

The Thermodynamics of Constrained Materials

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1. Introduction

In continuum mechanics an internal constraint is a limitation on the possible motions of a material point. Examples such as incompressibility and inextensibility have a long history. Indeed, the notion of incompressibility appears in the early work on fluid dynamics, while inextensibility is an essential ingredient in the theory of the catenary, in the theory of the elastica, and in certain theories of membranes. Constrained materials are generally simpler in their behavior than unconstrained materials. This fact has often been exploited in classical fluid dynamics, but it was not until the pioneering research of RIVLIN¹ that its importance in more general theories was realized.

The first truly general *mechanical* theory of internal constraints was developed by NOLL², who studied limitations of the form

$$\varphi(C)=0 \quad (C=F^T F) \quad (1.1)$$

on the deformation gradient F . NOLL assumes that the (Cauchy) stress T at time t is determined by the history F^t only to within a *reaction stress* \bar{T} that does no work in any motion satisfying the constraint; *i.e.*,

$$T = \hat{T}(F^t) + \bar{T},$$

and if

$$D = \text{sym}(\dot{F}F^{-1})$$

is the stretching tensor, then

$$\bar{T} \cdot D = 0 \quad (1.2)$$

in any motion satisfying (1.1). NOLL proves, as a consequence of this assumption, that \bar{T} must be a scalar multiple of the tensor $F \partial_C \varphi(C) F^T$:

$$\bar{T} = \alpha F \partial_C \varphi(C) F^T \quad (\alpha \text{ arbitrary}). \quad (1.3)$$

¹ RIVLIN obtained several exact solutions for incompressible elastic solids and for incompressible Reiner-Rivlin fluids. These solutions are discussed in detail by TRUESDELL & NOLL [1965, §§54–57, 119], where complete references to RIVLIN's work can be found. Later ADKINS & RIVLIN [1955] and RIVLIN [1955] developed a general theory of elastic bodies subject to certain inextensibility constraints. *Cf.* also GREEN & ADKINS [1960, Ch. VII].

² TRUESDELL & NOLL [1965, §30]. *Cf.* POINCARÉ [1889, §152], [1892, §33].

Constraints involving thermodynamic variables were first studied by GREEN, NAGHDI & TRAPP [1970].¹ These authors consider limitations of the form

$$A(\mathbf{F}, \theta) \cdot \mathbf{D} + B(\mathbf{F}, \theta) \dot{\theta} + c(\mathbf{F}, \theta) \cdot \mathbf{g} = 0, \quad (1.4)$$

where θ is the temperature and \mathbf{g} the temperature gradient. In place of NOLL's postulate they assume that the stress \mathbf{T} , the entropy η , and the heat flux \mathbf{q} are determined to within reactions $\bar{\mathbf{T}}$, $\bar{\eta}$, and $\bar{\mathbf{q}}$ that give rise to a null production of entropy² in any process satisfying the constraint; *i.e.*

$$\bar{\mathbf{T}} \cdot \mathbf{D} - \bar{\eta} \dot{\theta} - \frac{1}{\theta} \bar{\mathbf{q}} \cdot \mathbf{g} = 0 \quad (1.5)$$

in any process consistent with (1.4). They then establish appropriate forms for $\bar{\mathbf{T}}$, $\bar{\eta}$, and $\bar{\mathbf{q}}$ completely analogous to (1.3).

In this paper we develop a general thermodynamic theory of constrained materials. We do not use relations of the form (1.1) or (1.4) to define a constraint. Instead, we specify the class of functions $\mathbf{F}(t)$, $\theta(t)$, $\mathbf{g}(t)$ ($-\infty < t < \infty$) that the material point can undergo; if at some time t not all values of $\mathbf{D}(t)$, $\dot{\theta}(t)$, and $\mathbf{g}(t)$ are possible, the point is said to be constrained.

In order to motivate the underlying assumptions of our theory, let us first consider constitutive relations of the form³

$$\begin{aligned} \psi &= \hat{\psi}(\mathbf{F}^t, \theta^t, \mathbf{g}^t), \\ \mathbf{T} &= \hat{\mathbf{T}}(\mathbf{F}^t, \theta^t, \mathbf{g}^t) + \bar{\mathbf{T}}, \\ \eta &= \hat{\eta}(\mathbf{F}^t, \theta^t, \mathbf{g}^t) + \bar{\eta}, \\ \mathbf{q} &= \hat{\mathbf{q}}(\mathbf{F}^t, \theta^t, \mathbf{g}^t) + \bar{\mathbf{q}}, \end{aligned} \quad (1.6)$$

where ψ is the specific free-energy. Rather than adopt a principle such as (1.2) or (1.5) to determine the nature of the reactions $\bar{\mathbf{T}}$, $\bar{\eta}$, and $\bar{\mathbf{q}}$, we assume instead that there exists a *reaction set* $\mathcal{R}(\mathbf{F}^t, \theta^t)$, depending on the histories \mathbf{F}^t and θ^t , such that

$$\left(\bar{\mathbf{T}}, -\bar{\eta}, -\frac{1}{\theta} \bar{\mathbf{q}} \right) \in \mathcal{R}(\mathbf{F}^t, \theta^t) \quad (1.7)$$

at each time t . We then use the Clausius-Duhem inequality

$$\rho \dot{\psi} - \mathbf{T} \cdot \mathbf{D} + \eta \dot{\theta} + \frac{1}{\theta} \mathbf{q} \cdot \mathbf{g} \leq 0 \quad (1.8)$$

¹ TRAPP [1971] obtains several interesting exact solutions within the framework of this theory.

² A slightly different approach was taken by ANDREUSSI & PODIO GUIDUGLI [1972], who include a reaction free-energy $\bar{\psi}$, and who assume, in addition to (1.5), that the reactions give rise to zero energy production.

³ Following GREEN, NAGHDI, & TRAPP, we do *not* include a reaction term $\bar{\psi}$ in (1.6). Such a quantity could easily be included; we would then be led to the conclusion that $\bar{\psi}$ be constant in every process.

to determine restrictions on the *reaction functional* \mathcal{R} . We show that if the reaction sets are *closed under scalar multiplication*,¹ and if the reaction functional is, in a certain precise sense, *maximal*,² then:

(i) The reaction functional must reduce to a function of the present values of \mathbf{F} and θ .

(ii) The reaction sets are subspaces.

(iii) The reactions obey (1.5) in each process.

(iv) The extra entropy production³

$$\begin{aligned} \sigma_E = & -\rho \frac{d}{dt} \hat{\psi}(\mathbf{F}^t, \theta^t, \mathbf{g}^t) + \hat{\mathbf{T}}(\mathbf{F}^t, \theta^t, \mathbf{g}^t) \cdot \mathbf{D} \\ & - \hat{\eta}(\mathbf{F}^t, \theta^t, \mathbf{g}^t) \dot{\theta} - \frac{1}{\theta} \hat{\mathbf{q}}(\mathbf{F}^t, \theta^t, \mathbf{g}^t) \cdot \mathbf{g} \end{aligned} \quad (1.9)$$

must be non-negative in every process.

This last result, since it does not involve the reactions, can be used, in the standard manner,⁴ to establish restrictions on the response functionals $\hat{\psi}$, $\hat{\mathbf{T}}$, $\hat{\eta}$, and $\hat{\mathbf{q}}$.

Next, we define the concept of material symmetry, as applied to constrained materials, and we use this concept to define, in the usual way, the notions of isotropy and fluidity. We then prove that:

(v) For a fluid, the only possible deformation-temperature constraint is temperature-dependent compressibility, the only possible purely mechanical constraint is incompressibility.

(vi) For an isotropic material, the only possible constraint on the temperature gradient is $\mathbf{g} \equiv \mathbf{0}$ (perfect conductivity).

We begin by defining

$$\begin{aligned} \boldsymbol{\gamma} &= (\mathbf{F}, \theta), \quad \boldsymbol{\lambda} = (\mathbf{D}, \dot{\theta}, \mathbf{g}), \quad \boldsymbol{\rho} = (\boldsymbol{\gamma}, \boldsymbol{\lambda}), \\ \bar{\boldsymbol{\tau}} &= \left(\bar{\mathbf{T}}, -\bar{\eta}, -\frac{1}{\theta} \bar{\mathbf{q}} \right), \end{aligned}$$

where all of the above are functions of time. The function $\boldsymbol{\rho}$ is called a *process*, the values $\bar{\boldsymbol{\tau}}(t)$ of $\bar{\boldsymbol{\tau}}$ are called *reactions*. In view of these definitions, the extra entropy production σ_E defined by (1.9) is a functional of the process $\boldsymbol{\rho}$:

$$\sigma_E = \hat{\sigma}(\boldsymbol{\rho}),$$

and the Clausius-Duhem inequality (1.8) reduces to

$$\hat{\sigma}(\boldsymbol{\rho}) + \bar{\boldsymbol{\tau}} \cdot \boldsymbol{\lambda} \geq 0, \quad (1.10)$$

¹ This assumption is based on past experience with special theories of constrained materials. Indeed, in each of these theories, if $\bar{\boldsymbol{\tau}}$ is a reaction, then so is $\alpha \bar{\boldsymbol{\tau}}$ for every scalar α (cf. (1.3)).

² This assumption insures that the reactions have maximum indeterminacy compatible with the second law.

³ More precisely, $\sigma_E/\rho\theta$ is the specific extra entropy production.

⁴ The abstract formalism developed by GURTIN [1968] (see also TRUESDELL [1969, Ch. 3], COLEMAN & OWEN [1970]) can be applied, almost without change, to establish restrictions on the response functionals similar to those first arrived at by COLEMAN [1964].

where by (1.7)

$$\bar{\tau}(t) \in \mathcal{R}(\gamma^t) \quad (1.11)$$

at each time t . We take (1.10) and (1.11), rather than the more complicated expressions (1.6)–(1.8), as the starting point for our theory. We assume that γ has values in some set Γ , that λ has values in an inner product space A , and that $\mathcal{R}(\gamma^t) \subset A$. This allows us to develop a theory that is applicable not only to simple materials, but also to rods, multipolar media, and other more general materials.

2. Notation

Throughout this paper \mathbb{R} denotes the reals, \mathbb{R}^+ the strictly positive reals; we use the word “time” as a synonym for “real number”.

Let A be a set, and let

$$F(\mathbb{R}, A) = \text{the space of all functions from } \mathbb{R} \text{ into } A.$$

The **history** of $\gamma \in F(\mathbb{R}, A)$ up to time t is the function $\gamma^t: [0, \infty) \rightarrow A$ defined by

$$\gamma^t(s) = \gamma(t-s).$$

Given two functions $\beta, \gamma \in F(\mathbb{R}, A)$, we write $\beta \diamond \gamma$ for the function in $F(\mathbb{R}, A)$ defined by

$$\beta \diamond \gamma(t) = \begin{cases} \beta(t), & t < 0 \\ \gamma(t), & t \geq 0. \end{cases}$$

Let $\mathcal{P} \subset F(\mathbb{R}, A)$. We say that \mathcal{P} is **translation invariant** if given any $\gamma \in \mathcal{P}$ and any $h \in \mathbb{R}$, the function

$$t \mapsto \gamma(t+h) \quad (\mathbb{R} \rightarrow A)$$

also lies in \mathcal{P} . We shall apply the above definitions to a function class

$$\mathcal{P} \subset F(\mathbb{R}, A_1) \times F(\mathbb{R}, A_2)$$

and to functions in \mathcal{P} . This is done in the obvious manner: by identifying $F(\mathbb{R}, A_1) \times F(\mathbb{R}, A_2)$ with $F(\mathbb{R}, A_1 \times A_2)$.

Finally, when A is contained in an inner product space,

$$RC(\mathbb{R}, A) = \{\gamma \in F(\mathbb{R}, A): \gamma \text{ is right-continuous}\},$$

$$RD(\mathbb{R}, A) = \{\gamma \in F(\mathbb{R}, A): \gamma \text{ is right-differentiable}\},$$

and we write $\dot{\gamma}$ for the right-hand derivative of $\gamma \in RD(\mathbb{R}, A)$.

For convenience, we also use the following notation:

\mathcal{V} = the vector space associated with three-dimensional Euclidean space,

Lin = the space of all tensors (linear transformations) on \mathcal{V} ,

$$\text{Sym} = \{F \in \text{Lin}: F = F^T\},$$

$$\text{Skw} = \{F \in \text{Lin}: F = -F^T\},$$

$$\text{Lin}^+ = \{F \in \text{Lin}: \det F > 0\}$$

$$\text{Orth}^+ = \{Q \in \text{Lin}^+: Q^T Q = Q Q^T = \mathbf{1}\}$$

$$\text{Unim}^+ = \{H \in \text{Lin}^+: \det H = 1\}.$$

Of course, here \det is the determinant and F^T is the transpose of F . Further,

$$\text{sym } F = \frac{1}{2}(F + F^T)$$

is the symmetric part of F , tr is the trace operator, and

$$A \cdot B = \text{tr}(AB^T)$$

designates the inner product on Lin . Cartesian products of the above spaces will always be endowed with the natural inner product; e.g., for

$$(A, u), (B, v) \in \text{Lin} \times \mathcal{V},$$

$$(A, u) \cdot (B, v) = A \cdot B + u \cdot v.$$

3. Abstract Theory of Constraints

Throughout this section Γ is a set, Λ is an inner product space.

By a **process class** we mean a set

$$\mathcal{P} \subset F(\mathbb{R}, \Gamma) \times F(\mathbb{R}, \Lambda)$$

with the following properties:

(P₁) \mathcal{P} is translation invariant;¹

(P₂) if $\rho_1 = (\gamma_1, \lambda_1)$ and $\rho_2 = (\gamma_2, \lambda_2)$ belong to \mathcal{P} , and if $\gamma_1(0) = \gamma_2(0)$, then $\rho_1 \diamond \rho_2$ belongs to \mathcal{P} .

Let \mathcal{P} be a process class. For convenience, we write

$$\begin{aligned} \mathcal{P}_0 &= \{\rho_0 : \rho_0 = \rho(0) \quad \text{for some } \rho \in \mathcal{P}\}, \\ \Gamma_0 &= \{\gamma_0 : (\gamma_0, \lambda_0) \in \mathcal{P}_0 \quad \text{for some } \lambda_0\}, \\ \mathcal{P}^* &= \{\rho^* : \rho^* = \rho^0 \quad \text{for some } \rho \in \mathcal{P}\}, \\ \Gamma^* &= \{\gamma^* : (\gamma^*, \lambda^*) \in \mathcal{P}^* \quad \text{for some } \lambda^*\}, \end{aligned} \tag{3.1}^2$$

and, for $\gamma_0 \in \Gamma_0$,

$$\Lambda_0(\gamma_0) = \{\lambda_0 : (\gamma_0, \lambda_0) \in \mathcal{P}_0\}. \tag{3.2}$$

By (P₁), given any $\rho = (\gamma, \lambda) \in \mathcal{P}$ and any time t ,

$$\rho(t) \in \mathcal{P}_0, \quad \gamma(t) \in \Gamma_0, \quad \rho^t \in \mathcal{P}^*, \quad \gamma^t \in \Gamma^*, \quad \lambda(t) \in \Lambda_0(\gamma(t)).$$

Let $\rho \in \mathcal{P}$, $(\gamma_0, \lambda_0) \in \mathcal{P}_0$, $\rho^* \in \mathcal{P}^*$, and $\gamma^* \in \Gamma^*$. We use the following terminology: ρ is a **process**, γ_0 is a **site**, λ_0 is a **flux**, ρ^* is a **process history**, γ^* is a **site history**, Γ_0 is the **site cross section**, $\Lambda_0(\gamma_0)$ is the **flux cross section** at the site γ_0 . We say that \mathcal{P} is **constrained** if $\Lambda_0(\gamma_0)$ is a *proper* subset of Λ for some site $\gamma_0 \in \Gamma_0$, \mathcal{P} is **unconstrained** if $\Lambda_0(\gamma_0) = \Lambda$ for all $\gamma_0 \in \Gamma_0$.

By a functional for the **extra entropy production** on \mathcal{P} we mean a mapping

$$\hat{\sigma} : \mathcal{P} \rightarrow F(\mathbb{R}, \mathbb{R});$$

¹ Thus if \mathcal{P} is "constrained", the "constraints" cannot depend explicitly on the time.

² Here ρ^0 is the history of ρ up to time $t=0$.

in any process ρ , $\hat{\sigma}(\rho)$ is a real-valued function of time whose value $\hat{\sigma}(\rho)(t)$ at t is the extra entropy production at time t in the process ρ .

A **reaction functional** for \mathcal{P} is a mapping \mathcal{R} that assigns to each site history $\gamma^* \in \Gamma^*$ a non-empty set $\mathcal{R}(\gamma^*) \subset \Lambda$ with $\mathcal{R}(\gamma^*)$ closed under scalar multiplication. We call $\mathcal{R}(\gamma^*)$ the **reaction set** for γ^* ; the elements $\bar{\tau} \in \mathcal{R}(\gamma^*)$ are called **reactions**. If $\rho = (\gamma, \lambda)$ is a process, and if $\bar{\tau}: \mathbb{R} \rightarrow \Lambda$ satisfies $\bar{\tau}(t) \in \mathcal{R}(\gamma^t)$ for all t , then $(\rho, \bar{\tau})$ is called a **process-reaction pair** (for \mathcal{P} and \mathcal{R}). Given a process-reaction pair,

$$\bar{\sigma} = \bar{\tau} \cdot \lambda \tag{3.3}$$

is the *entropy production due to the reaction*.

Let $\hat{\sigma}$ be a functional for the extra entropy production on \mathcal{P} , and let \mathcal{R} be a reaction functional for \mathcal{P} . Then \mathcal{R} is **thermodynamically admissible** relative to $\hat{\sigma}$ if \mathcal{R} is the *maximal* reaction functional consistent with the following:

Dissipation Axiom. If $(\rho, \bar{\tau})$ is a process-reaction pair (for \mathcal{P} and \mathcal{R}) with $\rho = (\gamma, \lambda)$, then

$$\hat{\sigma}(\rho) + \bar{\tau} \cdot \lambda \geq 0.$$

The assumption of **maximality** is the requirement that: if \mathcal{R}' is another reaction functional for \mathcal{P} consistent with the dissipation axiom, then $\mathcal{R}' < \mathcal{R}$, i.e.

$$\mathcal{R}'(\gamma^*) \subset \mathcal{R}(\gamma^*)$$

for every $\gamma^* \in \Gamma^*$. Clearly, there exists *at most one* thermodynamically admissible reaction functional. Indeed, by the assumption of maximality, if both \mathcal{R} and \mathcal{R}' are thermodynamically admissible, then $\mathcal{R}' < \mathcal{R}$ and $\mathcal{R} < \mathcal{R}'$, so that $\mathcal{R} = \mathcal{R}'$.

Theorem 1. *Let \mathcal{P} be a process class, let $\hat{\sigma}$ be a functional for the extra entropy production on \mathcal{P} , and let \mathcal{R} be a reaction functional for \mathcal{P} . Then \mathcal{R} is thermodynamically admissible relative to $\hat{\sigma}$ if and only if:*

(i) *for every site history $\gamma^* \in \Gamma^*$*

$$\mathcal{R}(\gamma^*) = \Lambda_0(\gamma^*(0))^\perp; \tag{3.4}$$

(ii) *for every process*

$$\hat{\sigma}(\rho) \geq 0.$$

We postpone, until later, the proof of this theorem. The next corollary is a direct consequence.

Corollary 1. *Let \mathcal{P} and $\hat{\sigma}$ satisfy the hypotheses of the theorem, and let \mathcal{R} be a reaction functional for \mathcal{P} with \mathcal{R} thermodynamically admissible relative to $\hat{\sigma}$. Then:*

(i) *\mathcal{R} is thermodynamically admissible relative to every non-negative functional describing the extra entropy production on \mathcal{P} .*

(ii) *In each process-reaction pair the entropy production (3.3) due to the reaction is zero.*

(iii) *The reaction functional reduces to a function of the present site:*

$$\mathcal{R}(\gamma^*) = \mathcal{R}(\gamma^*(0)).$$

- (iv) For each site γ_0 the reaction set $\mathcal{R}(\gamma_0)$ is a subspace of Λ .
- (v) \mathcal{P} is unconstrained if and only if

$$\mathcal{R}(\gamma_0) = \{0\}$$

for every site γ_0 .

Given a process class \mathcal{P} and any $\hat{\sigma}: \mathcal{P} \rightarrow F(\mathbb{R}, \mathbb{R}^+)$, it is clear from the theorem and (i) of the corollary that the reaction functional \mathcal{R} defined by (3.4) is the *only* reaction functional for \mathcal{P} that is thermodynamically admissible relative to $\hat{\sigma}$. Thus, as would be expected, the reactions depend only on the nature of the constraint and are independent of the particular constitutive functional $\hat{\sigma}$ describing the extra entropy production. For this reason, the mapping \mathcal{R} defined on the site cross section Γ_0 by

$$\mathcal{R}(\gamma_0) = \Lambda_0(\gamma_0)^\perp \tag{3.5}$$

is called the **thermodynamically admissible reaction function** for \mathcal{P} .

With a view toward proving the theorem, we now establish

Lemma 1. *Let \mathcal{P} be a process class. Then given a site history $\gamma^* \in \Gamma^*$ and a flux $\lambda_0 \in \Lambda_0(\gamma^*(0))$, there exists a history λ^* such that*

$$(\gamma^*, \lambda^*) \in \mathcal{P}^*, \quad \lambda^*(0) = \lambda_0. \tag{3.6}$$

Proof. In view of (3.1)_{3,4}, there exists a process $\bar{\rho} = (\bar{\gamma}, \bar{\lambda})$ such that $\bar{\gamma}^0 = \gamma^*$; and, by (3.1)₁ and (3.2), there exists a process $\tilde{\rho} = (\tilde{\gamma}, \tilde{\lambda})$ such that $\tilde{\gamma}(0) = \gamma^*(0)$ ($= \bar{\gamma}(0)$) and $\tilde{\lambda}(0) = \lambda_0$. By (P₂), $\rho = (\gamma, \lambda) = \bar{\rho} \diamond \tilde{\rho}$ belongs to \mathcal{P} ; if we define $\lambda^* = \lambda^0$, then (γ^*, λ^*) satisfies (3.6). \square

Proof of Theorem 1. Assume first that (i) and (ii) hold. Then a simple calculation shows that \mathcal{R} and $\hat{\sigma}$ satisfy the dissipation axiom. To see that \mathcal{R} is maximal, let \mathcal{R}' be a reaction functional for \mathcal{P} consistent with the dissipation axiom. Choose $\rho^* = (\gamma^*, \lambda^*) \in \mathcal{P}^*$. By (3.1)₃ there exists a process $\rho = (\gamma, \lambda)$ such that $\rho^0 = \rho^*$. Let $\tau_0 \in \mathcal{R}'(\gamma^*)$ and define $\bar{\tau}: \mathbb{R} \rightarrow \Lambda$ by

$$\bar{\tau}(t) = \begin{cases} 0, & t = 0 \\ \tau_0, & t \neq 0. \end{cases}$$

Since \mathcal{R}' has values that are closed under scalar multiplication, 0 belongs to each reaction set; thus $(\rho, \bar{\tau})$ is a process-reaction pair (for \mathcal{P} and \mathcal{R}'), and we conclude from the dissipation axiom (applied at $t = 0$) that

$$\sigma(\rho)(0) + \tau_0 \cdot \lambda^*(0) \geq 0.$$

This inequality must hold for every $\tau_0 \in \mathcal{R}'(\gamma^*)$. Thus, since $\mathcal{R}'(\gamma^*)$ is closed under scalar multiplication,

$$\tau_0 \cdot \lambda^*(0) = 0$$

whenever $(\gamma^*, \lambda^*) \in \mathcal{P}^*$ and $\tau_0 \in \mathcal{R}'(\gamma^*)$. Thus letting $\lambda_0 \in \Lambda_0(\gamma^*(0))$, we conclude, with the aid of Lemma 1, that

$$\tau_0 \cdot \lambda_0 = 0;$$

hence $\mathcal{R}'(\gamma^*) \subset \Lambda_0(\gamma^*(0))^\perp$. Thus $\mathcal{R}' \subset \mathcal{R}$ and \mathcal{R} is maximal.

To prove the converse assertion, assume that \mathcal{R} is thermodynamically admissible relative to $\hat{\sigma}$. Then the dissipation axiom applied to a process-reaction pair $(\rho, \bar{\tau})$ with ρ arbitrary and $\bar{\tau} \equiv 0$ leads to (ii). Next, let \mathcal{S} be the reaction functional defined by

$$\mathcal{S}(\gamma^*) = A_0(\gamma^*(0))^\perp$$

for $\gamma^* \in \Gamma^*$. It then follows from (ii) and the assertion established in the last paragraph that \mathcal{S} is thermodynamically admissible relative to $\hat{\sigma}$. Thus, in view of the remark made in the paragraph preceding the theorem, $\mathcal{R} = \mathcal{S}$. \square

4. Mechanical Theory

a) General Theory

The mechanical theory of simple materials falls within our framework provided we let

$$\Gamma = \text{Lin}^+, \quad \Lambda = \text{Sym},$$

and identify

$$\gamma \leftrightarrow F, \quad \lambda \leftrightarrow D, \quad \bar{\tau} \leftrightarrow \bar{T},$$

where F is the deformation gradient, $D = \text{sym}(\dot{F}F^{-1})$ the stretching tensor, and \bar{T} the Cauchy reaction stress. Thus we assume that each process class \mathcal{P} under consideration is a subset of

$$\mathcal{F} = \{(F, D) : F \in RD(\mathbb{R}, \text{Lin}^+), D = \text{sym}(\dot{F}F^{-1})\}. \quad (4.1)$$

It is interesting to note that, by (ii) of Corollary 1,

$$\bar{T} \cdot D = 0$$

for every process-reaction pair; *i.e.*, the power expended by the reaction stress vanishes. This assertion is the starting point of the mechanical theory of constrained materials proposed by NOLL and discussed in the Introduction. Further, by (iii) of Corollary 1, the thermodynamically admissible reaction functional $\mathcal{R}(F^t)$ for a given process class $\mathcal{P} \subset \mathcal{F}$ must reduce to a function $\mathcal{R}(F(t))$ of the present value of F .

Generally, for the process classes of physical interest, the sites F_0 lie in a manifold $\mathcal{M} \subset \text{Lin}^+$. With this in mind, we introduce the following definition. A **constraint manifold** is a *connected* C^1 -manifold $\mathcal{M} \subset \text{Lin}^+$ with the following properties:

$$(M_1) \quad 1 \in \mathcal{M};$$

$$(M_2) \quad \text{if } F_0 \in \mathcal{M} \text{ and } Q \in \text{Orth}^+, \text{ then } QF_0 \in \mathcal{M}.$$

We denote by $\dot{\mathcal{M}}(F_0)$ the corresponding *tangent space* at $F_0 \in \mathcal{M}$.

Condition (M_1) is simply the requirement that the reference configuration be chosen judiciously; (M_2) asserts that \mathcal{M} be invariant under changes in frame, *i.e.*, that \mathcal{M} be objective.

Let $\mathcal{P} \subset \mathcal{F}$ be a process class, and let \mathcal{M} be a constraint manifold. We then say that \mathcal{P} is **compatible** with \mathcal{M} if the site and flux cross sections corresponding

to \mathcal{P} satisfy¹

$$\Gamma_0 = \mathcal{M},$$

$$A_0(F_0) = \{D_0 \in \text{Sym} : D_0 = \text{sym}(F' F_0^{-1}), F' \in \dot{\mathcal{M}}(F_0)\}, \quad F_0 \in \mathcal{M}. \quad (4.2)$$

The next result demonstrates that this notion is not empty.

Proposition 1. *Let \mathcal{M} be a constraint manifold, and let \mathcal{P} be the set of all pairs $(F, D) \in \mathcal{F}$ with $F \in RD(\mathbb{R}, \mathcal{M})$. Then \mathcal{P} is a process class compatible with \mathcal{M} .*

The proof of this proposition is based on

Lemma 2. *Let \mathcal{M} be a constraint manifold. Then given $F_0 \in \mathcal{M}$ and $F' \in \dot{\mathcal{M}}(F_0)$, there exists a function $F \in RD(\mathbb{R}, \mathcal{M})$ such that*

$$F(0) = F_0, \quad \dot{F}(0) = F'.$$

Proof. Since \mathcal{M} is a C^1 -manifold, there exists an $\alpha > 0$ and a class C^1 function $G: [-\alpha, \alpha] \rightarrow \mathcal{M}$ such that

$$G(0) = F_0, \quad \dot{G}(0) = F'.$$

Choose $F \in RD(\mathbb{R}, \mathcal{M})$ as follows: $F(t) = G(-\alpha)$ for $t < -\alpha$, $F(t) = G(t)$ for $-\alpha \leq t \leq \alpha$, and $F(t) = G(\alpha)$ for $t > \alpha$. \square

Proof of Proposition 1. It is a simple matter to verify that \mathcal{P} is a process class and that (4.2)₁ holds. To establish (4.2)₂ choose $F_0 \in \mathcal{M}$. Trivially,

$$A_0(F_0) \subset \mathcal{D} = \{D_0 \in \text{Sym} : D_0 = \text{sym}(F' F_0^{-1}), F' \in \dot{\mathcal{M}}(F_0)\}.$$

Choose $D_0 \in \mathcal{D}$. Then there exists an $F' \in \dot{\mathcal{M}}(F_0)$ such that

$$D_0 = \text{sym}(F' F_0^{-1}).$$

By Lemma 2 there exists an $F \in RD(\mathbb{R}, \mathcal{M})$ such that

$$F(0) = F_0, \quad \dot{F}(0) = F'.$$

If we let $D = \text{sym}(\dot{F} F^{-1})$, then $(F, D) \in \mathcal{P}$, and hence $D(t) \in A_0(F(t))$ for all t . But $D(0) = D_0$; thus $D_0 \in A_0(F_0)$, and hence $\mathcal{D} \subset A_0(F_0)$. Therefore $\mathcal{D} = A_0(F_0)$ and (4.2)₂ holds. \square

Proposition 2. *Let \mathcal{P} be a process class compatible with a constraint manifold \mathcal{M} . Then \mathcal{P} is constrained if and only if*

$$\dim \mathcal{M} \leq 8. \quad (4.3)$$

Again the proof is based on a lemma.

Lemma 3. *Let \mathcal{M} be a constraint manifold. Then*

$$\text{Skw} \subset \dot{\mathcal{M}}(\mathbf{1}). \quad (4.4)$$

¹ At first sight, it might appear that (4.2)₂ is a consequence of (4.1) and (4.2)₁. That this is not so is clear from the following counter-example: take \mathcal{P} equal to the set of all $(F, D) \in \mathcal{F}$ such that F is a constant function with value in \mathcal{M} . Then \mathcal{P} is a process class with $\Gamma_0 = \mathcal{M}$, but $A(F_0) \equiv \{0\}$.

Proof. By (M₁) and (M₂), $\text{Orth}^+ \subset \mathcal{M}$; and the proof follows from the fact that the tangent space to the manifold Orth^+ at $\mathbf{1} \in \text{Orth}^+$ is the space Skw . \square

Proof of Proposition 2. Assume that \mathcal{P} is constrained. Then for some $F_0 \in \mathcal{M}$, $\Lambda_0(F_0) \neq \text{Sym}$, and hence there exists a $D_0 \in \text{Sym}$, $D_0 \notin \Lambda_0(F_0)$. Let $F' = D_0 F_0$ (so that $D_0 = \text{sym}(F' F_0^{-1})$.) Then, by (4.2)₂, $F' \notin \dot{\mathcal{M}}(F_0)$; hence $\dot{\mathcal{M}}(F_0) \neq \text{Lin}$. But $\dot{\mathcal{M}}(F_0)$ is a subspace of Lin and $\dim \text{Lin} = 9$; thus $\dim \dot{\mathcal{M}} = \dim \dot{\mathcal{M}}(F_0) \leq 8$.

Conversely, assume that (4.3) holds. Then, in particular, $\dim \dot{\mathcal{M}}(\mathbf{1}) \leq 8$, and there exists an $F' \in \text{Lin}$ such that

$$F' \notin \dot{\mathcal{M}}(\mathbf{1}). \tag{4.6}$$

Let $D_0 = \text{sym } F'$ and assume that $D_0 \in \Lambda_0(\mathbf{1})$. Then there exists a $G' \in \dot{\mathcal{M}}(\mathbf{1})$ such that $D_0 = \text{sym } G'$. Thus $\text{sym } F' = \text{sym } G'$ and $F' = G' + W$, $W \in \text{Skw}$. By Lemma 3, $W \in \dot{\mathcal{M}}(\mathbf{1})$; thus, since $\dot{\mathcal{M}}(\mathbf{1})$ is a subspace, $F' = G' + W \in \dot{\mathcal{M}}(\mathbf{1})$, which contradicts (4.6). Thus $D_0 \notin \Lambda_0(\mathbf{1})$; hence $\Lambda_0(\mathbf{1}) \neq \text{Sym}$ and \mathcal{P} is constrained. \square

Given a constraint manifold \mathcal{M} , it is clear from (4.2)₂ that the (thermodynamically admissible) reaction function \mathcal{R} defined by (3.5) is the *same* for each process class \mathcal{P} compatible with \mathcal{M} . For this reason we call \mathcal{R} the reaction function *corresponding to \mathcal{M}* .

b) Examples

We now give some examples of constraint manifolds and use our previous results to determine the corresponding reaction functions.

(1) **Incompressibility.**¹ Here

$$\begin{aligned} \mathcal{M} &= \{F \in \text{Lin}^+ : \det F = 1\} = \text{Unim}^+, \\ \dot{\mathcal{M}}(F) &= \{F' \in \text{Lin} : \text{tr}(F' F^{-1}) = 0\}, \end{aligned}$$

and we conclude from (3.5) and (4.2)₂ that both $\Lambda_0(F)$ and the reaction set $\mathcal{R}(F)$ are independent of F , and, since $\mathbf{1} \cdot D = \text{tr } D$, that

$$\begin{aligned} \Lambda_0 &= \{D \in \text{Sym} : \text{tr } D = 0\}, \\ \mathcal{R} &= \{\alpha \mathbf{1} : \alpha \in \mathbb{R}\}. \end{aligned}$$

Thus each reaction stress $\bar{T} \in \mathcal{R}$ is an arbitrary pressure:

$$\bar{T} = -p \mathbf{1}.$$

(2) **Rigidity.** Here

$$\begin{aligned} \mathcal{M} &= \text{Orth}^+, \\ \Lambda_0 &= \{\mathbf{0}\}, \\ \mathcal{R} &= \text{Sym}, \end{aligned}$$

so that the reaction stress is an arbitrary symmetric tensor.

¹ Cf. TRUESDELL & NOLL [1965, §30].

(3) **Inextensibility**¹ in the direction e in the reference configuration, where e is a unit vector. For this example,

$$\begin{aligned}\mathcal{M} &= \{F \in \text{Lin}^+ : |Fe| = 1\}, \\ \dot{\mathcal{M}}(F) &= \{F' \in \text{Lin} : (F^T F') \cdot (e \otimes e) = 0\}, \\ \Lambda_0(F) &= \{D \in \text{Sym} : D \cdot (Fe \otimes Fe) = 0\}, \\ \mathcal{R}(F) &= \{\alpha(Fe \otimes Fe) : \alpha \in \mathbb{R}\},\end{aligned}$$

and the reaction stress

$$\bar{T} = \alpha(Fe \otimes Fe) \quad (\alpha \text{ arbitrary})$$

is an arbitrary pure tension (or compression) in the direction Fe .

(4) **Orthogonality preserving** with respect to the directions e and f in the reference configuration, where e and f are orthogonal unit vectors. Here

$$\begin{aligned}\mathcal{M} &= \{F \in \text{Lin}^+ : Fe \cdot Ff = 0\}, \\ \dot{\mathcal{M}}(F) &= \{F' \in \text{Lin} : (F^T F') \cdot \text{sym}(e \otimes f) = 0\}, \\ \Lambda_0(F) &= \{D \in \text{Sym} : D \cdot (e \otimes f) = 0\}, \\ \mathcal{R}(F) &= \{\alpha \text{sym}(Fe \otimes Ff) : \alpha \in \mathbb{R}\},\end{aligned}$$

and

$$\bar{T} = \alpha \text{sym}(Fe \otimes Ff) \quad (\alpha \text{ arbitrary})$$

is an arbitrary pure shear corresponding to the direction pair (Fe, Ff) .

c) Material Symmetry

Let \mathcal{M} be a constraint manifold. A tensor $H \in \text{Unim}^+$ is a **symmetry transformation** for \mathcal{M} provided

$$\mathcal{M} = \mathcal{M}H. \quad (4.7)$$

This definition, in conjunction with (3.1) and (4.2)₂, implies the following transformation laws: for every $F \in \mathcal{M}$ and every symmetry transformation H ,

$$\dot{\mathcal{M}}(FH) = \dot{\mathcal{M}}(F)H, \quad \Lambda_0(FH) = \Lambda_0(F), \quad \mathcal{R}(FH) = \mathcal{R}(F). \quad (4.8)$$

It is not difficult to verify that the set \mathcal{G} of all symmetry transformations is a subgroup of Unim^+ . We call \mathcal{G} the **symmetry group**² for \mathcal{M} , and we say that \mathcal{M} describes a **fluid** if

$$\mathcal{G} = \text{Unim}^+,$$

a **solid** if for some $P \in \mathcal{M}$

$$P \mathcal{G} P^{-1} \subset \text{Orth}^+,$$

¹ Cf. ADKINS & RIVLIN [1955], RIVLIN [1955], GREEN & ADKINS [1960, Ch. VII], TRUESDELL & NOLL [1965, §30].

² The definitions contained in this paragraph are due to NOLL [1958]; see also TRUESDELL & NOLL [1965, §§31–33]. In these definitions P describes the deformation gradient from the reference configuration to an *undistorted configuration*.

an isotropic material if for some $P \in \mathcal{M}$

$$\text{Orth}^+ \subset P \mathcal{G} P^{-1}.$$

The next theorem shows that for a fluid the only possible constraint is incompressibility.

Theorem 2. *Let \mathcal{M} describe a fluid. Then either each process class compatible with \mathcal{M} is unconstrained, or \mathcal{M} describes an incompressible fluid.*

Proof. Let

$$I = \{\alpha \in \mathbb{R} : \alpha \mathbf{1} \in \mathcal{M}\}.$$

Choose $F \in \text{Lin}^+$. Then $H = (\det F)^{\frac{1}{3}} F^{-1} \in \text{Unim}^+ = \mathcal{G}$, and by (4.7)

$$F \in \mathcal{M} \Rightarrow FH \in \mathcal{M} \Rightarrow (\det F)^{\frac{1}{3}} \mathbf{1} \in \mathcal{M} \Rightarrow (\det F)^{\frac{1}{3}} \in I.$$

On the other hand, since $H^{-1} \in \mathcal{G}$,

$$(\det F)^{\frac{1}{3}} \in I \Rightarrow (\det F)^{\frac{1}{3}} \mathbf{1} \in \mathcal{M} \Rightarrow (\det F)^{\frac{1}{3}} H^{-1} \in \mathcal{M} \Rightarrow F \in \mathcal{M}.$$

Thus

$$\mathcal{M} = \{F \in \text{Lin}^+ : (\det F)^{\frac{1}{3}} \in I\}. \tag{4.9}$$

Let $\varphi: \text{Lin}^+ \rightarrow \mathbb{R}$ be defined by $\varphi(F) = (\det F)^{\frac{1}{3}}$. Then φ is continuous, and by (4.9)

$$I = \varphi(\mathcal{M}), \quad \mathcal{M} = \varphi^{-1}(I).$$

Thus I is connected (since \mathcal{M} is). Assume that I has a non-empty interior \mathring{I} . Then $\varphi^{-1}(\mathring{I})$ is an open set in Lin , and it follows that $\mathcal{M}(F) = \text{Lin}$ and $\dim \mathcal{M} = 9$. We therefore conclude from Proposition 2 that if the process class \mathcal{P} induced by \mathcal{M} is constrained, then I must have an empty interior. The only connected sets in \mathbb{R} with this property are singletons. Thus, and by (M_1) , if \mathcal{P} is constrained, $I = \{1\}$, and \mathcal{M} describes an incompressible fluid. \square

5. Thermodynamical Theory

a) General Theory

Here we let

$$\Gamma = \text{Lin}^+ \times \mathbb{R}^+, \quad A = \text{Sym} \times \mathbb{R} \times \mathcal{V},$$

and identify

$$\gamma \leftrightarrow (F, \theta), \quad \lambda \leftrightarrow (D, \dot{\theta}, g), \quad \bar{\tau} \leftrightarrow \left(\bar{T}, -\bar{\eta}, -\frac{1}{\theta} \bar{q} \right),$$

where F is the deformation gradient, D the stretching tensor, θ the temperature, g the temperature gradient, \bar{T} the Cauchy reaction stress, $\bar{\eta}$ the reaction entropy, and \bar{q} the reaction heat flux. Thus we assume that each process class under consideration is a subset of

$$\mathcal{F} = \{(\gamma, \lambda) : \gamma = (F, \theta), \lambda = (D, \dot{\theta}, g), \gamma \in RD(\mathbb{R}, \Gamma), D = \text{sym}(\dot{F}F^{-1}), g \in F(\mathbb{R}, \mathcal{V})\}.$$

We conclude from (ii) of Corollary 1 that

$$\bar{T} \cdot \mathbf{D} - \bar{\eta} \dot{\theta} + \frac{1}{\theta} \bar{q} \cdot \mathbf{g} = 0 \tag{5.1}$$

in every process-reaction pair, which is the initial assumption of the theory proposed by GREEN, NAGHDI & TRAPP [1970]. Further, by (iii) of Corollary 1 the thermodynamically admissible reaction functional for any given process class must reduce to a function of the present values of \mathbf{F} and θ .

With a view toward generalizing the notion of a constraint manifold introduced in Section 4, let $(\mathcal{M}, \mathcal{N})$ be a pair consisting of:

- (i) a C^1 -manifold \mathcal{M} in $\text{Lin}^+ \times \mathbb{R}^+$ with tangent space $\dot{\mathcal{M}}(\mathbf{F}_0, \theta_0)$ at $(\mathbf{F}_0, \theta_0) \in \mathcal{M}$;
- (ii) a mapping \mathcal{N} that assigns to each $(\mathbf{F}_0, \theta_0) \in \mathcal{M}$ a non-empty subspace $\mathcal{N}(\mathbf{F}_0, \theta_0) \subset \mathcal{V}$.

Then $(\mathcal{M}, \mathcal{N})$ is a **constraint pair** provided the following three conditions are satisfied:

- (N₁) $(\mathbf{1}, \theta_0) \in \mathcal{M}$ for some $\theta_0 \in \mathbb{R}^+$;
- (N₂) if $(\mathbf{F}_0, \theta_0) \in \mathcal{M}$ and $\mathbf{Q} \in \text{Orth}^+$, then $(\mathbf{Q}\mathbf{F}_0, \theta_0) \in \mathcal{M}$ and $\mathbf{Q}^T \mathcal{N}(\mathbf{Q}\mathbf{F}_0, \theta_0) = \mathcal{N}(\mathbf{F}_0, \theta_0)$;
- (N₃) $\dim \mathcal{N}(\mathbf{F}_0, \theta_0)$ is the same for all $(\mathbf{F}_0, \theta_0) \in \mathcal{M}$ (we write $\dim \mathcal{N}$ for this number).

We shall study processes restricted by $(\mathcal{M}, \mathcal{N})$ in the following manner: $(\mathbf{F}(t), \theta(t)) \in \mathcal{M}$ and $\mathbf{g}(t) \in \mathcal{N}(\mathbf{F}(t), \theta(t))$ for all t . More precisely, a process class $\mathcal{P} (\subset \mathcal{F})$ is **compatible** with $(\mathcal{M}, \mathcal{N})$ if the site and flux cross sections corresponding to \mathcal{P} satisfy

$$\begin{aligned} \Gamma_0 &= \mathcal{M}, \\ \Lambda_0(\mathbf{F}_0, \theta_0) &= \mathcal{D}(\mathbf{F}_0, \theta_0) \times \mathcal{N}(\mathbf{F}_0, \theta_0), \quad (\mathbf{F}_0, \theta_0) \in \mathcal{M}, \end{aligned} \tag{5.2}^1$$

where

$$\mathcal{D}(\mathbf{F}_0, \theta_0) = \{(\mathbf{D}_0, \theta') : \mathbf{D}_0 = \text{sym}(\mathbf{F}'\mathbf{F}_0^{-1}), \quad (\mathbf{F}', \theta') \in \dot{\mathcal{M}}(\mathbf{F}_0, \theta_0)\}.$$

An example of a process class \mathcal{P} compatible with an arbitrary constraint pair $(\mathcal{M}, \mathcal{N})$ is furnished by the set of all pairs $(\gamma, \lambda) \in \mathcal{F}$ with $\gamma = (\mathbf{F}, \theta)$, $\lambda = (\mathbf{D}, \dot{\theta}, \mathbf{g})$, $(\mathbf{F}, \theta) \in \text{RD}(\mathbb{R}, \mathcal{M})$, $\mathbf{g} \in \text{RC}(\mathbb{R}, \mathcal{V})$, and $\mathbf{g}(t) \in \mathcal{N}(\mathbf{F}(t), \theta(t))$ for all $t \in \mathbb{R}$. The proof of this assertion is almost identical to the proof of Proposition 1.

Proposition 3. *Let \mathcal{P} be a process class compatible with a constraint pair $(\mathcal{M}, \mathcal{N})$. Then \mathcal{P} is constrained if and only if*

$$\dim \mathcal{M} \leq 8 \quad \text{or} \quad \dim \mathcal{N} \leq 2.$$

We omit the proof; it is completely analogous to the proof of Proposition 2.

The next theorem is a direct consequence of (3.5), (5.2), and the fact that $\mathcal{D}(\mathbf{F}_0, \theta_0)$ and $\mathcal{N}(\mathbf{F}_0, \theta_0)$ are subspaces of $\text{Sym} \times \mathbb{R}$ and \mathcal{V} , respectively.

¹ Of course, by (5.2) we mean that $(\mathbf{D}_0, \theta', \mathbf{g}_0) \in \Lambda_0(\mathbf{F}_0, \theta_0) \Leftrightarrow (\mathbf{D}_0, \theta') \in \mathcal{D}(\mathbf{F}_0, \theta_0)$ and $\mathbf{g}_0 \in \mathcal{N}(\mathbf{F}_0, \theta_0)$.

Theorem 3. *Let $(\mathcal{M}, \mathcal{N})$ be a constraint pair. Then the thermodynamically admissible reaction function \mathcal{R} is the same for each process class compatible with $(\mathcal{M}, \mathcal{N})$. Moreover,*

$$\mathcal{R}(\mathbf{F}_0, \theta_0) = \mathcal{T}(\mathbf{F}_0, \theta_0) \times \mathcal{Q}(\mathbf{F}_0, \theta_0)$$

for every $(\mathbf{F}_0, \theta_0) \in \mathcal{M}$, where

$$\begin{aligned} \mathcal{T}(\mathbf{F}_0, \theta_0) &= \mathcal{D}(\mathbf{F}_0, \theta_0)^\perp, \\ \mathcal{Q}(\mathbf{F}_0, \theta_0) &= \mathcal{N}(\mathbf{F}_0, \theta_0)^\perp. \end{aligned} \tag{5.3}$$

An interesting consequence of (5.3) is that

$$\bar{\mathbf{T}} \cdot \mathbf{D} - \bar{\eta} \dot{\theta} = 0, \quad \bar{\mathbf{q}} \cdot \mathbf{g} = 0$$

for every process-reaction pair, a result much stronger than our original result (5.1).

In view of Theorem 3, $\bar{\boldsymbol{\tau}} = \left(\bar{\mathbf{T}}, -\bar{\eta}, -\frac{1}{\theta_0} \bar{\mathbf{q}} \right)$ is a reaction, i.e. $\bar{\boldsymbol{\tau}} \in \mathcal{R}(\mathbf{F}_0, \theta_0)$, if and only if

$$(\bar{\mathbf{T}}, -\bar{\eta}) \in \mathcal{T}(\mathbf{F}_0, \theta_0), \quad \bar{\mathbf{q}} \in \mathcal{Q}(\mathbf{F}_0, \theta_0).$$

Thus the reaction function \mathcal{R} can be specified in terms of a reaction function \mathcal{T} for the stress and entropy and a reaction function \mathcal{Q} for the heat flux.

b) Examples

We now give several examples of \mathcal{M} and \mathcal{N} , and for each we determine the corresponding reaction functions \mathcal{T} and \mathcal{Q} . For convenience, we now write (\mathbf{F}, θ) , \mathbf{F}' , θ' , \mathbf{D} , and \mathbf{g} for arbitrary elements of \mathcal{M} , Lin, \mathbb{R} , Sym, and \mathcal{V} .

(1) **Temperature-dependent compressibility.**¹ Here \mathcal{M} is specified by a relation between $\det \mathbf{F}$ and θ ; i.e. there exists a non-empty subset \mathcal{J} of $\mathbb{R}^+ \times \mathbb{R}^+$ such that²

$$(\mathbf{F}, \theta) \in \mathcal{M} \Leftrightarrow (\det \mathbf{F}, \theta) \in \mathcal{J}.$$

In cases of practical interest there exists a class C^1 volume-temperature function $f: \mathbb{R}^+ \rightarrow \mathbb{R}^+$ with³ $f' \neq 0$ such that

$$(\det \mathbf{F}, \theta) \in \mathcal{J} \Leftrightarrow \det \mathbf{F} = f(\theta).$$

In this instance,

$$\begin{aligned} \dot{\mathcal{M}}(\mathbf{F}, \theta) &= \{(\mathbf{F}', \theta') : \text{tr}(\mathbf{F}' \mathbf{F}^{-1}) = m(\theta) \theta'\}, \quad m = f'/f, \\ \mathcal{D}(\mathbf{F}, \theta) &= \{(\mathbf{D}, \theta') : \text{tr} \mathbf{D} = m(\theta) \theta'\}, \\ \mathcal{T}(\mathbf{F}, \theta) &= \{(\bar{\mathbf{T}}, -\bar{\eta}) : (\bar{\mathbf{T}}, \bar{\eta}) = \alpha(\mathbf{1}, m(\theta)), \alpha \in \mathbb{R}\}. \end{aligned}$$

Thus \mathcal{D} and \mathcal{T} depend only on θ , the reaction stress is an arbitrary pressure

$$\bar{\mathbf{T}} = -p \mathbf{1},$$

¹ Cf. TRAPP [1971].

² The manifold structure on \mathcal{M} imposes certain restrictions on \mathcal{J} .

³ Here $f' = df/d\theta$. This should not be confused with \mathbf{F}' and θ' , which are not derivatives but arbitrary elements of Lin and \mathbb{R} .

and the corresponding reaction entropy is given by

$$\bar{\eta} = -m(\theta)p.$$

(2) **Temperature-dependent extensibility**¹ in the direction \mathbf{e} in the reference configuration, where \mathbf{e} is a unit vector. Here there exists a class C^1 function $f: \mathbb{R}^+ \rightarrow \mathbb{R}^+$ with $f' \neq 0$ such that

$$(\mathbf{F}, \theta) \in \mathcal{M} \Leftrightarrow \frac{1}{2} |\mathbf{F}\mathbf{e}|^2 = f(\theta).$$

For this case

$$\dot{\mathcal{M}}(\mathbf{F}, \theta) = \{(\mathbf{F}', \theta') : \mathbf{F}\mathbf{e} \cdot \mathbf{F}'\mathbf{e} = f'(\theta)\theta'\},$$

$$\mathcal{D}(\mathbf{F}, \theta) = \{(\mathbf{D}, \theta') : \mathbf{D} \cdot (\mathbf{F}\mathbf{e} \otimes \mathbf{F}\mathbf{e}) = f'(\theta)\theta'\},$$

$$\mathcal{T}(\mathbf{F}, \theta) = \{(T, -\bar{\eta}) : (T, \eta) = \alpha(\mathbf{F}\mathbf{e} \otimes \mathbf{F}\mathbf{e}, f'(\theta)), \alpha \in \mathbb{R}\},$$

so that the reaction stress

$$\bar{\mathbf{T}} = \alpha \mathbf{F}\mathbf{e} \otimes \mathbf{F}\mathbf{e} \quad (\alpha \text{ arbitrary})$$

is an arbitrary pure tension (or compression) in the direction $\mathbf{F}\mathbf{e}$, and the corresponding reaction entropy is given by

$$\bar{\eta} = \alpha f'(\theta).$$

(3) **Perfect conductivity.** Here the temperature gradient \mathbf{g} is constrained to be zero, so that

$$\mathcal{N}(\mathbf{F}, \theta) = \{\mathbf{0}\},$$

$$\mathcal{Q}(\mathbf{F}, \theta) = \mathcal{V},$$

and the reaction heat flux $\bar{\mathbf{q}}$ is completely arbitrary.

(4) **Perfect conductivity**² in the direction \mathbf{e} in the reference configuration, where \mathbf{e} is a unit vector. For this example,

$$\mathcal{N}(\mathbf{F}, \theta) = \{\mathbf{g} : \mathbf{F}\mathbf{e} \cdot \mathbf{g} = 0\},$$

$$\mathcal{Q}(\mathbf{F}, \theta) = \{\bar{\mathbf{q}} : \bar{\mathbf{q}} = \alpha \mathbf{F}\mathbf{e}, \alpha \in \mathbb{R}\},$$

so that the heat flux is an arbitrary vector

$$\bar{\mathbf{q}} = \alpha \mathbf{F}\mathbf{e} \quad (\alpha \text{ arbitrary})$$

parallel to $\mathbf{F}\mathbf{e}$.

c) Material Symmetry

Let $(\mathcal{M}, \mathcal{N})$ be a constraint pair. The **symmetry group** \mathcal{G} for $(\mathcal{M}, \mathcal{N})$ is the (group) of all $\mathbf{H} \in \text{Unim}^+$ such that

$$(\mathbf{F}, \theta) \in \mathcal{M} \Leftrightarrow (\mathbf{F}\mathbf{H}, \theta) \in \mathcal{M},$$

$$(\mathbf{F}, \theta) \in \mathcal{M} \Rightarrow \mathcal{N}(\mathbf{F}, \theta) = \mathcal{N}(\mathbf{F}\mathbf{H}, \theta). \quad (5.4)$$

¹ Cf. TRAPP [1971].

² Cf. GREEN, NAGHDI, & TRAPP [1970].

We say that $(\mathcal{M}, \mathcal{N})$ describes a **fluid** if

$$\mathcal{G} = \text{Unim}^+,$$

a **solid** if for some $(\mathbf{P}, \theta_0) \in \mathcal{M}$

$$\mathbf{P} \mathcal{G} \mathbf{P}^{-1} \subset \text{Orth}^+,$$

an **isotropic material** if for some $(\mathbf{P}, \theta_0) \in \mathcal{M}$

$$\text{Orth}^+ \subset \mathbf{P} \mathcal{G} \mathbf{P}^{-1}. \tag{5.5}$$

Clearly, the relations (4.8) have obvious analogs in the present theory.

The next result shows that when the material is isotropic, the only possible constraint for heat conduction is perfect conductivity.

Theorem 4. *Let $(\mathcal{M}, \mathcal{N})$ describe an isotropic material. Then either the temperature gradient is unconstrained ($\mathcal{N} \equiv \mathcal{V}$, $\mathcal{Q} \equiv \{\mathbf{0}\}$) or the material is a perfect conductor ($\mathcal{N} \equiv \{\mathbf{0}\}$, $\mathcal{Q} \equiv \mathcal{V}$).*

Proof. By hypothesis and (5.5), if $\mathbf{Q} \in \text{Orth}^+$, then

$$\mathbf{H} = \mathbf{P}^{-1} \mathbf{Q} \mathbf{P} \in \mathcal{G}.$$

Thus, since $(\mathbf{P}, \theta_0) \in \mathcal{M}$, we may conclude from (5.4) that

$$\mathcal{N}(\mathbf{P}, \theta_0) = \mathcal{N}(\mathbf{P}\mathbf{H}, \theta_0) = \mathcal{N}(\mathbf{Q}\mathbf{P}, \theta_0).$$

On the other hand, by (N_2)

$$\mathcal{N}(\mathbf{Q}\mathbf{P}, \theta_0) = \mathbf{Q} \mathcal{N}(\mathbf{P}, \theta_0).$$

Therefore

$$\mathcal{N}(\mathbf{P}, \theta_0) = \mathbf{Q} \mathcal{N}(\mathbf{P}, \theta_0)$$

for every $\mathbf{Q} \in \text{Orth}^+$, and the only two subspaces of \mathcal{V} with this property are $\{\mathbf{0}\}$ and \mathcal{V} . Thus $\mathcal{N}(\mathbf{P}, \theta_0)$ equals $\{\mathbf{0}\}$ or \mathcal{V} , and the proof follows from (N_3) . \square

The next theorem shows that for a fluid the only possible constraint for \mathbf{F} and θ is temperature-dependent compressibility.¹

Theorem 5. *Let $(\mathcal{M}, \mathcal{N})$ describe a fluid. Then either the deformation gradient and temperature are unconstrained ($\mathcal{M} \equiv \mathcal{V}$, $\mathcal{T} \equiv \{\mathbf{0}\}$), so that both the reaction stress and the reaction entropy vanish, or the material exhibits temperature-dependent compressibility.*

We omit the proof, which is similar to that of Theorem 2.

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¹ Theorem 4 also gives the possible constraints on the temperature gradient \mathbf{g} in the case of a fluid, since such a material is isotropic.

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