A demonstration of consistency of an entropy balance with balance of energy

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1. Introduction

The main purpose of this note is to demonstrate that a postulate for balance of entropy in thermomechanics—in the form introduced by Green and Naghdi [1]—is consistent with, and can be derived from, the balance of energy. However, additional results also emerge from our derivation which include the classical conservation laws of the mechanical theory for mass, momentum and moment of momentum.

After some preliminaries in section 2, our starting point in section 3 is a statement of balance of energy which at first has a slightly different form than the usual in that it also includes the rate of thermal energy due to heat density (see Eq. $(2.3)_2$); the latter may be regarded as the counterpart of the rate of kinetic energy in a purely mechanical theory. In this form of the balance of energy (or the First Law of thermodynamics), it is the specific Helmholtz free energy (and not the specific internal energy) which first occurs. However, after invoking the well-known relationship between these two specific energies (see Eq. $(3.11)_2$), we recover the usual form of the balance of energy in terms of the specific internal energy. In section 4, we turn to our main objective for deriving a balance of entropy from the balance of energy. Here, we designate certain quantities by the scalar m, the vector f, and the scalar ξ ; and later identify these, in the order listed, as internal generation of mass, internal force per unit mass and internal generation of entropy (see Eqs. (4.4) - (4.6)). These help to provide a clearer picture of the structure of the basic equations in thermomechanics; and eventually, in the context of a nonlocal theory, the first two, namely m and f, are set equal to zero. Also, in the course of our derivation in section 4, we first set aside the invariance conditions under superposed rigid body motions (hereafter abbreviated as s.r.b.m.), but these conditions are eventually utilized in order to deduce the balance of entropy in the form postulated in [1]. A part of the derivation which concerns the recovery of the mechanical conservation laws is presented only briefly in the latter part of section 4, since it is somewhat similar to the procedure and used previously with various degrees of generality by Green and Rivlin [2], by Naghdi [3, pp. 487–490] and by Green and Naghdi [4].

Two aspects of the present derivation are worth emphasizing. The inclusion of the rate of thermal energy (due to heat density) in the primitive form of the balance of energy in section 3, together with additional quantities introduced in section 4 (see Eqs. (4.4)-(4.6)), now provide clearer interpretations of the various derived results. Moreover, the balance of entropy in the present development emerges naturally instead of being a separate postulate motivated only by the form of the energy equation for an inviscid fluid [1].

2. Notations and preliminaries

Consider a body \mathscr{B} with particles (material points) X and identify X with its position X in a fixed reference configuration κ_0 in a three-dimensional Euclidean space \mathscr{E}^3 . Let x be the position vector in \mathscr{E}^3 occupied by the particle X in the current configuration κ at time t. Also let ϱ_0 and ϱ be, respectively, the mass density of \mathscr{B} in the configuration κ_0 and κ . A motion of \mathscr{B} is a sufficiently smooth and invertible mapping χ defined by $x = \chi(X, t)$. The particle velocity is defined by $v = \dot{x}$, where a superposed dot denotes material time differentiation holding X fixed. Let \mathscr{B} in its current configuration κ occupy a material volume \mathscr{R} bounded by a smooth closed surface $\partial \mathscr{R}$ and denote the volume occupied by any subset \mathscr{S}_t of \mathscr{B} in κ by a part $\mathscr{P} \subseteq \mathscr{R}$ bounded by a closed surface $\partial \mathscr{P}$.

Recalling the basic concepts of force, work and energy in classical continuum mechanics, we suppose that the body \mathscr{B} is acted upon by surface (or contact) forces \overline{t} per unit area of $\partial \mathscr{R}$ and by body forces b per unit mass throughout \mathscr{R} . The rates of work of these forces are defined for all v, respectively, by $\overline{t} \cdot v$ per unit area of $\partial \mathscr{R}$ and by $b \cdot v$ per unit mass in \mathscr{R} . Also, the kinetic energy per unit mass is defined by $\frac{1}{2}v \cdot v$ throughout \mathscr{R} . It is assumed that the externally applied force \overline{t} gives rise to a surface (contact) force t per unit area of $\partial \mathscr{P}$, defined by a corresponding rate of work¹ $t \cdot v$ for all v.

Next, in the context of thermomechanics, we admit the existence of an empirical temperature T and heat energy. Thus, a positive scalar variable θ is defined throughout \mathcal{R} which depends on T and on the kinematical and

¹ In addition to t, the external forces i could be assumed to give rise to internal body forces in \mathcal{P} , but it is not necessary to admit such internal body forces here.

thermal properties of the body restricted by the condition $(\partial \theta / \partial T) > 0$. Then, θ is invertible with respect to T and is adopted as a measure of temperature throughout \mathcal{R} . The external rates of supplies of heat to the body \mathcal{B} consist of a surface flux of heat $-\overline{h}$ per unit area of $\partial \mathcal{R}$ and volume rate of supply of heat r per unit mass throughout \mathcal{R} . These are accompanied by an external surface flux of entropy $-\overline{k} = -\overline{h}/\theta$ per unit area of $\partial \mathcal{R}$ and an external volume rate of supply of entropy $s = r/\theta$ per unit mass throughout \mathcal{R} . It is assumed that $-\overline{h}$ and $-\overline{k}$ give rise to a surface flux of heat -h into \mathcal{P} and measured per unit area of $\partial \mathcal{P}$, together with a surface flux of entropy $-k = -h/\theta$ per unit area? of $\partial \mathcal{P}$. Further, corresponding to the kinetic energy density in \mathcal{P} arising from mechanical concepts, there is a density of heat ζ together with an entropy density $\eta = \zeta/\theta$ per unit mass in \mathcal{R} .

In the remainder of this section, we record various expressions representing the kinetic energy, thermal energy due to ζ , heat supplies and rate of work contributions to any subset \mathscr{S}_t of the body in κ occupying a volume \mathscr{P} bounded by a closed surface $\partial \mathscr{P}$. The kinetic energy K and the thermal energy H due to the heat density $\zeta = \theta \eta$ per unit mass in \mathscr{S}_t are:

$$K(\mathscr{S}_{t}) = \int_{\mathscr{P}} \frac{1}{2} \varrho \boldsymbol{v} \cdot \boldsymbol{v} \, d\boldsymbol{v}, \quad H(\mathscr{S}_{t}) = \int_{\mathscr{P}} \varrho \theta \eta \, d\boldsymbol{v}.$$
(2.1)

The total rate of work R on \mathscr{S}_t due to rate of work by the body force **b** and the rate of work by the contact force **t** is

$$R(\mathscr{S}_t) = \int_{\mathscr{P}} \varrho \boldsymbol{b} \cdot \boldsymbol{v} \, d\boldsymbol{v} + \int_{\partial \mathscr{P}} \boldsymbol{t} \cdot \boldsymbol{v} \, d\boldsymbol{a}.$$
(2.2)

Similarly, the total rate of heat Q supplied to \mathcal{S}_t is

$$Q(\mathscr{S}_{t}) = \int_{\mathscr{P}} \varrho r \, dv - \int_{\partial \mathscr{P}} h \, da$$
$$= \int_{\mathscr{P}} \varrho \theta s \, dv - \int_{\partial \mathscr{P}} \theta k \, da.$$
(2.3)

Finally, for later reference, we introduce the total rate W at which internal energy (both due to rate of mechanical work and thermal energy) is generated in \mathcal{S}_t by

$$W(\mathscr{S}_{t}) = \int_{\mathscr{P}} \varrho w \, dv, \tag{2.4}$$

where w is density of internal energy.

² Internal volume of rate of supply of heat and entropy may also be generated in \mathcal{P} , but these are not considered here.

3. Balance of energy

The balance of energy (or the First Law of thermodynamics) for any part \mathscr{S}_t occupying a volume \mathscr{P} in κ may be stated as follows:

- (i) The total rate of work of external body forces in S_t plus the rate of work of surface traction on ∂S_t, plus energy due to external volume supply of heat in S_t and external surface flux of heat across ∂S_t, minus the total rate of change of kinetic energy and heat in S_t plus the total rate at which internal energy (mechanical and thermal) is generated in S_t is zero.
- (ii) The total heat energy Q and mechanical work R supplied to or extracted from \mathcal{S}_t in a cycle is zero.

A cycle referred to in (ii) is a thermomechanical process, during a closed interval of time $I = [t_1, t_2]$ with $t_1 < t_2$, involving various kinematical, kinetical and thermal variables, which define the state of any part of the body and which assume the same values at the beginning and end of the cycle at times t_1 and t_2 . For example, the body could be completely at rest at the beginning and end of the cycle, with the same values of the kinematical and kinetical variables.

In adopting a balance of energy for \mathscr{G}_t in the form stated in (i) and (ii), it is tacitly assumed that the theory under discussion is a local theory, i.e., any internal forces or rate of supplies of heat generated in \mathscr{G}_t , as well as quantities such as t and k, do not depend on kinematical quantities outside \mathscr{G}_t . Some modifications are necessary in order to discuss a nonlocal theory.

In view of the statement (i) and the definitions (2.1)-(2.4), the balance of energy may be stated in the form

$$-\frac{d}{dt}\left\{K(\mathscr{S}_t) + H(\mathscr{S}_t)\right\} + R(\mathscr{S}_t) + Q(\mathscr{S}_t) + W(\mathscr{S}_t) = 0.$$
(3.1)

Observing that the time rates of change of kinetic energy \dot{K} and of thermal energy \dot{H} take the same values at the beginning $(t = t_1)$ and end $(t = t_2)$ of any cycle during the time interval $I = [t_1, t_2]$, from the statement (ii) and an expression resulting from integration of (3.1) with respect to t between the limits t_1 and t_2 we obtain

$$\oint_{t_1}^{t_2} W(\mathscr{S}_t) \, dt = 0, \tag{3.2}$$

where we have also used (2.4). The result (3.2) must hold for all \mathscr{P} and for any cycle during the time interval $I = [t_1, t_2]$. If the time integral in (3.2) is taken over any thermomechanical process which is not a cycle during the

closed time interval $[t_1, t]$, the integral is nonzero and will not depend on the path but only on the state of the body at time t (and t_1) so that

$$\int_{t_1}^t W(\mathscr{S}_t) \, dt = -\Psi(\mathscr{S}_t),\tag{3.3}$$

with Ψ defined by

$$\Psi(\mathscr{S}_t) = \int_{\mathscr{P}} \varrho \psi \, dv. \tag{3.4}$$

The scalar potential ψ on the right-hand side of (3.4), as becomes evident later, is known as the specific Helmholtz free energy. It follows from (3.3) that

$$W(\mathscr{S}_{t}) = -\frac{d}{dt} \Psi(\mathscr{S}_{t})$$
(3.5)

and then by virtue of (2.4) and (3.4) we also have

$$-\int_{\mathscr{P}} \varrho w \, dv = \frac{d}{dt} \int_{\mathscr{P}} \varrho \psi \, dv, \tag{3.6}$$

which holds for every part \mathcal{P} . Hence, with the usual continuity assumptions we may deduce the local result

$$\varrho J w = -\overline{\varrho J \psi},\tag{3.7}$$

where $J = \det F$ and $F = \partial \chi / \partial X$ stands for the deformation gradient. With the help of (3.5) or (3.6), the balance of energy in the form (3.1) can be reduced to

$$-\frac{d}{dt}\left\{K(\mathscr{S}_{t}) + H(\mathscr{S}_{t}) + \Psi(\mathscr{S}_{t})\right\} + R(\mathscr{S}_{t}) + Q(\mathscr{S}_{t}) = 0, \qquad (3.8)$$

or equivalently to

$$-\frac{d}{dt} \int_{\mathscr{P}} \left[\frac{1}{2} \boldsymbol{v} \cdot \boldsymbol{v} + \boldsymbol{\psi} + \eta \theta \right] \varrho \, dv + \int_{\mathscr{P}} (s\theta + \boldsymbol{b} \cdot \boldsymbol{v}) \varrho \, dv + \int_{\partial \mathscr{P}} (\boldsymbol{t} \cdot \boldsymbol{v} - k\theta) \, da = 0.$$
(3.9)

Before closing this section, we indicate the relationship between (3.9) and the usual form of balance of energy. For this purpose, we introduce a specific internal energy ε and define internal energy E by

$$E(\mathscr{S}_t) = \int_{\mathscr{P}} \varrho \varepsilon \, dv \tag{3.10}$$

Then, after setting

$$E(\mathscr{S}_t) = \Psi(\mathscr{S}_t) + H(\mathscr{S}_t), \quad \varepsilon = \psi + \eta\theta, \tag{3.11}$$

the balance equation (3.9) can be rewritten in its usual form in terms of ε after also replacing $s\theta$ and $k\theta$ by r and h, respectively.

4. A derivation of conservation laws of thermomechanics from the balance of energy (3.9)

From the balance of energy (3.9) we derive here a general balance of entropy, as well as the mechanical conservation laws of the classical continuum mechanics. We first apply the balance of energy (3.9) to an elementary tetrahedron and using the usual smoothness assumptions, we deduce that

$$(\boldsymbol{t} - \boldsymbol{T}\boldsymbol{n}) \cdot \boldsymbol{v} - (\boldsymbol{k} - \boldsymbol{p} \cdot \boldsymbol{n})\boldsymbol{\theta} = 0, \tag{4.1}$$

where *n* is the outward unit normal to $\partial \mathscr{P}$. As will be seen below, the second order tensor *T* in (4.1) is the (Cauchy) stress tensor, and *p* is an entropy flux vector which is related to the usual heat flux vector *q* by $p = q\theta$. With the help of (4.1) and the divergence theorem, the energy balance (3.9) may be reduced to

$$\overline{\mathscr{E}} = \int_{\mathscr{P}} \left\{ -(\dot{\varrho} + \varrho \operatorname{div} \boldsymbol{v}) [\frac{1}{2} \boldsymbol{v} \cdot \boldsymbol{v} + \psi + \eta \theta] + (-\varrho \dot{\boldsymbol{v}} + \varrho \boldsymbol{b} + \operatorname{div} \boldsymbol{T}) \cdot \boldsymbol{v} 4 - \varrho \boldsymbol{\lambda} \cdot \boldsymbol{\omega} + \boldsymbol{T} \cdot \boldsymbol{D} + (-\varrho \dot{\eta} + \varrho \boldsymbol{s} - \operatorname{div} \boldsymbol{p}) \theta - \rho \cdot \operatorname{grad} \theta - \varrho (\dot{\psi} + \eta \dot{\theta}) \right\} dv = 0,$$

$$(4.2)$$

where $\overline{\mathscr{E}}$ defines the integral in (4.2), "div" stands for the divergence operator with respect to the place x keeping t fixed, grad $\theta = \partial \theta / \partial x$ is the temperature gradient, D is the rate of deformation tensor, W is the spin tensor, $\omega = \operatorname{curl} v$ is the vorticity vector and

$$-\varrho\Gamma = \frac{1}{2}(T - T^{T}), \quad \lambda \times a = \Gamma a, \quad \omega \times a = 2Wa$$
(4.3)

for all arbitrary vectors **a**. Also, in (4.2) and (4.3), the notation T^{T} stands for the transpose of the second order tensor T, Γ is a skew-symmetric second order tensor with λ being the corresponding axial vector.

We now define a vector f and scalars ξ and m by the equations

$$m = \dot{\varrho} + \varrho \, \operatorname{div} \boldsymbol{v},\tag{4.4}$$

$$\varrho \boldsymbol{f} = \varrho \boldsymbol{v} + \boldsymbol{m} \boldsymbol{v} - \varrho \boldsymbol{b} - \operatorname{div} \boldsymbol{T}, \tag{4.5}$$

$$\varrho\xi = \varrho\dot{\eta} + m\eta - \varrho s + \operatorname{div} \boldsymbol{p}. \tag{4.6}$$

Then, after adding and subtracting $mv \cdot v$ to and from the integrand of (4.2) and using (4.4)-(4.5), (4.2) and hence (3.9) reduces to

$$\mathscr{E} = \int_{\mathscr{P}} \left\{ \frac{1}{2} m \boldsymbol{v} \cdot \boldsymbol{v} - m \boldsymbol{\psi} - \varrho \boldsymbol{f} \cdot \boldsymbol{v} - \varrho \boldsymbol{\lambda} \cdot \boldsymbol{\omega} + \boldsymbol{T} \cdot \boldsymbol{D} - \varrho \boldsymbol{\xi} \theta - \boldsymbol{p} \cdot \operatorname{grad} \theta - \varrho (\dot{\boldsymbol{\psi}} + \eta \dot{\theta}) \right\} d\boldsymbol{v} = 0.$$

$$(4.7)$$

Since \mathscr{E} (defined by the left-hand side of (3.9))—in accordance with statement (i) of section 3—represents the sum of all energies displayed in (3.1), the reduced expression (4.7) enables us to give an interpretation and meaning to *m*, *f* and ξ which so far are defined only mathematically by (4.4), (4.5) and (4.6). It is convenient to provide here interpretations as to what each term in the integrand of the integral in (4.7) represents. A list of these interpretations is as follows:

- $T \cdot D$: rate of work of internal stress T
- $-p \cdot \text{grad } \theta$: rate of internal generation of heat due to entropy flux vector p
 - $-\varrho f \cdot v$: rate of work by an internal force f per unit mass
 - $-\varrho\lambda\cdot\omega$: rate of work by an internal couple per unit mass
 - $-\varrho \xi \theta$: rate of supply of energy due to an internal generation of entropy
 - $-m\psi$: rate of supply of energy due to an internal generation of mass

In a complete theory it is necessary to specify constitutive equations for T, p, f, ξ, m , as well as for ψ and η (or θ). Then, equations (4.4)–(4.6) represent field equations for balances of mass, momentum and entropy, respectively, and these equations cease to be merely definitions of m, f, ξ . It should be noted that in this approach there is, at this stage, a nonzero internal force f and internal couple λ although only stress vectors were applied to the surface. As will be seen presently, these internal forces will be zero. However, if the theory had been a nonlocal theory these quantities would not be zero and would have been present in the original energy balance (3.1) since they are affected by material outside \mathcal{P} , unless \mathcal{P} is the entire region occupied by the body as a whole (see, for example, [4]).

Since (4.7) must hold for every part \mathcal{P} , assuming that the integrand is continuous, we may deduce the local equation

$$\frac{1}{2}m\boldsymbol{v}\cdot\boldsymbol{v} - m\boldsymbol{\psi} - \varrho\boldsymbol{f}\cdot\boldsymbol{v} - \varrho\boldsymbol{\lambda}\cdot\boldsymbol{\omega} + \boldsymbol{T}\cdot\boldsymbol{D} - \varrho\boldsymbol{\xi}\boldsymbol{\theta} - \boldsymbol{p}\cdot\operatorname{grad}\boldsymbol{\theta} - \varrho(\boldsymbol{\psi} + \eta\boldsymbol{\theta}) = 0.$$
(4.8)

Given constitutive equations for T, p, η, m, f, ξ , the equations (4.4)–(4.6) with specified values for the external force and external supply of entropy

and suitable boundary and initial conditions are sufficient to determine the velocity (or the displacement) and temperature fields. Moreover, as in the paper of Green and Naghdi [1], the reduced energy equation (4.8) must be regarded as an identity which provides some restrictions on constitutive equations.

It will be observed that the balance of momentum in (4.5) contains the extra internal force f and is, therefore, somewhat different from that in the usual approach which postulates a momentum balance at the outset. Moreover, the entropy balance (4.6) appears here naturally consistent with a general balance of energy instead of being a postulate with only a limited motivation (based on the form of the energy equation for an inviscid fluid) as in [1].

In order to relate the second order tensor T to the stress vector t and the vector p to the surface flux of entropy k, we return to (4.1) and examine its implication under s.r.b.m. Under such motions of the body moves to the configuration κ^+ which differs from κ only by a rigid motion. Thus, by considering a special s.r.b.m. in which the particle velocity v^+ in κ^+ differs from v by only a constant rigid body translational velocity and after an appeal to well-known invariance conditions, we readily obtain

$$t = Tn, \quad k = p \cdot n. \tag{4.9}$$

The first of (4.9) is a standard result in continuum mechanics and identifies T as the Cauchy stress tensor, while the second of (4.9) relates the surface flux of entropy $k(=h/\theta)$ defined in section 2 to the entropy flux vector p.

As noted in section 1, it is known that from the energy equation and the invariance conditions under s.r.b.m., the field equations for mass conservation and the linear momentum may be recovered in the forms (4.4) and (4.5) with

$$m = 0, \quad f = O,$$
 (4.10)

and that the equation for moment of momentum may be recovered with $\lambda = o$ or equivalently with

$$\boldsymbol{\Gamma} = \boldsymbol{O} \quad \text{or} \quad \boldsymbol{T} = \boldsymbol{T}^T. \tag{4.11}$$

It should be emphasized that the local equations for mass conservation and linear momentum, namely (4.4) and (4.5) together with (4.9) and (4.10), are obtained here using a special s.r.b.m. in which v^+ differs from v by only a constant rigid body translational velocity; and that the result (4.11) corresponding to the local form of the consequence of moment of momentum is obtained using a special s.r.b.m. in which the skew-symmetric part of the velocity gradient in κ^+ differs from that in κ by a constant rigid body angular velocity. Of course, the results discussed in this paragraph may alternatively be derived directly from (4.8).

Before closing this section, it may be observed that the basic structure of (4.6) together with its interpretation as a balance of entropy—consistent with the reduced energy equation (4.7)—was established prior to any consideration of invariance under s.r.b.m. Furthermore, the use of a particular s.r.b.m. and associated invariance conditions in connection with (4.9) and (4.10) is very mild indeed. With this background, by invoking $(4.10)_1$ once more, the second term on the right-hand side of (4.6) vanishes and we obtain

$$\varrho\xi = \varrho\dot{\eta} - \varrho s + \operatorname{div} \boldsymbol{p},\tag{4.12}$$

which is the local form of the balance of entropy postulated in [1].

5. Additional remarks

Most of the existing literature on thermodynamics does not admit an entropy balance but postulates an entropy inequality, such as the Clausius-Duhem or similar inequalities, where often the concept of entropy first appears. An alternative procedure in [1] makes use of an entropy balance as an independent balance law in the form (4.12). In this approach, after elimination of the heat supply r and the body force b with the use of the local equation for balance of entropy and the equations of motion, the local balance of energy results in a reduced energy equation. The latter is then regarded as an identity for all thermomechanical processes and is used to place restrictions on constitutive equations. Additional restrictions which arise from the Second Law of thermodynamics can also be imposed with profit on the constitutive equations, but these are not discussed here either. Instead reference is made to the discussion of this aspect of the subject in [5] after suppressing the electrodynamic effects.

The entropy flux p in (4.6) and (4.12) is clearly defined through $(4.9)_2$ or equivalently through q/θ , where the positive temperature θ depends on empirical temperature T and may also depend on a particular material. At this stage θ is not an absolute temperature. It frequently happens, however, that after full discussion of constitutive equations for a given material, the temperature θ can be proved to depend only on the empirical temperature T. Then, by imposing also the condition that the scalar θ is an increasing function of T, i.e., $\partial \theta/\partial T > 0$, it can be concluded that θ is an absolute temperature of the particular class of materials discussed but not necessarily for *all* materials. Some authors have claimed that a definition of the form q/θ for an entropy flux is not always true. However, in general, such a quantity cannot be measured directly. Sometimes claim is made in regard to the form of entropy flux on the basis of comparison with kinetic theory, but macroscopic definitions used in kinetic theory do not necessarily coincide with those used here or other developments in thermomechanics.

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Abstract

It is shown in this note that a general balance of entropy postulated previously with only a limited motivation (based on the form of the energy equation for an inviscid fluid) is consistent with, and can be derived from, a general balance of energy. In this derivation, an early form of entropy balance does not make use of invariance conditions under superposed rigid body motions. However, with the help of the latter invariance conditions, additional results are also derived which provide some insight on the structure of the basic equations in thermomechanics.

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