# On the Thermomechanics of Interstitial Working

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Dedicated to J. L. Ericksen on his 60<sup>th</sup> birthday

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# 1. Introduction

In order to model fluid capillarity effects, the Dutch physicist KORTEWEG formulated in 1901 a constitutive equation for the Cauchy stress that included density gradients. Specifically, KORTEWEG proposed for study a compressible fluid model in which the "elastic" or "equilibrium" portion of the Cauchy stress tensor T is given by

$$T = T(\varrho, \theta, \operatorname{grad} \varrho, \operatorname{grad}^2 \varrho),$$

$$= (-p + \alpha \, \varDelta \varrho + \beta |\operatorname{grad} \varrho|^2) \, \mathbf{1} + \delta \operatorname{grad} \varrho \otimes \operatorname{grad} \varrho + \gamma \operatorname{grad}^2 \varrho,$$
(1.1)

where  $\varrho = \varrho(\mathbf{x}, t)$  is the density of the fluid at the place  $\mathbf{x}$  at time t, where grad  $\varrho$ and grad<sup>2</sup>  $\varrho$  are, respectively, the first and second (spatial) gradients of  $\varrho$  with respect to  $\mathbf{x}$  (with  $\Delta \varrho = \text{tr} (\text{grad}^2 \varrho) = \text{the Laplacian of } \varrho$ ), and where  $p, \alpha, \beta, \delta$ , and  $\gamma$  are material functions of  $\varrho$  and the temperature  $\theta$ . To model viscous effects in the dynamic response of his fluids, KORTEWEG added to the right-hand side of (1.1) the classic form of CAUCHY and POISSON, *i.e.*,  $\lambda(\text{tr } D) \mathbf{1} + 2\mu D$ , where **D** is the usual stretching tensor of hydrodynamics, and where  $\lambda$  and  $\mu$ , the usual viscosity coefficients, may depend on  $\rho$  and  $\theta$ .

In modern terminology, KORTEWEG's form (1.1) is a special example of an elastic material of grade N in which, in order to model more complex spatial interaction effects in a material, the constitutive quantities (here T) are permitted to depend not only on the first gradient of the deformation, the strain, but also on all gradients of the deformation less than or equal to the integer N. Thus, in particular, KORTEWEG'S (1.1) gives the stress in a very special elastic material of grade 3, and in recent years such higher grade materials have been intensively studied [1-21]. In particular, theories of KORTEWEG's type have been employed not only to model capillarity effects but also to analyze the structure of liquid-vapour phase transitions under both static [11, 12] and dynamic [13-17] conditions. A troubling aspect of all these higher-grade models, however, is that they are in general incompatible with the usual continuum theory of thermodynamics—indeed, KORTEWEG's model (1.1) is incompatible with conventional thermodynamics unless all the nonclassical coefficients,  $\alpha$ ,  $\beta$ ,  $\delta$ , and  $\gamma$  vanish identically!

To describe this incompatibility in more detail, let us identify the material particles of a continuous body  $\mathscr{B}$  with the positions  $X \in E$  they occupy in a fixed reference configuration  $B \subseteq E$ , where E is a three-dimensional Euclidean point space. We recall then that in conventional continuum thermodynamics the material body  $\mathscr{B}$  is completely characterized by its **process class**  $\mathbb{P}(\mathscr{B})$  which consists of certain ordered 8-tuples of functions,

$$\pi = \{ \boldsymbol{\chi}, \theta, \varepsilon, \eta, T, q, b, r \} \in \mathbb{P}(\mathcal{B}),$$

defined on  $B \times \mathbb{R}$  which, for every subdomain  $P \subseteq B$ , satisfy the balance of linear momentum

$$\frac{d}{dt} \int_{P_t} \varrho \dot{\mathbf{x}} \, dv = \int_{\partial P_t} T\mathbf{n} \, da + \int_{P_t} \varrho \mathbf{b} \, dv, \qquad (1.2)$$

the balance of energy

$$\frac{d}{dt} \int_{P_t} \varrho(\varepsilon + \frac{1}{2} \dot{\mathbf{x}} \cdot \dot{\mathbf{x}}) \, dv = \int_{\partial P_t} (\dot{\mathbf{x}} \cdot \mathbf{T} \mathbf{n} - \mathbf{q} \cdot \mathbf{n}) \, d\mathbf{a} + \int_{P_t} \varrho(\dot{\mathbf{x}} \cdot \mathbf{b} + \mathbf{r}) \, dv, \quad (1.3)$$

and the Clausius-Duhem inequality

$$\frac{d}{dt} \int_{P_t} \varrho \eta \, dv \ge - \int_{\partial P_t} \frac{q \cdot \mathbf{n}}{\theta} \, da + \int_{P} \varrho \, \frac{r}{\theta} \, dv, \qquad (1.4)$$

where, during the process  $\pi$  at the particle X at time t,

- (i)  $x = \chi(X, t) \in E$  is the motion,
- (ii)  $\theta = \theta(X, t) (> 0)$  is the absolute temperature,
- (iii)  $\varepsilon = \varepsilon(X, t)$  is the specific internal energy per unit mass,
- (iv)  $\eta = \eta(X, t)$  is the specific *entropy* per unit mass,

(v) T = T(X, t) is the (symmetric\*) Cauchy stress tensor, (vi)  $q = q(X, t) \in V$  is the heat flux vector, (vii)  $b = b(X, t) \in V$  is the specific body force per unit mass, (viii) r = r(X, t) is the radiant heating per unit mass,

where V is the translation space of E. In the axioms (1.2)-(1.4),  $\dot{x} \equiv \frac{\partial}{\partial t} \chi(X, t)$ denotes the velocity,  $S_t \equiv \chi(S, t)$  for any  $S \subseteq B$ , and  $n = n(x, t) \in V$  is the outer unit normal to  $\partial P_t$ . As earlier,  $\varrho = \varrho(X, t)$  denotes the mass density which, by conservation of mass, satisfies

$$\varrho(X, t) = \frac{\varrho_{\mathbf{R}}(X)}{|\det F(X, t)|}, \qquad (1.5)$$

where  $\varrho_R$  is a positive function given once and for all along with the body  $\mathscr{B}$  and the reference configuration B, and where

$$F = F(X, t) \equiv \nabla \chi(X, t)$$

is the deformation gradient \*\* which we always take to be nonsingular.

When sufficient smoothness is assumed and (1.5) is taken into account, it is easily shown that (1.2)-(1.4) are equivalent to the local conditions

$$\operatorname{div} \boldsymbol{T} + \varrho \boldsymbol{b} = \varrho \ddot{\boldsymbol{x}}, \tag{1.6}$$

$$\varrho \dot{\varepsilon} = T \cdot L - \operatorname{div} q + \varrho r, \qquad (1.7)$$

$$\varrho(\dot{\varepsilon} - \theta \dot{\eta}) - T \cdot L + \frac{q \cdot g}{\theta} \leq 0,$$
 (1.8)

where  $g = \operatorname{grad} \theta$  is the spatial temperature gradient and  $L = \operatorname{grad} \dot{x} = \dot{F}F^{-1}$  is the spatial velocity gradient. Moreover, a superposed dot (e.g.,  $\dot{\varepsilon}$ ) denotes the material time derivative of the indicated quantity  $\left(\dot{\varepsilon} \equiv \frac{\partial}{\partial t} \varepsilon(X, t)\right)$ , while the divergence operator in (1.6) and (1.7) is the contraction of the spatial gradient operator grad (·).

Now suppose we postulate a constitutive structure like KORTEWEG's in (1.1) indeed, by (1.5), suppose we consider even the much more general case in which  $\varepsilon$ ,  $\eta$ , T, and q are given functions of F,  $\theta$ ,  $\nabla F$ ,  $\nabla^2 F$ , and g, *i.e.*,

$$egin{aligned} & arepsilon & = \hat{arepsilon}(F,\, heta,\,
abla F,\,
abla^2 F,\,g), \ & \eta & = \hat{\eta}(F,\, heta,\,
abla F,\,
abla^2 F,\,g), \ & T & = \hat{T}(F,\, heta,\,
abla F,\,
abla^2 F,\,g), \ & q & = \hat{q}(F,\, heta,\,
abla F,\,
abla^2 F,\,g), \end{aligned}$$

<sup>\*</sup> For the materials we study here, standard arguments show that this assumed symmetry of T is equivalent to the usual principle of *balance of angular momentum*. For the more general materials studied by DUNN in [31], the stress tensor T need no longer be symmetric.

<sup>\*\*</sup> Throughout our work " $\nabla$ " will denote differentiation with respect to the *particle* X in B while "grad" will denote differentiation with respect to the *place* x in  $B_i$ .

so our material is elastic and of grade three. Then standard arguments\* (or specialization of results we obtain below) show that the inequality (1.8) forces  $\varepsilon$ ,  $\eta$ , and T to depend on at most F and  $\theta$ , and further, in terms of the Helmholtz free energy  $\psi = \hat{\psi}(F, \theta) = \varepsilon - \theta \eta$ , the relations

$$\eta = -\hat{\psi}_{\theta}(F, \theta)$$
 and  $T = \rho \hat{\psi}_{F}(F, \theta) F^{T}$ 

must hold. In particular, T cannot depend on  $\nabla F$ ,  $\nabla^2 F$ , or g, and this clearly rules out KORTEWEG's model (1.1) unless  $\alpha \equiv \beta \equiv \delta \equiv \gamma \equiv 0$ .

What is required then is a new, broader thermodynamic structure that admits nontrivial KORTEWEG type materials and, more generally, materials of arbitrary grade. While there are several such broader thermodynamic structures, we confine our attention in the present paper to a particularly simple and attractive one, which moreover does a minimum of violence to the classic conceptual structure embodied in (1.2)-(1.4). Indeed, an important feature of the theory we present here is that the purely mechanical principles of linear and angular momentum balance, as well as the purely thermal Clausius-Duhem inequality, are preserved in their standard forms.\*\* In particular, for the materials governed by our theory, the net local force and the net local torque actions exerted on the boundary of any subbody of  $\mathscr{B}$  will be delivered in exactly the standard way by the symmetric Cauchy stress tensor T.

All that we will modify, then, is the energy balance (1.3). Our idea is to follow a line of thought for energetic calculations which is similar to one found useful by ERICKSEN [22] in his work on liquid crystals and which, in fact, was suggested (and discarded) by TOUPIN [1] in his work on materials with couple-stresses.\*\*\* Specifically, for each process  $\pi$  we are going to posit the existence of a rate of supply of mechanical energy, the **interstitial working** u = u(X, t; n), defined for all  $(X, t) \in B \times \mathbb{R}$  and all unit vectors n, such that the balance of energy (1.3) for each subdomain P is replaced by

$$\frac{d}{dt} \int_{P_t} \varrho(\varepsilon + \frac{1}{2} \dot{\mathbf{x}} \cdot \dot{\mathbf{x}}) \, dv = \int_{\partial P_t} (T \mathbf{n} \cdot \dot{\mathbf{x}} + u - q \cdot \mathbf{n}) \, da + \int_{P_t} \varrho(\mathbf{b} \cdot \dot{\mathbf{x}} + r) \, dv. \quad (1.9)$$

Thus, in addition to the usual working  $Tn \cdot \dot{x}$  of the surface tractions Tn on  $\partial P_t$  and the flow of heat  $-q \cdot n$  through  $\partial P_t$ , we are allowing spatial interactions of longer range to engender a rate of supply u of mechanical energy across every material surface in  $\mathcal{B}$ .

At the foundation level the interstitial density u is distinguished from  $\dot{x} \cdot Tn$ ,

<sup>\*</sup> See, for instance, Theorem 1 of ERINGEN in [4] or the much more far-reaching theorem of GURTIN [3] on the impossibility of long range spatial interaction in any elastic material. For an early paper on the impossibility of certain spatial interactions in a purely thermal context, see the study [32] by COLEMAN & MIZEL.

<sup>\*\*</sup> We remark, however, that it is not clear to us that this much of the classical structure can be preserved if internal interactions have sufficiently long range. In particular, genuinely nonlocal internal interactions would seem to us to render meaningless the usual concepts of stress and heat flux.

<sup>\*\*\*</sup> Our idea is also related to certain aspects of the energetics of multipolar media; see GREEN & RIVLIN [33, 34].

the working of the surface tractions, by the fact that we shall here require u to be *objective* \* under a frame change, \* *i.e.*,

$$u^{*}(X, t^{*}; \nu^{*}) = u(X, t; \nu)$$
(1.10)

where  $t^* = t - a$  for a fixed, constant shift a in the time scale, and where  $v^* = Q(t) v$  for a time-dependent, proper orthogonal tensor Q = Q(t). The requirement that u be objective is central to the present analysis; we regard it, in fact, as a constitutive assumption that delimits the modes of interstitial working that may take place within the body. (In a theory of polar media, for example, such objectivity for u would be unnatural, and (1.10) would require replacement by an alternative postulate, governing the transformation of u under frame changes. Several such alternative postulates and the materials to which they give rise are studied in [31].) Also at the foundational level, the interstitial working u is distinguished from the influx of heat,  $-q \cdot n$ , in that it is only the latter quantity that appears in the Clausius-Duhem inequality. Additional properties of u, which will further distinguish it from both  $\dot{x} \cdot Tn$  and  $-q \cdot n$  as well as further motivate our interpretation of it as a rate of supply of *mechanical* energy, will emerge in a moment when we discuss constitutive structure.

Now, in fact, u = u(X, t; n) cannot really depend on n in an arbitrary fashion: an analogue of a standard theorem due to CAUCHY tells us that the balance law (1.9) can hold for all subdomains  $P \subseteq B$  if and only if u(X, t; n) is linear in n, *i.e.*, there must exist a vector field u = u(X, t) with values in V such that

$$u(X, t; n) = u(X, t) \cdot n \tag{1.11}$$

for every unit vector n. It is in terms of this interstitial work flux u, rather than the scalar density u, that we shall henceforth formulate our theory, and we note straightway that (1.10) and (1.11) imply that u is objective, *i.e.*,

$$u^{*}(X, t^{*}) = Q(t) u(X, t), \qquad (1.12)$$

under a frame change.

It is interesting to look at our introduction of u in a more abstract way. In the conventional thermodynamics which is embodied in (1.2)-(1.4), the surface energy flux h, beyond that due to the working of the surface tractions, is just the heat flux q and is thus inextricably linked to the surface entropy flux j which is just  $q/\theta$ . Our introduction of the interstitial work flux u has severed this link since now h = q - u while j is still given by  $q/\theta$ . Mathematically therefore our theory includes and is equivalent to either a theory in which h was kept equal to (interpreted as) the heat flux q but the entropy flux j was taken to be given by  $q/\theta - k$ , where k would represent a flux of entropy due to longer range spatial interactions, or a theory in which longer range spatial interactions resulted in neither h nor j having any simple dependence on (interpretation in terms

<sup>\*</sup> For an explanation of these concepts and their application to the other 8 quantities constituting a process  $\pi$ , the reader should see the treatise [23]. In [23] the stronger postulate of objectivity under frame changes corresponding to both proper and improper, time-dependent, orthogonal tensors Q(t) is adopted.

of) the heat flux q (which, in fact, would then disappear from this theory\*). Thus, although motivated differently, our theory has formal similarities to that of MÜLLER [24].\*\*

It is also interesting to note that, while it has seemed natural to us to keep the (vectorial) heat flux q and introduce the (scalar) surface supply u, one might wish to start not with the general fluxes, h and j, above of energy and entropy but rather with just scalar surface supplies, h = h(X, t; v) and j = j(X, t; v), respectively. In this more general setting, Cauchy's theorem, applied to the resulting form of balance of energy, yields the existence of a flux h = h(X, t) such that

$$h(X, t; v) = h(X, t) \cdot v;$$

it does *not* however yield, when applied to the corresponding new form of the Clausius-Duhem inequality, the existence of a flux j = j(X, t) such that

$$j(X, t; v) = j(X, t) \cdot v,$$

unless one makes the additional postulate that the function  $j(X, t; \cdot)$  satisfies the condition  $j(X, t; -\nu) = -j(X, t; \nu)$ , i.e., one must postulate that the internal surface entropy supply conforms with the law of "action-reaction".

For us then, the process class  $\mathbb{P}(\mathcal{B})$  of a body will consist of processes  $\pi$  which are certain ordered 9-tuples of functions on  $B \times \mathbb{R}$ ,

$$\boldsymbol{\pi} = \{\boldsymbol{\chi}, \boldsymbol{\theta}, \boldsymbol{\varepsilon}, \boldsymbol{\eta}, \boldsymbol{T}, \boldsymbol{q}, \boldsymbol{u}, \boldsymbol{b}, \boldsymbol{r}\},\$$

with the physical interpretations and mathematical properties we have discussed above, and which satisfy the balance of linear momentum (1.2), the Clausius-Duhem inequality (1.4), the conservation of mass (1.5), and the balance of energy in the new form (1.9). Paralleling (1.6)–(1.8), it is easy to show then that (1.2), (1.4), and (1.9) are, given sufficient smoothness and (1.5), equivalent to the local conditions

$$\operatorname{div} \boldsymbol{T} + \varrho \boldsymbol{b} = \varrho \ddot{\boldsymbol{x}}, \tag{1.13}$$

$$\varrho \dot{\varepsilon} = \mathbf{T} \cdot \mathbf{L} - \operatorname{div} \mathbf{q} + \operatorname{div} \mathbf{u} + \varrho \mathbf{r}, \qquad (1.14)$$

$$\varrho(\dot{\varepsilon} - \theta\dot{\eta}) - T \cdot L - \operatorname{div} u + \frac{q \cdot g}{\theta} \leq 0.$$
 (1.15)

<sup>\*</sup> Note that, in terms of this last alternative, our theory can be seen as a way offeintroducing the heat flux q by *defining*  $q \equiv \theta j$  and then u = q - h. The first alternative theory, of course, is just the reintroduction of the heat flux q by the identifications  $q \equiv h$  and then  $k \equiv q/\theta - j$ .

As these alternative but equivalent theories suggest, outside the traditional structure (1.2)-(1.4) the identification of the "real" heat flux is a rather subtle affair.

<sup>\*\*</sup> ERINGEN also seems to have had in mind breaking the usual link between h and j, cf. (2.21) in [4]. However, except for suggesting chemical reactions, he gives little guidance for identifying such "non-simple processes." For a related discussion of these issues in the context of mixture theory, but with a point of view similar to that adopted here, see GURTIN & VARGAS [35]. By nonlocal considerations, ERINGEN [25, 27] and ERINGEN & EDELEN [26] have recently suggested a rationale for even more drastically altering *all* of the local balance laws (1.5)–(1.8). A very similar, but less specific, modification was discussed in [28].

In terms of the Helmholtz free energy  $\psi = \psi(X, t) \equiv \varepsilon - \theta \eta$ , the inequality (1.15) is readily seen to be equivalent to

$$\varrho(\dot{\psi} + \eta\dot{\theta}) - T \cdot L - \operatorname{div} u + \frac{q \cdot g}{\theta} \leq 0.$$
 (1.16)

We will refer to (1.16) as the *dissipation inequality*, and we will study the thermodynamic consequences of (1.3)-(1.16) for the constitutive structure arising from the assumption that  $\varepsilon(X, t)$ ,  $\eta(X, t)$ , T(X, t), q(X, t), and u(X, t) are, for every  $\pi \in \mathbb{P}(\mathcal{B})$ , given by smooth functions of F,  $\theta$ ,  $\nabla F$ ,  $\nabla^2 F$ , g, and  $\dot{F}$ , i.e.,

$$\begin{split} \varepsilon &= \hat{\varepsilon}(F, \theta, \nabla F, \nabla^2 F, g, F), \\ \eta &= \hat{\eta}(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}), \\ T &= \hat{T}(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}), \\ q &= \hat{q}(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}), \\ u &= \hat{u}(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}). \end{split}$$
(1.17)<sub>1-5</sub>

Of course, once  $\hat{\epsilon}(\cdot)$  and  $\hat{\eta}(\cdot)$  are given, the relation  $\psi \equiv \epsilon - \theta \eta$  determines a function  $\hat{\psi}(\cdot)$  such that

$$\psi = \hat{\psi}(F, \theta, \nabla F, \nabla^2 F, g, F). \star$$
(1.17)<sub>6</sub>

The common, open domain  $\mathscr{I}$  of the response functions  $\hat{\varepsilon}(\cdot)$ ,  $\hat{\eta}(\cdot)$ ,  $\hat{T}(\cdot)$ ,  $\hat{q}(\cdot)$ ,  $\hat{u}(\cdot)$ , and  $\hat{\psi}(\cdot)$  of (1.17) is a matter of some delicacy. While the topological structure of  $\mathscr{I}$  will be further delineated at the appropriate places in Sections 2 and 4 and in Appendix A, we observe here that  $\mathscr{I}$  constitutes a tacit restriction on the process class  $\mathbb{P}(\mathscr{B})$  since any process  $\pi$  in  $\mathbb{P}(\mathscr{B})$  must be such that its associated motion and temperature field,  $\chi(\cdot, \cdot)$  and  $\theta(\cdot, \cdot)$ , satisfy

$$(\nabla \chi, \theta, \nabla^2 \chi, \nabla^3 \chi, \text{grad } \theta, \nabla \dot{\chi}) (X, t) \in \mathscr{I}$$

for all  $(X, t) \in B \times \mathbb{R}$ . Accordingly, we will henceforth call two maps,  $\chi(\cdot, \cdot)$  and  $\theta(\cdot, \cdot)$ , a **motion** and a **temperature field**, respectively, *only* if they conform with this restriction.

The presence of the strain rate  $\dot{F}$  in  $(1.17)_5$  is of crucial importance for our entire theory and is suggested by our interpretation of  $u = u \cdot n$  as a rate of supply of mechanical energy due to spatial interactions of longer range than those reflected in the usual mechanical energy supply rate  $\dot{x} \cdot Tn$  (=  $(T^T \dot{x}) \cdot n$ ), arising from the working of the surface tractions. Indeed, based on the formal analogy to  $(T^T \dot{x}) \cdot n$ , one might even want to require that the form

$$\boldsymbol{u} \cdot \boldsymbol{n} = \hat{\boldsymbol{u}}(\boldsymbol{F}, \theta, \nabla \boldsymbol{F}, \nabla^2 \boldsymbol{F}, \boldsymbol{g}, \boldsymbol{F}) \cdot \boldsymbol{n}$$

<sup>\*</sup> Note that for simplicity we study only the case where the response functions  $\hat{\varepsilon}(\cdot)$ ,  $\hat{\eta}(\cdot)$ ,  $\hat{\eta}(\cdot)$ ,  $\hat{\eta}(\cdot)$ ,  $\hat{u}(\cdot)$ ,  $\hat{u}(\cdot)$ , and  $\hat{\psi}(\cdot)$  are the same for each particle  $X \in B$ . Thus, we suppose that the material of which our body  $\mathscr{B}$  is composed is homogeneous and that B is one of its homogeneous reference configurations. Correspondingly, we henceforth assume that the function  $\varrho_{\mathbf{R}}(X)$  of (1.5) is also independent of X.

be linear in  $\dot{F}$ , but we shall not make this assumption. Instead, in Section 2 we will *prove* that  $\hat{u}(\cdot)$  can be at most *affine* in  $\dot{F}$  and g; indeed, we will show that u decomposes into three distinct parts:

$$u = \hat{u}(F, \theta, \nabla F, \nabla^2 F, g, F),$$
  
=  $\nabla \dot{F} + \Omega g + w^{\mathrm{E}}$  (1.18)

where  $\mathbf{V} = \mathbf{V}(F, \theta, \nabla F)$  is a third order tensor, where  $\Omega = \Omega(F, \theta, \nabla F, \nabla^2 F)$  is a skew, second order tensor, and where  $\mathbf{w}^{\mathrm{E}} = \mathbf{w}^{\mathrm{E}}(F, \theta, \nabla F, \nabla^2 F)$  is independent of g and  $\dot{F}$ . Moreover, we will show that  $\hat{\psi}(\cdot)$ , the response function for the free energy, can depend on at most F,  $\theta$ , and  $\nabla F$ ,

$$\psi = \hat{\psi}(F, \theta, \nabla F), \qquad (1.19)$$

and that the tensor  $\mathbb{V}(F, \theta, \nabla F)$  is completely determined by  $\hat{\psi}(\cdot)$  and vanishes at a given point  $(F, \theta, \nabla F)$  if and only if  $\hat{\psi}_{\nabla F}(F, \theta, \nabla F)$  vanishes (see our (2.7) and (2.8)). Thus, the "dynamic" part  $v \equiv \nabla F$  of u, besides involving the *time rate* of the strain F in a surprisingly simple way, also depends in an interesting fashion upon the sensitivity of the Helmholtz free energy to *local distortions* of the strain.

The decomposition (1.18) tells us that there are three distinct mechanisms for the production of the interstitial flux u. While, for many materials, we believe the dominant (sole?) mechanism to be that associated with the dynamic part  $\nabla \dot{F}$ , we find it interesting that thermodynamics delivers a "static" part of u,  $w \equiv \Omega g + w^{E}$ , consisting of the "purely thermal" term  $\Omega g$  and the "equilibrium" term  $w^{E}$ . Here we show that these two terms must be such that together they satisfy the relation

div 
$$\boldsymbol{w} = \frac{\boldsymbol{q}^{\mathrm{E}} \cdot \boldsymbol{g}}{\theta}$$

for every motion-temperature pair  $(\chi, \theta)$   $(\cdot, \cdot)$ , where  $q^{E}$ , the *equilibrium heat flux*, is given by

$$q^{\mathrm{E}} = q^{\mathrm{E}}(F, \, heta, \, 
abla F, \, 
abla^2 F) \equiv \hat{q}(F, \, heta, \, 
abla F, \, 
abla^2 F, \, 0, \, 0).$$

Thus, if the material does not support an equilibrium flux of heat (and so  $q^E \equiv 0$ ) then w is divergence-free and thus drops out of the energy equation (1.14) and the dissipation inequality (1.16). Conversely, if the material does not support a static (*i.e.* rest) interstitial flux (and so  $w \equiv 0$ ), as would be the case if we postulated that

$$F=0 \Rightarrow u=0$$

then we see that neither can it support an equilibrium flux of heat.\*

As we have seen, in our theory the Helmholtz free energy turns out to act as a potential for the dynamic part of u. We shall also see that  $\hat{\psi}(\cdot)$  fulfills its classic role of acting as a potential for the entropy  $\eta$  and, in the "elastic" case when  $\hat{T}(\cdot)$  and  $\hat{q}(\cdot)$  are independent of  $\hat{F}$ , for the stress T. Indeed, in Section 2 we show that an *entropy relation* of the classic form always holds in our materials, *viz*.

$$\eta = -\hat{\psi}_{\theta}(F, \theta, \nabla F), \qquad (1.20)$$

<sup>\*</sup> We note that the following work can be materially simplified on a first reading if one adopts this postulate throughout. Indeed in this case several subsections and paragraphs set in pica type, as well as Appendices B and C, can be omitted.

and, in Section 3, we show that, in terms of the Cartesian components  $T_{ij}$ ,  $F_{ix}$ , and  $F_{ix\beta}$  of, respectively, T, F, and  $\nabla F$ , the following stress relation must hold whenever  $\hat{T}(\cdot)$  and  $\hat{q}(\cdot)$  are independent of  $\dot{F}$ :

$$T_{ij} = \varrho [\hat{\psi}_{F_{i\alpha}} F_{j\alpha} + \hat{\psi}_{F_{i\alpha\beta}} F_{j\alpha\beta} + (F_{i\alpha} F_{j\beta} F_{\lambda k}^{-1} \hat{\psi}_{F_{k\alpha\beta}})_{,\lambda} - (F_{i\alpha} \hat{\psi}_{F_{j\alpha\beta}} + F_{j\alpha} \hat{\psi}_{F_{i\alpha\beta}})_{,\beta}]. \star$$

$$(1.21)$$

By (1.20) it is clear that, like the free energy, the entropy  $\eta$  and the energy  $\varepsilon = \psi + \theta \eta$  can depend on at most F,  $\theta$ , and  $\nabla F$ . Perhaps more interesting is the stress relation (1.21): it tells us that, while the stress  $T = \hat{T}(F, \theta, \nabla F, \nabla^2 F, g)$  in an elastic material of grade 3 can depend on all five of its arguments, it can depend on g and  $\nabla^2 F$  at most *affinely*.

In the general nonelastic or viscous case, matters are more subtle: while the entropy relation (1.20) continues to hold, the general dependence of  $\hat{T}(\cdot)$ and  $\hat{q}(\cdot)$  on  $\dot{F}$  now permits us to establish the stress relation (1.21) only at states of "local equilibrium," *i.e.*, only at states  $(F, \theta, \nabla F, \nabla^2 F, g, F)$  where  $g = \dot{F} = 0$ . Thus, as in simpler theories,\*\* the inclusion of viscous effects through constitutive dependence on  $\dot{F}$  makes only a portion of the stress T determined by the free energy  $\psi$ .

In Section 4 we introduce a subclass of our general materials (1.17). These are the materials of Korteweg type and arise when the constitutive equations of (1.17) are specialized to

$$\varepsilon = \overline{\varepsilon}(\varrho, \theta, d, S, g, L),$$

$$\eta = \overline{\eta}(\varrho, \theta, d, S, g, L),$$

$$T = \overline{T}(\varrho, \theta, d, S, g, L),$$

$$q = \overline{q}(\varrho, \theta, d, S, g, L),$$

$$u = \overline{u}(\varrho, \theta, d, S, g, L),$$

$$\psi = \overline{\psi}(\varrho, \theta, d, S, g, L),$$
(1.22)

where  $d \equiv \operatorname{grad} \varrho$ ,  $S = S^T \equiv \operatorname{grad}^2 \varrho$ , and  $L = \dot{F}F^{-1} = \operatorname{grad} x$ . As is clear, such materials include more than the original proposal (1.1) by KORTEWEG. We shall find however that the form (1.1) is inconsistent with the thermodynamic structure laid down here unless fairly specific relations hold among its coefficients.

As in the more general case already discussed, thermodynamics requires that S, g, and L drop out of  $\overline{\varepsilon}(\cdot)$ ,  $\overline{\eta}(\cdot)$ , and  $\overline{\psi}(\cdot)$ . and indeed that

$$\begin{split} \psi &= \bar{\psi}(\varrho,\,\theta,\,d),\\ \eta &= -\bar{\psi}_{\theta}(\varrho,\,\theta,\,d),\\ \varepsilon &= \bar{\psi}(\varrho,\,\theta,\,d) - \theta \bar{\psi}_{\theta}(\varrho,\,\theta,\,d). \end{split} \tag{1.23}$$

<sup>\*</sup> In (3.3) and (3.4) we give, respectively, alternative forms for T and for the Piola-Kirchhoff stress tensor  $T^{R}$  associated with T.

<sup>\*\*</sup> See, for example, the study [29] by COLEMAN & MIZEL.

Further, for materials of Korteweg type, the dynamic part u of the interstitial work flux u is just  $\varrho \bar{\varrho \psi}_d$ . Indeed, we shall show that

$$u = -\varrho^{2}(\operatorname{tr} L) \,\overline{\psi}_{d}(\varrho, \,\theta, \,d) + \overline{w}(\varrho, \,\theta, \,d, \,S, \,g), \qquad (1.24)$$
$$= \varrho \dot{\varrho} \overline{\psi}_{d} + \overline{w},$$

where this last holds by mass conservation in the form  $\dot{\varrho} = -\varrho$  (tr L). Moreover the static portion  $\boldsymbol{w} = \overline{\boldsymbol{w}}(\cdot)$  of  $\boldsymbol{u}$  can also, for materials of Korteweg type, be shown to have a very specific structure. In fact, in addition to our earlier remark that  $\boldsymbol{w}$  is always divergence-free in any material that has a null equilibrium heat flux, the function  $\overline{\boldsymbol{w}}(\cdot)$  must (i) vanish identically if the material possesses a center of symmetry\*, and, in any case, (ii) always depend on the local strain distortion in a rather simple and explicit way, in fact vanishing at any point where the local measure of distortion,  $\boldsymbol{d} = \operatorname{grad} \varrho$ , vanishes. See our (4.7).

For elastic materials of Korteweg type (*i.e.*, when  $T(\cdot)$  and  $\overline{q}(\cdot)$  do not depend on the velocity gradient L), the general form (1.21) for the Cauchy stress reduces to just

$$T = (-\varrho^{2}\overline{\psi}_{\varrho} + \varrho \ d \cdot \overline{\psi}_{d} + \varrho^{2} \operatorname{div} \overline{\psi}_{d}) \ 1 - \varrho \ d \otimes \overline{\psi}_{d},$$
  
$$= \{-\varrho^{2}\overline{\psi}_{\varrho} + \varrho \operatorname{div} (\varrho\overline{\psi}_{d})\} \ 1 - \varrho \ d \otimes \overline{\psi}_{d},$$
(1.25)

a constitutive form that turns out to have several pleasant and highly desirable properties. While the reader should refer to Sections 3 and 4 for a complete treatment, we note here that, firstly, the form (1.25) avoids the overdetermined character of equilibrium solutions that SERRIN [18] found typically to hold for KORTEWEG's original model (1.1). Secondly, since  $\psi$  is objective under a frame change, the function  $\overline{\psi}(\varrho, \theta, d)$  can depend on d only through its squared magnitude  $M \equiv d \cdot d$ . That is,

$$\psi = \overline{\psi}(\varrho, \theta, d) = \psi(\varrho, \theta, M)$$

and so (1.24) and (1.25) take on the more explicit respective forms

$$\boldsymbol{u} = \dot{\varrho}\boldsymbol{c}\,\boldsymbol{d} + \boldsymbol{\bar{w}},\tag{1.26}_1$$

$$T = \{-\varrho^2 \psi_{\varrho} + \varrho \operatorname{div} (c \, d)\} \, \mathbf{1} - c \, d \otimes d, \qquad (1.26)_2$$
$$= \{-\varrho^2 \psi_{\varrho} + \varrho c_{\varrho} M + \varrho c_{\theta} g \cdot d + 2\varrho c_M \, d \otimes d \cdot \operatorname{grad}^2 \varrho + \varrho c \, \varDelta \varrho\} \, \mathbf{1} - c \, d \otimes d,$$

where  $c = c(\varrho, \theta, M) \equiv 2\varrho \psi_M(\varrho, \theta, M)$  is usually called the *surface tension coefficient*. We see from  $(1.26)_2$  that, in addition to entering into T only affinely, g and  $\operatorname{grad}^2 \varrho$  affect only the isotropic portion of the stress in any elastic material of Korteweg type. These materials are thus somewhat different from KORTEWEG'S (1.1): the form  $(1.26)_2$  has no term like KORTEWEG'S  $\gamma$  grad<sup>2</sup>  $\varrho$  and has delicate links among the coefficients that correspond to  $\alpha$ ,  $\beta$ , and  $\delta$  in (1.1). As we shall see in Section 4, the exact structural details of (1.25) and/or  $(1.26)_2$  have important consequences for the theory and, we feel, suggest (1.25) as a model superior to KORTEWEG'S (1.1). Lastly, we remark that, even for viscous materials of Korte-

<sup>\*</sup> That is, if  $\overline{w}(\cdot)$  is an odd function of d and g jointly.

we gtype (for which L does not drop out of  $\overline{T}(\cdot)$  and  $\overline{q}(\cdot)$ ), the forms (1.25) and (1.26)<sub>2</sub> turn out to give the stress at any particle X that is in "local equilibrium" in the sense that g = L = 0 at X.

If we set  $p = p(\varrho, \theta) \equiv \varrho^2 \psi_{\varrho}(\varrho, \theta, 0)$ , a little manipulation shows that (1.26)<sub>2</sub> can be written as

$$T = \left\{-p(\varrho, \theta) + \varrho c_{\varrho}M + \frac{1}{2}\int_{0}^{M} \left[c - \varrho c_{\varrho}\right] dM + \varrho c \, \varDelta \varrho + \varrho c_{\theta}g \cdot d + 2\varrho c_{M}d \otimes d \cdot \operatorname{grad}^{2}\varrho\right\} 1 - cd \otimes d.$$

The important special case where c is independent of M corresponds precisely to KORTE-WEG'S original assumptions and yields here the specialization

$$T = \{-p(\varrho, \theta) + \varrho c \, \varDelta \varrho + \frac{1}{2} (\varrho c)_{\varrho} M + \varrho c_{\theta} g \cdot d\} \, 1 - c \, d \otimes d. \tag{1.27}$$

Comparing this with (1.1), we see that now

$$\alpha = \varrho c, \quad \beta = \frac{1}{2} (\varrho c)_o, \quad \delta = -c, \quad \gamma = 0,$$

formulae noted earlier by AIFANTIS & SERRIN [11] for the connection they have with the variational theory of VAN DER WAALS.

Finally, and as we have already indicated, there are several points in our analysis where thermodynamics and objectivity under frame changes are found to impose strong restrictions on the functional form of the interstitial work flux u. The precise representation theorems necessitated by these restrictions are developed in our Appendices A, B, and C, and the techniques and results of these appendices will, we feel, be found to be of interest in their own right. (This is, perhaps, particularly true of Appendix C, which may be read independently of the rest of our text.)

We close this Introduction with a few brief remarks concerning the connection of our work with some earlier theories that admitted gradients of deformations beyond the first into their constitutive equations. First, and closest to ours in generality, is the work of TOUPIN in 1962 and 1964 on elastic materials with couplestresses [1, 2]. In [1] TOUPIN formulated general laws governing the balance of linear momentum, angular momentum, and energy in a continuum capable of generating couple-stresses and spin momenta. TOUPIN was thus mainly interested in materials for which the usual symmetry of the Cauchy stress fails-in direct opposition to our point of view here. However, in his footnote on page 394 of [1], TOUPIN apparently envisaged the importance of at least the dynamic part uof our interstitial work flux, though in fact he then proceeded to cast this term out of his analysis (apparently as not germane to higher gradient effects and/or couple-stresses). As our work clearly shows, however, the presence of u gives a very convenient mechanism for energy, entropy, and stress to depend on higher gradients of the deformation, and thus the final sentence of TOUPIN's footnote on page 398 of [1], namely

"Our analysis shows that if the energy depends on these higher derivatives of the displacement, then, in general, the principal part of the couple-stress cannot vanish in such a material."

seems to us to require modification.

In his second paper, considering only static, mechanical effects, TOUPIN [2] postulated a principle of virtual work for an elastic material whose storedenergy density W per unit reference volume is to depend on both F and  $\nabla F$ . He finds the resulting equilibrium equations and boundary conditions necessitated by this principle of virtual work and identifies the quantity

$$W_{F_{i\alpha}} - (W_{F_{i\alpha\beta}})_{\beta} \tag{1.28}$$

as the Piola-Kirchhoff stress in his material. As a glance at our (3.4) makes clear, \* this is quite different from the Piola-Kirchhoff stress of the materials we study here. Moreover, TOUPIN finds very nonstandard boundary conditions for his theory which, among other things, require that the stress tensor no longer deliver the surface tractions, even on arbitrary subbodies within his materials. Additionally, TOUPIN's form (1.28) fails to deliver symmetric Cauchy stresses even in materials that are nominally "fluid-like" (e.g., materials of Korteweg type) where the concept of couple-stresses would seem inappropriate. The theory we present here, even restricted to just elastic materials, thus seems to us to have several advantages over those of TOUPIN.

Restricting their attention to, in our terminology, rather special and essentially elastic materials of Korteweg type, FIXMAN in 1967 [5], and FELDERHOF in 1970 [6], also studied certain higher grade constitutive models. FIXMAN's approach was to use a mechanical variational principle to find a certain "internal conservative force" which he then required to be the divergence of the elastic stresses in his materials. He then inferred\*\* that these stresses are of the form

$$(-p+2\lambda[\varrho^2 \, \varDelta \varrho+\varrho M])\,\mathbf{1}-2\lambda \varrho \, \boldsymbol{d} \otimes \boldsymbol{d}, \qquad (1.29)$$

where  $d = \operatorname{grad} \varrho$ ,  $M = |d|^2$ , and  $\lambda$  is a constant. This, of course, is exactly the form that emerges from our (1.27) if we take  $c = 2\lambda \varrho$ .

FELDERHOF, on the other hand, used both a minimum principle and a variational principle based on a certain Lagrangian to find, respectively, the equilibrium equations and the dynamic momentum equations that governed his materials. He then observed\*\*\* that each of these two sets of equations was compatible with a stress tensor of the form

$$-(p + c_1 a \varrho \, \Delta \varrho + (\frac{1}{2} + c_1) \, a M) \, \mathbf{1} + c_1 a \, \mathbf{d} \otimes \mathbf{d} + (1 + c_1) \, a \varrho \mathbf{S}, \quad (1.30)$$

where  $S = \text{grad}^2 \rho$ , where *a* is a determined constant in his theory, but where  $c_1$  is a completely arbitrary parameter.<sup>†</sup> While FELDERHOF did not resolve this

<sup>\*</sup> For comparison with our theory, we identify W with the *isothermal* stored-energy of the material. Hence  $W = \varrho_R \psi$ .

<sup>\*\*</sup> See his equations (30) and (31).

<sup>\*\*\*</sup> See his equation (4.7) and note that FELDERHOF's "pressure tensor" is the negative of our T.

<sup>&</sup>lt;sup>†</sup> That is, the value of  $c_1$  does not affect the divergence of (1.30).

indeterminancy of the stress, a glance at our  $(1.26)_2$  shows that the form (1.30) will be compatible with the thermodynamic structure laid down here only if  $c_1 = -1$ , \* which results in the form

$$(-p + a\varrho \,\varDelta \varrho + \frac{1}{2}aM) \,\mathbf{1} - a \,d \,\otimes d, \tag{1.31}$$

and this is precisely what emerges from our (1.27) if we take c = a. (We remark that FIXMAN'S (1.29) and FELDERHOF'S (1.30) and (1.31) are mutually exclusive, but that this is merely a consequence of their assuming slightly different forms for their respective energies' dependence on  $M = |\operatorname{grad} \varrho|^2$ .)

It is, perhaps, worth making explicit what is but tacit in FELDERHOF's multiplicity of forms (1.30) for the stress: Since they can be stated without even any *concept* of internal stress, virtual work principles like that of TOUPIN, mechanical variational principles like that of FIXMAN, and minimum and Lagrangian variational principles like those used by FELDERHOF are fundamentally unable ever to tell one what the stresses are in a body to which they apply. This, of course, may be viewed as a strength of these principles, since they are thus compatible with a multiplicity of materials, having different forms of stresses. Our point here, however, is that the most they can do in this regard is to *suggest* a form for the stress *up to a divergence-free term*—and they can do even this only if one is prepared to adjoin to them CAUCHY's concept of stress and the momentum equations based on it. Thus, TOUPIN's form (1.28), FIXMAN's form (1.29), and even FELDERHOF's forms (1.30) are all suspect to us: each of these forms may require the addition of a divergence-free form to give the "real" stress in their respective materials.

Finally, there is the work of BLINOWSKI [7–10] on (in our therminology) elastic materials of Korteweg type. Restricting his attention to isothermal processes, BLINOWSKI in [7] and [8] formulated an energy principle containing a surface flux term which was linear in  $L = \text{grad } \dot{x}$ . BLINOWSKI's isothermal energy principle thus contains a term like the dynamic part v of our interstitial work flux but, as we have seen, for materials of Korteweg type v must not only be linear in L but also of the very special form

$$-(\operatorname{tr} L) \varrho^2 \overline{\psi}_d.$$

As a consequence of his overly general form for v, BLINOWSKI was able in [7] and [8] to derive forms for the stress only up to divergence-free terms. \*\* In [9], however, working within a theory of mixtures and without giving any reason or discussing its connection with his earlier work, BLINOWSKI replaced his general form for v with

(tr *L*) *p*,

where p is just a vector. Modulo terms that depend on the mixture, he was then able to find that  $p = -\varrho^2 \overline{\psi}_d$  as well as an explicit form for the Cauchy stress T. It was apparently this more specialized form (tr L) p which BLINOWSKI had in mind in [10], where he returned to the study of a single-component material and used a form for T equivalent to our (1.26)<sub>2</sub>.

<sup>\*</sup> Such thermodynamic compatibility would also require FELDERHOF to set  $c_0 = 1$  in his (2.7) so as to conform with our (1.23).

<sup>\*\*</sup> In [8] he seems to assert otherwise but we are unable to follow his argument.

### 2. Thermodynamic Compatibility: General Results

We seek now the thermodynamic restrictions imposed on the constitutive functions of (1.17) by the fact that every process  $\pi \in \mathbb{P}(\mathcal{B})$  must be such that the balance of mass (1.5), the balance of linear momentum (1.13), the balance of energy (1.14), and the dissipation inequality (1.16) must hold throughout  $\pi$ . To find these restrictions we need to ensure that  $\mathbb{P}(\mathcal{B})$  is sufficiently large; we thus adopt what is now in effect a classical point of view: Specifically, let **any** motion  $\chi(\cdot, \cdot)$  and **any** temperature  $\theta(\cdot, \cdot)$  be assigned on  $B \times \mathbb{R}$ ; then (1.5) and the constitutive equations (1.17) enable one to calculate an associated density  $\varrho(\cdot, \cdot)$ , energy  $\varepsilon(\cdot, \cdot)$ , entropy  $\eta(\cdot, \cdot)$ , stress  $T(\cdot, \cdot)$ , heat flux  $q(\cdot, \cdot)$ , interstitial work flux  $u(\cdot, \cdot)$ , and a free energy  $\psi(\cdot, \cdot)$ . Entering these fields into the balance laws (1.13) and (1.14), we may in turn calculate an associated body force  $b(\cdot, \cdot)$  and radiant heating  $r(\cdot, \cdot)$ . We thus have produced an ordered 9-tuple of functions on  $B \times \mathbb{R}$ , *viz.*, and in a notation that anticipates our next axiom,

$$\pi_{(\mathbf{x}, \theta)} \equiv \{ \mathbf{\chi}, \theta, \varepsilon, \eta, T, q, u, b, r \};$$

we call it the ordered 9-tuple **induced** by the motion-temperature pair  $(\chi, \theta)$  and observe that it automatically meets balance of mass, linear momentum, and energy.

We now make the fundamental hypothesis that every induced 9-tuple  $\pi_{(\chi,\theta)}$ is a process, \* *i.e.*, it belongs to the process class  $\mathbb{P}(\mathscr{B})$ , and so must (also) satisfy the dissipation inequality (1.16). This is an **Axiom of Size** on the process class  $\mathbb{P}(\mathscr{B})$  and ensures that  $\mathbb{P}(\mathscr{B})$  is suitably rich in processes. As a consequence, we may now assert that the response functions  $\hat{\varepsilon}(\cdot)$ ,  $\hat{\eta}(\cdot)$ ,  $\hat{T}(\cdot)$ ,  $\hat{q}(\cdot)$ ,  $\hat{u}(\cdot)$  and  $\hat{\psi}(\cdot)$  of (1.17) must be such that, by the chain rule,

$$\varrho[\hat{\psi}_{\mathbf{F}}(\Lambda)\cdot\dot{\mathbf{F}} + \{\hat{\psi}_{\theta}(\Lambda) + \hat{\eta}(\Lambda)\}\dot{\theta} + \hat{\psi}_{\nabla\mathbf{F}}(\Lambda)\cdot\nabla\dot{\mathbf{F}} + \hat{\psi}_{\mathbf{g}}(\Lambda)\cdot\dot{\mathbf{g}} + \hat{\psi}_{\nabla^{2}\mathbf{F}}(\Lambda)\cdot\nabla^{2}\dot{\mathbf{F}} \\
+ \hat{\psi}_{\mathbf{F}}(\Lambda)\cdot\ddot{\mathbf{F}}] - \hat{\mathbf{T}}(\Lambda)\,\mathbf{F}^{-1^{T}}\cdot\dot{\mathbf{F}} - \hat{u}_{\theta}(\Lambda)\cdot\mathbf{g} - \hat{u}_{\mathbf{g}}(\Lambda)\cdot\mathbf{G} - [\hat{u}_{\mathbf{F}}(\Lambda)\times\nabla\mathbf{F} \\
+ \hat{u}_{\nabla\mathbf{F}}(\Lambda)\times\nabla^{2}\mathbf{F} + \hat{u}_{\nabla^{2}\mathbf{F}}(\Lambda)\times\nabla^{3}\mathbf{F} + \hat{u}_{\mathbf{F}}(\Lambda)\times\nabla\dot{\mathbf{F}}]\cdot\mathbf{F}^{-1^{T}} + \frac{\hat{q}(\Lambda)\cdot\mathbf{g}}{\theta} \leq 0. \quad (2.1)$$

must hold at every  $(X, t) \in B \times \mathbb{R}$  for every motion  $\chi(\cdot, \cdot)$  and every temperature field  $\theta(\cdot, \cdot)$ . Here  $\Lambda \equiv (F, \theta, \nabla F, \nabla^2 F, g, F) \in \mathscr{I}$  and  $G \equiv \operatorname{grad}^2 \theta$ , while for any two tensors of order *n*,  $\Gamma$  and  $\Phi$ , we define  $\Gamma \times \Phi$  to be the second order tensor such that (in Cartesian components)

$$(\boldsymbol{\Gamma} \times \boldsymbol{\Phi})_{ij} = \Gamma_{ipq...t} \Phi_{pq...tj}.$$

Also, in writing (2.1) we have used the fact that " $\nabla$ " and "." commute, *e.g.*,  $\overline{\nabla F} = \nabla F$ , *etc.* 

Let T denote the set of second-order tensors defined on the translation space V, and let  $T_s$  and  $T^+$  denote those subsets of T consisting in, respectively, symmetric tensors and invertible tensors with positive determinant. Let  $T_{ns}$  denote the set of  $n^{\text{th}}$  order tensors defined on V which are symmetric in their last n-1 places.

<sup>\*</sup> There is now a one-to-one correspondence between motion-temperature pairs  $(\chi, \theta)$  and processes  $\pi \in \mathbb{P}(\mathscr{B})$ . We thus here make contact with other, alternative axiomatizations of thermomechanics that identify processes with  $(\chi, \theta)$  pairs.

For a given point  $\Lambda$  in the constitutive domain  $\mathscr{I}$ , we can always find a motion  $\chi(\cdot, \cdot)$ , a temperature field  $\theta(\cdot, \cdot)$ , and a particle-time pair  $(X_0, t_0) \in B \times \mathbb{R}$  such that

$$(\mathbf{F}, \theta, \nabla \mathbf{F}, \nabla^2 \mathbf{F}, \mathbf{g}, \mathbf{F}) (\mathbf{X}_0, t_0) = \Lambda$$

while at  $(X_0, t_0)$  the seven quantities  $\dot{\theta} \in \mathbb{R}$ ,  $\nabla \mathbf{F} \in T_{3s}$ ,  $\nabla^2 \mathbf{F} \in T_{4s}$ ,  $\dot{g} \in V$ ,  $\mathbf{F} \in T$ ,  $G \in T_s$ , and  $\nabla^3 \mathbf{F} \in T_{5s}$  are independent of  $\Lambda$  and arbitrary. It thus follows that (2.1) is essentially linear in these seven variables. We see therefore that (2.1) implies that, at each  $\Lambda \in \mathcal{I}$ ,

$$\hat{\psi}_{\theta}(\Lambda) + \hat{\eta}(\Lambda) = 0, \quad \hat{\psi}_{\mathbf{g}}(\Lambda) = 0, \hat{\psi}_{\nabla^{2}\mathbf{F}}(\Lambda) = 0, \quad \hat{\psi}_{\mathbf{F}}(\Lambda) = 0,$$

$$(2.2)$$

and

$$\varrho \hat{\psi}_{\nabla F}(\Lambda) \cdot \nabla F = (\hat{u}_{F}(\Lambda) \times \nabla F) \cdot F^{-1^{T}}, 
\hat{u}_{g}(\Lambda) \cdot G = 0, 
(\hat{u}_{\nabla^{2}F}(\Lambda) \times \nabla^{3}F) \cdot F^{-1^{T}} = 0,$$
(2.3)

where  $\nabla F$ , G, and  $\nabla^3 F$  in (2.3) are arbitrary elements of, respectively,  $T_{3s}$ ,  $T_s$ , and  $T_{5s}$ .

What remains now of the dissipation inequality is the restriction that

$$\{\varrho\hat{\psi}_{\mathbf{F}}(\Lambda) - \hat{\mathbf{T}}(\Lambda) \mathbf{F}^{-1}\} \cdot \dot{\mathbf{F}} - \{\hat{\mathbf{u}}_{\mathbf{F}}(\Lambda) \times \nabla \mathbf{F} + \hat{\mathbf{u}}_{\nabla \mathbf{F}}(\Lambda) \times \nabla^{2} \mathbf{F}\} \cdot \mathbf{F}^{-1} - \hat{\mathbf{u}}_{\theta} \cdot \mathbf{g} + \frac{\hat{q}(\Lambda) \cdot \mathbf{g}}{\theta} \leq 0,$$
(2.4)

which we will call the reduced dissipation inequality.

The conditions  $(2.2)_{2,3,4}$  tell us that  $\hat{\psi}(\cdot)$  is *locally* independent of  $\nabla^2 F$ , g, and  $\dot{F}$ . We now assume that the domain  $\mathscr{I}$  is of the form  $\mathscr{S}' \times T_{4s} \times V \times T$ , where  $\mathscr{S}'$  is some open subset of  $T^+ \times \mathbb{R}^+ \times T_{2s}$  (and where for brevity we shall frequently set  $\mathscr{S} = \mathscr{S}' \times T_{4s}$ ). Although stronger than needed here and in subsequent arguments, this assumption endows  $\mathscr{I}$  with sufficient connectivity properties to enable to us integrate  $(2.2)_{2,3,4}$  and so conclude that  $\hat{\psi}(\cdot)$  is globally independent of  $\nabla^2 F$ , g, and  $\dot{F}$ , *i.e.*,

$$\psi = \hat{\psi}(F, \theta, \nabla F).$$

In addition,  $(2.2)_1$  now shows that  $\hat{\eta}(\cdot)$  enjoys the same independence and that in fact the *entropy relation* 

$$\eta = \hat{\eta}(F, \theta, \nabla F) = -\hat{\psi}_{\theta}(F, \theta, \nabla F)$$

holds. It easily follows that

$$\varepsilon = \hat{\varepsilon}(F, \theta, \nabla F) = \hat{\psi}(F, \theta, \nabla F) - \theta \hat{\psi}_{\theta}(F, \theta, \nabla F).$$

Thus,  $\eta$  and  $\varepsilon$  are completely determined by the response function  $\hat{\psi}(\cdot)$  for the free energy.

The conditions  $(2.3)_{1,2,3}$  are harder to analyze; we begin with  $(2.3)_1$  which is of overarching importance to all of our subsequent results. In terms of Cartesian components,  $(2.3)_1$  is the requirement that

$$\varrho \hat{\psi}_{F_{i\alpha\beta}}(F,\,\theta,\,\nabla F) \,\Gamma_{i\alpha\beta} = \frac{\partial \hat{u}_j}{\partial \dot{F}_{i\alpha}}(F,\,\theta,\,\nabla F,\,\nabla^2 F,\,g,\,\dot{F}) \,F_{\beta j}^{-1} \Gamma_{i\alpha\beta} \tag{2.5}$$

for all  $\Gamma_{i\alpha\beta}$  with  $\Gamma_{i\alpha\beta} = \Gamma_{i\beta\alpha}$ , and where we have used that  $\hat{\psi}(\cdot)$  depends only on F,  $\theta$ , and  $\nabla F$ . If we eliminate  $\Gamma_{i\alpha\beta}$  from (2.5) we find the equivalent condition

$$\frac{1}{2} \left\{ \frac{\partial \hat{u}_j}{\partial \dot{F}_{i\alpha}} F_{\beta j}^{-1} + \frac{\partial \hat{u}_j}{\partial \dot{F}_{i\beta}} F_{\alpha j}^{-1} \right\} = \varrho \hat{\psi}_{F_{i\alpha\beta}}, \qquad (2.6)$$

since  $\hat{\psi}_{F_{i\alpha\beta}} = \hat{\psi}_{F_{i\beta\alpha}}$ . In Appendix A we show, by using the objectivity of u under a frame change, that the system of equations (2.6) is uniquely solvable for  $\hat{u}_{\dot{F}}$  and, indeed, taht

$$\frac{\partial u_i}{\partial \dot{F}_{jx}}(F,\theta,\nabla F,\nabla^2 F,g,\dot{F}) = \varrho\{\hat{\psi}_{F_{k\beta\delta}}F_{\alpha k}^{-1}F_{i\beta}F_{j\delta} + \hat{\psi}_{F_{j\alpha\beta}}F_{i\beta} - \hat{\psi}_{F_{i\alpha\beta}}F_{j\beta}\}, \quad (2.7)$$

where  $\hat{\psi}_{F_{ix\beta}} = \hat{\psi}_{F_{ix\beta}}(F, \theta, \nabla F)$ . We conclude at once that  $\hat{u}_{\dot{F}}$  is independent of  $\nabla^2 F$ , **g**, and  $\dot{F}$ ; thus (2.7) is easily integrated, showing that  $\hat{u}(\cdot)$  depends on  $\dot{F}$  at most affinely, *i.e.*,

$$u = \hat{u}(F, \theta, \nabla F, \nabla^2 F, g, F),$$
  
=  $\mathbf{V}(F, \theta, \nabla F) \dot{F} + \hat{w}(F, \theta, \nabla F, \nabla^2 F, g),$  (2.8)

where the Cartesian components  $V_{ijx}$  of the third-order tensor V are given by the right-hand side of (2.7), and where  $(V\dot{F})_i = V_{ijx}\dot{F}_{jx}$ . As we show in Appendix A,  $V(F, \theta, \nabla F)$  vanishes at  $(F, \theta, \nabla F)$  if and only if  $\hat{\psi}_{\nabla F}(F, \theta, \nabla F)$  vanishes there, *i.e.*, the dynamic portion v of the interstitial work flux u vanishes identically only when the sensitivity of the free energy to local spatial variations of F is stationary.

If we now enter (2.8) into the remaining restrictions  $(2.3)_{2,3}$ , we find that  $\hat{w}(\cdot)$  must meet the conditions

$$\hat{w}_{g}(F, \theta, \nabla F, \nabla^{2}F, g) \cdot G = 0,$$

$$(\hat{w}_{\nabla^{2}F}(F, \theta, \nabla F, \nabla^{2}F, g) \times \nabla^{3}F) \cdot F^{-1} = 0,$$
(2.9)

for all  $(F, \theta, \nabla F, \nabla^2 F, g)$  in  $\mathscr{S} \times V$ , for all  $G \in T_s$ , and for all  $\nabla^3 F \in T_{5s}$ . As is well known (and as is easily proved with the more general techniques we introduce in Appendix C), the condition  $(2.9)_1$  means that the dependence of  $\hat{w}(\cdot)$  on g can be at most affine, with skew linear part, *i.e.*,

$$\hat{w}(F, heta, 
abla F, 
abla^2 F, g) = \Omega g + w^{\mathrm{E}}$$

where  $\Omega = \Omega(F, \theta, \nabla F, \nabla^2 F)$  is skew, and where  $w^{\rm E} = w^{\rm E}(F, \theta, \nabla F, \nabla^2 F)$ =  $\hat{w}|_{g=0}$  is the "equilibrium part" of w. Thus, (2.9)<sub>2</sub> now becomes the requirement

- ^

that

$$(\boldsymbol{\Omega}_{\nabla^{2}F}(F, \theta, \nabla F, \nabla^{2}F) \times (\boldsymbol{g} \otimes \nabla^{3}F)) \cdot F^{-1^{T}} = 0,$$
  
$$(\boldsymbol{w}_{\nabla^{2}F}^{\mathrm{E}}(F, \theta, \nabla F, \nabla^{2}F) \times \nabla^{3}F) \cdot F^{-1^{T}} = 0,$$
  
(2.10)

and we have proven that the interstitial work flux is of the form

$$u = \mathbf{V}\dot{F} + \mathbf{\Omega}g + w^{\mathrm{E}}.$$

As a consequence, the reduced dissipation inequality (2.4) has become the requirement that

$$\{\varrho\hat{\psi}_{F} - \hat{T}F^{-1}^{T}\} \cdot \dot{F} - g \cdot \nabla_{\theta}\dot{F} - \{\nabla_{F} \times (\dot{F} \otimes \nabla F) + \nabla_{\nabla F} \times (\dot{F} \otimes \nabla^{2}F)\} \cdot F^{-1}^{T} - \{\Omega_{F} \times (g \otimes \nabla F) + \Omega_{\nabla F} \times (g \otimes \nabla^{2}F)\} \cdot F^{-1}^{T} - \{w_{F}^{E} \times \nabla F + w_{\nabla F}^{E} \times \nabla^{2}F\} \cdot F^{-1}^{T} - w_{\theta}^{E} \cdot g + \frac{\hat{q} \cdot g}{\theta} \leq 0,$$

$$(2.11)$$

where  $\hat{T}(\cdot)$  and  $\hat{q}(\cdot)$  are evaluated at  $(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}) \in \mathcal{I}$ ,  $\mathscr{I}$  where  $\Omega(\cdot)$ and  $w^{\mathrm{E}}(\cdot)$  are evaluated at  $(F, \theta, \nabla F, \nabla^2 F) \in \mathscr{S}$ , and where  $\hat{\psi}(\cdot)$  and  $\mathbb{V}(\cdot)$  are evaluated at  $(F, \theta, \nabla F) \in \mathscr{S}'$ . We also note that the term  $g \cdot \Omega_{\theta} g$  is absent from (2.11) because  $\Omega$  is skew.

By putting  $g = \dot{F} = 0$  in (2.11), we see that, in addition to  $(2.10)_2$ ,  $w^{\rm E}(\cdot)$  must also satisfy

$$\{\boldsymbol{w}_{\boldsymbol{F}}^{\mathrm{E}}(\boldsymbol{F},\,\theta,\,\nabla\boldsymbol{F},\,\nabla^{2}\boldsymbol{F})\times\nabla\boldsymbol{F}\,+\,\boldsymbol{w}_{\nabla\boldsymbol{F}}^{\mathrm{E}}(\boldsymbol{F},\,\theta,\,\nabla\boldsymbol{F},\,\nabla^{2}\boldsymbol{F})\times\nabla^{2}\boldsymbol{F}\}\cdot\boldsymbol{F}^{-1}^{T}\geq0\,,\qquad(2.12)$$

for all  $(F, \theta, \nabla F, \nabla^2 F) \in \mathscr{S}$ . It now follows by a result of OLVER [36, 37] that equality must hold in (2.12), *i.e.* 

$$\{\boldsymbol{w}_{\boldsymbol{F}}^{\mathrm{E}} \times \nabla \boldsymbol{F} + \boldsymbol{w}_{\nabla \boldsymbol{F}}^{\mathrm{E}} \times \nabla^{2} \boldsymbol{F}\} \cdot \boldsymbol{F}^{-1^{T}} \equiv \boldsymbol{0}, \qquad (2.13)$$

for all  $(F, \theta, \nabla F, \nabla^2 F) \in \mathscr{S}$ . We shall give an independent proof of this in Appendix B for materials of Korteweg type; here we just note that  $(2.10)_2$  and (2.13) together imply that

$$\operatorname{div} \boldsymbol{w}^{\mathrm{E}} \equiv \boldsymbol{w}^{\mathrm{E}}_{\boldsymbol{ heta}} \cdot \boldsymbol{g},$$

for every motion-temperature pair  $(\chi, \theta)$   $(\cdot, \cdot)$ . In particular therefore, (2.11) now takes the simpler form

$$\{ \varrho \hat{\psi}_{\mathbf{F}} - \hat{\mathbf{T}} \mathbf{F}^{-1} \} \cdot \dot{\mathbf{F}} - \{ \mathbf{V}_{\mathbf{F}} \times (\dot{\mathbf{F}} \otimes \nabla \mathbf{F}) + \mathbf{V}_{\nabla \mathbf{F}} \times (\dot{\mathbf{F}} \otimes \nabla^{2} \mathbf{F}) \} \cdot \mathbf{F}^{-1}^{T} - \mathbf{g} \cdot \mathbf{V}_{\theta} \dot{\mathbf{F}} - \{ \boldsymbol{\Omega}_{\mathbf{F}} \times (\mathbf{g} \otimes \nabla \mathbf{F}) + \boldsymbol{\Omega}_{\nabla \mathbf{F}} \times (\mathbf{g} \otimes \nabla^{2} \mathbf{F}) \} \cdot \mathbf{F}^{-1}^{T} - \boldsymbol{w}_{\theta}^{\mathrm{E}} \cdot \mathbf{g} + \frac{\hat{\mathbf{q}} \cdot \mathbf{g}}{\theta} \leq 0.$$

$$(2.14)$$

<sup>\*</sup> It is useful to recall here that div  $(\cdot) = J^{-1} \nabla \cdot (JF^{-1}(\cdot))$ ,  $J \equiv \det F$ . From OLVER's work, it now follows that  $(2.10)_2$  and (2.12) not only imply (2.13) but also completely determine the structure of the function  $JF^{-1}w^{\rm E}(F, \theta, \nabla F, \cdot)$ . We do not require the explicit form of this function here but, for materials of Korteweg type, the reader may read it off from our (4.7).

If we replace  $\dot{F}$  and g in (2.14) by, respectively,  $h\dot{F}$  and hg, h > 0, divide the resulting inequality by h and let  $h \searrow 0$ , then we obtain an inequality which is linear in both  $\dot{F}$  and g. Thus, it follows easily that for any tensor  $\dot{F}$ 

$$\{\varrho\hat{\psi}_{\mathbf{F}}(\mathbf{F},\,\theta,\,\nabla \mathbf{F}) - \hat{\mathbf{T}}(\mathbf{F},\,\theta,\,\nabla \mathbf{F},\,\nabla^{2}\mathbf{F},\,\mathbf{0},\,\mathbf{0})\,\mathbf{F}^{-1}^{T}\}\cdot\dot{\mathbf{F}} \\ = \{\mathbf{V}_{\mathbf{F}}(\mathbf{F},\,\theta,\,\nabla \mathbf{F})\times(\dot{\mathbf{F}}\,\otimes\,\nabla \mathbf{F}) + V_{\nabla \mathbf{F}}(\mathbf{F},\,\theta,\,\nabla \mathbf{F})\times(\dot{\mathbf{F}}\,\otimes\,\nabla^{2}\mathbf{F})\}\cdot\mathbf{F}^{-1}^{T}, \quad (2.15)_{1}$$

and for any vector g

$$\frac{1}{\theta} \hat{q}(F, \theta, \nabla F, \nabla^2 F, 0, 0) \cdot g$$

$$= \{ \Omega_F(F, \theta, \nabla F, \nabla^2 F) \times (g \otimes \nabla F) + \Omega_{\nabla F}(F, \theta, \nabla F, \nabla^2 F) \times (g \otimes \nabla^2 F) \} \cdot F^{-1^T}$$

$$+ w_{\theta}^{\mathrm{E}}(F, \theta, \nabla F, \nabla^2 F) \cdot g. \qquad (2.15)_2$$

The equation  $(2.15)_1$  may be solved to determine the equilibrium portion

$$T^{\mathrm{E}} = T^{\mathrm{E}}(F, \theta, \nabla F, \nabla^{2}F) \equiv T(F, \theta, \nabla F, \nabla^{2}F, 0, 0)$$

of the viscous stress  $\hat{T}(\cdot)$ . The reader should turn to Section 3 for a discussion of this equilibrium stress, since it is but the specialization, when g = 0, of our formulae (3.2) (3.4) which turn out to give the response for the stress T in those of our materials which are elastic. The result  $(2.15)_2$  is easily solved for equilibrium heat flux

$$q^{ ext{E}} = q^{ ext{E}}(F, heta,
abla F,
abla^2 F) \equiv \hat{q}(F, heta,
abla F,
abla^2 F,0,0),$$

which, in particular, need not vanish unless  $\Omega(\cdot)$  and  $w^{E}(\cdot)$  are of a structure special enough to make the right hand side of  $(2.15)_2$  vanish identically. In Section 4 we shall see that this is precisely what happens in materials of Korteweg type which possess a center of symmetry.

Before leaving  $(2.15)_2$  we note one further consequence of it,  $(2.10)_{1,2}$ , (2.13), and the fact that  $\Omega$  is skew. Indeed, we see that, for any motion  $\chi(\cdot, \cdot)$  and any temperature field  $\theta(\cdot, \cdot)$ , we have that

div 
$$\boldsymbol{w} = \operatorname{div} \hat{\boldsymbol{w}}(\nabla \boldsymbol{\chi}, \theta, \nabla^2 \boldsymbol{\chi}, \nabla^3 \boldsymbol{\chi}, \operatorname{grad} \theta),$$
  

$$= \operatorname{div} \{ \boldsymbol{\Omega} \operatorname{grad} \theta + \boldsymbol{w}^{\mathrm{E}} \},$$

$$= \frac{1}{\theta} q^{\mathrm{E}}(\nabla \boldsymbol{\chi}, \theta, \nabla^2 \boldsymbol{\chi}, \nabla^3 \boldsymbol{\chi}) \cdot \operatorname{grad} \theta,$$

$$= \frac{q^{\mathrm{E}} \cdot \boldsymbol{g}}{\theta}$$
(2.16)

which nicely relates the equilibrium heat flux to the contribution of w, the static part of u, to the energy equation. In particular, *if the equilibrium heat flux is al*ways zero, then div w always vanishes -w drops out of the energy equation! Additionally, whether  $q^E$  is zero or not, we see that div w vanishes whenever the temperature field is spatially uniform. We now use  $(2.15)_{1,2}$  to reduce (2.14) further. We see at once that the reduced dissipation inequality now takes the form

$$\{ \hat{T}(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}) - \hat{T}(F, \theta, \nabla F, \nabla^2 F, 0, 0) \} F^{-1T} \cdot \dot{F} + g \cdot \nabla_{\theta}(F, \theta, \nabla F) \dot{F}$$

$$\geq \frac{1}{\theta} \{ \hat{q}(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}) - \hat{q}(F, \theta, \nabla F, \nabla^2 F, 0, 0) \} \cdot g, \qquad (2.17)$$

which, except for the term  $g \cdot \nabla_{\theta} \dot{F}$ , does not explicitly involve any part of the interstitial work flux u. Further reductions of the inequality (2.17) now suggest themselves, but we defer them until Section 4 where they can be studied in the context of the classical assumptions concerning the structure of the viscous part of the stress.

#### 3. General Elastic Materials

Suppose we apply the reduced dissipation inequality in the form (2.11) to those of our materials which are **elastic** in the classic sense that  $\hat{T}(\cdot)$  and  $\hat{g}(\cdot)$  are independent of  $\dot{F}$ . In this case (2.11) is then linear in F, and we therefore conclude that

$$\{\varrho\hat{\psi}_{F}(F,\,\theta,\,\nabla F) - \hat{T}(F,\,\theta,\,\nabla F,\,\nabla^{2}F,\,g)\,F^{-1}\,F - g\cdot \nabla_{\theta}(F,\,\theta,\,\nabla F)\,\dot{F} \qquad (3.1)$$
$$-\{\nabla_{F}(F,\,\theta,\,\nabla F)\times(\dot{F}\otimes\nabla F) + \nabla_{\nabla F}(F,\,\theta,\,\nabla F)\,(\dot{F}\otimes\nabla^{2}F)\}\cdot F^{-1}\,F \equiv 0$$

for all  $(F, \theta, \nabla F, \nabla^2 F, g) \in \mathscr{S} \times V$  and for all tensors  $\dot{F}$ , and where  $\mathbb{V}_{ij\alpha}(F, \theta, \nabla F)$ is given by the right-hand side of (2.7). We can solve (3.1) for the Cauchy stress  $T = \hat{T}(F, \theta, \nabla F, \nabla^2 F, g)$ , but, before doing so, we note one of the interesting consequences of (3.1), even in its implicit form. Specifically, since any of our materials, elastic or not, has been shown to satisfy  $\varepsilon = \hat{\varepsilon} = \hat{\psi} - \theta \hat{\psi}_{\theta}$ , where  $\hat{\psi} = \hat{\psi}(F, \theta, \nabla F)$ , we conclude that always

$$\dot{arepsilon} = \hat{arphi}_{oldsymbol{F}} \cdot oldsymbol{F} + \hat{arphi}_{
abla oldsymbol{F}} \cdot 
abla oldsymbol{F} + heta \dot{\eta}$$

where we have also used the entropy relation,  $\eta = -\hat{\psi}_{\theta}$ . Further,  $\boldsymbol{u} = \boldsymbol{V}\dot{\boldsymbol{F}} + \boldsymbol{w}$ , and therefore the energy equation (1.14) for any one of our materials is just

$$\begin{split} \varrho\{\hat{\psi}_{F}\cdot\dot{F} + \hat{\psi}_{\nabla F}\cdot\nabla\dot{F} + \theta\dot{\eta}\} \\ &= T\cdot L + g\cdot \nabla_{\theta}\dot{F} + \{V_{F}\times(\dot{F}\otimes\nabla F) + \nabla_{\nabla F}\times(\dot{F}\otimes\nabla^{2}F) + \nabla\times\nabla\dot{F}\}\cdot F^{-1^{T}} \\ &+ \operatorname{div}\boldsymbol{w} - \operatorname{div}\boldsymbol{q} + \varrho r. \end{split}$$

But, by (2.3)<sub>1</sub> and (2.7),  $\rho \hat{\psi}_{\nabla F} \cdot \nabla \dot{F} = (\nabla \times \nabla \dot{F}) \cdot F^{-1^T}$ . Thus, when the material is elastic so (3.1) also holds, the energy equation is just

$$egin{aligned} arrho & heta & ext{if} \ & arrho & arrho & arrho \ & arrho & arrho & arrho \ & arrho & arrho & arrho & arrho \ & arrho & arrho & arrho \ & arrho$$

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where we have used (2.16). Thus, regardless of the sensitivity of our materials to spatial interactions of longer range, those that are elastic obey an energy equation of exactly the same form as that used in first-grade theories of thermoelasticity (with the exception of the presence of the term due to the equilibrium heat flux  $q^{E}$ ).

We return to (3.1) and solve it for the Cauchy stress T. After a lengthy and somewhat tedious calculation, we find that, in terms of its Cartesian components T is given by

$$T_{ij} = \varrho [\hat{\psi}_{F_{i\alpha}} F_{j\alpha} + \hat{\psi}_{F_{i\alpha\beta}} F_{j\alpha\beta} + (\hat{\psi}_{F_{k\alpha\beta}} F_{i\alpha} F_{j\beta} F_{\lambda k}^{-1})_{,\lambda} - (\hat{\psi}_{F_{j\alpha\beta}} F_{i\alpha} + \hat{\psi}_{F_{i\alpha\beta}} F_{j\alpha})_{,\beta}], \star \qquad (3.2)_1 = \varrho \hat{\psi}_{F_{i\alpha}} F_{j\alpha} + \varrho \hat{\psi}_{F_{i\alpha\beta}} F_{j\alpha\beta} - \{\varrho (\hat{\psi}_{F_{i\alpha\beta}} F_{j\alpha} F_{k\beta} + \hat{\psi}_{F_{j\alpha\beta}} F_{k\alpha} F_{i\beta} - \hat{\psi}_{F_{k\alpha\beta}} F_{j\alpha} F_{i\beta})\}_{,k}, \qquad (3.2)_2$$

where lower case Greek (Latin) indces have been used to denote the components of the particle X (of the place x), and where a comma has been used to indicate partial differentiation. Now  $(3.2)_1$  is equivalent to

$$T_{ij} = \varrho[\{\hat{\psi}_{F_{i\alpha}} - (\hat{\psi}_{F_{i\alpha\beta}})_{,\beta}\}F_{j\alpha} + (\hat{\psi}_{F_{k\alpha\beta}}F_{i\alpha}F_{j\beta}F_{\lambda k}^{-1})_{,\lambda} - (\hat{\psi}_{F_{j\alpha\beta}}F_{i\alpha})_{,\beta}].$$
(3.3)

Thus, if we recall that the Piola-Kirchhoff stress tensor  $T^{R}$  associated with T is given by

$$T^{\mathrm{R}} = |\det F| \ TF^{-1^{T}},$$

we see that the representation (3.3) yields

$$T_{i\alpha}^{\mathbf{R}} = \varrho_{\mathbf{R}}[\hat{\psi}_{F_{i\alpha}} - (\hat{\psi}_{F_{i\alpha\beta}})_{,\beta} + F_{j\alpha}^{-1}(\hat{\psi}_{F_{k\delta\beta}}F_{i\delta}F_{j\beta}F_{k}^{-1})_{,\lambda} - F_{j\alpha}^{-1}(\hat{\psi}_{F_{j\delta\beta}}F_{i\delta})_{,\beta}],$$

and after a little manipulation, this last line may be written in the form

$$T_{i\alpha}^{\mathbf{R}} = \varrho_{\mathbf{R}}[\hat{\psi}_{F_{i\alpha}} - (\hat{\psi}_{F_{i\alpha\beta}})_{,\beta} + (\{\hat{\psi}_{F_{j\lambda\alpha}}F_{\beta j}^{-1} - \hat{\psi}_{F_{j\lambda\beta}}F_{\alpha j}^{-1}\}F_{i\lambda})_{,\beta}].$$
(3.4)

The forms (3.2)-(3.4) possess an interesting structure. First, of course, is the fact that, as in the usual first-grade theory of elasticity, the free energy response function  $\hat{\psi}(\cdot)$  completely determines the response function for  $\hat{T}(\cdot)$ . Second is the fact that, while  $\hat{T}(F, \theta, \nabla F, \nabla^2 F, g)$  can involve  $\nabla^2 F$  and g, it can do so only as these two variables are produced by the indicated differentiations with respect to  $X^{\lambda}$  and  $X^{\beta}$ . Thus g and  $\nabla^2 F$  enter into the stress at most *affinely*. Third, note that, while we have always assumed the Cauchy stress to be symmetric, nowhere in our analysis have we ever used this assumption. We see, however, by (3.2) that the symmetry of T is precisely equivalent to the symmetry in i and j of the term

$$\hat{\psi}_{F_{i\alpha}}F_{j\alpha}+\hat{\psi}_{F_{i\alpha\beta}}F_{j\alpha\beta}.$$

<sup>\*</sup> In deriving the compact expression  $(3.2)_1$  we used repeatedly the fact that  $\hat{\psi}(\cdot)$  does not depend explicitly on the particle X. Similarly in going from  $(3.2)_1$  to  $(3.2)_2$  we have used the assumption that  $\varrho_R$  is independent of X.

Equivalently, the symmetry of T is exactly the condition that

$$\hat{\psi}_{F}(F,\,\theta,\,\nabla F)\cdot WF + \hat{\psi}_{\nabla F}(F,\,\theta,\,\nabla F)\cdot W\nabla F \equiv 0 \tag{3.5}$$

for all  $(F, \theta, \nabla F)$  and all skew tensors W. But, as is well known and easily proven, (3.5) holds if and only if

$$\hat{\psi}(QF, \theta, Q\nabla F) = \hat{\psi}(F, \theta, \nabla F)$$

for all proper, orthogonal tensors Q, *i.e.*, as in the usual first-grade theory of elasticity, the symmetry of the Cauchy stress tensor is equivalent to the objectivity of  $\hat{\psi}(\cdot)$  under a frame change for any of our materials which are elastic. Fourth, note that the term

$$(\hat{\psi}_{F_{j\lambda\alpha}}F_{\beta j}^{-1}-\hat{\psi}_{F_{j\lambda\beta}}F_{\alpha j}^{-1})F_{i\lambda}$$

whose divergence with respect to  $X^{\beta}$  appears in (3.4) is skew in  $\alpha$  and  $\beta$ . Therefore, it contributes nothing to  $T_{i\alpha,\alpha}^{R}$  and

$$T_{i\alpha,\alpha}^{\mathbf{R}} = \varrho_{\mathbf{R}}[(\hat{\psi}_{F_{i\alpha}})_{,\alpha} - (\hat{\psi}_{F_{i\alpha\beta}})_{,\alpha\beta}].$$
(3.6)

If we glance back at TOUPIN's form (1.28) for the Piola-Kirchhoff stress  $T^R$ , we see at once that, in isothermal problems, our theory and Toupin's will yield the same field equation for linear momentum balance in an elastic material; it is only at the more subtle levels of energetics (which restricts the stress power  $T \cdot L$ ) and boundary conditions (which restrict the traction Tn) where differences between the two theories' forms for the stress will manifest themselves.

Fifth, and finally, if we compare the expression (3.1) for the stress in an elastic material to the expression  $(2.15)_1$  for the equilibrium stress in one of our general materials, we see that they differ only in the term  $\mathbf{g} \cdot \mathbb{V}_{\theta}(\mathbf{F}, \theta, \nabla \mathbf{F}) \dot{\mathbf{F}}$  in (3.1). Thus, with care being taken to set  $\mathbf{g} = 0$  in them, each of the expressions (3.2)-(3.4) may also be used to calculate the equilibrium stresses in any one of the general materials of Section 2.

# 4. Materials of Korteweg Type

In the present section we seek the specializations of the results in Sections 2 and 3 that occur when the constitutive equations of (1.17) are replaced by the simpler forms of (1.22). Materials of this class will be said to be of **Korteweg type**. Not surprisingly, the restrictions of thermodynamics take much simpler forms for them.

First, the results of  $(2.3)_{2,3,4}$  show that, for a material of Korteweg type, the free energy  $\psi = \psi(\varrho, \theta, d, S, g, L)$  can depend only on  $\varrho$ ,  $\theta$ , and d, i.e.,

$$\psi = \overline{\psi}(\varrho, \theta, d), \star \tag{4.1}$$

<sup>\*</sup> Paralleling the discussion in Section 2, we now assume that the constitutive domain  $\mathscr{I}$  of the response functions in (1.22) is of the form  $\mathscr{S}' \times T_s \times V \times T$ , where  $\mathscr{S}'$  is an open subset of  $(0, \infty) \times (0, \infty) \times V$ .

where  $d = \operatorname{grad} \varrho$ . It then follows from  $(2.2)_1$  and the definition of the Helmholtz free energy  $\psi$  that  $\eta$  and  $\varepsilon$  are given by

$$\eta = \overline{\eta}(\varrho, \theta, d) = -\overline{\psi}_{\theta}(\varrho, \theta, d), \qquad (4.2)$$

and

$$\varepsilon = \overline{\varepsilon}(\varrho, \theta, d) = \overline{\psi}(\varrho, \theta, d) - \theta \overline{\psi}_{\theta}(\varrho, \theta, d),$$

respectively.

Second, we note that (1.5) implies that

$$d_i = (\operatorname{grad} \varrho)_i = \varrho_{,\alpha} F_{\alpha i}^{-1} = -\varrho F_{\alpha i}^{-1} F_{\beta j}^{-1} F_{j\beta\alpha};$$

a simple calculation then gives that for materials of Korteweg type

$$\hat{\psi}_{F_{ilphaeta}} = -rac{1}{2} arrho \{F_{lpha l}^{-1} F_{eta j}^{-1} \overline{\psi}_{d_j} + F_{eta l}^{-1} F_{lpha j}^{-1} \overline{\psi}_{d_j}\}.$$

Thus, by (A.9) of Appendix A, we find that

$$\frac{\partial \bar{u}_i}{\partial L_{jk}} = \frac{\partial \hat{u}_i}{\partial F_{jx}} F_{kx} = -\varrho^2 \bar{\psi}_{d_i} \delta_{jk};$$

hence  $u = \overline{u}(\varrho, \theta, d, S, g, L)$  must be of the form

$$\begin{split} \boldsymbol{\mu} &= -\varrho^2(\operatorname{tr} \boldsymbol{L}) \, \overline{\psi}_d(\varrho, \, \theta, \, d) + \overline{\boldsymbol{w}}(\varrho, \, \theta, \, d, \, S, \, g), \\ &= \varrho \overline{\varrho} \overline{\psi}_d + \boldsymbol{w}, \end{split}$$
(4.3)

where we have used conservation of mass in the form  $\dot{\varrho} = -\varrho$  (tr L).

Consequently, for materials of Korteweg type, the dynamic part of the interstitial work flux u is just the simple term  $\varrho \dot{\varrho} \overline{\psi}_d$ , which we see vanishes for a particle X if and only if X is instantaneously experiencing no change in density or is instantaneously in a state  $(\varrho, \theta, d)$  at which  $\overline{\psi}(\varrho, \theta, \cdot)$  is stationary.

The restrictions  $(2.3)_{2,3}$ , when specialized to materials of Korteweg type, show that the static part of u must be such that

$$\overline{w}_{g} \cdot G \equiv 0,$$

$$\overline{w}_{s} \cdot \Gamma \equiv 0,$$
(4.4)

for every  $G \in T_s$ , for every completely symmetric third order tensor  $\mathbb{T}$ , and for all  $(\varrho, \theta, d, S, g)$  in  $\mathscr{G} \times V$ , where  $\mathscr{G} = \mathscr{G}' \times T_s$ .

Also, of course, the reduced dissipation inequality (2.4) must hold for materials of Korteweg type. However, since it is rather cumbersome to specialize that inequality directly, we return to its original form (1.16) and enter the results of (4.1)–(4.4). This yields

$$\varrho\{\overline{\psi}_{\varrho}\dot{arrho}+\overline{\psi}_{d}\cdot\dot{d}\}-\overline{T}\cdot L-\mathrm{div}\left\{\varrho\dot{arrho}\overline{\psi}_{d}+\overline{w}
ight\}+rac{\overline{q}\cdot g}{ heta}\leq0,$$

or, equivalently,

$$[\overline{T}(\Lambda) + \varrho \ d \otimes \overline{\psi}_d + \{\varrho^2 \overline{\psi}_\varrho - \varrho \ \operatorname{div} (\varrho \overline{\psi}_d)\} \mathbf{1}] \cdot \mathbf{L} + \overline{w}_\varrho \cdot d + \overline{w}_\varrho \cdot g + \overline{w}_d \cdot S - \frac{\overline{q}(\Lambda) \cdot g}{\theta} \ge 0, \quad (4.5)$$

where we have used mass conservation in the form  $\dot{\varrho} = -\varrho \operatorname{tr} L$  and the fact that grad  $(\dot{\varrho}) = \dot{d} + L^T d$ , and where here, of course,  $\Lambda = (\varrho, \theta, d, S, g, L)$ .

Let  $\overline{w}^{E} = \overline{w}^{E}(\rho, \theta, d, S) \equiv \overline{w}(\rho, \theta, d, S, 0)$  and, in (4.5), set L = g = 0 to find the restriction (cf. (2.12))

$$w_o^{\mathsf{E}}(\varrho,\,\theta,\,d,\,S)\cdot d + w_d^{\mathsf{E}}(\varrho,\,\theta,\,d,\,S)\cdot S \ge 0, \tag{4.6}$$

for all  $(o, \theta, d, S) \in \mathcal{G}$ . In our Appendices B and C this restriction on  $\overline{w}(\cdot)$ , as well as those due to (4.4), are analyzed in full detail. As a result of (i) these thermodynamic restrictions, (ii) the objectivity of u under a frame change, and (iii) the assumption, which we henceforth make, that the domain  $\mathcal{S}$  is of the form  $\mathscr{S}'' \times V \times T_s$  for some open subset  $\mathscr{S}''$  of  $(0,\infty) \times (0,\infty)$ , it turns out that  $\overline{w}(\cdot): \mathscr{G} \times V \to V$  can be at most of the form

$$\boldsymbol{w} = \boldsymbol{\bar{w}}(\varrho, \theta, \boldsymbol{d}, \boldsymbol{S}, \boldsymbol{g}) = (\omega_1 \, \boldsymbol{d} + \omega_2 \boldsymbol{S} \, \boldsymbol{d}) \times \boldsymbol{g} + r \, \boldsymbol{d} \times (\boldsymbol{S} \, \boldsymbol{d}), \tag{4.7}$$

for scalar-valued functions  $\omega_1$ ,  $\omega_2$ , and r of  $\varrho$ ,  $\theta$ , and  $M = |d|^2$ . Thus, for materials of Korteweg type, the purely thermal part of w is just  $(\omega_1 d + \omega_2 S d) \times g$ , while the equilibrium part of w is just  $w^{E} = r d \times (S d)$ . By (4.7), we see at once that, if the material possesses a center of symmetry for  $\overline{w}(\cdot)$ , i.e., if

$$\overline{w}(\varrho, \, heta, \, -d, \, S, \, -q) = -\overline{w}(\varrho, \, heta, \, d, \, S, \, g),$$

then  $\omega_1, \omega_2$ , and r must vanish identically, and so

$$w = \overline{w}(o, \theta, d, S, g) \equiv 0.$$

In other words, for any material of Korteweg type which possesses a center symmetry, the interstitial work flux u reduces to its dynamic part alone:

$$u = \varrho \dot{\varrho} \overline{\psi}_d.$$

For materials of Korteweg type that do not possess a center of symmetry for  $\overline{w}(\cdot)$ , little can be said about the functions  $\omega_1$ ,  $\omega_2$ , and r. However, a calculation based on (4.7) shows that

$$\overline{w}_{\varrho} \cdot d + \overline{w}_{\theta} \cdot g + \overline{w}_{d} \cdot S = (r_{\theta} - 2\omega_{1M} + \omega_{2\varrho}) g \cdot d \times (S d), \qquad (4.8)$$

and hence, for any density field  $\rho(x, t)$  and any temperature field  $\theta(x, t)$ ,

$$\operatorname{div} \overline{w}(\varrho, \theta, d, S, g) = (r_{\theta} - 2\omega_{1M} + \omega_{2\varrho}) g \cdot d \times (S d)$$

where  $d = \operatorname{grad} \varrho$ ,  $S = \operatorname{grad}^2 \varrho$ , and  $g = \operatorname{grad} \theta$ , and where we have used the fact  $\vec{w}(\cdot)$  satisfies (4.4). Upon comparing this last with (2.16), we also see that in materials of Korteweg type

$$q^{\mathrm{E}} = q^{\mathrm{E}}(\varrho, \theta, d, S) \equiv \overline{q}(\varrho, \theta, d, S, 0, 0),$$
  
=  $\theta(r_{\theta} - 2\omega_{1M} + \omega_{2\varrho}) d \times (S d).$  (4.9)

Thus, if

а

then div w drops out of the local laws 
$$(1.14)$$
- $(1.16)$  and the material cannot support  
a flux of heat at any particle locally in equilibrium. Conversely, if (4.10) fails then a  
nonuniform density field will cause a flux of heat (even when  $g = L = 0$ ) at any place  
where grad  $\rho$  and grad<sup>2</sup>  $\rho$  are nonzero (unless grad  $\rho$  happens to be an eigenvector  
of grad<sup>2</sup>  $\rho$ ).

 $r_{ heta}-2\omega_{1M}+\omega_{2a}\equiv 0,$ 

(4.10)

By (4.8) and (4.9), we now see that the reduced dissipation inequality (4.5) may now be written in the form

$$[\overline{T}(\Lambda) + \varrho \ d \otimes \overline{\psi}_d + \{\varrho^2 \overline{\psi}_\varrho - \varrho \ \text{div} \ (\varrho \overline{\psi}_d)\} \ \mathbf{1}] \cdot \mathbf{L} \ge \frac{1}{\theta} \{\overline{q}(\Lambda) - \overline{q}(\varrho, \theta, d, S, 0, 0\} \cdot \mathbf{g}$$

$$(4.11)$$

where  $\Lambda = (\varrho, \theta, d, S, g, L)$ . If we now take g = 0, replace L with hL, h > 0, divide the resulting form of (4.11) by h, and let  $h \searrow 0$ , we find that, in addition to the *equilibrium heat flux relation* (4.9), the following *equilibrium stress relation* must hold:

$$T = T(\varrho, \theta, d, S, 0, 0),$$

$$= -\{\varrho^2 \overline{\psi}_{\varrho} - \varrho \overline{\psi}_{d} \cdot d - \varrho^2 [\overline{\psi}_{d\varrho} \cdot d + \overline{\psi}_{dd} \cdot S]\} 1 - \varrho \ d \otimes \overline{\psi}_{d},$$

$$(4.12)$$

for any material of Korteweg type. The form (4.12) has many important properties which we shall discuss momentarily in the context of elastic materials of Korteweg type. We merely observe here that, due to the presence of the term  $\varrho d \otimes \overline{\psi}_d$ in (4.12), our material can support shear stresses in equilibrium.\*

Entering (4.12) into (4.11) yields

$$\{\overline{T}(\varrho, \theta, d, S, g, L) - \overline{T}(\varrho, \theta, d, S, 0, 0) - \varrho^{2}(\overline{\psi}_{d\theta} \cdot g) 1\} \cdot L$$

$$\geq \frac{1}{\theta} \{\overline{q}(\varrho, \theta, d, S, g, L) - \overline{q}(\varrho, \theta, d, S, 0, 0)\} \cdot g,$$
(4.13)

as our final form of the reduced dissipation inequality. Upon replacing g and L with, respectively, hg and hL,  $h \neq 0$ , dividing the resulting form of (4.13) by  $h^2$ , and then letting  $h \rightarrow 0$ , we find that

$$\overline{T}_{L} \cdot (L \otimes L) + \overline{T}_{g} \cdot (L \otimes g) - \varrho^{2} (\operatorname{tr} L) \, \overline{\psi}_{d\theta} \cdot g \geq \frac{1}{\theta} \{ \overline{q}_{g} \cdot (g \otimes g) + \overline{q}_{L} \cdot (g \otimes L) \},$$
(4.14)

where the gradients  $\overline{T}_L$ ,  $\overline{T}_g$ ,  $\overline{q}_L$ , and  $\overline{q}_g$  are evaluated at  $(\varrho, \theta, d, S, 0, 0)$  and where  $\overline{\psi}_{d\theta}$  is evaluated at  $(\varrho, \theta, d)$ . The inequality (4.14) is a quadratic form in *L* and *g*; as such, necessary and sufficient conditions for its satisfaction are just

$$\begin{aligned} \overline{T}_{L} \cdot (L \otimes L) &\geq 0, \\ \overline{q}_{g} \cdot (g \otimes g) &\leq 0, \end{aligned} \tag{4.15}$$

 $4[\overline{T}_{L} \cdot (L \otimes L)] \left[ -\frac{1}{\theta} \, \overline{q}_{g} \cdot (g \otimes g) \right]$   $\geq \left[ \overline{T}_{g} \cdot (L \otimes g) - \varrho c_{\theta} \, (\mathrm{tr} \, L) \, (d \cdot g) - \frac{1}{\theta} \, \overline{q}_{L} \cdot (g \otimes L) \right]^{2}$ 

$$T = \tau(a \otimes b + b \otimes a), \quad \tau \equiv 0,$$

for perpendicular unit vectors a and b.

<sup>\*</sup> It is easy to see, however, that (4.12) does not allow the material to support states of *simple shear*, in which

for all tensors L and all vectors g. In writing (4.15)<sub>3</sub> we have used that, by objectivity,  $\psi = \overline{\psi}(\varrho, \theta, d) = \psi(\varrho, \theta, M), M \equiv |d|^2$ , so that  $\varrho \overline{\psi}_d = \varrho 2\psi_M d = c d$ , where  $c \equiv 2\varrho \psi_M$  is the surface tension coefficient.

The conditions  $(4.15)_{1,2}$  are quite easy to interpret:  $(4.15)_1$  is just the assertion that, at equilibrium, the viscosity tensor  $\overline{T}_L(\varrho, \theta, d, S, g, L)$  is positive semidefinite;  $(4.15)_2$  just asserts that the conductivity tensor  $\overline{q}_g(\varrho, \theta, d, S, g, L)$  is negative semi-definite under the same circumstances. The condition  $(4.15)_3$  is harder to interpret in any generality. We note only the form it takes in materials that (i) enjoy an initial separation of effects (*i.e.*,  $\overline{T}_g = \overline{q}_L = 0$  at least in equilibrium), and (ii) have a viscosity tensor  $\overline{T}_L$  and a conductivity tensor  $\overline{q}_g$  such that the classical forms

$$\begin{split} \overline{T}_L \cdot (L \otimes L) &= \lambda \, (\mathrm{tr} \, D)^2 + 2\mu (\mathrm{tr} \, D^2), \\ \overline{q}_g \cdot (g \otimes g) &= -\varkappa \, |g|^2, \end{split}$$

hold at least in equilibrium. Here D is the symmetric part of L, and  $\lambda$ ,  $\mu$ , and  $\varkappa$  are given functions of  $\varrho$ ,  $\theta$ , and M. In this case, it is well known that  $(4.15)_1$  holds if and only if  $3\lambda + 2\mu \ge 0$  and  $\mu \ge 0$ , while  $(4.15)_2$  holds if and only if  $\varkappa \ge 0$ . The condition  $(4.15)_3$  is now the requirement that

$$4\varkappa \{\lambda(\operatorname{tr} D)^2 + 2\mu(\operatorname{tr} D^2)\} |g|^2 \geq \theta^2 \varrho_{\theta}^2 (\operatorname{tr} D)^2 (d \cdot g)^2$$

for all symmetric tensors D, all vectors g, all vectors d, and all values of the arguments  $\rho$ ,  $\theta$ , and  $M = |d|^2$  of the functions c,  $\lambda$ ,  $\mu$ , and  $\varkappa$ . The necessary and sufficient condition for this particular form of  $(4.15)_3$  is easily seen to be

$$4lpha \{\lambda + rac{2}{3}\mu\} \ge heta^2 arrho_{ heta}^2 M$$

In particular, the dependence of the surface tension coefficient c on temperature is mildly regulated by the viscosities  $\lambda$  and  $\mu$  and by the thermal conductivity  $\varkappa$ . Even more specially: if  $c_{\theta}$  is independent of M and if  $\varkappa$ ,  $\lambda$ , and  $\mu$  are bounded as  $M \nearrow \infty$ , then we see easily that  $c_{\theta}$  in fact must vanish. Conversely, if  $c_{\theta} \neq 0$ then neither  $\varkappa$  nor  $\lambda + \frac{2}{3}\mu$  can vanish unless M = 0.

#### 5. Elastic Materials of Korteweg Type

Paralleling the analysis of Section 3, let us now consider materials of Korteweg type in which viscous effects are absent. Thus our material will now be assumed to be **elastic** in the sense that neither  $\overline{T}(\cdot)$  nor  $\overline{q}(\cdot)$  depends on L. In this case the inequality (4.11) is now linear in  $\dot{F}$ , and hence we find

$$T = \overline{T}(\varrho, \theta, d, S, g),$$

$$= -\{\varrho^2 \overline{\psi}_{\varrho} - \varrho \overline{\psi}_{d} \cdot d - \varrho^2 [\overline{\psi}_{\varrho d} \cdot d + \overline{\psi}_{d\theta} \cdot g + \overline{\psi}_{dd} \cdot S]\} \mathbf{1} - \varrho d \otimes \overline{\psi}_{d},$$
(5.1)

for all  $(\varrho, \theta, d, S, g) \in \mathscr{S} \times V$ . All that now remains of the reduced dissipation inequality is the requirement that

$$\{\overline{q}(\varrho,\,\theta,\,d,\,S,\,g)-\overline{q}(\varrho,\,\theta,\,d,\,S,\,0)\}\cdot g\leq 0,\tag{5.2}$$

*i.e.*, any excess heat flux over its equilibrium value is always directed against the temperature gradient.

We have already observed in our Introduction how the stress relation (5.1) may be written in the form (1.27), which brings out the role of the surface tension coefficient  $c \equiv 2\varrho \psi_M$  as well as drawing attention to the structural similarities and differences (5.1) enjoys when compared with KORTEWEG's original proposal (1.1). In addition, the form (5.1) possesses another extremely important property. To exhibit it, let us rewrite (5.1) in the form

$$T = \varrho\{-\varrho \overline{\psi}_{\varrho} + \operatorname{div} (\varrho \overline{\psi}_{d})\} \mathbf{1} - \varrho \mathbf{d} \otimes \overline{\psi}_{d},$$
  
=  $\varrho\{\operatorname{div} (\varrho \overline{\psi}_{d}) - (\varrho \overline{\psi})_{\varrho} + \psi\} \mathbf{1} - \varrho \mathbf{d} \otimes \overline{\psi}_{d}.$  (5.3)

Therefore, we compute that, for any density field  $\varrho = \varrho(\mathbf{x}, t)$  and any temperature field  $\theta = \theta(\mathbf{x}, t)$ , we have

div 
$$T = \varrho \operatorname{grad} \left\{ \operatorname{div} \left( \varrho \overline{\psi}_d \right) - \left( \varrho \overline{\psi} \right)_{\varrho} \right\} + \operatorname{grad} \left( \varrho \psi \right) + \left\{ \operatorname{div} \left( \varrho \overline{\psi}_d \right) - \left( \varrho \overline{\psi} \right)_{\varrho} \right\} d$$
  
 $- \operatorname{div} \left( \varrho \overline{\psi}_d \right) d - \left( \operatorname{grad}^2 \varrho \right) \left( \varrho \overline{\psi}_d \right),$   
 $= \varrho \operatorname{grad} \left\{ \operatorname{div} \left( \varrho \overline{\psi} \right)_d - \left( \varrho \overline{\psi} \right)_{\varrho} \right\} + \left( \varrho \overline{\psi} \right)_{\theta} g,$ 

$$= -\varrho \operatorname{grad} \mu + \left( \varrho \overline{\psi} \right)_{\theta} g,$$
(5.4)

where, in terms of the Helmholtz free energy per unit current volume  $\varrho \psi$ , we have defined the (chemical) potential

$$\mu \equiv (\varrho \overline{\psi})_d - \operatorname{div} (\varrho \overline{\psi})_\varrho.$$

In terms of  $\mu$  and  $\varrho \overline{\psi}$ , (5.3) may be written in the form

$$T = (\varrho \,\overline{\psi} - \varrho \mu) \, \mathbf{1} - \mathbf{d} \, \otimes (\varrho \overline{\psi})_{\mathbf{d}}. \tag{5.5}$$

The potential  $\mu$  thus not only determines a portion of the stress—it also, by (5.4), essentially determines all of div T whenever the temperature field is spatially uniform. It follows that in isothermal problems the equations of motion (1.13) take the form

$$- \operatorname{grad} \mu + b = \ddot{x},$$

for any elastic material of Korteweg type; i.e., elastic materials of Korteweg type, when the temperature field is uniform, obey equations of motion of the same general structure as those for the perfect fluid of Euler in a barotropic flow. More specially, we see that whenever the body force **b** is derivable from a potential,  $\mathbf{b} = -\text{grad } \phi(\mathbf{x}, t)$ , the acceleration field will be a gradient, and, as a result, much of classical hydrodynamics will carry over at once to elastic materials of Korteweg type. More specially still: whenever the temperature field is uniform, the body motionless, and  $\mathbf{b} = -\text{grad } \phi(\mathbf{x})$ , the equations of equilibrium for our material admit of the first integral

$$\mu + \phi = \text{constant} \equiv k$$
,

i.e.

$$\operatorname{div}\left(\varrho\overline{\psi}\right)_{d}-(\varrho\overline{\psi})_{\varrho}=\phi(\boldsymbol{x})-k.$$

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Thus, the equilibrium configurations of our material, instead of being governed by 3 third-order partial differential equations (div  $T = \text{grad } \phi$ ) for the single scalar field  $\varrho$ , which would usually result in  $\varrho$  being overdetermined, \* are in fact governed by a single partial differential equation of second order.

#### Appendix A

In this appendix we wish to show that if the interstitial work flux  $u = u(F, \theta, \nabla F, \nabla^2 F, g, \dot{F})$  is objective under frame changes and satisfies the restriction (2.6) on  $u_{\dot{F}}$ , namely

$$\frac{1}{2} \left\{ \frac{\partial \hat{u}_j}{\partial \dot{F}_{i\alpha}} F_{\beta j}^{-1} + \frac{\partial \hat{u}_j}{\partial \dot{F}_{i\beta}} F_{\alpha j}^{-1} \right\} = \varrho \hat{\psi}_{F_{i\alpha\beta}}, \qquad (2.6)$$

then  $\hat{u}_{\dot{F}}$  must be given by

- -

$$rac{\partial u_i}{\partial \dot{F}_{jlpha}} = \varrho \{ \hat{\psi}_{F_{keta\delta}} F_{lpha k}^{-1} F_{ieta} F_{j\delta} + \hat{\psi}_{F_{jlphaeta}} F_{ieta} - \hat{\psi}_{F_{ilphaeta}} F_{jeta} \}.$$

We begin by noting that (2.6) may be written in the equivalent form

$$\frac{1}{2} \left( \frac{\partial \hat{u}_i}{\partial \dot{F}_{kx}} F_{jx} + \frac{\partial \hat{u}_j}{\partial \dot{F}_{kx}} F_{ix} \right) = \varrho \hat{\psi}_{F_{kx}\beta} F_{i\alpha} F_{j\beta}.$$
(A.1)

Next, we observe that the objectivity of u means that  $\hat{u}(\cdot)$  satisfies the functional equation

$$\hat{u}(QF,\,\theta,\,Q\nabla F,\,Q\nabla^2 F,\,Qg,\,Q\dot{F}+\dot{Q}F)=Q\hat{u}(F,\,\theta,\,\nabla F,\,\nabla^2 F,\,g,\,\dot{F}),^{\star\star} \quad (A.2)$$

for all  $(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}) \in \mathscr{I}$  and for all proper orthogonal tensor-valued functions  $Q(\tau)$ , where  $\dot{Q} = \frac{d}{d\tau} Q(\tau)$ . If we take  $Q(\tau) = e^{\tau W}$ , where W is skew, and evaluate (A.2) at  $\tau = 0$ , we see that

$$\hat{u}(F,\theta,\nabla F,\nabla^2 F,g,\dot{F}+WF)=\hat{u}(F,\theta,\nabla F,\nabla^2 F,g,\dot{F})$$
(A.3)

for all skew tensor W. If we now in (A.3) replace W with hW, differentiate with respect to h, and evaluate at h = 0, we find that

$$\frac{\partial u_i}{\partial F_{j\alpha}}(F,\,\theta,\,\nabla F,\,\nabla^2 F,\,g,\,F)\,W_{jk}F_{k\alpha}=0$$

 $(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}) \in \mathscr{I} \Rightarrow (QF, \theta, Q \nabla F, Q \nabla^2 F, Qg, \dot{Q}F + Q\dot{F}) \in \mathscr{I}.$ 

<sup>\*</sup> In [18], SERRIN has shown that precisely such overdetermination occurs for KOR-TEWEG's form (1.1) unless a very special relation holds among the nonclassical coefficients  $\alpha$ ,  $\beta$ ,  $\delta$ , and  $\gamma$ .

<sup>\*\*</sup> To assert (A.2), of course, requires that we assume  $\mathscr{I}$  is mapped into itself under a frame change, *i.e.*,

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for all  $(F, \theta, \nabla F, \nabla^2 F, g, \dot{F}) \in \mathscr{I}$  and for all skew W. Equivalently,

$$\frac{\partial \hat{u}_i}{\partial \dot{F}_{j\alpha}} F_{k\alpha} \text{ is symmetric in } j \text{ and } k.$$
(A.4)

Now set

$$H_{ijk} = \frac{\partial u_i}{\partial \dot{F}_{j\alpha}} F_{k\alpha} \quad and \quad D_{ijk} = \varrho \hat{\psi}_{F_{k\alpha\beta}} F_{i\alpha} F_{j\beta},$$

so that (A.1) and (A.4) are, respectively, just the conditions that

$$\frac{1}{2}(H_{ikj} + H_{jki}) = D_{ijk}$$
 (A.5)<sub>1</sub>

and

$$H_{ijk}$$
 is symmetric in j and k. (A.5)<sub>2</sub>

By  $(A.5)_2$  we see that  $(A.5)_1$  may now be written in the form

$$\frac{1}{2}(H_{ijk} + H_{jik}) = D_{ijk},.$$
 (A.6)

Note that  $D_{ijk}$  is automatically symmetric in *i* and *j* since  $\hat{\psi}_{F_{k\alpha\beta}} = \hat{\psi}_{F_{k\beta\alpha}}$ .

Now (A.6) just asserts that for each fixed k, k = 1, 2, 3,  $H_{ijk}$  has  $D_{ijk}$  as its symmetric part, *i.e.*,

$$H_{ijk} = D_{ijk} + W_{ijk}, \tag{A.7}$$

where each  $W_{ijk}$ , k = 1, 2, 3, is skew in *i* and *j*. But by (A.5)<sub>2</sub>  $H_{ijk}$  is symmetric in *j* and *k*, and this will let us calculate  $W_{ijk}$  in terms of the  $D_{pqr}$ . Indeed, by (A.5)<sub>2</sub> and (A.7),

$$D_{ijk} + W_{ijk} = H_{ijk} = H_{ikj} = D_{ikj} + W_{ikj},$$
  
 $W_{ijk} - W_{ikj} = D_{ikj} - D_{ijk}.$  (A.8)<sub>1</sub>

and so

But if we permute indices in  $(A.8)_1$ , we find that

$$W_{jik} - W_{jki} = D_{jki} - D_{jik},$$
 (A.8)<sub>2</sub>

and

$$W_{kji} - W_{kij} = D_{kij} - D_{kji}.$$
 (A.8)<sub>3</sub>

Thus, upon adding  $(A.8)_1$ ,  $(A.8)_2$ , and  $(A.8)_3$ , and exploiting the fact that  $W_{ijk}$  is skew in *i* and *j*, we find that

$$2W_{kji} = D_{ikj} - D_{ijk} + D_{jki} - D_{jik} + D_{kij} - D_{kji},$$
  
=  $2D_{ikj} - 2D_{ijk},$ 

where the last holds because  $D_{iik}$  is symmetric in *i* and *j*.

We have thus proven that

$$W_{ijk}=D_{kij}-D_{kji},$$

and so, by (A.7),

$$H_{ijk} = D_{ijk} + D_{kij} - D_{kji}.$$

But this last is exactly the assertion that

$$\frac{\partial u_i}{\partial \dot{F}_{j\alpha}} F_{k\alpha} = \varrho \left\{ \hat{\psi}_{F_{k\alpha\beta}} F_{i\alpha} F_{j\beta} + \hat{\psi}_{F_{j\alpha\beta}} F_{k\alpha} F_{i\beta} - \hat{\psi}_{F_{i\alpha\beta}} F_{k\alpha} F_{j\beta} \right\},\tag{A.9}$$

which, modulo multiplication by  $F_{\lambda k}^{-1}$ , is what we wished to prove.

Before we leave (A.9), it is interesting to note that, while it trivially implies that  $\hat{u}_{\dot{F}}$  vanishes whenever  $\hat{\psi}_{\nabla F}$  vanishes, the converse of this is also true, *i.e.*,  $\hat{u}_{\dot{F}}$  vanishes only if  $\hat{\psi}_{\nabla F}$  vanishes. Indeed, if  $\hat{u}_{\dot{F}}$  vanishes, then  $H_{ijk} = 0$  and hence

$$D_{ijk} + D_{kij} - D_{kjl} = 0. (A.10)$$

But, if we now permute indices in this equation 2 at a time, we arrive at 3 additional equations, each equivalent to (A.10). When all 4 of these equations are added and account is taken of the symmetry  $D_{ijk} = D_{jik}$ , we find that

$$D_{ijk} + D_{kij} = 0;$$

thus, by (A.10), we must have  $D_{kii} = 0$ , and so  $\hat{\psi}_{\nabla F}$  must vanish as claimed.

# Appendix B

In this and the following appendix, we analyze and solve the requirement of objectivity under frame changes and the restrictions (4.4) and (4.6) imposed by thermodynamics on  $\overline{w}(\cdot): \mathscr{G} \times V \to V$ , the static part of the interstitial work flux in a material of Korteweg type. Our analysis leans heavily on the structure of the set  $\mathscr{G}$ , the domain of  $\overline{w}(\cdot, \cdot, \cdot, \cdot, g)$ . Accordingly, and as indicated in Section 4, we now assume that  $\mathscr{G}$  has the special form

$$\mathscr{G} = \mathscr{G}'' \times V \times T_s,$$

where  $\mathscr{G}''$  is an open subset of  $(0,\infty)\times(0,\infty)$ . Thus, for each  $(\varrho,\theta)\in\mathscr{G}''$ , the function  $w = \overline{w}(\varrho, \theta, d, S, g)$  is defined for every d and g in V and for every  $S \in T_s$ .

Now, the thermodynamic restriction  $(4.4)_2$ , that

$$\overline{w}_s \cdot \Gamma \equiv 0, \tag{4.4}_2$$

is of independent interest, as well as being somewhat intricate to analyze. That analysis is thus the subject of Appendix C, and we begin here with its central conclusion: the function  $w = \overline{w}(\varrho, \theta, d, S, g)$  satisfies (4.4)<sub>2</sub> if and only if  $\overline{w}(\varrho, \theta, d, \cdot, g)$  is of the form

$$\begin{split} \overline{w} &= w(\varrho, \theta, d, S, g), \\ &= a(\varrho, \theta, d, g) + b(\varrho, \theta, d, g) [S] + S^* c(\varrho, \theta, d, g), \end{split}$$
(B.1)

for vector-valued functions  $a(\cdot)$ ,  $b(\cdot)$ , and  $c(\cdot)$ , where  $S^*$  denotes the adjugate\* of the symmetric tensor S, and where  $b(\varrho, \theta, d, g)$  [·] is linear\*\* and meets

 $e \cdot b(\varrho, \theta, d, g) [e \otimes e] = 0$  for every unit vector e. Since (B.1) tells us that

<sup>\*</sup> This is defined in Appendix C.

<sup>\*\*</sup> This notation for linear functions is explained and motivated in Appendix C.

 $\overline{w}(\cdot)$  is a polynomial of degree 2 in S, we see that  $(4.4)_1$ , which states that  $\overline{w}_g$  is skew, can hold if and only if

$$\begin{array}{c} a_{g}(\varrho, \, \theta, \, d, \, g), \\ b_{g}(\varrho, \, \theta, \, d, \, g) \, [S], \\ S^{*}c_{g}(\varrho, \, \theta, \, d, \, g), \end{array} \right\} are \ all \ skew \tag{B.2}$$

for all  $(\varrho, \theta, d, S, g) \in \mathscr{G} \times V$ .

Let us look first at  $(B.2)_3$ : If we take S = 1, then  $(B.2)_3$  tells us that  $c_g = -c_g^T$ . Thus  $(B.2)_3$  now yields

$$S^*c_g = -c_g^T S^{*T} = c_g S^*,$$

where we have used the facts that  $S^* = S^{*^T}$ , since S is symmetric, and that  $c_g = -c_g^T$ . That is, (B.2)<sub>3</sub> tells us that  $c_g$  is a skew tensor that commutes with any symmetric tensor which is an adjugate. Even if attention is limited to symmetric S which are invertible, it is now quite easy to show that  $c_g(\varrho, \theta, d, g)$  must vanish identically, *i.e.*,

$$\boldsymbol{c} = \boldsymbol{c}(\varrho, \theta, \boldsymbol{d}).$$

The remaining two restriction,  $(B.2)_{1,2}$ , as we saw in Section 2, just mean that  $a(\varrho, \theta, d, \cdot)$  and  $b(\varrho, \theta, d, \cdot)$  [S] are affine, with skew linear parts. Thus, (4.4) holds if and only if

$$w = \overline{w}(\varrho, \theta, d, S, g),$$
  
=  $p(\varrho, \theta, d) + \Omega_1(\varrho, \theta, d) g + r(\varrho, \theta, d) [S] + \Omega_2(\varrho, \theta, d) [S] g + S^*c(\varrho, \theta, d),$   
=  $p(\varrho, \theta, d) + \omega_1(\varrho, \theta, d) \times g + r(\varrho, \theta, d) [S] + \omega_2(\varrho, \theta, d) [S] \times g + S^*c(\varrho, \theta, d),$   
(B.3)

where we have introduced the axial vectors  $\omega_1$  and  $\omega_2$  which correspond to the skew tensors  $\Omega_1$  and  $\Omega_2$ , respectively, and where

and

$$e \cdot r(\varrho, \theta, d) [e \otimes e] = 0,$$
  
 $e \times \omega_2(\varrho, \theta, d) [e \otimes e] = 0,$  (B.4)

for every unit vector e, since our original function,  $b(\cdot)$  of (B.1), satisfied  $e \cdot b(\varrho, \theta, d, g) [e \otimes e] = 0$ .

We now turn to the restrictions imposed on  $\overline{w}(\cdot)$  by (4.6). Indeed, by (B.3), we see that  $w^{\rm E} = \overline{w}^{\rm E}(\varrho, \theta, d, S) \equiv \overline{w}(\varrho, \theta, d, S, 0)$  is given by

$$w^{\mathrm{E}} = p(\varrho, \theta, d) + r(\varrho, \theta, d) [S] + S^* c(\varrho, \theta, d)$$

Consequently, (4.6) is just the requirement that

$$p_{\varrho}(\varrho, \theta, d) \cdot d + r_{\varrho}(\varrho, \theta, d) [S] \cdot d + \{S^* c_{\varrho}(\varrho, \theta, d)\} \cdot d$$

$$+ p_{d}(\varrho, \theta, d) \cdot S + r_{d}(\varrho, \theta, d) [S] \cdot S + c_{d}(\varrho, \theta, d) \cdot S^{*T} S \ge 0,$$
(4.6)

for all  $(\varrho, \theta, d, S) \in \mathscr{G}'' \times V \times T_s$ , where  $r(\cdot)$  satisfies (B.4)<sub>1</sub>. As we indicated earlier<sup>\*</sup>, and, as we will now show, one consequence of (4.6) is that it holds if and only if its left-hand side vanishes identically. Additionally, we shall see that interesting chaining identities are imposed by (4.6) on the functions  $p(\cdot)$ ,  $r(\cdot)$ , and  $c(\cdot)$ .

First, since  $S = S^T$ , the Cayley-Hamilton theorem yields  $S^{*T}S = S^*S =$  (det S) 1. Thus (4.6), which is cubic in S, holds for all  $S \in T_s$  if and only if

$$\operatorname{tr} \boldsymbol{c}_{\boldsymbol{d}}(\varrho,\,\theta,\,\boldsymbol{d})\equiv 0, \qquad (B.5)_1$$

and

$$p_{\varrho}(\varrho, \theta, d) \cdot d + r_{\varrho}(\varrho, \theta, d) [S] \cdot d + \{S^*c_{\varrho}(\varrho, \theta, d)\} \cdot d + p_{d}(\varrho, \theta, d) \cdot S + r_{d}(\varrho, \theta, d) [S] \cdot S \ge 0, \qquad (B.5)_2$$

for all  $(\varrho, \theta, d, S) \in \mathscr{G}'' \times V \times T_s$ . Next, if we put  $S = \alpha e \otimes e$ ,  $\alpha \in \mathbb{R}$  and  $e \in V$ , a simple calculation gives that  $S^* = 0$ , while  $r_d(\varrho, \theta, d) [e \otimes e] \cdot e \otimes e$  is seen to vanish by  $(B.4)_1$ . Hence, for  $S = \alpha e \otimes e$ ,  $(B.5)_2$  yields that

$$p_o(\varrho, \theta, d) \cdot d + \alpha \{r_o(\varrho, \theta, d) [e \otimes e] \cdot d + p_d(\varrho, \theta, d) \cdot e \otimes e\} \ge 0$$

for all  $(\varrho, \theta, d) \in \mathscr{G}'' \times V$ , for all  $\alpha \in \mathbb{R}$ , and for all  $e \in V$ . It is thus clear that the coefficient of  $\alpha$  in this last must vanish identically, or, equivalently, by the spectral theorem,

$$\boldsymbol{r}_{o}(\varrho,\,\theta,\,d)\,[S]\cdot\boldsymbol{d}+\boldsymbol{p}_{d}(\varrho,\,\theta,\,d)\cdot\boldsymbol{S}\equiv\boldsymbol{0},\tag{B.6}$$

for all  $(\varrho, \theta, d, S) \in \mathscr{G}'' \times V \times T_s$ . The identity (B.6) means that the inequality (B.5)<sub>2</sub> has been reduced to the condition

$$p_{\varrho}(\varrho, \theta, d) \cdot d + d \cdot S^* c_{\varrho}(\varrho, \theta, d) + r_{d}(\varrho, \theta, d) [S] \cdot S \geq 0.$$
(B.7)

Now replace S in (B.7) with  $S + \alpha e \otimes e$ ; a simple calculation then gives

$$\alpha[d \cdot \{Se \otimes e + e \otimes eS - S - (\operatorname{tr} S) e \otimes e + \{(\operatorname{tr} S) - S \cdot e \otimes e\} 1\} c_e + r_d[S] \cdot e \otimes e + r_d[e \otimes e] \cdot S] + p_e \cdot d + d \cdot S^* c_e + r_d[S] \cdot S \ge 0$$

for all  $\alpha \in \mathbb{R}$  and all unit vectors  $e \in V$ , and where we have again used  $(B.4)_1$  to set  $r_d[e \otimes e] \cdot e \otimes e = 0$ . It is clear that this last inequality can hold only if the coefficient multiplying  $\alpha$  vanishes identically, *i.e.*, by the spectral theorem, only, if

$$d \cdot \{S_1 S_2 + S_2 S_1 - (\operatorname{tr} S_1) S_2 - (\operatorname{tr} S_2) S_1\} + \{(\operatorname{tr} S_1) (\operatorname{tr} S_2) - \operatorname{tr} (S_1 S_2)\} 1\} c_{\varrho} + r_d[S_1] \cdot S_2 + r_d[S_2] \cdot S_1 \equiv 0 \quad (B.8)$$

for all  $(\varrho, \theta, d) \in \mathscr{G}'' \times V$  and for any two symmetric tensors  $S_1$  and  $S_2$ . Upon selecting  $S_1 = S_2 = S$  in (B.8), we find that  $d \cdot S^*c_{\varrho} + r_d[S] \cdot S \equiv 0$ , and thus (B.7) has been reduced to just the condition

$$\boldsymbol{p}_{\varrho}(\varrho,\,\theta,\,\boldsymbol{d})\cdot\boldsymbol{d}\geq0\tag{B.9}$$

for all  $(\varrho, \theta, d) \in \mathscr{S}'' \times V$ .

<sup>\*</sup> See our discussion of the more general inequality (2.12).

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Summarizing our discussion to this point, we see that  $p(\cdot)$ ,  $r(\cdot)$ , and  $c(\cdot)$  have been shown to satisfy (B.4)<sub>1</sub> and (4.6) if and only if the three identities (B.5)<sub>1</sub>, (B.6), and (B.8) and the inequality (B.9) hold (and then (4.6) reduces to just (B.9)). However, a little more is true: in (B.6) replace d with  $\tau d$  and take  $S = d \otimes d$ to find that

$$\mathbf{p}_{d}(\varrho,\,\theta,\,\tau\,\,d)\cdot\,d\,\otimes\,d=d\cdot\frac{d}{d\tau}\,\mathbf{p}(\varrho,\,\theta,\,\tau\,\,d)=0$$

for all  $(\varrho, \theta, d) \in \mathscr{G}'' \times V$  and for all  $\tau \in \mathbb{R}$ , since  $r_{\varrho}(\varrho, \theta, \tau d) [d \otimes d] \cdot d$ vanishes due to  $(B.4)_1$ . If we now integrate this last equation from  $\tau = 0$ to  $\tau = 1$ , we see that

$$\boldsymbol{d} \cdot \boldsymbol{p}(\varrho, \theta, \boldsymbol{d}) = \boldsymbol{d} \cdot \boldsymbol{p}(\varrho, \theta, 0). \tag{B.10}$$

Consequently, (B.9) holds if and only if  $d \cdot p_{\varrho}(\varrho, \theta, 0) \ge 0$  for all  $(\varrho, \theta, d) \in \mathscr{G}'' \times V$ . Clearly, we must then have  $p_{\varrho}(\varrho, \theta, 0) \equiv 0$ , and hence  $d \cdot p_{\varrho}(\varrho, \theta, d) \equiv 0$ , *i.e.*, (B.9) holds if and only if its left-hand side is identically zero.

We now have shown that, as claimed, (4.6) holds if and only if its left-hand side vanishes identically and that this occurs if and only if the four chained identities (B.5)<sub>1</sub>, (B.6), (B.8), and  $p_e(\varrho, \theta, 0) = 0$  are satisfied.

Finally, note that, since  $\overline{u}(\cdot)$  is objective under a frame change, its static part  $\overline{w}(\cdot)$  must also be objective. Hence

$$\overline{w}(\varrho, \theta, Q d, QSQ^{T}, Qg) = Q\overline{w}(\varrho, \theta, d, S, g), \qquad (B.11)$$

for all  $(\varrho, \theta, d, S, g) \in \mathscr{S} \times V$  and for all proper, orthogonal Q. In terms of the representation (B.3), it is easy to see that (B.11) is equivalent to the five conditions:

$$p(\varrho, \theta, Q d) = Qp(\varrho, \theta, d),$$
  

$$\omega_1(\varrho, \theta, Q d) = (\det Q) Q\omega_1(\varrho, \theta, d),$$
  

$$r(\varrho, \theta, Q d) [QSQ^T] = Qr(\varrho, \theta, d) [S],$$
  

$$\omega_2(\varrho, \theta, Q d) [QSQ^T] = (\det Q) Q\omega_2(\varrho, \theta, d) [S],$$
  

$$c(\varrho, \theta, Q d) = Qc(\varrho, \theta, d),$$
  
(B.12)

for all  $(\rho, \theta, d, S) \in \mathcal{S}$ , and where det Q = +1 since Q is proper.

As is well known, the functional equations  $(B.12)_{1,2,5}$  are readily solved:

$$p = p(\varrho, \theta, d) = P(\varrho, \theta, M) d,$$
  

$$\omega_1 = \omega_1(\varrho, \theta, d) = \omega_1(\varrho, \theta, M) d,$$
  

$$c = c(\varrho, \theta, d) = C(\varrho, \theta, M) d,$$
  
(B.13)

for scalar-valued functions, P,  $\omega_1$ , and C of  $\varrho$ ,  $\theta$ , and  $M = |d|^2$ , defined on  $\mathscr{S}'' \times [0, \infty)$ . But now, when the restriction (B.10) from thermodynamics is applied to the form (B.13)<sub>1</sub>, it follows easily that  $P(\cdot)$  must vanish identically. Similarly, when the restriction (B.5)<sub>1</sub> from thermodynamics is applied to the form

 $(B.13)_3$ , one finds that  $C(\varrho, \theta, \cdot)$  must be such that  $3C + 2MC_M = 0$ ; hence  $C(\varrho, \theta, M) = C(\varrho, \theta, 1) M^{-3/2}$ , which is defined on  $\mathscr{S}'' \times [0, \infty)$  if and only if  $C(\cdot) \equiv 0$ . Thus we have shown that

$$p(\cdot) \equiv c(\cdot) \equiv 0,$$

and, as a consequence, the restrictions (B.6) and (B.8) are now just

$$\begin{aligned} \mathbf{r}_{\varrho}(\varrho,\,\theta,\,d)\,[\mathbf{S}]\cdot\mathbf{d} &\equiv 0,\\ \mathbf{r}_{\mathbf{d}}(\varrho,\,\theta,\,d)\,[\mathbf{S}_{1}]\cdot\mathbf{S}_{2} + \mathbf{r}_{\mathbf{d}}(\varrho,\,\theta,\,d)\,[\mathbf{S}_{2}]\cdot\mathbf{S}_{1} &\equiv 0, \end{aligned} \tag{B.14}$$

respectively, for all  $(\varrho, \theta, d) \in \mathscr{G}'' \times V$  and for all symmetric tensors  $S, S_1$ , and  $S_2$ .

The functional equation of  $(B.12)_{3,4}$  can also be solved; one finds that any function f = f(d)[S], defined for vectors  $d \in V$  and symmetric tensors S on V which is linear in S and satisfies the requirement

$$f(Q d) [QSQ^{T}] = Qf(d) [S]$$
(B.15)

for all proper, orthogonal tensors Q, must be of the form

$$f = f(d) [S] = \{S \cdot (F_1 \ 1 + F_2 \ d \otimes d) \ 1 + F_3 S\} \ d + F_4 \ d \times (S \ d), \quad (B.16)$$

for scalar-valued functions  $F_i$ , i = 1, 2, 3, 4, of  $M = |\mathbf{d}|^2$  alone.\*

When the representation (B.16) is applied to  $r(\varrho, \theta, d)$  [S], one finds that the restriction (B.4)<sub>1</sub> forces the terms corresponding to  $F_1$ ,  $F_2$ , and  $F_3$  to satisfy  $F_1 + F_3 = F_2 = 0$ . Therefore

$$\mathbf{r} = \mathbf{r}(\varrho, \theta, \mathbf{d}) [\mathbf{S}] = r \, \mathbf{d} \times (\mathbf{S} \, \mathbf{d}) + r_1 \{\mathbf{S} - (\operatorname{tr} \, \mathbf{S}) \, \mathbf{l}\} \, \mathbf{d},$$

where the scalar-valued functions r and  $r_1$  depend on  $\varrho$ ,  $\theta$ , and  $M = |d|^2$  and are defined on  $\mathscr{S}'' \times [0, \infty]$ . When this form for  $r(\cdot)$  is put into the restriction (B.14)<sub>2</sub> with  $S_1 = e_1 \otimes e_1$  and  $S_2 = e_2 \otimes e_2$ , where  $e_1$  and  $e_2$  are mutually perpendicular unit vectors pependicular to d, one finds that  $r_1$  must vanish identically. Consequently,  $r(\cdot)$  must be of the form

$$\boldsymbol{r} = \boldsymbol{r}(\varrho, \theta, d) [\boldsymbol{S}] = \boldsymbol{r} \, \boldsymbol{d} \times (\boldsymbol{S} \, \boldsymbol{d}),$$

and, moreover, this form for  $r(\cdot)$  satisfies the restrictions  $(B.14)_{1,2}$  identically.

Lastly, when the representation (B.16) is applied to  $\omega_2(\varrho, \theta, d)$  [S] and the restriction (B.4)<sub>2</sub> is taken into account, one finds that the terms corresponding to  $F_1$ ,  $F_2$ , and  $F_4$  must all vanish. Hence,

$$\boldsymbol{\omega}_2 = \boldsymbol{\omega}_2(\varrho, \theta, d) [S] = \boldsymbol{\omega}_2 S d,$$

<sup>\*</sup> When (B.15) is required to hold for all orthogonal tensors, proper or not, the representation (B.16), without the term  $d \times (S d)$ , is a consequence of a more general theorem of NoLL [30], who studied the consequences of (B.15) for arbitrary functions f = f(d, S) in the case where Q can be any orthogonal tensor. The representation (B.16) appears to be new.

for a scalar-valued function  $\omega_2$  of  $\varrho$ ,  $\theta$ , and  $M = |\boldsymbol{d}|^2$ , which is defined on  $\mathscr{G}'' \times [0, \infty]$ .

Summarizing our results, we see that thermodynamics, the objectivity of the interstitial work flux  $\boldsymbol{u}$  under frame changes, and the assumption that  $\mathscr{S} = \mathscr{S}'' \times V \times T_s$ , together imply that  $\overline{\boldsymbol{w}}(\cdot)$  is at most of the form

$$w = \overline{w}(\varrho, \theta, d, S, g),$$
  
=  $\omega_1 d \times g + r d \times (S d) + \omega_2(S d) \times g,$ 

for scalar-valued functions  $\omega_1$ , r, and  $\omega_2$  of  $\varrho$ ,  $\theta$ , and  $M = |d|^2$ . We have proven the representation (4.7).

#### Appendix C

Let  $T_s$  denote the set of symmetric second-order tensors defined on a three dimensional inner product space V. Let  $w(\cdot): T_s \to V$  be once continuously differentiable. We show here that, if in addition

$$w_s(S) \cdot \Gamma = 0 \tag{C.1}$$

for all  $S \in T_s$  and all completely symmetric third-order tensors  $\mathbb{T}$ , then  $w(\cdot)$  must be of the form

$$w(S) = a + b[S] + S^*c,$$
 (C.2)

where *a* and *c* are constant vectors, where  $b[\cdot]$  is a linear function<sup>\*</sup> satisfying  $e \cdot b[e \otimes e] = 0$  for every unit vector *e*, and where *S*<sup>\*</sup> is the adjugate of *S*.<sup>\*\*</sup> Conversely, it is easy to see that if (C.2) holds then (C.1) is satisfied.

To begin the proof that (C.1) implies (C.2), let us take  $\Gamma$  in (C.1) to be of the form  $r \otimes r \otimes r$  for  $r \in V$ . In this case (C.1) tells us that

$$\mathbf{r} \cdot \mathbf{w}_{\mathbf{s}}(S) \left[ \mathbf{r} \otimes \mathbf{r} \right] = 0 \tag{C.3}$$

for any  $S \in T_s$  and any  $r \in V$ . If we replace S in (C.3) by  $S + \tau r \otimes r$ , we see that (C.3) asserts that

$$\frac{d}{d\tau} \mathbf{r} \cdot \mathbf{w}(\mathbf{S} + \tau \mathbf{r} \otimes \mathbf{r}) = \mathbf{0}$$

$$A^* = A^2 - IA + II1,$$

where I and II are, respectively, the first and second principal invariants of A. By the Cayley-Hamilton theorem, it then follows that

$$A^*A = AA^* = (\det A) \mathbf{1}.$$

<sup>\*</sup> Throughout this and our earlier Appendix B, we use square brackets to denote linear functions. Thus  $f[\cdot]$  is a linear function of one variable,  $f[\cdot, \cdot]$  is a bilinear functions of two variables, *etc.* Similarly, while we write  $w_s(S)$  for the gradient of  $w(\cdot)$  at S, we will write  $w_s(S)$  [ $\cdot$ ] for the *differential* of  $w(\cdot)$  at S.

<sup>\*\*</sup> For any second-order tensor A on the three-dimensional inner product space V, we may define the adjugate  $A^*$  of A by

for all  $\tau \in \mathbb{R}$ , for all vectors r, and for all symmetric tensors S. We thus see that  $r \cdot w(S + \tau r \otimes r)$  is independent of  $\tau$ , *i. e.*,

$$\mathbf{r} \cdot \mathbf{w}(\mathbf{S} + \tau \mathbf{r} \otimes \mathbf{r}) = \mathbf{r} \cdot \mathbf{w}(\mathbf{S}) \tag{C.4}$$

for all  $\tau$ , r, and S.

Now differentiate (C.3) and (C.4) with respect to r in the direction r', yielding

$$\mathbf{r}' \cdot \mathbf{w}_{s}(S) \left[ \mathbf{r} \otimes \mathbf{r} \right] + \mathbf{r} \cdot \mathbf{w}_{s}(S) \left[ \mathbf{r}' \otimes \mathbf{r} + \mathbf{r} \otimes \mathbf{r}' \right] = 0, \quad (C.5)$$

$$r' \cdot w(S + \tau r \otimes r) + r \cdot w_s(S + \tau r \otimes r) [\tau(r' \otimes r + r \otimes r')] = r' \cdot w(S),$$

respectively. In (C.5)<sub>2</sub> replace  $S + \tau r \otimes r$  by S and subtract (C.5)<sub>1</sub>, multiplied by  $\tau$ , from the result to obtain

$$r' \cdot w(S) - \tau r' \cdot w_s(S) [r \otimes r] = r' \cdot w(S - \tau r \otimes r)$$

or, since the vector  $\mathbf{r}'$  is arbitrary,

$$w(S + \alpha r \otimes r) = w(S) + w_s(S) [\alpha r \otimes r], \qquad (C.6)$$

where we have replaced  $-\tau$  by  $\alpha$ . We remark that (C.6) holds for every symmetric tensor S, every vector r, and every real number  $\alpha$ ; by repeated application of (C.6) we now complete the proof of the representation (C.2).

We note first that (C.6) enables us to assert that  $w(\cdot)$  is infinitely differentiable. Indeed, if S' is any symmetric tensor, let  $\sum_{i=1}^{3} s'_i e'_i \otimes e'_i$  be its spectral representation; by (C.6) it then follows that

$$w_{s}(S)[S'] = \sum_{i=1}^{3} \{w(S + s'_{i}e'_{i} \otimes e'_{i}) - w(S)\},\$$

and so  $w_s(\cdot)$  [S'] is, for each  $S' \in T_s$ , continuously differentiable on  $T_s$ . Moreover, the differential  $w_{ss}(S)$  [S', S''] of  $W_s(S)$  [S'] is easily seen to be symmetric in S' and S''. Similarly, the third differential  $w_{sss}(S)$  [ $\cdot, \cdot, \cdot$ ] is easily seen to exist and be symmetric in all three of its arguments. Higher-order differentials of  $w(\cdot)$  also exist but we shall not need them.

If we successively take S = 0,  $S = \beta s \otimes s$ , and  $S = \beta s \otimes s + \gamma t \otimes t$ in (C.6), we find that

$$w(\alpha r \otimes r) = w(0) + w_s(0) [\alpha r \otimes r],$$
  

$$w(\alpha r \otimes r + \beta s \otimes s) = w(\beta s \otimes s) + w_s(\beta s \otimes s) [\alpha r \otimes r],$$
 (C.7)  

$$w(\alpha r \otimes r + \beta s \otimes s + \gamma t \otimes t)$$

$$= w(\beta s \otimes s + \gamma t \otimes t) + w_s(\beta s \otimes s + \gamma t \otimes t) [\alpha r \otimes r],$$

respectively. We differentiate (C.7)<sub>2</sub> and (C.7)<sub>3</sub> with respect to  $\beta$  and evaluate the result at  $\beta = 0$ , so obtaining

$$w_{s}(\alpha r \otimes r) [s \otimes s] = w_{s}(0) [s \otimes s] + w_{ss}(0) [\alpha r \otimes r, s \otimes s],$$
(C.8)

 $w_{s}(\alpha r \otimes r + \gamma t \otimes t) [s \otimes s] = w_{s}(\gamma t \otimes t) [s \otimes s] + w_{ss}(\gamma t \otimes t) [\alpha r \otimes r, s \otimes s],$ 

respectively. Next, we differentiate  $(C.8)_2$  with respect to  $\gamma$  and evaluate the result at  $\gamma = 0$ , so concluding that

$$w_{ss}(\alpha r \otimes r) [s \otimes s, t \otimes t] = w_{ss}(0) [s \otimes s, t \otimes t] + w_{sss}(0) [\alpha r \otimes r, s \otimes s, t \otimes t].$$
(C.9)

After some relabeling,  $(C.7)_{1,2}$  and  $(C.8)_1$  may be combined to show that  $w(\beta s \otimes s + \gamma t \otimes t) = w(0) + w_s(0) [\beta s \otimes s + \gamma t \otimes t] + w_{ss}(0) [\beta s \otimes s, \gamma t \otimes t].$ (C.10)

Similarly, after some relabeling,  $(C.8)_{1,2}$  and (C.9) may be combined to show that

$$w_{s}(\beta s \otimes s + \gamma t \otimes t) [r \otimes r] = w_{s}(0) [r \otimes r] + w_{ss}(0) [r \otimes r, \gamma t \otimes t] + w_{ss}(0) [r \otimes r, \beta s \otimes s] + w_{sss}(0) [r \otimes r, \beta s \otimes s, \gamma t \otimes t].$$
(C.11)

If we now put (C.10) and (C.11) into  $(C.7)_3$ , we see that we have shown that

$$w(\alpha r \otimes r + \beta s \otimes s + \gamma t \otimes t) = w(0) + w_s(0) [\alpha r \otimes r + \beta s \otimes s + \gamma t \otimes t] + w_{ss}(0) [\alpha r \otimes r, \beta s \otimes s] + w_{ss}(0) [\alpha r \otimes r, \gamma t \otimes t]$$
(C.12)  
+  $w_{ss}(0) [\beta s \otimes s, \gamma t \otimes t] + w_{sss}(0) [\alpha r \otimes r, \beta s \otimes s, \gamma t \otimes t],$ 

for any three real numbers  $\alpha$ ,  $\beta$ , and  $\gamma$  and for any three vectors r, s, and t in V.

Now, by the spectral theorem, any symmetric tensor S can be written as  $S = \sum_{i=1}^{3} s_i e_i \otimes e_i$  for eigenvalues  $s_i$  and associated, mutually perpendicular, eigenvectors  $e_i$ . If we substitute the spectral form for S into (C.12), we see that for any  $S \in T_S$ ,

$$w(S) = w(0) + w_{s}(0) [S] + (s_{1}s_{2}) w_{ss}(0) [e_{1} \otimes e_{1}, e_{2} \otimes e_{2}] + (s_{1}s_{3}) w_{ss}(0) [e_{1} \otimes e_{1}, e_{3} \otimes e_{3}] + (s_{2}s_{3}) w_{ss}(0) [e_{2} \otimes e_{2}, e_{3} \otimes e_{3}] + (s_{1}s_{2}s_{3}) w_{sss}(0) [e_{1} \otimes e_{1}, e_{2} \otimes e_{2}, e_{3} \otimes e_{3}],$$
(C.13)

*i.e.*,  $w(\cdot)$  is at most a cubic polynomial form in the eigenvalues of S. But even more is true-indeed,

$$w_{sss}(0) [e_1 \otimes e_1, e_2 \otimes e_2, e_3 \otimes e_3] = 0$$
(C.14)

for every choice of mutually perpendicular unit vectors  $e_1$ ,  $e_2$ , and  $e_3$  in V. To see this we need only return to (C.3) and differentiate that equation with respect to S in the direction S'. We find that

$$\mathbf{r} \cdot \mathbf{w}_{ss}(S) \left[ \mathbf{r} \otimes \mathbf{r}, S' \right] = 0. \tag{C.15}$$

If we differentiate (C.15) with respect to S in the direction S'', we also see that

$$\mathbf{r}\cdot\mathbf{w}_{sss}(S)\left[\mathbf{r}\,\otimes\,\mathbf{r},\,S',\,S''\right]=0.$$

In this last line we now take  $S' = s \otimes s$  and  $S'' = t \otimes t$  and use the symmetry of  $w_{sss}(S)$  [ $\cdot, \cdot, \cdot$ ]. We conclude that  $w_{sss}(S)$  [ $r \otimes r, s \otimes s, t \otimes t$ ] is is perpendicular to r, to s, and to t. A fortiori, when r, s, and t form a basis for V,

$$w_{sss}(S) [r \otimes r, s \otimes s, t \otimes t] = 0$$

at every  $S \in T_s$ . We have proven (C.14).

Next, let us take  $S' = s \otimes s$  in (C.15) and use the symmetry of  $w_{ss}(S)$  [ $\cdot, \cdot$ ]. We conclude that  $w_{ss}(S)$  [ $r \otimes r, s \otimes s$ ] is always perpendicular to both r and s. Thus, for any orthonormal basis  $\{e_i; i = 1, 2, 3\}$  of V and for every  $S \in T_s$ 

$$w_{ss}(S) [e_i \otimes e_i, e_i \otimes e_i]$$
 is parallel to  $e_k$  (C.16)

for all  $i \neq j \neq k \neq i$ . In addition, if we differentiate (C.5) with respect to S in the direction  $r \otimes r$  and then invoke (C.15) with  $S' = r' \otimes r + r \otimes r'$ , we find that  $r' \cdot w_{ss}(S) [r \otimes r, r \otimes r] = 0$ . Since r' is arbitrary, this requires that

$$w_{ss}(S) [r \otimes r, r \otimes r] = 0.$$
 (C.17)

at every  $S \in T_s$  and for every  $r \in V$ .

Now let  $\{e_i, i = 1, 2, 3\}$  be any orthonormal basis for V. Since  $1 = \sum_{i=1}^{3} e_i \otimes e_i$ , an easy calculation, based on the bilinearity and symmetry of  $w_{ss}(S)$  [ $\cdot, \cdot$ ], gives

$$\frac{1}{2} w_{ss}(S) [1, 1] = w_{ss}(S) [e_1 \otimes e_1, e_2 \otimes e_2] + w_{ss}(S) [e_1 \otimes e_1, e_3 \otimes e_3] + w_{ss}(S) [e_2 \otimes e_2, e_3 \otimes e_3],$$
(C.18)

where (C.17) has been used to drop the terms  $w_{ss}(S) [e_i \otimes e_i, e_i \otimes e_i]$ , i = 1, 2, 3. Thus, by (C.16) and (C.18),

$$\boldsymbol{w}_{ss}(0) \left[\boldsymbol{e}_{i} \otimes \boldsymbol{e}_{i}, \boldsymbol{e}_{j} \otimes \boldsymbol{e}_{j}\right] = \left\{ \frac{1}{2} \boldsymbol{w}_{ss}(0) \left[\boldsymbol{1}, \boldsymbol{1}\right] \cdot \boldsymbol{e}_{k} \right\} \boldsymbol{e}_{k}, \quad (C.19)$$

for  $i \neq j \neq k \neq i$ .

With (C.14) and (C.19), the representation (C.13) now becomes

 $w(S) = w(0) + w_s(0) [S] + \{s_1s_2e_3 \otimes e_3 + s_1s_3e_2 \otimes e_2 + s_2s_3e_1 \otimes e_1\} \frac{1}{2}w_{ss}(0) [1, 1],$ which, with  $a \equiv w(0)$ ,  $b[\cdot] \equiv w_s(0) [\cdot]$ , and  $c \equiv \frac{1}{2}w_{ss}(0) [1, 1]$ , is exactly the representation (C.2) which we were to prove (since  $s_1s_2e_3 \otimes e_3 + s_1s_3e_2 \otimes e_2 + s_2s_3e_1 \otimes e_1$  is just the adjugate  $S^*$  of  $S = \sum_{i=1}^3 s_ie_i \otimes e_i$ ). The condition that  $e \cdot b[e \otimes e] = 0$  is, of course, just the requirement (C.3) at S = 0.

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