THERMODYNAMIC RESTRICTIONS IN NON-LINEAR RATE TYPE MATERIALS

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ABSTRACT

Although one-sided rate type (differential type) materials have received attention in the literature, the restrictions which should be applied have not been finally resolved. The author seeks to clarify this situation, examining first thermomechanical, and then, thermodynamic, processes.

1. INTRODUCTION

Much recent and not so recent literature has appeared purporting to treat one-sided rate type materials (materials of the differential type) wherein the stress and other dependent variables are a function of, say, the deformation gradient or strain and their nth order higher time derivative.

Other than problems associated with coordinate frame indifference and material indifference[1] (material isotropy groups)[2] which have essentially been solved except for some remaining disagreement on use of improper rotations[3] the major problem lies in the thermodynamic restrictions applicable to such materials. Two parts of this question need answering. First, does the second law of thermodynamics in the form of the Clausius–Duhem inequality (CDI) apply to materials undergoing irreversible non-equilibrium thermomechanical processes? Secondly, what are the physical implications of the various initial constitutive assumptions with respect to the type of material described?

It is intended herein to offer an alternative to the first question and hopefully clarify the second.

In essence, it will be shown that one-sided rate type materials depending on deformation gradients, temperature and temperature gradients, as well as the higher time derivatives of these quantities will always be reducible to nothing more than non-linear Kelvin solids showing no relaxation properties. For materials of this type the inclusion of hidden variables is essential to the relaxation process (creep, however, can occur without interval variables).

1.1 Notations and definitions

The notations and definitions used herein are similar to those of Truesdell and Noll's NLFT[1]. We denote vectors and spatial points by boldface Latin miniscules; q, x ... Sets, bodies and regions are denoted by script majuscules, $\mathscr{B}$, $\mathscr{R}$. Tensors (linear transformations) and material points are given in boldface Latin majuscules, F, T, X. Configurations and mappings are given

in boldface Greek minuscules, χ, ξ. Where repeated indices are used, summation over 1, 2, 3 is implied. Transpose of $\mathbf{F}$ is $\mathbf{F}^T$ and its inverse is $\mathbf{F}^{-1}$. The trace (spur) is written $\mathbf{tr}\mathbf{A} = A_{ii}$ and the determinant of the matrix representation of $\mathbf{A}$ is $\mathbf{det}\mathbf{A}$. Present time is taken as $\mathbf{t}$ and previous time is τ.

We define a *body* $\mathcal{B}$ as a smooth manifold (continuum) of elements (*particles*) $\mathbf{X}$ whose coordinates in some reference are also $\mathbf{X}$. *The configuration* χ of $\mathcal{B}$ are the elements of a set of one-to-one (invertible) mappings of $\mathcal{B}$ into a three-dimensional Euclidian point space $\mathscr{E}$. The *spatial point* $\mathbf{x}$ is called the place occupied by the particle $\mathbf{X}$,

$$\mathbf{x} = \chi(\mathbf{X}); \mathbf{X} = \chi^{-1}(\mathbf{x}) \tag{1.1}$$

and $\mathbf{X}$ above is the particle whose place is $\mathbf{x}$.

The region of space, $\chi(\mathcal{B})$, into which the body is mapped is called the region occupied by the body $\mathcal{B}$ in the configuration χ. *The reference configuration*, its volume element and its surface area element are $\mathscr{R}$, $\mathscr{V}$, $\mathscr{S}$ respectively. The *deformed configuration*, its volume element and its surface area element (where χ is not the identity mapping) are $\mathbf{r}$, $\mathbf{v}$, $\mathbf{s}$ respectively.

A *motion* of body $\mathcal{B}$ is a one-parameter family of configurations with the real parameter $\mathbf{t}$, time. Thus

$$\mathbf{x} = \chi(\mathbf{X}, \mathbf{t}); \mathbf{X} = \chi^{-1}(\mathbf{x}, \mathbf{t}) \tag{1.2}$$

We assume the existence and continuity of any derivatives wherever needed.

Critical to the entire theory is the *concept of localization*. A curve $\mathscr{C}$ in $\mathscr{R}$ is deformed by 1.1 into a curve $\mathbf{c}$ in $\mathbf{r}$. If $\mathbf{dX}$ is an *element of arc* along $\mathscr{C}$, using the rule for change of variables in an integral,

$$\int_{\mathscr{C}} [\ldots] \, dX^K = \int_{\mathbf{c}} [\ldots] \, X,_k^K \, dx^k \tag{1.3}$$

with

$$X,_k^K \equiv \partial X^K/\partial x_k \tag{1.4}$$

The spatial field $\mathbf{dx}$ is thus defined in terms of the material field $\mathbf{dX}$ by

$$dX^K = X,_k^k \, dx^k \tag{1.5}$$

whose solution for $\mathbf{dx}$ is

$$dx^k = x,_K^k \, dX^K \tag{1.6}$$

In equation 1.6 $\mathbf{dx}$ is a field deformed with the material whose determination requires knowledge of the deformation in a neighbourhood of $\mathbf{x}$.

The $x,_k^k$ are the components of the *deformation gradient*, $\mathbf{F}$. Uniqueness of 1.6 is assured by the postulate of a positive definite bounded volume element such that

$$0 < (dv/dV) = J = \det \mathbf{F} < \infty \tag{1.7}$$

where ρ is the density.

Thus, $\mathbf{dx}$ is the vector at $\mathbf{x}$ into which the vector $\mathbf{dX}$ at $\mathbf{X}$ is deformed by the linear transformation, 1.6.

We shall deal herein only with *simple materials*, i.e. those whose response is affected by only $\mathbf{F}$ and not its gradients[†].

We have defined, therefore, the deformation gradient $\mathbf{F} = \mathbf{GRAD}\ \chi$ at and with respect to $\mathbf{X}$ relative to the deformed configuration, $\mathbf{r}$.

The symbol $\mathbf{grad} \cdot$ is used to denote the gradient at $\mathbf{X}$ with respect to $\mathbf{x}$.

The usual material derivative and spatial derivative definitions are used.

For a homogeneous continuum, considered here, explicit dependence upon $\mathbf{X}$ is not required in any of the ensuing constitutive equations.

Polar decomposition of $\mathbf{F}$ results in

$$\mathbf{F} = \mathbf{RU} \text{ or } \mathbf{F} = \mathbf{VR} \tag{1.8}$$

where $\mathbf{R}$ is an orthogonal rotation tensor and $\mathbf{U}$ and $\mathbf{V}$ are right and left positive definite, symmetric stretch tensors respectively.

The *right and left Cauchy–Green strain tensors* are

$$\mathbf{C} = \mathbf{F}^{\mathsf{T}}\mathbf{F} = \mathbf{U}^2, \mathbf{B} = \mathbf{FF}^{\mathsf{T}} = \mathbf{V}^2 \tag{1.9}$$

With κ as a reference configuration at time t_0 and $\chi(t)$ and $\chi(\tau)$ the configurations at times t and τ, the usual composition of mappings defines the *relative deformation gradient* as

$$\mathbf{F}(\tau) = \mathbf{F}_{(t)}(\tau)\ \mathbf{F}(t)$$

where

$$\mathbf{F}(\tau): \kappa \rightarrow \chi(\tau);\ \mathbf{F}(t): \kappa \rightarrow \chi(t);\ \mathbf{F}_{(t)}(\tau): \chi(t) \rightarrow \chi(\tau) \tag{1.10}$$

so that

$$\mathbf{F}_{(t)}(\tau) = \mathbf{F}(\tau)\ \mathbf{F}(t)^{-1} \tag{1.11}$$

We may thus express the *relative deformation gradient rate* evaluated at present time t as

$$\mathbf{L}(t) \equiv \dot{\mathbf{F}}_{(t)}(t) = \frac{\partial}{\partial \tau} \dot{\mathbf{F}}_{(t)}(\tau)\big|_{\tau = t} = \dot{\mathbf{F}}(t)\ \mathbf{F}(t)^{-1} \tag{1.12}$$

which is simply the spatial velocity gradient

$$\mathbf{grad}\ \dot{\mathbf{x}} \tag{1.13}$$

Similarly, the spatial gradient of the nth acceleration is then

$$\mathbf{L}_n(t) = \frac{\partial \overset{(n)}{\mathbf{x}}}{\partial \mathbf{x}} = \overset{(n)}{\mathbf{F}}_{(t)}(t) = \mathbf{grad}\ \overset{(n)}{\mathbf{x}}\ n = 1, 2, .. \tag{1.14}$$

with

$$\mathbf{L}_0 = \mathbf{I};\ \mathbf{L}_1 = \mathbf{L}$$

[†] It may be noted that non-simple materials subjected to pure homogeneous deformations are also covered by our restriction.

Employing polar decomposition on the relative deformation gradient and differentiating, we can then define the *stretching*, **D**, and the *spin*, **W**, as

$$\mathbf{D} = \dot{\mathbf{U}}_{(t)}(t) = \tfrac{1}{2}(\mathbf{L} + \mathbf{L}^{\mathsf{T}})$$
$$\mathbf{W} = \dot{\mathbf{R}}_{(t)}(t) = \tfrac{1}{2}(\mathbf{L} - \mathbf{L}^{\mathsf{T}}) \tag{1.15}$$

D is obviously the symmetric part of **L** and is sometimes called the rate of deformation tensor.

A useful relationship is easily derived

$$\mathbf{tr}\mathbf{D} = \mathbf{tr}\mathbf{L} = \operatorname{div}\dot{\mathbf{x}} = \frac{1}{\mathbf{V}}\frac{d\mathbf{V}}{dt} \tag{1.16}$$

where **V** is here the present volume.

An inner product $\mathbf{A}\cdot\mathbf{B}$ can be represented as $\mathbf{tr}\mathbf{A}^{\mathsf{T}}\mathbf{B}$. Also

$$\mathbf{tr}\mathbf{A}^{\mathsf{T}}\mathbf{B} = \mathbf{tr}\mathbf{B}^{\mathsf{T}}\mathbf{A}, \ \mathbf{tr}\mathbf{A}\mathbf{B}\mathbf{C} = \mathbf{tr}\mathbf{B}\mathbf{C}\mathbf{A}.$$

The *Cauchy stress tensor*, $\mathbf{T} = \mathbf{T}(\mathbf{X}, t)$ is the stress per unit area in the deformed configuration. For non-polar materials herein considered, the usual balance of moment of momenta yields $\mathbf{T} = \mathbf{T}^{\mathsf{T}}$, hence **T** is symmetric. We also define the *specific body force* $\mathbf{b} = \mathbf{b}(\mathbf{X}, t)$ per unit mass as a field force extended on the body $\mathscr{B}$ at **X** by causes outside of $\mathscr{B}$.

The thermodynamic variables to be employed are not in accord with the 1948 I.U.P.A.C. and I.U.P.A.P. recommendations because of the obvious conflict with the mechanical variables. We define here:

(1) The *total internal energy* in the body $\mathscr{B}$ as **E** which is an additive set function of the portions of the body with units (mass) (length)^2 (time)$^{-2}$. The localization of **E** leads to the *specific internal energy*, ε, at a point **X** per unit mass with dimension (length)^2 (time)$^{-1}$.

(2) The *total entropy*, $\mathbf{N}(\mathbf{X}, t)$ as above with its localization to *specific entropy*, $\eta = \eta(\mathbf{X}, t)$ per unit mass.

(3) The *absolute temperature*, $\theta = \theta(\mathbf{X}, t)$ which, unless otherwise specified, is the translational temperature.

(4) The *heat flux vector*, $\mathbf{q} = \mathbf{q}(\mathbf{X}, t)$ whose units are energy per unit area per unit time = (mass) (time)$^{-3}$ where an outwardly directed unit normal vector $\tilde{\mathbf{n}}$ is used, the total flux of heat over an element of body surface area **s** is

$$\oint_s \mathbf{q}\cdot\tilde{\mathbf{n}}\,\mathbf{ds} \tag{1.17}$$

which by the Green–Gauss theorem yields

$$\int_v \operatorname{div}\mathbf{q}\,\mathbf{dv} \tag{1.18}$$

with dimension energy/unit time and represents the *rate at which heat is leaving the* body surface, **s**. The integrated heat flux is **Q**.

(5) The *specific heat supply* $\mathbf{r} = \mathbf{r}(\mathbf{X}, t)$ per unit mass per unit time absorbed by the body $\mathscr{B}$ at **X** from external non-conductive sources or internal point sources (whose existence is not pertinent at this point).

(6) The *internal state vector*, φ or α, whose scalar components in $\varphi = (\varphi_1, \varphi_2, \ldots \varphi_n)$ are the internal state variables. This vector may be considered as a hidden variable wherein it is capable of energy transfer.

2. THERMOMECHANICAL PROCESSES

The notation used above is due to Coleman and Gurtin[4]. The impetus for the specific approach used resulted from conversations with R. S. Rivlin and J. Meixner.

2.1 Energy inequality restrictions

The set of three mechanical functions, motion x, stress T and body force b with the stated localization of motion plus the six thermal functions listed above and defined for all particles X in $\mathscr{B}$ over all time t is called a *thermomechanical process* if and only if the set satisfies the usual local laws of balance of momentum

$$\text{div } T + \rho b = \rho \ddot{x} \qquad (2.1)$$

and the *balance of energy*

$$\rho \dot{\varepsilon} = T \cdot L - \text{div } q + \rho r \qquad (2.2)$$

Thus, a sufficient condition for a thermomechanical process is one wherein only x, T, ε, q, η, θ and φ are prescribed and b and r are found from equations 2.1 and 2.2.

Consider now the integral of 2.2 over some finite interval of time which for convenience will be taken as $t\varepsilon[0, t]$. We shall take the state of the body at all times $t\varepsilon(-\infty, 0]$ as a thermomechanical *fiducial state* wherein we postulate at all points X and times $t \star \leqslant 0$

$$\theta(X, t \star) = \theta_0(X, t \star) \quad Q(X, t \star) = Q_0(X, t \star)$$

$$T(X, t \star) = 0 \qquad\qquad F(X, t \star) = 1$$

$$L = \dot{L} = \ldots = L^{(n)}(X, t \star) = 0 \qquad\qquad (2.3)$$

$$\varepsilon(X, t \star) = \varepsilon_0(X, t \star)$$

Equation 2.3 implies a homothermal field. θ_0 could be taken equal to zero without loss of generality. Conditions 2.3_3 and 2.3_4 imply no initial stress nor strain, and 2.3_5 implies no motion at times $t \leqslant 0$. Equation 2.3_2, wherein Q is the energy per unit volume, simply implies a fiducial state for the heat content which, without loss of generality, may be taken as $Q_0 = 0$.

The relation 2.3_6 is based on the fact that energy may be defined only to within an arbitrary constant[10]. In this case, if we either take $\theta = 0$ and $Q_0 = 0$ implying $\varepsilon_0 = 0$ or take ε_0 as a *fiducial energy level below which we cannot go by any thermomechanical process*, integration of 2.2 then gives

$$\rho\varepsilon(X, t) = \int_{t_0}^{t} T \cdot L \, d\tau - \int_{t_0}^{t} \text{div } q \, d\tau + \int_{t_0}^{t} \rho r \, d\tau, \, t_0 \leqslant t\star \qquad (2.4)$$

We now *postulate* with the definitions given above

$$\varepsilon(X, t) \geqslant 0 \qquad (2.5)$$

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which we call the first inequality of thermomechanics or the *energy inequality*. Note that expression 2.5 holds in non-equilibrium conditions.

The thermal implications of 2.5 are rather obvious and perhaps trivial. Letting no mechanical motion ensue we have from 2.5 and 2.4

$$- \int_{t_0}^{t} \text{div } \mathbf{q} \, d\tau + \int_{t_0}^{t} \rho r \, d\tau \geqslant 0 \tag{2.6}$$

Letting

$$- \int_{-\infty}^{t_0} \text{div } \mathbf{q} \, d\tau = - \Delta \mathbf{Q}^{\text{OUT}} = \Delta \mathbf{Q}^{\text{IN}} \tag{2.7}$$

where $\Delta \mathbf{Q}^{\text{IN}}$ is the amount of energy conducted as heat into the body at time t_0. Also we have

$$\int_{-\infty}^{t_0} \rho r \, d\tau = \Delta \hat{\mathbf{Q}}^{\text{IN}} \tag{2.8}$$

which is the amount of energy brought into the body by external radiation. Then we write for the energy (in the form of heat) in the body at time t_0

$$\mathbf{Q}_0 = \Delta \mathbf{Q}^{\text{IN}} + \Delta \hat{\mathbf{Q}}^{\text{IN}} \tag{2.9}$$

During the non-mechanical process from t_0 to the present time t we have from 2.4 and 2.9 with $t_0 = 0$

$$\rho \varepsilon(\mathbf{X}, t) = - \int_{t_0}^{t} \text{div } \mathbf{q} \, d\tau + \int_{t_0}^{t} \rho r \, d\tau \geqslant 0 \tag{2.10}$$

With the interpretation

$$- \int_{t_0}^{t} \text{div } \mathbf{q} \, d\tau = - \Delta \mathbf{Q}^{\text{OUT}}(t_0, t)$$
$$\int_{t_0}^{t} \rho r \, d\tau = \Delta \hat{\mathbf{Q}}^{\text{IN}}(t_0, t) \tag{2.11}$$

equation 2.10 becomes

$$- \Delta \mathbf{Q}^{\text{OUT}}(t_0, t) + \Delta \hat{\mathbf{Q}}^{\text{IN}}(t_0, t) + \mathbf{Q}_0 \geqslant 0 \tag{2.12}$$

which can be written with $\Delta \hat{\mathbf{Q}}^{\text{IN}} = - \Delta \hat{\mathbf{Q}}^{\text{OUT}}$ as

$$\Delta \mathbf{Q}^{\text{OUT}}(t_0, t) + \Delta \hat{\mathbf{Q}}^{\text{OUT}}(t_0, t) \leqslant \mathbf{Q}_0 \tag{2.13}$$

Thus, no more net heat may be lost through conduction and radiation over a time interval than was originally in the body at the beginning of the interval under zero mechanical processes.

The mechanical implications are given for the condition of no radiation and no heat transfer over the interval $[0, t]$. Since these heat processes are assumed independent in that we can in principle ensure that

$$\int_{t_0}^{t} \text{div } \mathbf{q} = 0; \int_{t_0}^{t} \rho r \, d\tau = 0 \tag{2.14}$$

this above restriction does not reduce the generality of the results.

Assume for illustrative purposes that the constitutive equation for the stress tensor, $\mathbf{T}$, is that of a one-sided linear rate type material wherein

$$\mathbf{T} = \mathbf{a}_0 \mathbf{B} + \mathbf{a}_1 \mathbf{L} + \mathbf{a}_2 \mathbf{L}_{(2)} + \ldots + \mathbf{a}_n \mathbf{L}_{(n)} \tag{2.15}$$

where $\mathbf{B} = \mathbf{B}^{\text{T}}$ is the left Cauchy–Green symmetric strain tensor and the

$L_{(n)}$ are the spatial gradients of the nth time derivative of the velocity with the a_n constants. Equations 2.4, 2.5 and 2.14 then are

$$\varepsilon(X, t) = \int_{t_0}^{t} T \cdot L \, d\tau \geqslant 0 \qquad (2.16)$$

The expression $T \cdot L$ with 2.15 therefore becomes

$$T \cdot L = a_0 B \cdot L + a_1 L \cdot L + a_2 L_2 \cdot L + a_3 L_3 \cdot L + \ldots \qquad (2.16a)$$

The first term on the right is then $B \cdot L = \text{tr}BL$ and from elementary operations

$$\text{tr}BL = \text{tr}L^T B = \text{tr}(F^T)^{-1}\dot{F}^T FF^T = \text{tr}\dot{F}^T F \qquad (2.17)$$

The integral of $\text{tr}\dot{F}^T F = \dot{F} \cdot F$ may be evaluated by considering first

$$\frac{\partial}{\partial \tau} \text{tr}F^T F = \text{tr}\frac{\partial}{\partial \tau} F^T F = 2\text{tr}\dot{F}^T F \qquad (2.18)$$

Thus we may write, using the definition of an integral and $B = V^2 = FF^T$,

$$\int_{t_0}^{t} a_0 B \cdot L \, d\tau = \int_{t_0}^{t} \frac{a}{2} \cdot \frac{\partial}{\partial \tau} \text{tr}V^2 \, d\tau = \frac{a_0}{2} \text{tr}V^2 = \frac{a_0}{2}(I_1 - 3) \qquad (2.19)$$

where $\text{tr}V^2 = \text{tr}B$ is the left Cauchy–Green stretch tensor which is strictly positive definite, hence $a_0 \geqslant 0$.

The second term, $a_1 L \cdot L$, in the integral is $\int_{t_0}^{t} L \cdot L \, d\tau$, $L(t_0) = 0$ (2.20)

which, by the basic definition of an inner product is positive definite in the argument and, hence, the integral is positive definite. Thus $a_1 \geqslant 0$.

The third term $a_2 L_{(2)} \cdot L$ may be similarly determined using the relation

$$\int \frac{\partial}{\partial \tau} \text{tr}L^T L \, d\tau = \int \text{tr}\frac{\partial}{\partial \tau} L^T L \, d\tau = \int L \cdot \dot{L} \, d\tau = L \cdot L \Big|_{t_0}^{t} \qquad (2.21)$$

Therefore $a_2 \geqslant 0$. All remaining terms of the form $L_{(n)} \cdot L$ with $n > 2$ cannot be shown to be positive definite for all arbitrary $L_{(n)}$ and L, hence

$$a_3 = a_4 = \ldots \ldots = a_n = 0 \qquad (2.22)$$

A comment is in order here. Assuming, for the linear rate expressions of T, other forms of the strain such as C, the right Cauchy–Green strain tensor and F, the deformation gradient, one cannot show that $a_0 \geqslant 0$. Similarly, in the operations for determining the existence of a_2, the velocity gradient L only enters through its symmetric part $L^{(s)} = \frac{1}{2}(L + L^T) \equiv D$ the stretching tensor. Thus, the energy inequality restricts the linear rate Cauchy stress tensor to

$$T = a_0 B + a_1 D + a_2 L_{(2)}^{(s)} \qquad (2.23)$$

where $L_{(2)}^{(s)}$ is the symmetric part of $\dot{L}$.

This result has been obtained without recourse to the second law of thermodynamics, the CDI, and does therefore hold rigorously in non-equilibrium conditions. The details were suggested by J. Meixner[5].

One may, with considerably more algebraic effort, generalize the linear

rate constitutive equation used previously as an illustrative example. Using a theorem of Rivlin[6], one may show that the symmetric Cauchy stress tensor $\mathbf{T}$ is expressible as a polynomial isotropic tensor function of, for example, the left Cauchy–Green strain tensor $\mathbf{B}$ and the symmetric part of the relative deformation gradient rate, $\mathbf{D}$. Then we may express this general non-linear relationship as

$$\mathbf{T} = \psi_0\mathbf{1} + \psi_1\mathbf{B} + \psi_2\mathbf{L} + \psi_3\mathbf{B}^2 + \psi_4\mathbf{D}^2$$
$$+ \psi_5(\mathbf{BD} + \mathbf{DB}) + \psi_6(\mathbf{B}^2\mathbf{D} + \mathbf{DB}^2) \qquad (2.24)$$
$$+ \psi_7(\mathbf{BD}^2 + \mathbf{D}^2\mathbf{B}) + \psi_8(\mathbf{B}^2\mathbf{D}^2 + \mathbf{D}^2\mathbf{B}^2)$$

where the coefficients $\psi_0 \ldots \psi_8$ are polynomials of the set of irreducible invariants of the two symmetric tensors, $\mathbf{B}$ and $\mathbf{D}$. The specific form for the irreducible invariants in this case is

$$\mathrm{tr}\mathbf{B}, \mathrm{tr}\mathbf{B}^2, \mathrm{tr}\mathbf{B}^3, \mathrm{tr}\mathbf{D}, \mathrm{tr}\mathbf{D}^2, \mathrm{tr}\mathbf{D}^3$$
$$\mathrm{tr}(\mathbf{BD}), \mathrm{tr}(\mathbf{BD}^2), \mathrm{tr}(\mathbf{B}^2\mathbf{D}), \mathrm{tr}(\mathbf{B}^2\mathbf{D}^2) \qquad (2.25)$$

Referring to the energy inequality condition 2.16 and, for simplicity, assuming on the basis of physical experience that the coefficients ψ_α are so slowly varying with time as to be approximated by constants (an admittedly totally unwarranted mathematical assumption) it can then be shown by arguments similar to those previously used herein that

$$\mathbf{T}(\mathbf{B}, \mathbf{D}) = \psi_1\mathbf{B} + \psi_2\mathbf{D} + \psi_3\mathbf{B}^2 + \psi_5(\mathbf{BD} + \mathbf{DB}) + \psi_6(\mathbf{B}^2\mathbf{D} + \mathbf{DB}^2)$$
$$(2.26)$$

A more general consideration produces the result, with constant coefficients,

$$\mathbf{T}(\mathbf{B}, \mathbf{D}) = \sum_{k=1}^{n} a_k\mathbf{B}^k + \sum_{k=1}^{n} c_k(\mathbf{D})^{2k-1} + \mathbf{L}_{(2)}\sum_{k=0}^{n} b_k(\mathbf{D})^{2k} \qquad (2.27)$$

In both of the above equations the existence of a rest configuration requires $\psi_0 = 0$. One can remove the $\mathbf{L}_{(2)}$ dependence in the stress, $\mathbf{T}$, by use of such schemes as assuming the body force derivable from a scalar potential. However, this assumption, while removing explicit dependence on $\mathbf{L}_{(2)}$, introduces an implicit dependence on **grad grad T** and the gradient of the scalar potential. This device is not to be recommended. Thus, the minimal reduction in dependent variables obtained by the use of the energy inequality yields for the Cauchy stress

$$\mathbf{T} = \mathbf{f}[\mathbf{B}, \mathbf{D}, \mathbf{L}_{(2)}] \qquad (2.28)$$

An equivalent form is

$$\mathbf{T} = \mathbf{f}[\mathbf{B}, \mathbf{A}_{(1)}, \mathbf{L}_{(2)}] \qquad (2.29)$$

where $\mathbf{A}_{(1)}$ is the Rivlin–Ericksen[2] deformation rate tensor related to $\mathbf{D}$ and $\mathbf{D}_{(2)}$ by

$$\mathbf{D} = \tfrac{1}{2}\mathbf{A}_{(1)} \quad \mathbf{D}_{(2)} = \tfrac{1}{2}(\mathbf{A}_{(2)} - \tfrac{1}{2}\mathbf{A}_{(1)}^2) \qquad (2.30)$$

and to $\mathbf{L}$ and $\mathbf{L}_2$ by

$$\mathbf{A}_{(1)} = \mathbf{L} + \mathbf{L}^T \quad \mathbf{A}_{(2)} = \mathbf{L}_{(2)} + \mathbf{L}_{(2)}^T + 2\mathbf{L}^T\mathbf{L} \qquad (2.31)$$

It is this dependence of $\mathbf{A}_{(2)}$ on $\mathbf{L}^T\mathbf{L}$ which precludes $\mathbf{A}_{(2)}$ being compatible with the energy inequality for the cases considered.

2.2 Material isotropy restrictions

The assumed isotropy of the material and the principle of coordinate frame indifference requires that any properly formulated physical law be invariant in form under the pertinent subgroup of unitary transformations. For our situation, requiring invariance of form under the proper orthogonal subgroup of transformations $\mathbf{G}$ (all real rotations) where $\det \mathbf{G} = +1$ precludes stress dependence on $\mathbf{L}$ or $\mathbf{L}_{(2)}$. The forms $\mathbf{D}_{(2)}$ and $\mathbf{A}_{(2)}$ of 2.30 and 2.31 are, however, acceptable. However, the energy inequality restrictions do not allow the $\mathbf{L}^T\mathbf{L}$ term in the stress equation. Thus, expression 2.29 can be reduced to a non-linear function

$$\mathbf{T} = \mathbf{f}[\mathbf{B}, \mathbf{A}_{(1)}] \qquad (2.32)$$

We call a thermomechanical process which satisfies the constitutive equations an *admissible thermomechanical process*.

3. THERMODYNAMIC PROCESSES

In order to develop the discussion relative to relaxation in one-sided rate type materials, we shall refer to results of Coleman and Gurtin[4] without presenting the details of development.

3.1 Equipresence

We shall employ herein Meixner's *strong principle of equipresence* wherein all constitutive equations shall initially contain the same terms[1] and each term shall depend on the same order of the derivatives[7]. Thus, since $\mathbf{B}$ is a function of $\mathbf{F}$ which is $\mathbf{GRAD}\ \mathbf{x}$ and $\mathbf{A}_{(1)}$ is, so to speak, $\dot{\mathbf{F}}$ we require the constitutive functionals for stress, $\mathbf{T}$, heat flux $\mathbf{q}$ and any other dependent variables, $\mathbf{P}$, to be of the form using 2.32

$$\mathbf{P} = \tilde{\mathbf{P}}(\mathbf{x}, \dot{\mathbf{x}}, \mathbf{F}, \dot{\mathbf{F}}, \theta, \dot{\theta}, \mathbf{grad}\ \theta, \mathbf{grad}\ \dot{\theta}) \qquad (3.1)$$

where we have not included the internal state variable φ as yet.

The material isotropy and the localization postulate immediately eliminate specific dependence on $\mathbf{x}$, $\dot{\mathbf{x}}$ so that with 2.32 and $\mathbf{g} \equiv \mathbf{grad}$ relation 3.1 becomes

$$\mathbf{P} = \tilde{\mathbf{P}}(\mathbf{B}, \mathbf{A}_{(1)}, \theta, \dot{\theta}, \mathbf{g}, \dot{\mathbf{g}}) \qquad (3.2)$$

Note that $\dot{\theta}$ need not necessarily appear since $\dot{\mathbf{x}}$ did not appear. Rather the gradients and time derivatives of the gradients appear.

3.2 Clausius–Duhem restrictions

While agreeing fully with Meixner's[7] and Rivlin's[3] comments regarding

the absence of thermodynamic validity for the Clausius–Duhem entropy rate inequality in the differential form

$$d\eta \geqslant \sum d\varepsilon/\theta \qquad (3.3)$$

where we use $d\varepsilon$ as the increment of energy addition of any sort, Coleman's thermodynamics of non-equilibrium processes rests essentially on the axiom that 3.3 holds at all times. Coleman[4] following a standard procedure asserts that the rate of entropy growth γ of a system equals the rate of specific entropy growth minus the rate of heat addition divided by absolute temperature. The key axiom is then that the rate of entropy growth, γ, is nonnegative[10] at every instant of time. Thus

$$\rho\gamma \equiv \rho\dot{\eta} - \left[\frac{\rho r}{\theta} - \operatorname{div}\left(\frac{q}{\theta} \right) \right] \geqslant 0 \qquad (3.4)$$

Defining the Piola–Kirchhoff non-symmetric stress tensor as $\mathbf{S} = \rho^{-1}\mathbf{T}(\mathbf{F}^{\mathbf{T}})^{-1}$ in order to remove conveniently the term ρ from the final equation gives the energy balance as

$$\rho\dot{\varepsilon} = \rho r - \operatorname{div}\mathbf{q} + \rho\mathbf{S}\cdot\dot{\mathbf{F}} \qquad (3.5)$$

Eliminating ρr from 3.4 and 3.5 after carrying out the operation indicated in $\operatorname{div}\mathbf{q}/\theta$ results in

$$\dot{\eta} \geqslant \frac{\dot{\varepsilon}}{\theta} - \frac{\mathbf{S}\cdot\dot{\mathbf{F}}}{\theta} - \frac{1}{\rho\theta^2}\mathbf{q}\cdot\mathbf{g} \qquad (3.6)$$

From Coleman[4] we note that:

$$\dot{\eta} \geqslant 0 \text{ when } \dot{\mathbf{F}} = \dot{\varepsilon} = \mathbf{g} = 0$$
$$\dot{\varepsilon} \leqslant 0 \text{ when } \dot{\mathbf{F}} = \dot{\eta} = \mathbf{g} = 0 \qquad (3.7)$$

Thus we see that in a typical stress relaxation test with homothermal conditions, the specific internal energy can decrease and the entropy can increase.

Introducing a *Helmholtz free energy* function ψ where

$$\psi = \varepsilon - \theta\eta \qquad (3.8)$$

and taking the partial derivative of ψ where $\dot{\psi} = \sum_{i=1}^{n} \partial_{\varphi_i}\psi \cdot \dot{\varphi}_i$ (with φ_i as any selected independent variable) and $\partial_\varphi\psi \equiv \partial\psi/\partial\varphi$ we then equate the coefficients above to those obtained by writing $\dot{\psi}$ in terms of 3.8 and 3.6. The result is then with a constitutive equation of form 3.2

$$\theta\gamma = (\mathbf{S} - \partial_{\mathbf{F}}\psi)\cdot\dot{\mathbf{F}} - (\partial_\theta\psi + \eta)\dot{\theta} - \frac{1}{\rho\theta}\mathbf{q}\cdot\mathbf{g} - \sum_{i=1}^{n} \partial_{\varphi_i}\psi\cdot\dot{\varphi}_i \geqslant 0 \quad (3.9)$$

Specifically in a form 3.2 we have

$$\psi = \psi(\mathbf{F}, \dot{\mathbf{F}}, \theta, \dot{\theta}, \mathbf{g}, \dot{\mathbf{g}}, \sum_1^n \varphi_i, \sum_1^n \dot{\varphi}_i) \qquad (3.10)$$

with $\eta, \mathbf{S}, \mathbf{q}$ of the same form.

Not only then is the usual result

$$\mathbf{S} = -\partial_\mathbf{F}\psi \; ; \eta = -\partial_\theta\psi \tag{3.11}$$

obtained, based on independence of the dependent variables, but in general

$$\partial_{\varphi_i}\psi = 0 \text{ for } 1 \leqslant i \leqslant n \tag{3.12}$$

which in our case removes any dependence on $\mathbf{g}$ or any φ_i in ψ. Similarly

$$\partial_{\dot{\varphi}_i}\psi = 0 \quad 1 \leqslant i \leqslant n \tag{3.13}$$

removing any dependence on $\dot{\varphi}_i$ whatever $\dot{\varphi}_i$ may be including it being $\dot{\mathbf{F}}, \dot{\theta}, \dot{\mathbf{g}}$.

Some authors[8,9] have interpreted the case where derivatives are used to imply that the entropy inequality simply drops the dependence on $\varphi^{(k)}$ to the level $\varphi^{(k-1)}$. This is not only untrue for independent variables, but logical deduction, i.e. recycling the equation with $\varphi^{(k-1)}$ dependence, would lead to $\varphi^{(k-2)}$ dependence until 3.12 or 3.13 conditions prevailed. In general

$$\partial_{\varphi_i^{(k)}}\psi = 0 \quad \mathbf{k} = 1, 2, \dots, \quad i = 1, 2, \dots$$

It is this above fact that has led[8] to the often quoted statement that one-sided rate materials cannot exhibit stress relaxation. The solution to this paradox is twofold. First, where all the variables in 3.10 are independent then relation 3.10 can be reduced to

$$\psi = \psi(\mathbf{F}, \theta) \tag{3.15}$$

a so-called caloric equation of state. Defining, as usual, the elastic, $_\mathbf{E}\mathbf{S}$, and dissipative $_\mathbf{D}\mathbf{S}$ stress components of $\mathbf{S} = {}_\mathbf{E}\mathbf{S} + {}_\mathbf{D}\mathbf{S}$ yields by equation 3.9

$$_\mathbf{E}\mathbf{S} = \partial_\mathbf{F}\psi \text{ and } {}_\mathbf{D}\mathbf{S} \cdot \dot{\mathbf{F}} \geqslant 0 \tag{3.16}$$

Implying, since $\mathbf{S}$ and $\dot{\mathbf{F}}$ are jointly continuous, that $_\mathbf{D}\mathbf{S} \to 0$ when $\dot{\mathbf{F}} \to 0$, i.e. no relaxation under constant strain. Again this is strictly correct and points out the fact that any one-sided formulation in any number of independent variables and their higher derivatives degenerates to nothing more than an equivalence to a two-element non-linear Kelvin–Voigt solid which can exhibit creep but no stress relaxation excepting a jump relaxation when $\dot{\mathbf{F}} \to 0$. Secondly, the situation may be resolved by simply removing the independence from one or more of the variables entering into, say 3.2. This may be done by specifying one of the derivatives of φ_i as dependent, i.e.

$$\dot{\varphi}_i = \mathbf{f}(\mathbf{B}, \mathbf{A}_{(1)}, \dots, \varphi_i, \dots) \tag{3.17}$$

Then a dissipation, σ, inequality will arise from 3.9 leading to a term

$$\sigma = -\partial_{\varphi_i}\psi \cdot \mathbf{f} \geqslant 0, \; \therefore \sigma \geqslant 0 \tag{3.18}$$

for homothermal fields, $\mathbf{g} = 0$.

We now see that dropping the artifice of 3.16 and expressing the rate of change of stress, $\dot{\mathbf{S}}$ as

$$\mathbf{S}\dot{\mathbf{F}} = \partial_\mathbf{F}\psi \cdot \dot{\mathbf{F}} + \partial_{\varphi_i}\psi \cdot \dot{\varphi}_i \tag{3.19}$$

and with $\dot{\mathbf{F}} = 0$ and 3.18 where $\dot{\varphi}_i = \mathbf{f}$, not necessarily integrable

$$\dot{\mathbf{S}}\mathbf{F} = \partial_{\varphi_i}\psi \cdot \dot{\varphi}_i \leqslant 0 \qquad (3.20)$$

Thus, the introduction of a dependence in time of even one φ_i leads to 3.20 which states that the stress must decrease in a stress relaxation test. Needless to say, the dependence of $\dot{\varphi}$ requires a proper statement of initial conditions.

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