase of entropy has been formulated by considering the evolution in the intrinsic state space. It is proved that the principle of the increase of entropy places thermodynamic restrictions on the evolution introduced in the general material structure. This result is of great importance to the thermodynamic theory of materials.

Celem obecnej pracy jest zbadanie ograniczeń termodynamicznych dla jednoznacznej struktury materialnej. Jest to możliwe dzięki koncepcji metody przygotowania. W pierwszej części pracy uogólniono rezultaty pracy [31] dla przypadku procesu termodynamicznego. Zdefiniowano jednoznaczną strukturę materialną w cząsteczce X ciała $\mathscr{B}$ i sformułowano ogólną zasadę determinizmu dla procesów termodynamicznych. W części drugiej pracy wprowadzono topologię w przestrzeni metody przygotowania oraz warunki gładkości dla rozpatrywanych procesów i funkcji (funkcjonałów) konstytutywnych. Jako podstawę ograniczeń termodynamicznych przyjęto zasadę dysypacyjną w postaci nierówności Clausiusa-Duhema. W części trzeciej wykazano, że z zasady dysypacyjnej wynikają dwa podstawowe kryteria, a mianowicie kryterium doboru funkcji konstytutywnych oraz kryterium osiągalności stanów wewnętrznych. Wyprowadzono również zasadę wzrostu entropii jako prosty rezultat zasady dysypacyjnej. Zasadę wzrostu entropii sformułowano rozpatrując ewolucję w przestrzeni stanów wewnętrznych. Wykazano, że z zasady tej wynikają ograniczenia termodynamiczne dla funkcji ewolucji wprowadzonej w ogólnej strukturze materialnej. Rezultat ten ma podstawowe znaczenie dla termodynamicznej teorii materiałów.

Целью настоящей работы является исследование термодинамических ограничений для однозначной материальной структуры. Это возможно благодаря концепции метода подготовки. В первой части работы обобщены результаты работы [31] на случай термодинамического процесса. Определена однозначная материальная структура в частице X тела $\mathscr{B}$ и сформулирован общий принцип причинности для термодинамических процессов. Во второй части работы введена топология в пространстве метода подготовки, а также условия гладкости для рассматриваемых процессов и определяющих функций (функционалов). За основу термодинамических ограничений принят диссипативный принцип в виде неравенства Клаузиуса-Дюгема. В третьей части показано, что из диссипативного принципа следуют два основных критерия, именно критерий подбора определяющих функций и критерий достижимости внутренних состояний. Выведен тоже принцип возрастания энтропии как простой результат диссипативного принципа. Принцип возрастания энтропии сформулирован рассматривая эволюцию в пространстве внутренних состояний. Показано, что из этого принципа вытекают термодинамические ограничения для функции эволюции, введенной в общей материальной структуре. Этот результат имеет основное значение для термодинамической теории материалов.

1. Introduction

IN ALL thermodynamic considerations for dissipative materials the thermodynamic restrictions have been investigated based on a precisely selected method of preparation together with rules of physical interpretation for the method of preparation assumed.

The main objective of the present paper is to investigate thermodynamic requirements for a general unique material structure without introducing particular realizations of the method of preparation space. We need only assume the topology for the method of preparation space and of course, the smoothness requirements for processes and the response functions (functionals) considered.

The secondary purpose of this paper is to show some connection between rational and classical formulations of the principles of thermodynamics.

Particular attention is given to the discussion of the consequences of the dissipation principle assumed in the form of the Clausius-Duhem inequality. An attempt is made to examine the criterion of the selection of the response functions (functionals) and the accessibility criterion in the intrinsic state space and to study the principle of the increase of entropy. The importance of these principles for the evolution considered in the intrinsic state space is shown. The results obtained have fundamental implications for the thermodynamic theory of dissipative materials.

2. Local thermodynamic process

The consideration of a global thermodynamic process for a body $\mathscr{B}$ gives the following equations describing a local thermodynamic process in a particle X (cf. Refs. [27, 29]):

$$(2.1) \qquad \text{Div}[F(t)T(t)] + \varrho b(t) = \varrho \ddot{x}(t),$$

$$(2.2) \qquad T(t) = T(t)^T,$$

$$(2.3) \qquad \frac{1}{2} \text{tr}[T(t)\check{C}(t)] - \text{Div}\, q(t) - \varrho[\dot{\psi}(t) + \vartheta(t)\dot{\eta}(t) + \dot{\vartheta}(t)\eta(t)] + \varrho r(t) = 0,$$

$$(2.4) \qquad -\dot{\psi}(t) - \dot{\vartheta}(t)\eta(t) + \frac{1}{2\varrho} \text{tr}[T(t)\dot{C}(t)] - \frac{1}{\varrho\,\vartheta(t)} \cdot q(t) \cdot \nabla\vartheta(t) \geq 0,$$

where $F(t)$ denotes the value of the deformation gradient of a particle X at time t and is determined by the function of motion χ by the relation

$$(2.5) \qquad F(t) = \nabla\chi(X, t),$$

if ∇ denotes gradient with respect to the material coordinates X (the particle X is identified with its position X in a fixed reference configuration $\varkappa$, see Fig. 1), $T(t)$ is the value of the Piola-Kirchhoff stress tensor of X at t, $b(t)$ the value of the density of the body force of X at t, ϱ denotes the mass density in the reference configuration $\varkappa$, $C(t)$ the value of the right Cauchy-Green deformation tensor in X at t, $q(t)$ is the value of the heat flux vector per unit surface in the reference configuration $\varkappa$ in X at t, $\psi(t)$ denotes the value of the specific free energy per unit mass in X at t, $\eta(t)$ the value of the specific entropy per unit mass in X at t, $\vartheta(t)$ is the value of absolute temperature in X at t, $r(t)$ the value of the heat

supply per unit mass and unit time in X at t, dot denotes differentiation with respect to time and the operator Div is computed with respect to the material coordinates X.

The Eqs. (2.1) and (2.2) are called Cauchy's laws of motion, the Eq. (2.3) represents the first local law of thermodynamics and the inequality (2.4) represents the second law of thermodynamics and is called the Clausius-Duhem inequality.

DEFINITION 1. *The three values*

$$(2.6) \qquad g = \big(C(t), \vartheta(t), \nabla\vartheta(t)\big)$$

computed in a particle X *at the instant of time* $t \in [0, d_P]$ *we shall call the local, deformation-temperature configuration of* X *at time* t.
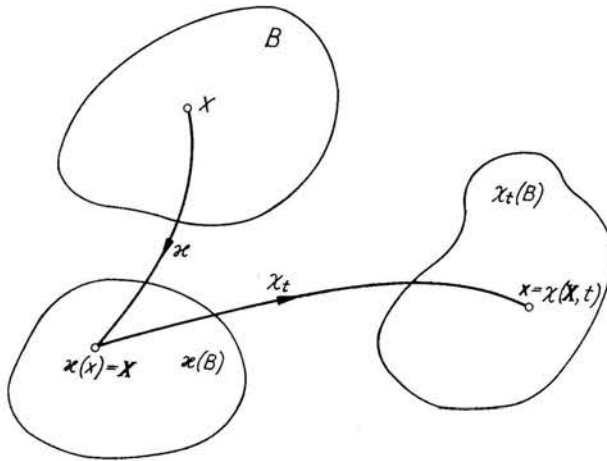

FIG. 1.

A set of all possible local configurations of a particle X will be denoted by $\mathscr{G}$ and will be called the configuration space (the deformation-temperature configuration space).

DEFINITION 2. *The four values*

$$(2.7) \qquad s = \big(\psi(t), \eta(t), T(t), q(t)\big)$$

given in a particle X *at time* $t \in [0, d_Z]$ *we shall call the local response of* X *at time* t.

A set of all possible local responses of a particle X will be denoted by $\mathscr{S}$ and will be called the response space.

We shall consider processes in the configuration space $\mathscr{G}$ and processes in the response space $\mathscr{S}$.

A process ([1])

$$(2.8) \qquad P \equiv (C, \vartheta, \nabla\vartheta): [0, d_P] \to \mathscr{G}$$

will determine the change of the deformation-temperature configuration of a particle X in the interval of time $[0, d_P]$. A number d_P will be called the duration of the process P, and $P^i = P(0)$ and $P^f = P(d_P)$ the initial and final values of the process P, respectively.

([1]) For a thorough discussion of properties of a process and for the definitions of a segment of the given process P and the continuation of the process P_1 with P_2, see W. NOLL [26].

A process

$$(2.9) \qquad \qquad Z \equiv (\psi, \eta, T, q) : [0, d_Z] \to \mathscr{S}$$

will determine the change of the response of a particle X in the interval of time $[0, d_Z]$, i.e., the change of the free energy, the entropy, the Piola-Kirchhoff stress, and the heat flux.

It is important to note that if the deformation-temperature configuration g and the response s of a particle X at time t are known and we have the function of motion χ, then we can determine the value of the body force $b(t)$ from the first of Cauchy's laws of motion (2.1) and the value of the heat supply per unit mass and unit time $r(t)$ from the first local law of thermodynamics (2.3).

Let us denote by

$$(2.10) \qquad \qquad \Pi \equiv \{ P | P : [0, d_P] \to \mathscr{G} \}$$

a set of all deformation-temperature configuration processes, and by

$$(2.11) \qquad \qquad \mathscr{Z} \equiv \{ Z | Z : [0, d_Z] \to \mathscr{S} \}$$

a set of all response processes for a particle X.

DEFINITION 3. *Every pair* $(P, Z) \in \Pi \times \mathscr{Z}$ *such that* $\mathrm{Dom}\, P = \mathrm{Dom}\, Z$ *and for every instant of time* $t \in [0, d_P]$ *the dissipation principle in the form of the Clausius-Duhem inequality* (2.4) *is satisfied, will be called a local thermodynamic process.*

3. Method of preparation

In a class of local thermodynamic processes we shall consider a subset which will be compatible with the internal constitutive assumptions describing the internal physical constitution of a body $\mathscr{B}$, i.e. compatible with a material (^{2}) of a body $\mathscr{B}$. Such a subset of a local thermodynamic process space will be called admissible for the constitutive assumptions in question.

To discuss the general relation between processes $P \in \Pi$ and $Z \in \mathscr{Z}$ which defines a material structure of a body $\mathscr{B}$ let us introduce a space $\mathscr{K}$ connected with the configuration space $\mathscr{G}$ in such a way that elements of the space $\mathscr{K}$, which will be denoted by $k \in \mathscr{K}$, are the method of preparation of the corresponding configurations g from $\mathscr{G}$. The space $\mathscr{K}$ will be called the method of preparation space (^{3}).

A main objective of thermodynamics of continuous media is to predict the response of a particle X of a body $\mathscr{B}$, of which physical properties are known, at the end of a deformation-temperature process. We can give an answer to this question if, and only if, we have full information about particle X before the test, i.e. before a deformation-temperature process. This information, which is needed for unique prediction of a future response of a particle X for every deformation-temperature process, is called the method of pre-

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(^{2}) A material as defined by W. NOLL [26] is an equivalence class of material structures, the equivalence being material isomorphy, cf. also Ref. [32].

(^{3}) For a notion of the method of preparation see Refs. [28–31], cf. also P. W. BRIDGMAN [5] and R. GILES [19]. The precise definition of the method of preparation space for a pure mechanical process was first given in Ref. [31]. We generalize here the presentation from Ref. [31] to a thermodynamic process.

paration of the actual deformation-temperature configuration. In other words the method of preparation should give the additional information required to define uniquely the internal state of a particle X of a body $\mathscr{B}$ during the local thermodynamic process.

It will be shown that a method of preparation of the deformation-temperature configuration of a particle X is needed to describe the internal dissipation of a material. This is a very important feature of the notion of the method of preparation.

Several different methods of preparation may correspond to one configuration, but it is very important that for a given method of preparation of the initial configuration only one response process corresponds to one deformation-temperature process beginning at this configuration.

DEFINITION 4. *A non-empty set $\mathscr{K}$ will be called the method of preparation space for a particle X if*

$$\bigvee_{\Sigma \subset \mathscr{G} \times \mathscr{K}} \bigvee_{\mathfrak{R}:(\Sigma \times \Pi)^{\bullet} \to \mathscr{Z}} \bigwedge_{g \in \mathscr{G}} \bigwedge_{P \in \Pi_g} \bigvee_{\mathscr{K}_g \subset \mathscr{K}} \mathfrak{R}(g, \cdot, P): \mathscr{K}_g \to \mathscr{Z}_P \text{ is bijection,}$$

where

(3.2) $$(\Sigma \times \Pi)^{*} \equiv \{(\sigma, P) \in \Sigma \times \Pi | \bigvee_{\mathscr{K}_{Pi} \subset \mathscr{K}} \sigma \in \{P^i\} \times \mathscr{K}_{Pi}\},$$

(3.3) $$\Pi_g \equiv \{P \in \Pi | P^i = g\},$$

and $\mathscr{Z}_P$ is a subset of $\mathscr{Z}$ corresponding to the process P.

DEFINITION 5. *A set*

(3.4) $$\Sigma \equiv \bigcup_{g \in \mathscr{G}} \{g\} \times \mathscr{K}_g, \quad \mathscr{K}_g \subset \mathscr{K}$$

(constructed by Definition 4) is called the intrinsic state space ([4]) of a particle X.

The element $\sigma \in \Sigma$ is a pair of the deformation-temperature configuration and the method of preparation, i.e.

(3.5) $$\sigma \equiv (P(t), A(t)) = (g, k), \quad g \in \mathscr{G}, \quad k \in \mathscr{G}_g,$$

where by A we denote a process in the method of preparation space $\mathscr{K}$, i.e., A: $[0, d_P] \to \mathscr{K}$.

We define two mappings as follows

(3.6) $$\hat{G} \equiv \text{pr}_{\mathscr{G}}: \quad \Sigma \to \mathscr{G},$$

(3.7) $$\hat{K} \equiv \text{pr}_{\mathscr{K}}: \quad \Sigma \to \mathscr{K},$$

which determine the projections from the instrinsic state space Σ on the configuration space $\mathscr{G}$ and on the method of preparation space $\mathscr{K}$, respectively.

([4]) The intrinsic state space Σ is due to Ref. [31]. It plays a similar role in the theory as the state space introduced by W. NOLL [26]. The difference between these two notions of state is in the conception of the method of preparation. The elements of the intrinsic state space are pairs. Every pair consists of the local configuration and its method of preparation. There is no notion of the method of preparation in NOLL's conception of state. The idea of splitting every element of the intrinsic state space into the local configuration and its method of preparation allows us to characterize precisely the intrinsic state of a particle X and is of great importance for the development of thermodynamics of dissipative material structure.

([5]) The mappings $\hat{G}$ and $\hat{K}$ were first introduced for a purely mechanical case, the former by W. NOLL [26] and the latter in Ref. [31].

4. General principle of determinism

The notion of a method of preparation is connected with a general principle of determinism in mechanics of continua. The principle of determinism can be stated as follows: Between an initial deformation-temperature configuration, its method of preparation, a deformation-temperature process beginning at this configuration and a response process of a particle X, there exists a functional relationship. This functional relation will describe a unique material structure in a particle X of a body $\mathscr{B}$.

According to Definition 4 there exists a mapping

$$(4.1) \qquad\qquad \Re:(\Sigma \times \Pi)^* \rightarrow \mathscr{Z}.$$

The mapping $\Re$ is called the constitutive mapping.

The constitutive mapping $\Re:(\Sigma \times \Pi)^* \rightarrow \mathscr{Z}$ has the property as follows

$$(4.2) \qquad \bigwedge_{\substack{\sigma_1,\sigma_2 \in \Sigma \\ \hat{G}(\sigma_1)=\hat{G}(\sigma_2)}} \bigwedge_{P \in \Pi_g} \{(\sigma_i, P) \in (\Sigma \times \Pi)^*, \ i = 1,2 \wedge \Re(\sigma_1, P) = \Re(\sigma_2, P)\}$$

$$\Rightarrow \hat{K}(\sigma_1) = \hat{K}(\sigma_2).$$

DEFINITION 6. *The system* $(\mathscr{G}, \Pi, \Sigma, \Re)$ *is called a unique material structure in a particle* X *of a body* $\mathscr{B}$.

The constitutive mapping $\Re$ with the property (4.2) expresses a general principle of determinism for dissipative continuum body.

A general principle of determinism: A unique response process $Z \in \mathscr{Z}$ corresponds to every deformation-temperature process $P \in \Pi$ beginning at the given intrinsic state $\sigma \in \Sigma$.

This statement of a principle of determinism is very general. It concerns thermodynamic processes and is valid for the arbitrary method of preparation space introduced.

Let us assume that a unique material structure is given. If we have the initial intrinsic state and the deformation-temperature process beginning at this intrinsic state we are interested then in the intrinsic state at the end of the process. The problem will be solved if the mapping between the intrinsic state at the end of the deformation-temperature process and the initial intrinsic state be given.

DEFINITION 7. *It is said that the mapping*

$$(4.3) \qquad\qquad \hat{e}:(\Sigma \times \Pi)^* \rightarrow \Sigma$$

is the evolution function, if for every pair $(\sigma, P) \in (\Sigma \times \Pi)^*$ *the equation*

$$(4.4) \qquad\qquad \Re(\hat{e}(\sigma, P), P^f_{(0)}) = [\Re(\sigma, P)]^f$$

is satisfied, where $[\Re(\sigma, P)]^f$ *denotes the final value of the response process* $Z = \Re(\sigma, P)$ *and* $P^f_{(0)}$ *is the deformation-temperature process of duration zero.*

In practical applications it will be convenient to have mapping from the intrinsic state space Σ into the response space $\mathscr{S}$. So, it is useful to define a new mapping

$$(4.5) \qquad\qquad \hat{S}:\Sigma \rightarrow \mathscr{S}$$

by the expression

$$(4.6) \qquad\qquad \hat{S}(\sigma) \equiv \Re(\sigma, \hat{G}(\sigma)_{(0)}).$$

The principle of determinism can be expressed by the relation [6]

$$(4.7) \qquad s = Z(t) = \hat{S}(\hat{e}(\sigma_0, P)) = \hat{S}(\sigma)$$

for every $(\sigma_0, P) \in (\Sigma \times \Pi)^*$, see Fig. 2.

This principle of determinism can be stated as follows:

A unique value of the response $s \in \mathscr{S}$ (i.e. unique values of the free energy $\psi(t)$, the entropy $\eta(t)$, the Piola-Kirchhoff stress tensor $T(t)$ and the heat flux vector $q(t)$) corresponds to every intrinsic state $\sigma \in \Sigma$.

The mapping $\hat{S}$ is called the response function.

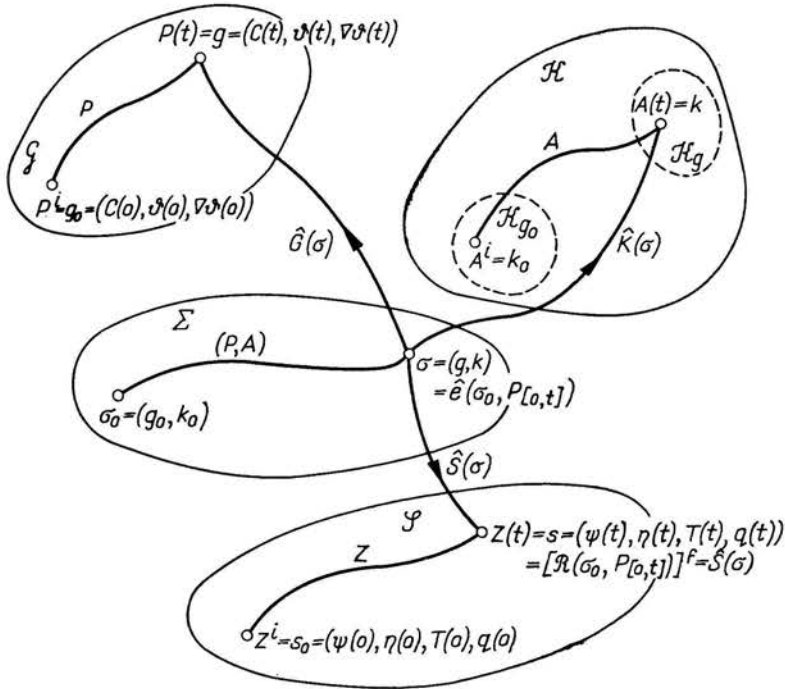The system $(\mathscr{G}, \Pi, \Sigma, \hat{S}, \hat{e})$ is also a unique material structure in a particle X.

Fig. 2.

The response function $\hat{S}$ represents the free energy response function $\hat{\Psi}$, the entropy response function $\hat{N}$, the stress response function $\hat{T}$ and the heat flux response function $\hat{Q}$, i.e.

$$(4.8) \qquad \hat{S} \equiv \{\hat{\Psi}, \hat{N}, \hat{T}, \hat{Q}\}.$$

DEFINITION 8. *A local thermodynamic process compatible with a unique material structure will be called an admissible process.*

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[6] It is noteworthy that both mappings $\hat{e}$ and $\hat{S}$ are similar to those introduced by W. NOLL [26] in a purely mechanical consideration but in the present theory, as in Ref. [31], the mappings $\hat{e}$ and $\hat{S}$ are generated by the constitutive mapping $\mathfrak{R}$.

5. Consequences of the dissipation principle

According to Definition 3, every local thermodynamic process has to satisfy the dissipation principle in the form of the Clausius-Duhem inequality (2.4).

Using Definition 8 of an admissible process we may state now the main problem of the thermodynamics of materials ([7]): In an assigned class of processes and within an assigned class of response functions (functionals) $\hat{\mathbf{S}} \equiv \{\hat{\mathbf{\Psi}}, \hat{\mathbf{N}}, \hat{\mathbf{T}}, \hat{\mathbf{Q}}\}$ to determine those that satisfy the Clausius-Duhem inequality (2.4).

Thus, it can be said that the main problem of the thermodynamics of materials is to determine an admissible thermodynamic process.

It is noteworthy that the answer to the main problem of the thermodynamics of materials depends on the topology assumed for the method of preparation space.

It will be proved that the dissipation principle will imply two fundamental criteria in the theory of materials.

1. The criterion of the selection of response functions (functionals) $\hat{\mathbf{S}} = \{\hat{\mathbf{\Psi}}, \hat{\mathbf{N}}, \hat{\mathbf{T}}, \hat{\mathbf{Q}}\}$ ([8]).

2. The criterion of the accessibility of an intrinsic state σ from the given initial intrinsic state σ_0 ([9]).

Both these criteria are main consequences of the dissipation principle.

6. Topological and smoothness assumptions

To investigate restrictions placed on a local thermodynamic process by the dissipation principle we assume:

1. The space of the method of preparation $\mathcal{K}$ is complete metrizable topological space ([10]).

2. Processes $\mathbf{P} \in \Pi$ considered in the configuration space $\mathcal{G}$ are continuously differentiable, i.e. for every time $t \in [0, d_P]$ exists the derivative $\frac{d}{d\tau} \mathbf{P}(\tau)|_{\tau=t} = \dot{\mathbf{P}}(t)$. The derivative $\dot{\mathbf{P}}(t)$ determines the rate of change of the process $\mathbf{P}$ at t.

3. Processes $\mathbf{A}$ considered in the method of preparation space $\mathcal{K}$ are continuously differentiable, i.e. for every time $t \in [0, d_P]$ exists the derivative $\frac{d}{d\tau} \mathbf{A}(\tau)|_{\tau=t} = \dot{\mathbf{A}}(t)$. The derivative $\dot{\mathbf{A}}(t)$ determines the rate of change of the process $\mathbf{A}$ at t.

([7]) Cf. B. D. COLEMAN and W. NOLL [10] and C. TRUESDELL [36].

([8]) It seems that C. ECKART [17] was the first who understood properly the consequences of the Clausius-Duhem inequality for constitutive assumptions. Further development of his idea was done by B. D. COLEMAN and W. NOLL [10], B. D. COLEMAN [11], B. D. COLEMAN and M. E. GURTIN [12], B. D. COLEMAN and V. J. MIZEL [13] and B. D. COLEMAN and D. R. OWEN [14].

([9]) The exploration of similar criterion to this has been recently taken, in another connection, by B. D. COLEMAN and D. R. OWEN [15].

([10]) For the exact meaning of the mathematical terms introduced please consult the book by J. L. KELLEY [20].

4. The rate $\dot{\mathbf{A}}(t)$ for $t \in [0, d_P]$ is idependent of the rate $\dot{\mathbf{P}}(t)$, i.e. we may assume that

(6.1) $$\dot{\mathbf{A}}(t) = \hat{\alpha}(\sigma) = \hat{\alpha}(\mathbf{P}(t), \mathbf{A}(t)), \quad t \in [0, d_P].$$

Under this assumption the rate of change of the process $\mathbf{A}$ in the method of preparation space $\mathscr{K}$ is completely determined by the actual intrinsic state $\sigma \in \Sigma$.

Two interesting cases can be considered:

(6.2)
$$\begin{array}{ll} \text{(i)} & \mathbf{A}(0) = k_0 \in \mathscr{K}, \\ \text{(ii)} & \mathbf{A}(-\infty) = k_{-\infty} \in \mathscr{K}. \end{array}$$

The differential equation (6.1) is called the evolution equation in the method of preparation space $\mathscr{K}$ and together with appropriate initial value (i) or (ii) for the given deformation-temperature process $\mathbf{P}: [0, d_P] \to \mathscr{G}$ completely determines the evolution of internal states, i.e. the evolution function $\hat{\mathbf{e}}: (\Sigma \times \Pi)^* \to \Sigma$.

The differential equation (6.1) with the initial value (i) leads to the unique material structure with internal state variables, and the initial value problem (6.1) and (ii) is iso-morphic with the unique material structure with memory ([11]).

5. A real value free energy response function $\hat{\Psi}$ defined on $\Sigma \subset \mathscr{G} \times \mathscr{K}$ is continuously differentiable on Σ with respect to the topology in Σ, i.e. the gradients $\partial_{\mathbf{P}(t)}\hat{\Psi}$ and $\partial_{\mathbf{A}(t)}\hat{\Psi}$ exist and are continuous functions on Σ. This property is called a chain rule property.

The deformation-temperature configuration space $\mathscr{G}$ has properties of a thirteen-dimensional vector space $\mathscr{V}_{13}$, hence it is a complete normed space (a topology of $\mathscr{G}$ is implied by a natural norm).

The intrinsic state space Σ with a topology implied by the topology assumed for $\mathscr{K}$ and the natural topology of $\mathscr{G}$ will be denoted by $\mathscr{D}$.

For future applications it will be useful to assume stronger topology for $\mathscr{K}$, namely that $\mathscr{K}$ is a complete normed space (a Banach space). Since $\mathscr{G}$ is also a complete normed space, hence Σ will have properties of a complete normed space denoted by $\hat{\mathscr{D}}$.

In the following we shall assume that the response functions (functionals) $\hat{\mathbf{S}} \equiv \{\hat{\Psi}, \hat{\mathbf{N}}, \hat{\mathbf{T}}, \hat{\mathbf{Q}}\}$ are defined on a set $\mathscr{D}$ (or $\hat{\mathscr{D}}$).

To state precisely, a chain rule property for the free energy response function (functional) $\hat{\Psi}$ is assumed with respect to the topology of $\mathscr{D}$ (or $\hat{\mathscr{D}}$).

It follows from the above assumptions that in each admissible local thermodynamic process

(6.3) $$\dot{\psi}(t) = \frac{d}{d\tau} \hat{\Psi}(\mathbf{P}(\tau), \mathbf{A}(\tau))|_{\tau=t} = \partial_{\mathbf{P}(t)}\hat{\Psi}(\cdot) * \dot{\mathbf{P}}(t) + \partial_{\mathbf{A}(t)}\hat{\Psi}(\cdot) \square \dot{\mathbf{A}}(t),$$

where

(6.4) $$\partial_{\mathbf{P}(t)}\hat{\Psi}(\cdot) * \dot{\mathbf{P}}(t) \equiv \mathbf{tr}[\partial_{\dot{C}(t)}\hat{\Psi}(\cdot)\dot{C}(t)] + \partial_{\vartheta(t)}\hat{\Psi}(\cdot)\dot{\vartheta}(t) + \partial_{\nabla\vartheta(t)}\hat{\Psi}(\cdot) \cdot \overline{\nabla\dot{\vartheta}(t)},$$

and $\partial_{\mathbf{A}(t)}\hat{\Psi}(\cdot) \square \dot{\mathbf{A}}(t)$ denotes a linear function (functional) with respect to $\dot{\mathbf{A}}(t)$. The result of $\partial_{\mathbf{A}(t)}\hat{\Psi}(\cdot) \square \dot{\mathbf{A}}(t)$ does depend on the realization of the method of preparation space $\mathscr{K}$ and on the topology induced in $\mathscr{K}$.

([11]) Cf. W. KOSIŃSKI and W. WOJNO [21] and M. J. LEITMAN and V. J. MIZEL [25].

To make clear our reasoning let us consider two examples.

1. If $\mathcal{K}$ is the past history function space then $\partial_{A(t)}\hat{\Psi}(\cdot) \square \dot{A}(t) = \delta\hat{\Psi}(\cdot | \dot{A}(t))$ denotes the Frechet derivative (in a Banach function space), i.e. the linear functional with respect to $\dot{A}(t)$. This realization of the method of preparation space leads to the unique material structure with memory (cf. Ref. [22]).

2. If $\mathcal{K}$ is a finite-dimensional vector space then $\partial_{A(t)}\hat{\Psi}(\cdot) \square \dot{A}(t) = \partial_{A(t)}\hat{\Psi}(\cdot) \cdot \dot{A}(t)$ denotes the scalar product in $\mathcal{K}$. This realization of the method of preparation space leads to the unique material structure with internal state variables (cf. Ref. [22]).

7. Constitutive restrictions

The dissipation principle requires that (2.4) hold at every time $t \in [0, d_P]$. We may use the Eqs. (4.7), (4.8) and (6.3) to write (2.4) in the form

$$(7.1) \quad \frac{1}{2\varrho}\,\mathbf{tr}\{[T(t) - 2\varrho\,\partial_{C(t)}\hat{\Psi}]\dot{C}(t)\} - [\eta(t) + \partial_{\vartheta(t)}\hat{\Psi}]\dot{\vartheta}(t)$$

$$- \partial_{\nabla\vartheta(t)}\hat{\Psi} \cdot \overline{\nabla\dot{\vartheta}(t)} - \partial_{A(t)}\hat{\Psi} \square \dot{A}(t) - \frac{1}{\varrho\,\vartheta(t)}\,q(t) \cdot \nabla\vartheta(t) \geqslant 0.$$

Since $\dot{C}(t)$, $\dot{\vartheta}(t)$ and $\overline{\nabla\dot{\vartheta}(t)}$ can be selected independently and may be arbitrarily chosen ([12]) hence the inequality (7.1) yields the results as follows

$$\partial_{\nabla\vartheta(t)}\Psi \equiv 0, \quad T(t) = 2\varrho\,\partial_{C(t)}\hat{\Psi}(\cdot), \quad \eta(t) = -\partial_{\vartheta(t)}\hat{\Psi}(\cdot),$$

$$(7.2)$$

$$- \partial_{A(t)}\hat{\Psi}(\cdot) \square \dot{A}(t) - \frac{1}{\varrho\,\vartheta(t)}\,\hat{Q}(\sigma) \cdot \nabla\vartheta(t) \geqslant 0,$$

satisfied at every time $t \in [0, d_P]$.

Let us introduce the following notations

$$\hat{d}(\sigma) = -\partial_{A(t)}\hat{\Psi}(\cdot) \square \dot{A}(t) - \frac{1}{\varrho\,\vartheta(t)}\,\hat{Q}(\sigma) \cdot \nabla\vartheta(t),$$

$$(7.3)$$

$$\hat{i}(\sigma) = -\frac{1}{\vartheta(t)}\,\partial_{A(t)}\hat{\Psi}(\cdot) \square \dot{A}(t).$$

The mapping $\hat{d}: \Sigma \to R^+$ (where R^+ denotes the set of non-negative real numbers) is called the general dissipation function, and the value $\hat{d}(\sigma)$ denotes the value of the general dissipation function at the intrinsic state $\sigma \in \Sigma$.

The mapping $\hat{i}: \Sigma \to R$ (the set of real numbers) is called the internal dissipation function, and $\hat{i}(\sigma)$ is its value at the intrinsic state $\sigma \in \Sigma$.

([12]) To prove this statement we can use a similar procedure to that of B. D. Coleman and M. E. Gurtin [12] and K. C. Valanis [37] for a material with internal state variables, or that of C. C. Wang and R. M. Bowen [38] for a non-linear material with quasi-elastic response.

The inequality $(7.2)_6$ is called the general dissipation inequality and using the Eqs. $(7.3)_1$ and $(7.3)_2$ it can be written in the form

$$(7.4) \qquad \hat{d}(\sigma) = \vartheta(t)\hat{i}(\sigma) - \frac{1}{\varrho\,\vartheta(t)}\,\hat{\mathbf{Q}}(\sigma) \cdot \nabla\vartheta(t) \geqslant 0.$$

The four results $(7.2)_1$ to $(7.2)_4$ express the criterion of the selection of the response functions (functionals) $\hat{\mathbf{S}} \equiv \{\hat{\Psi}, \hat{\mathbf{N}}, \hat{\mathbf{T}}, \hat{\mathbf{Q}}\}$ which can be stated as follows:

Choosing the free energy response function $\hat{\Psi}$ which is independent of the actual temperature gradient $\nabla\vartheta(t)$ and the heat flux response function $\hat{\mathbf{Q}}$ such that the general dissipation inequality (7.4) is satisfied at every instant of time $t \in [0, d_P]$ or for every intrinsic state σ determined by the relation $\sigma = \hat{\mathbf{e}}(\sigma_0, \mathbf{P}_{[0,t]})$, where σ_0 denotes the initial intrinsic state and $\mathbf{P}_{[0,t]}$ the segment of the given deformation-temperature process $\mathbf{P}$, the response stress function $\hat{\mathbf{T}}$ and the response entropy function $\hat{\mathbf{N}}$ are uniquely determined by the relations $(7.2)_2$ and $(7.2)_3$.

It is noteworthy that for the case $q(t) \equiv 0$ or $\nabla\vartheta(t) \equiv 0$ for $t \in [0, d_P]$ the general dissipation inequality (7.4) takes the particular form

$$(7.5) \qquad \hat{i}(\sigma) = -\frac{1}{\vartheta(t)}\,\partial_{A(t)}\hat{\Psi}(\cdot)\,\square\,\dot{A}(t) \geqslant 0, \quad t \in [0, d_P]$$

which is called the internal dissipation inequality.

We can return now to the discussion of the notion of the method of preparation as such information which is required for the description of the internal dissipation of an inelastic material. The expression $(7.3)_2$ which defines the value of the internal dissipation at the intrinsic state σ shows that full information given in the method of preparation, i.e. $A(t) = k$ and the evolution equation $\dot{A}(t) = \hat{\alpha}(\sigma)$, essentially determines the internal dissipation for this intrinsic state.

If there is no need to introduce any information in the method of preparation this case corresponds to an ideal material without internal dissipation — this ideal material is called a perfectly elastic material.

8. Accessibility criterion

Let us assume that the initial intrinsic state $\sigma_0 \in \Sigma$ is known, and let us choose an arbitrary intrinsic state $\sigma^* \in \Sigma$, see Fig. 3. The question arises whether the intrinsic state σ^* is accessible from the initial intrinsic state σ_0, or in other words, what is the condition of accessibility of σ^* from σ_0.

If the intrinsic state σ^* is accessible from the initial intrinsic state σ_0, then the deformation-temperature process $\mathbf{P}$ has to exist which generates the process in the method of preparation space $A: [0, d_P] \rightarrow \mathcal{K}$ such that

$$(8.1) \qquad \sigma_0 = (\mathbf{P}(0), A(0)) = (g_0, k_0) \quad \text{and} \quad \sigma^* = (\mathbf{P}(d_P), A(d_P)) = (g^*, k^*),$$

and for every instant of time $t \in [0, d_P]$ the dissipation principle is satisfied.

The response of a material corresponding to the intrinsic state σ^* is determined by the constitutive relation

(8.2)
$$Z(d_P) = \hat{S}(\hat{e}(\sigma_0, P)) = \hat{S}(\sigma^*).$$

Since the deformation-temperature process P is assumed to be known and this process generates a process A in the method of preparation space $\mathcal{K}$, hence the dissipation principle will give fundamental restriction on the process A: $[0, d_P] \rightarrow \mathcal{K}$.

The dissipation principle requires that for a given process P such a process A: $[0, d_P] \rightarrow \mathcal{K}$ be chosen that the general dissipation inequality

(8.3)
$$\hat{d}(\sigma) \geqslant 0, \quad \sigma = (P(t), A(t)) = (g, k)$$

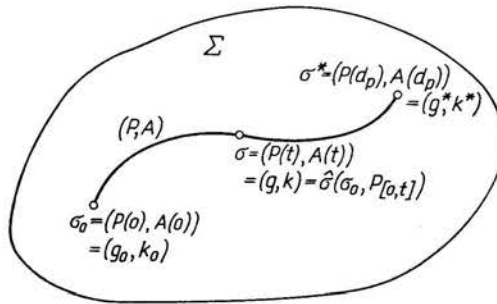for every instant of time $t \in [0, d_P]$ must be satisfied.

FIG. 3.

This is the second fundamental criterion obtained as the result of the dissipation principle.

Accessibility criterion: An arbitrary intrinsic state $\sigma^* \in \Sigma$ is accessible from the initial intrinsic state $\sigma_0 \in \Sigma$ if there exists a pair of processes (P, A): $[0, d_P] \rightarrow \mathcal{G} \times \mathcal{K}$ such that the following conditions are satisfied:

$$(P(0), A(0)) = (g_0, k_0) = \sigma_0, \quad (P(d_P), A(d_P)) = (g^*, k^*) = \sigma^*,$$

(8.4)
$$\hat{d}(P(t), A(t)) = -\frac{1}{\vartheta(t)} \partial_{A(t)} \hat{\Psi}(\cdot) \square \dot{A}(t) - \frac{1}{\varrho \vartheta(t)} \hat{Q}(\sigma) \cdot \nabla \vartheta(t) \geqslant 0$$

for every instant of time $t \in [0, d_P]$.

It is noteworthy that the accessibility criterion places some restrictions on the evolution function $\hat{e}$: $(\Sigma \times \Pi)^* \rightarrow \Sigma$. Indeed, if we assume the deformation-temperature process P such that the intrinsic state $\sigma^* = \hat{e}(\sigma_0, P)$ be accessible from the initial intrinsic state σ_0 by this process P, then the condition $(8.4)_2$ represents the restriction on the evolution function $\hat{e}$.

This conclusion is obvious if the condition $(8.4)_2$ is written in the form

(8.5)
$$\hat{d}(\hat{e}(\sigma_0, P_{[0,t]})) \geqslant 0 \quad \text{for} \quad t \in [0, d_P].$$

9. Principle of the increase of entropy

Let us consider the intrinsic state space Σ. In this space we choose the initial intrinsic state σ_0 and an arbitrary intrinsic state σ. Let us assume that there exists a pair of processes (P, A): $[0, d_P] \to \mathcal{G} \times \mathcal{K}$ such that

(9.1) $(P(0), A(0)) = (g_0, k_0) = \sigma_0$ and $(P(t), A(t)) = (g, k) = \sigma.$

The pair of the processes (P, A) is represented in the intrinsic state space Σ by the curve $\mathcal{L}$, see Fig. 4.
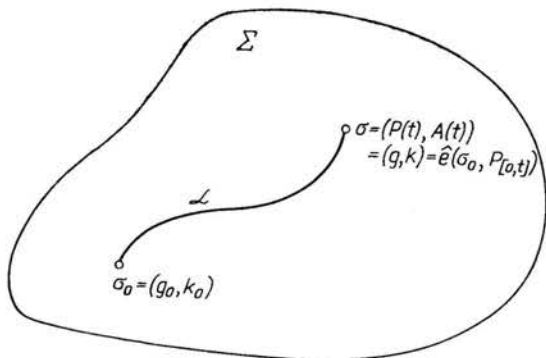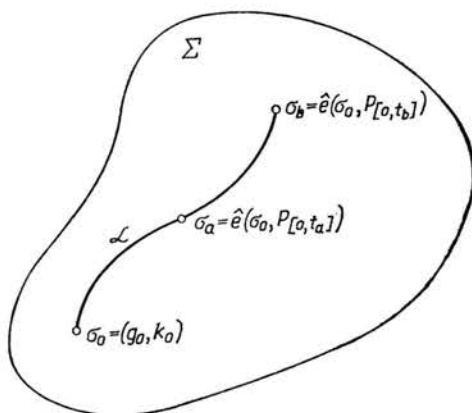

FIG. 4.   FIG. 5.

We define the curvilinear integral along the curve $\mathcal{L}$ which due to natural time parametrization can be written in the form

(9.2) $\mathscr{J}(\sigma_0, \sigma) = \int_0^t \hat{d}(P(\tau), A(\tau)) d\tau = \int_0^t \hat{d}(\hat{e}(\sigma_0, P_{[0,\tau]})) d\tau, \quad t \in [0, d_P].$

In a similar way we can define the integral

(9.3) $\mathscr{I}(\sigma_0, \sigma) = \int_0^t \hat{i}(P(\tau), A(\tau)) d\tau = \int_0^t \hat{i}(\hat{e}(\sigma_0, P_{[0,\tau]})) d\tau, \quad t \in [0, d_P].$

The integrals $\mathscr{J}(\sigma_0, \sigma)$ and $\mathscr{I}(\sigma_0, \sigma)$ are called the general dissipation integral and the internal dissipation integral, respectively.

Let us consider in the internal state space Σ two states σ_a and σ_b which lie on the curve $\mathcal{L}$, see Fig. 5. The state σ_a corresponds to the instant of time $t_a \in [0, d_P]$ and the state σ_b to the instant $t_b \in [0, d_P]$, and of course $t_b > t_a$.

The dissipation principle requires that

(9.4) $\mathscr{J}(\sigma_0, \sigma_b) - \mathscr{J}(\sigma_0, \sigma_a) \geqslant 0.$

Principle of the increase of entropy: For all σ_a, $\sigma_b \in \Sigma$, σ_b is accessible from σ_a if, and only if, the general dissipation integral of σ_b is not less than that of σ_a.

8*

It is important to note that the internal dissipation integral (9.3) is a measure of the irreversibility of a local thermodynamic process for the case when $q(t) \equiv 0$ or $\nabla \vartheta(t) \equiv 0$ for $t \in [0, d_P]$ and may be interpreted as the empirical entropy ([13]) or as the irreversibility function ([14]).

If we assume this interpretation and the condition $q(t) \equiv 0$ for $t \in [0, d_P]$ we can state the principle of increase of entropy in the form as follows (cf. P. RASTALL [35]): For all σ_a, $\sigma_b \in \Sigma$, σ_b is adiabatically accessible from σ_a if, and only if, the empirical entropy of σ_b is not less than that of σ_a.

The principle of the increase of entropy was first formulated by M. PLANCK [33, 34].

10. Discussion

It is worth pointing out some features of the thermodynamics of materials presented. We started from the dissipation principle in the form of the Clausius-Duhem inequality and we deduced two fundamental criteria for the thermodynamics of materials, namely the criterion of the selection of the response functions (functionals) occurring in the mathematical statement of the general principle of determinism and the accessibility criterion in the intrinsic state space Σ.

The accessibility criterion is connected with the Caratheodory formulation of the second law of thermodynamics ([15]).

As a consequence of the dissipation principle we also deduced the principle of the increase of entropy. Appropriate interpretation of the general dissipation integral (or the internal dissipation integral) led to the very old statement of the second law of thermodynamics first presented by M. PLANCK ([16]).

It is very important to stress that all considerations concerned a general unique material structure before a particular realization of the method of preparation was given.

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([13]) The clear meaning of the empirical entropy can be found in the papers by H. A. BUCHDAHL [6, 7], cf. also H. A. BUCHDAHL and W. GREVE [8], L. B. COOPER [16], P. RASTALL [35] and J. B. BOYLING [2, 3].

([14]) The concept of the irreversibility function was introduced by R. GILES [19].

([15]) Cf. C. CARATHEODORY [9]. Caratheodory's formulation of classical thermodynamics has been developed further by M. BORN [4], H. A. BUCHDAHL [6, 7], G. FULK and H. JUNG [18], B. BERNSTEIN [1], H. A. BUCHDAHL and W. GREVE [8], P. T. LANDSBERG [23, 24], J. L. COOPER [16], P. RASTALL [35] and J. B. BOYLING [2, 3].

([16]) Cf. M. PLANCK [33, 34]. Extension of Planck's idea has been done by H. A. BUCHDAHL [6], P. RASTALL [35] and J. B. BOYLING [2, 3].

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