

## A NOTE ON ONSAGER'S RELATIONS

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**Abstract.** A nonlinear viscoelastic material with the heat flux obeying a generalization of Cattaneo's law is considered. It is shown that for slow processes with small gradients of temperature the exact constitutive equations can be approximated by those of a linear viscous material with Fourier heat conduction. As a consequence of the thermodynamic restrictions on the original constitutive equations, the approximate constitutive equations are shown to satisfy the principle of local equilibrium for energy and entropy, and the kinetic coefficients giving the viscous stress and heat flux vector satisfy Onsager's relations.

**1. Introduction.** In this paper I consider constitutive equations of the form

$$\mu(t) = M(\mathbf{F}(t), \theta(t)) + \int_0^\infty m(\mathbf{F}(t), \mathbf{F}(t-s), \theta(t), \mathbf{G}^t(s), s) ds. \quad (1.1)$$

Here  $\mathbf{F}(t)$ ,  $\theta(t)$  are the present values of the deformation gradient and of the absolute temperature,  $\mathbf{F}(t-s)$  are the values of the deformation gradient prior to  $t$  ( $s > 0$ ), and  $\mathbf{G}_t(s)$  are the values of the summed history of the gradient of temperature  $\mathbf{g} = \mathbf{g}(t) = \nabla\theta(t)$ , defined by

$$\mathbf{G}^t(s) = \int_0^s \mathbf{g}(t-s') ds'. \quad (1.2)$$

$M(\cdot)$  and  $m(\cdot)$  are the constitutive functions. The constitutive equations of the form (1.1) are postulated for the entropy, energy, Helmholtz free energy, Piola-Kirchhoff stress, and the referential heat flux.

As far as the dependence on the mechanical variable,  $\mathbf{F}$ , is concerned, the material exhibits a viscoelastic type of behavior. While there is a vast literature on models qualitatively similar to the one given above (see, e.g., Coleman and Noll [4], Coleman [3]), the above specific form of the dependence on  $\mathbf{F}(t)$ ,  $\mathbf{F}(t-s)$  has been proposed recently by Gurtin and Hrusa [7, 8], who call constitutive assumptions of the type (1.1) single-integral laws. The dependence on the thermal variables is instantaneous in the temperature, and the dependence on the history of temperature through the summed history  $\mathbf{G}^t$  is typical for models that exhibit finite speeds of propagation of

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thermal disturbances. The well-known modification by Cattaneo [2] of Fourier's law of heat conduction is included as a special case in (1.1), but Fourier's law itself is not included. Thermodynamics of rigid heat conductors with the heat flux dependent on the summed histories of the gradient of temperature was examined by Gurtin and Pipkin [9], Coleman, Fabrizio and Owen [5], and Brandon and Hrusa [1]. I also refer to these papers for further reference.

In this paper I extend first some of the results of [1, 9] to deformable bodies, and then I proceed to consider the approximations of the constitutive equations (1.1) appropriate for slow processes with small gradients of temperature. I shall show that the approximate constitutive equations are

$$\mu(t) = M(\mathbf{F}(t), \theta(t)) + \mathbf{K}(\mathbf{F}(t), \theta(t))\dot{\mathbf{F}}(t) + \mathbf{L}(\mathbf{F}(t), \theta(t))\mathbf{g}(t), \quad (1.3)$$

where the kinetic coefficients  $\mathbf{K}$  and  $\mathbf{L}$  are explicitly determined by the form of the function  $m$  in (1.1) (cf. Eqs. (3.6), (3.7) in Sec. 3). The constitutive equations (1.3) are typical for Newton-type viscous materials with Fourier heat conduction. The main purpose of the paper is to show that if the material (1.1) obeys the Clausius-Duhem inequality, then

- (1) the approximate constitutive equations obey the Clausius-Duhem inequality with a positive production of entropy given by a quadratic form in the nonequilibrium parameters  $\dot{\mathbf{F}}, \mathbf{g}$ ;
- (2) the approximate constitutive equations for the energy, entropy, and Helmholtz free energy obey the principle of local equilibrium (i.e., are independent of  $\dot{\mathbf{F}}, \mathbf{g}$ );
- (3) the matrix of kinetic coefficients occurring in the approximate constitutive equations for the stress and the heat flux vector obeys Onsager's type of symmetry.

Assertions (1)–(3) are usually starting postulates in the linear irreversible thermodynamics [6]. It is interesting to note that the conclusions (1)–(3) apparently do not follow from the general theory of materials with fading memory with unspecified form of the response functionals.

**2. Single-integral laws.** For notational simplicity the set of all deformation gradients is identified with the set  $\text{Lin}^+$  of all three-dimensional second-order tensors  $\mathbf{F}$  with  $\det \mathbf{F} > 0$ , the set of all absolute temperatures  $\theta$  with  $R^{++} = (0, +\infty)$ , and the set of all referential gradients of temperature  $\mathbf{g}$  with the three-dimensional vector space  $\mathcal{V}$  with scalar product. A *process* is any triplet of continuous and continuously differentiable functions  $(\mathbf{F}, \theta, \mathbf{g})$  of time  $t \in R$  with values in  $\text{Lin}^+ \times R^{++} \times \mathcal{V}$  such that for each  $t \in R$  the ranges of the functions  $(\mathbf{F}, \theta, \mathbf{g})$  and  $(\dot{\mathbf{F}}, \dot{\theta}, \dot{\mathbf{g}})$  on  $(-\infty, t]$  are contained in a compact subset of  $\text{Lin}^+ \times R^{++} \times \mathcal{V}$ .

For a given process  $(\mathbf{F}, \theta, \mathbf{g})$  and time  $t \in R$ , the *summed history*  $\mathbf{G}^t$  of the *gradient of temperature* up to  $t$  is defined to be the function  $\mathbf{G}^t$  on  $[0, +\infty)$  given by (1.2); as a consequence we have  $\mathbf{G}^t(0) = \mathbf{0}$ .  $\bar{\mathbf{G}}$  will standardly denote the indefinite integral of  $\mathbf{g}$ ,  $\dot{\bar{\mathbf{G}}} = \mathbf{g}$ , normalized by  $\bar{\mathbf{G}}(0) = \mathbf{0}$ . Then

$$\mathbf{G}^t(s) = \bar{\mathbf{G}}(t) - \bar{\mathbf{G}}(t - s). \quad (2.1)$$

We shall deal with the constitutive equations giving the present value of the dependent quantity  $\mu(t)$  at time  $t$  by the expression of the form (1.1) where  $M$  is a function on  $\text{Lin}^{++} \times R^{++}$  and  $m$  a function on  $\text{Lin}^+ \times \text{Lin}^+ \times R^{++} \times \mathcal{V} \times R^{++}$  subject to the decay conditions to be specified below. To simplify the notation, when dealing with expressions like (1.1), we shall often write  $\mathbf{F}, \theta, \mathbf{g}$  for  $\mathbf{F}(t), \theta(t), \mathbf{g}(t)$ , respectively,  $\mathbf{H}$  for  $\mathbf{F}(t-s)$ , and  $\mathbf{G}$  for  $\mathbf{G}^t(s)$  ( $s > 0$ ). The typical argument of  $M$  is thus  $(\mathbf{F}, \theta)$  and the typical argument of  $m$  is  $(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s)$ . The partial derivatives of  $M$  with respect to  $\mathbf{F}$  and  $\theta$  are denoted by  $\partial_{\mathbf{F}}M, \partial_{\theta}M$ , respectively, and the partial derivatives of  $m$  with respect to  $\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s$  are denoted by  $\partial_{\mathbf{F}}m, \partial_{\mathbf{H}}m, \partial_{\theta}m, \partial_{\mathbf{G}}m, m'$ , respectively.

The functions  $M$  and  $m$  are not uniquely determined by the correspondence  $(\mathbf{F}, \theta, \mathbf{g}) \mapsto \mu$ , where  $\mu$  is as in (1.1), and it turns out [8] that one can use this freedom in the choice of  $M, m$  to impose a *normalization condition*

$$m(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) = 0 \tag{2.2}$$

for every  $\mathbf{F} \in \text{Lin}^+, \theta > 0, s > 0$ . Indeed, given a pair  $(\tilde{M}, \tilde{m})$  not necessarily satisfying (2.2), then the pair  $(M, m)$  given by

$$M(\mathbf{F}, \theta) = \tilde{M}(\mathbf{F}, \theta) + \int_0^\infty \tilde{m}(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) ds, \\ m(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) = \tilde{m}(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) - \tilde{m}(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s)$$

shall satisfy (2.2) and give the same values of  $\mu$ .

To state the decay conditions on  $m$ , the concept of dominance similar to that in [7, 8, 1] will be used: a function  $w$  on  $\text{Lin}^+ \times \text{Lin}^+ \times R^{++} \times \mathcal{V} \times R^{++}$  is said to be *locally dominated* if for every compact set  $C$  in  $\text{Lin}^+ \times \text{Lin}^+ \times R^{++} \times \mathcal{V} \times R^{++}$  there exists an integrable function  $f$  on  $R^{++}$  such that

$$|w(\mathbf{F}, \mathbf{H}, \theta, \mathbf{g}, s)| \leq f(s) \tag{2.3}$$

for every  $(\mathbf{F}, \mathbf{H}, \theta, \mathbf{g}) \in C$  and  $s > 0$ .

**DEFINITION 2.1.** Given functions  $M$  on  $\text{Lin}^+ \times R^{++}$  and  $m$  on  $\text{Lin}^+ \times \text{Lin}^+ \times R^{++} \times \mathcal{V} \times R^{++}$  with values in a finite-dimensional vector space, (1.1) is said to be a *single-integral law* if  $M$  is continuously differentiable,  $m$  twice continuously differentiable, the normalization condition (2.2) holds, the functions

$$m, \partial_{\mathbf{F}}m, \partial_{\mathbf{H}}m, \partial_{\theta}m, \partial_{\mathbf{G}}m, s \partial_{\mathbf{G}}m, s \partial_{\theta}m \tag{2.4}$$

are locally dominated, and for every process  $(\mathbf{F}, \theta, \mathbf{g})$  and every  $t \in R$ , one has

$$m(\mathbf{F}(t), \mathbf{F}(t-s), \theta(t), \mathbf{G}^t(s), s) \rightarrow 0 \tag{2.5}$$

as  $s \rightarrow +\infty$  and as  $s \rightarrow 0+$ .

Note that for  $s \rightarrow 0+$ , the argument of  $m$  in (2.5) converges to  $(\mathbf{F}(t), \mathbf{F}(t), \theta(t), \mathbf{0}, 0)$  and the limit (2.5) for  $s \rightarrow 0+$  is therefore consistent with the normalization (2.2), which is assumed to hold only for  $s > 0$ , as  $m$  is not assumed to be defined for  $s = 0$ . Definition 2.1 differs only in technical details from the definitions given in [7, 8]. The domination conditions say first of all that the influence of the remote past is small; technically, they are adjusted so as to ensure that all the integrals occurring in

the statements and proofs of the results are absolutely convergent. In particular, the assumption that  $m$  itself is dominated ensures that the integral in (1.1) is convergent for every process and every time; the dominance of the partial derivatives of  $m$  with respect to  $\mathbf{F}$ ,  $\mathbf{H}$ ,  $\theta$ , and  $\mathbf{G}$  ensures the continuous differentiability of  $\mu$  with respect to  $t$  and that the time derivative of the integral in (1.1) is given by the time derivative of the integrand with respect to  $t$ . The dominance of  $s \partial_{\mathbf{H}} m$ ,  $s \partial_{\mathbf{G}} m$  permits one first of all to define the kinetic coefficients  $\mathbf{K}$ ,  $\mathbf{L}$  by formulas (3.6), (3.7) in Sec. 3 and second to use the dominated convergence theorem in the proof of Proposition 3.1. Finally, the limits (2.5) are used in the proof of the sufficiency of the thermodynamic restrictions stated in Proposition 4.1 for the validity of the dissipation inequality.

**3. Kinetic coefficients.** The two terms on the right-hand side of (1.1) have clearly distinguished meanings. Namely, they give the equilibrium and the nonequilibrium parts of the response, respectively. Indeed, if the process corresponds to a local equilibrium up to  $t_0$ , i.e., if

$$\mathbf{F}(t) = \mathbf{F}(t_0), \quad \theta(t) = \theta(t_0), \quad \mathbf{g}(t) = 0 \quad (3.1)$$

for all  $t \leq t_0$ , then the normalization condition (2.2) ensures that the integral in (1.1) vanishes for all  $t \leq t_0$  and the response is determined by  $M$  alone:

$$\mu(t) = M(\mathbf{F}(t_0), \theta(t_0)) \quad (3.2)$$

for all  $t \leq t_0$ .

Given a process  $(\mathbf{F}, \theta, \mathbf{g})$  and  $\alpha \in (0, 1]$ , we define a new process  $(\mathbf{F}_\alpha, \theta_\alpha, \mathbf{g}_\alpha)$  given by

$$\mathbf{F}_\alpha(t) = \mathbf{F}(\alpha t), \quad \theta_\alpha(t) = \theta(\alpha t), \quad \mathbf{g}_\alpha(t) = \alpha \mathbf{g}(\alpha t), \quad (3.3)$$

$t \in R$ . The process  $(\mathbf{F}_\alpha, \theta_\alpha, \mathbf{g}_\alpha)$  corresponds to a *temporal retardation of the deformation-temperature path and to a temporal retardation and simultaneous mollification of the temperature gradients*. Roughly, as  $\alpha \rightarrow 0$ , the process "approaches equilibrium". The time-evolution of the quantity  $\mu$  corresponding to the process  $(\mathbf{F}_\alpha, \theta_\alpha, \mathbf{g}_\alpha)$  is the function  $\mu_\alpha$ , defined by

$$\mu_\alpha(t) = M(\mathbf{F}_\alpha(t), \theta_\alpha(t)) + \int_0^\infty m(\mathbf{F}_\alpha(t), \mathbf{F}_\alpha(t-s), \theta_\alpha(t), \mathbf{G}_\alpha^t(s), s) ds, \quad (3.4)$$

where  $\mathbf{G}_\alpha^t$  is the summed history of the gradient of temperature corresponding to  $(\mathbf{F}_\alpha, \theta_\alpha, \mathbf{g}_\alpha)$ , i.e.,

$$\begin{aligned} \mathbf{G}_\alpha^t(s) &= \int_0^s \mathbf{g}_\alpha(t-s') ds' \\ &= \int_0^s \mathbf{g}(\alpha(t-s')) ds' \\ &= \int_0^{\alpha s} \mathbf{g}(\alpha t - s'') ds'' \\ &= \mathbf{G}^{\alpha t}(\alpha s) = \overline{\mathbf{G}}(\alpha t) - \overline{\mathbf{G}}(\alpha t - \alpha s), \end{aligned} \quad (3.5)$$

where  $\overline{\mathbf{G}}$  is the indefinite integral of  $\mathbf{g}$  normalized by  $\overline{\mathbf{G}}(0) = \mathbf{0}$ .

Proposition 3.1, below, shows that as  $\alpha \rightarrow 0$ , the single-integral law (3.4) for  $\mu_\alpha$  can be approximated by a much simpler equation (3.8) with no genuine memory effects. We define the *kinetic coefficients*  $\mathbf{K}$ ,  $\mathbf{L}$ , of the single-integral law (1.1), to be the functions of  $(\mathbf{F}, \theta) \in \text{Lin}^+ \times R^{++}$  given by

$$\mathbf{K}(\mathbf{F}, \theta) = - \int_0^\infty \partial_{\mathbf{H}} m(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s ds, \tag{3.6}$$

$$\mathbf{L}(\mathbf{F}, \theta) = - \int_0^\infty \partial_{\mathbf{G}} m(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s ds. \tag{3.7}$$

PROPOSITION 3.1. In the situation described above, one has

$$\begin{aligned} \mu_\alpha(t) = & M(\mathbf{F}_\alpha(t), \theta_\alpha(t)) + \mathbf{K}(\mathbf{F}_\alpha(t), \theta_\alpha(t)) \cdot \dot{\mathbf{F}}_\alpha(t) \\ & + \mathbf{L}(\mathbf{F}_\alpha(t), \theta_\alpha(t)) \cdot \mathbf{g}_\alpha(t) + o(\alpha, t), \end{aligned} \tag{3.8}$$

where  $o(\alpha, t)/\alpha \rightarrow 0$  as  $\alpha \rightarrow 0$  for every  $t \in R$ . Here  $\dot{\mathbf{F}}_\alpha$  is the time-derivative of  $\mathbf{F}_\alpha$ .

Hence the nonequilibrium part of the response can be approximated by linear dependences on the "nonequilibrium parameters"  $\dot{\mathbf{F}}$ ,  $\mathbf{g}$ . The starting form of the constitutive equations was chosen so as to obtain the asymptotic form (3.8). More general starting constitutive equations lead to more general approximate constitutive equations. For instance, the inclusion of  $\theta(t - s)$  in the integrand in (1.1) would lead to (3.8) with the right-hand side augmented by the term linear in  $\dot{\theta}$ . The above proposition is based on Coleman and Noll's idea of retardation, [4], although the situation considered by them is not exactly the one considered here.

*Proof.* Using the homogeneity of time, it is enough to verify the assertion of the proposition for  $t = 0$ . We then have

$$\mu_\alpha(0) = M(\mathbf{F}_0, \theta_0) + \int_0^\infty m(\mathbf{F}_0, \mathbf{F}(-\alpha s), \theta_0, -\overline{\mathbf{G}}(-\alpha s), s) ds,$$

where  $\mathbf{F}_0 = \mathbf{F}(0)$ ,  $\theta_0 = \theta(0)$ , and  $\overline{\mathbf{G}}$  is as in (3.5). Defining  $o(\alpha) = o(\alpha, 0)$  by (3.8), our goal is to verify that  $o(\alpha)/\alpha \rightarrow 0$  as  $\alpha \rightarrow 0$ . Using (3.6), (3.7),  $\mathbf{g}_\alpha(0) = \alpha \mathbf{g}(0)$ ,  $\dot{\mathbf{F}}_\alpha(0) = \alpha \dot{\mathbf{F}}(0)$ , we have

$$\begin{aligned} o(\alpha)/\alpha = & \frac{1}{\alpha} \left\{ \int_0^\infty m(\mathbf{F}_0, \mathbf{F}(-\alpha s), \theta_0, -\overline{\mathbf{G}}(-\alpha s), s) ds \right. \\ & + \int_0^\infty \partial_{\mathbf{H}} m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s) s ds \cdot \alpha \dot{\mathbf{F}}(0) \\ & \left. - \int_0^\infty \partial_{\mathbf{G}} m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s) s ds \cdot \alpha \mathbf{g}(0) \right\}. \end{aligned}$$

Since  $m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s) = 0$ , we can write the last expression as

$$\begin{aligned} o(\alpha)/\alpha = & \int_0^\infty \frac{1}{\alpha} (m(\mathbf{F}_0, \mathbf{F}(-\alpha s), \theta_0, -\overline{\mathbf{G}}(-\alpha s), s) - m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s)) ds \\ & + \int_0^\infty (\partial_{\mathbf{H}} m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s) s \cdot \dot{\mathbf{F}}(0) - \partial_{\mathbf{G}} m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s) s \cdot \mathbf{g}(0)) ds. \end{aligned}$$

Fixing  $s > 0$  and applying the mean value theorem to the function

$$\alpha \mapsto m(\mathbf{F}_0, \mathbf{F}(-\alpha s), \theta_0, -\overline{\mathbf{G}}(-\alpha s), s)$$

in the obvious way, we obtain the existence of a  $\vartheta = \vartheta(\alpha, s) \in (0, 1)$  such that

$$\begin{aligned} o(\alpha)/\alpha = & \int_0^\infty (\partial_{\mathbf{H}} m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s) s \cdot \dot{\mathbf{F}}(0) \\ & - \partial_{\mathbf{H}} m(\mathbf{F}_0, \mathbf{F}(-\alpha\vartheta s), \theta_0, -\overline{\mathbf{G}}(-\alpha\vartheta s), s) s \cdot \dot{\mathbf{F}}(-\alpha\vartheta s) \\ & - \partial_{\mathbf{G}} m(\mathbf{F}_0, \mathbf{F}_0, \theta_0, \mathbf{0}, s) s \cdot \mathbf{g}(0) \\ & + \partial_{\mathbf{G}} m(\mathbf{F}_0, \mathbf{F}(-\alpha\vartheta s), \theta_0, -\mathbf{G}(-\alpha\vartheta s), s) s \cdot \mathbf{g}(-\alpha\vartheta s)) ds. \end{aligned} \quad (3.9)$$

As  $\alpha \rightarrow 0$ , the integrand converges to 0 for every  $s > 0$ . Since the multiples by  $s$  of the partial derivatives occurring in (3.9) are assumed to be dominated, the dominated convergence theorem implies  $o(\alpha)/\alpha \rightarrow 0$  as  $\alpha \rightarrow 0$ .  $\square$

**4. Constitutive assumptions and thermodynamic restrictions.** A *thermodynamic process* of a material element is specified by the time-evolutions of the following quantities:

- $\mathbf{F}$  deformation gradient,
- $\theta$  absolute temperature,
- $\mathbf{g}$  gradient of temperature,
- $\varepsilon$  specific internal energy,
- $\eta$  specific entropy,
- $\psi$  specific Helmholtz free energy,
- $\boldsymbol{\sigma}$  Piola-Kirchhoff stress,
- $\boldsymbol{\xi}$  referential heat flux vector.

It is assumed that  $(\mathbf{F}, \theta, \mathbf{g})$  satisfies the restrictions imposed on the process in Sec. 2 and that the remaining quantities are given by the single-integral laws

$$\varepsilon = E(\mathbf{F}, \theta) + \int_0^\infty e(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) ds, \quad (4.1)$$

$$\eta = H(\mathbf{F}, \theta) + \int_0^\infty h(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) ds, \quad (4.2)$$

$$\psi = P(\mathbf{F}, \theta) + \int_0^\infty p(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) ds, \quad (4.3)$$

$$\boldsymbol{\sigma} = \mathbf{S}(\mathbf{F}, \theta) + \int_0^\infty \mathbf{s}(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) ds, \quad (4.4)$$

$$\boldsymbol{\xi} = \mathbf{Q}(\mathbf{F}, \theta) + \int_0^\infty \mathbf{q}(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) ds, \quad (4.5)$$

where  $\varepsilon, \eta, \psi, \boldsymbol{\sigma}, \boldsymbol{\xi}$  stand for  $\varepsilon(t), \eta(t), \psi(t), \boldsymbol{\sigma}(t), \boldsymbol{\xi}(t)$ , and the meaning of the arguments of the integrands in (4.1)–(4.5) has been explained in Sec. 2. The *constitutive functions*

$$E, e, H, h, P, p, \mathbf{S}, \mathbf{s}, \mathbf{Q}, \mathbf{q} \quad (4.6)$$

have appropriate codomains given by the interpretation of the left-hand sides of (4.1)–(4.5). The definition relation  $\varepsilon = \psi + \theta\eta$  for the Helmholtz free energy implies the following relations among the constitutive functions for  $\varepsilon, \psi$ , and  $\eta$ :

$$E(\mathbf{F}, \theta) = P(\mathbf{F}, \theta) + \theta H(\mathbf{F}, \theta) \quad (4.7)$$

and

$$e(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) = p(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) + \theta h(\mathbf{F}, \mathbf{H}, \theta, \mathbf{G}, s) \tag{4.8}$$

on their domains. The material element specified by the constitutive functions (4.6) is said to be *compatible with thermodynamics* if the dissipation inequality

$$\dot{\psi} \leq \boldsymbol{\sigma} \cdot \dot{\mathbf{F}} - \eta \dot{\theta} - \boldsymbol{\xi} \cdot \mathbf{g} / \theta \tag{4.9}$$

holds for every process satisfying the constitutive equations (4.1)–(4.5). For simplicity the density of the material element in the reference configuration is assumed to be equal to 1. I refer to Gurtin and Hrusa [7, 8] for the discussion of the assumption that the entropy and the free energy are given by the single-integral laws.

**PROPOSITION 4.1.** The material element is compatible with thermodynamics if and only if the following relations hold among the constitutive functions throughout their domains:

$$\mathbf{S} = \partial_{\mathbf{F}} P, \quad \mathbf{s} = \partial_{\mathbf{F}} p, \tag{4.10}$$

$$H = -\partial_{\theta} P, \quad h = -\partial_{\theta} p, \tag{4.11}$$

$$\mathbf{Q} = \mathbf{0}, \quad \mathbf{q} = -\theta \partial_{\mathbf{G}} p, \tag{4.12}$$

$$p' \leq 0. \tag{4.13}$$

The stress and the entropy relations (4.10) and (4.11) are essentially instances of the results obtained by Coleman [3] within the framework of the general theory of materials with fading memory. The particular form given above is a consequence of the postulated form of the constitutive equations and appears first in Gurtin and Hrusa [7, 8]. The heat flux relations (4.12) are instances of the result of Gurtin and Pipkin [9] obtained within the framework of materials with the dependence on the summed history of the gradient of temperature via unspecified functionals. The particular form given above is first given by Brandon and Hrusa [1] for one-dimensional rigid heat conductors. Formally, relations (4.10)–(4.13) can be obtained from the abstract results of Gurtin and Hrusa [8] by identifying their paths with triplets  $(\mathbf{F}, \theta, \overline{\mathbf{G}})$ , where  $\overline{\mathbf{G}}$  is the indefinite integral of  $\mathbf{g}$ ; the values of their single-integral law  $\mathcal{M}(f^t)$  with the values of the triplets  $(\boldsymbol{\sigma}, -\eta, -\boldsymbol{\xi}/\theta)$ , with the integrand written in the form  $m(\mathbf{F}(t), \mathbf{F}(t-s), \theta(t), \overline{\mathbf{G}}(t) - \overline{\mathbf{G}}(t-s), s)$ , and with their thermodynamic potential identified with  $\psi$ . Noting that  $\dot{f} = (\dot{\mathbf{F}}, \dot{\theta}, \dot{\overline{\mathbf{G}}}) = (\dot{\mathbf{F}}, \dot{\theta}, \mathbf{g})$ , we see that the dissipation inequality (4.9) takes the form

$$\dot{\psi} \leq \mathcal{M}(f^t) \cdot \dot{f}(t),$$

which is the abstract dissipation inequality of Gurtin and Hrusa [8]. The above proposition then is the equivalence (a)  $\Leftrightarrow$  (c) of Theorem 1 of [8]. Strictly speaking, the technical assumptions differ slightly from those of [8], but it is an easy matter to modify the arguments given in [8] to make them applicable in the present context.

Also the following result follows easily from the results of [8]:

**PROPOSITION 4.2.** Suppose that the material element is compatible with thermodynamics. Then

- (1) everywhere on the domain of  $p$ ,

$$p \geq 0; \tag{4.14}$$

(2) the following relations hold for every  $\mathbf{F} \in \text{Lin}^+$ ,  $\theta > 0$ ,  $s > 0$ :

$$\partial_{\mathbf{H}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) = \partial_{\mathbf{G}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) = \mathbf{0}, \quad (4.15)$$

$$\partial_{\mathbf{H}} \partial_{\mathbf{F}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) = -\partial_{\mathbf{F}}^2 p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s), \quad (4.16)$$

$$\partial_{\mathbf{H}} \partial_{\mathbf{G}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) = -\partial_{\mathbf{F}} \partial_{\mathbf{G}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s); \quad (4.17)$$

(3) the matrix

$$\begin{bmatrix} \partial_{\mathbf{F}}^2 p, & \partial_{\mathbf{F}} \partial_{\mathbf{G}} p \\ \partial_{\mathbf{F}} \partial_{\mathbf{G}} p, & \partial_{\mathbf{G}}^2 p \end{bmatrix},$$

when evaluated at  $(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s)$ , is positive-semidefinite for every  $\mathbf{F} \in \text{Lin}^+$ ,  $\theta > 0$ ,  $s > 0$ .  $\square$

Item (1) is one of the assertions of Lemma 1 of Gurtin and Hrusa [8]. Items (2), (3), as they stand, do not occur in [8], but easily follow from their noting that for every  $s > 0$  the function

$$(\mathbf{F}', \mathbf{H}, \mathbf{G}) \mapsto p(\mathbf{F}', \mathbf{H}, \theta, \mathbf{G}, s)$$

has a minimum at  $(\mathbf{F}', \mathbf{H}, \mathbf{G}) = (\mathbf{F}, \mathbf{F}, \mathbf{0})$  (cf. (3.11) of [8] and the proof of Theorem 4 of [8]). (4.15) is then vanishing of the first partial derivatives at minimum; (4.16), (4.17) follow from (4.15) by differentiating. Finally Assertion (3) is the positive-semidefiniteness of the second differential at minimum.

### 5. The principle of local equilibrium, production of entropy, and Onsager's relations.

Along with the exact constitutive equations (4.1)–(4.5) we shall now consider the *approximate constitutive equations*

$$\bar{\varepsilon} = E(\mathbf{F}, \theta), \quad (5.1)$$

$$\bar{\eta} = H(\mathbf{F}, \theta), \quad (5.2)$$

$$\bar{\psi} = P(\mathbf{F}, \theta), \quad (5.3)$$

$$\bar{\boldsymbol{\sigma}} = \mathbf{S}(\mathbf{F}, \theta) + \mathbf{K}^\sigma(\mathbf{F}, \theta) \cdot \dot{\mathbf{F}} + \mathbf{L}^\sigma(\mathbf{F}, \theta) \cdot \mathbf{g}, \quad (5.4)$$

$$\bar{\boldsymbol{\xi}} = \mathbf{K}^\xi(\mathbf{F}, \theta) \cdot \dot{\mathbf{F}} + \mathbf{L}^\xi(\mathbf{F}, \theta) \cdot \mathbf{g}, \quad (5.5)$$

where the *kinetic coefficients*  $\mathbf{K}^\sigma$ ,  $\mathbf{L}^\sigma$  for the stress and  $\mathbf{K}^\xi$ ,  $\mathbf{L}^\xi$  for the heat flux are given according to the prescription of Proposition 3.1:

$$\mathbf{K}^\sigma(\mathbf{F}, \theta) = - \int_0^\infty \partial_{\mathbf{H}} \mathbf{s}(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds, \quad (5.6)$$

$$\mathbf{L}^\sigma(\mathbf{F}, \theta) = \int_0^\infty \partial_{\mathbf{G}} \mathbf{s}(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds, \quad (5.7)$$

$$\mathbf{K}^\xi(\mathbf{F}, \theta) = - \int_0^\infty \partial_{\mathbf{H}} \mathbf{q}(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds, \quad (5.8)$$

$$\mathbf{L}^\xi(\mathbf{F}, \theta) = \int_0^\infty \partial_{\mathbf{G}} \mathbf{q}(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds. \quad (5.9)$$

In (5.5) the equilibrium contribution to the heat flux is already omitted in view of (4.12)<sub>1</sub>. A priori, there is no reason for omitting the kinetic terms in the constitutive equations (5.1)–(5.3) for the internal energy, entropy, and the Helmholtz free energy,

but it will be seen soon that the kinetic coefficients for these quantities vanish as a consequence of the compatibility of the exact constitutive equations (4.1)–(4.5) with thermodynamics. That is, equations (5.1)–(5.3) approximate the exact constitutive equations to the same degree of accuracy as (5.4) and (5.5) for retarded and mollified processes.

Let  $\varepsilon_\alpha, \eta_\alpha, \psi_\alpha, \sigma_\alpha, \xi_\alpha$  be the exact response to  $(\mathbf{F}_\alpha, \theta_\alpha, \mathbf{g}_\alpha)$  and let  $\bar{\varepsilon}_\alpha, \bar{\eta}_\alpha, \bar{\psi}_\alpha, \bar{\sigma}_\alpha, \bar{\xi}_\alpha$  be the response to  $(\mathbf{F}_\alpha, \theta_\alpha, \mathbf{g}_\alpha)$  according to (5.1)–(5.5).

**PROPOSITION 5.1.** If the material element given by the exact constitutive equations (4.1)–(4.5) is compatible with thermodynamics, then the functions  $\varepsilon_\alpha, \eta_\alpha, \psi_\alpha, \sigma_\alpha, \xi_\alpha$  differ by the terms of order  $o(\alpha)$  (with  $o(\alpha)/\alpha \rightarrow 0$  for  $\alpha \rightarrow 0$ ) from the functions  $\bar{\varepsilon}_\alpha, \bar{\eta}_\alpha, \bar{\psi}_\alpha, \bar{\sigma}_\alpha, \bar{\xi}_\alpha$ .

The absence of the kinetic coefficients in (5.1)–(5.3) is often called the principle of local equilibrium in the linear thermodynamics of irreversible processes. The proof of Proposition 5.1 will be given after the subsequent proposition, which describes the properties of the approximate constitutive equations.

**PROPOSITION 5.2.** If the material element given by the exact constitutive equations (4.1)–(4.5) is compatible with thermodynamics, then

- (1) for every process  $(\mathbf{F}, \theta, \mathbf{g})$  the approximate response  $\bar{\varepsilon}, \bar{\eta}, \bar{\psi}, \bar{\sigma}, \bar{\xi}$ , given by (5.1)–(5.5) satisfies

$$\theta \dot{\bar{\eta}} = \dot{\bar{\varepsilon}} - \bar{\sigma} \cdot \dot{\mathbf{F}} + \bar{\xi} \cdot \mathbf{g}/\theta + \theta \gamma, \tag{5.10}$$

$$\dot{\bar{\psi}} = \dot{\bar{\sigma}} \cdot \mathbf{F} - \bar{\eta} \dot{\theta} - \bar{\xi} \cdot \mathbf{g}/\theta - \theta \gamma, \tag{5.11}$$

where  $\gamma$ , the production of entropy, satisfies

$$\gamma \geq 0; \tag{5.12}$$

- (2) the equilibrium response functions  $P, H, \mathbf{S}, E$  satisfy

$$\mathbf{S} = \partial_{\mathbf{F}} P, \quad H = -\partial_\theta P,$$

or equivalently

$$\theta dH = dE - \mathbf{S} \cdot d\mathbf{F}, \quad dP = \mathbf{S} \cdot d\mathbf{F} - H d\theta;$$

- (3) the production of entropy  $\gamma$  is given by

$$\gamma = \Lambda \mathbf{X} \cdot \mathbf{X}, \tag{5.13}$$

where  $\mathbf{X} = (\dot{\mathbf{F}}, \dot{\theta})$  and  $\Lambda$  is the matrix of kinetic coefficients given by

$$\Lambda = \begin{bmatrix} \mathbf{K}^\sigma/\theta, & \mathbf{L}^\sigma/\theta \\ -\mathbf{K}^\xi/\theta^2, & -\mathbf{L}^\xi/\theta^2 \end{bmatrix};$$

- (4) the matrix of kinetic coefficients is positive-semidefinite and symmetric.

By assertion (1) the approximate model is compatible with thermodynamics, (2) is the Gibbs equation for the equilibrium variables, (3) is the quadratic expression for the production of entropy in terms of the nonequilibrium variables  $\mathbf{X}$ , and (4) is the Onsager symmetry of the kinetic coefficients.

*Proof of Proposition 5.1.* In view of Proposition 3.1 the proof amounts to showing that the kinetic coefficients  $\mathbf{K}^\psi$ ,  $\mathbf{L}^\psi$ ,  $\mathbf{K}^\eta$ ,  $\mathbf{L}^\eta$ ,  $\mathbf{K}^\varepsilon$ ,  $\mathbf{L}^\varepsilon$  for the single-integral laws for  $\psi$ ,  $\eta$ , and  $\varepsilon$  vanish. Using (3.6), (3.7) for  $\psi$  and (4.15), we have

$$\begin{aligned}\mathbf{K}^\psi &= - \int_0^\infty \partial_{\mathbf{H}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds = 0, \\ \mathbf{L}^\psi &= \int_0^\infty \partial_{\mathbf{G}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds = 0.\end{aligned}$$

Next, using (3.6), (3.7) for  $\eta$  and (4.11), (4.15), we have

$$\begin{aligned}\mathbf{K}^\eta &= - \int_0^\infty \partial_{\mathbf{H}} \mathbf{h}(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds \\ &= \int_0^\infty \partial_{\mathbf{H}} \partial_\theta p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds \\ &= \partial_\theta \int_0^\infty \partial_{\mathbf{H}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds = 0,\end{aligned}$$

and similarly

$$\begin{aligned}\mathbf{L}^\eta &= \int_0^\infty \partial_{\mathbf{G}} h(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds \\ &= - \int_0^\infty \partial_{\mathbf{G}} \partial_\theta p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds \\ &= - \partial_\theta \int_0^\infty \partial_{\mathbf{G}} p(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s) s \, ds = 0.\end{aligned}$$

Finally, using the definition relation (4.8) we deduce that

$$\mathbf{K}^\varepsilon = \mathbf{K}^\psi + \theta \mathbf{K}^\eta, \quad \mathbf{L}^\varepsilon = \mathbf{L}^\psi + \theta \mathbf{L}^\eta$$

and hence  $\mathbf{K}^\varepsilon = 0$ ,  $\mathbf{L}^\varepsilon = 0$  follow from the preceding considerations.  $\square$

*Proof of Proposition 5.2.* Item (2) is just the restatement of (4.10)<sub>1</sub> and (4.11)<sub>1</sub>. Using these relations one finds by a direct computation that (5.10), (5.11) hold with  $\gamma$  given by (5.13). This proves Assertion (3). Therefore, the proof of Assertion (1) will be complete if one shows that the matrix  $\Lambda$  is positive-semidefinite, which is part of Assertion (4). Hence, the only thing that now remains to be proved is Assertion (4).

To prove it, note that using the definitions of the kinetic coefficients (5.6)–(5.9),  $\Lambda$  can be written as

$$\Lambda = \frac{1}{\theta} \int_0^\infty \begin{bmatrix} -\partial_{\mathbf{H}} \mathbf{s}, & \partial_{\mathbf{G}} \mathbf{s} \\ \frac{1}{\theta} \partial_{\mathbf{H}} \mathbf{q}, & -\frac{1}{\theta} \partial_{\mathbf{G}} \mathbf{q} \end{bmatrix} s \, ds,$$

where the matrix elements are evaluated at the argument  $(\mathbf{F}, \mathbf{F}, \theta, \mathbf{0}, s)$ . Using (4.10)<sub>2</sub>, (4.11)<sub>2</sub>, the matrix in the integrand can be converted to

$$\begin{bmatrix} -\partial_{\mathbf{F}} \partial_{\mathbf{H}} p, & \partial_{\mathbf{F}} \partial_{\mathbf{G}} p \\ -\partial_{\mathbf{H}} \partial_{\mathbf{G}} p, & \partial_{\mathbf{G}}^2 p \end{bmatrix}$$

which in conjunction with (4.16), (4.17) leads to

$$\begin{bmatrix} \partial_{\mathbf{F}}^2 p, & \partial_{\mathbf{F}} \partial_{\mathbf{G}} p \\ \partial_{\mathbf{F}} \partial_{\mathbf{G}} p, & \partial_{\mathbf{G}}^2 p \end{bmatrix}.$$

To summarize,

$$\Lambda = \frac{1}{\theta} \int_0^\infty \begin{bmatrix} \partial_{\mathbf{F}}^2 p, & \partial_{\mathbf{F}} \partial_{\mathbf{G}} p \\ \partial_{\mathbf{G}} \partial_{\mathbf{F}} p, & \partial_{\mathbf{G}}^2 p \end{bmatrix} s \, ds.$$

The interchangeability of the second partial derivatives gives the symmetry of  $\Lambda$  and Item (3) of Proposition 4.2 asserts its positive-semidefinite character.  $\square$

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