On Entropy Flux of Anisotropic Elastic Bodies

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Abstract
The framework of irreversible thermodynamics is fundamental in development of constitutive models. One of the important aspects of the extended irreversible thermodynamics is the relationship between the entropy flux and the heat flux, especially for phenomena far from equilibrium. In this paper, we demonstrate that the assumption that Lagrange multiplier conjugated to the energy balance equation (in the expression for the second law of thermodynamics) is a function of temperature \( \Lambda^e(\theta) \) is a sufficient condition to derive the entropy flux–heat flux relation for all isotropic materials as well as for a number of crystal classes including transverse isotropy, orthotropy, triclinic systems and rhombic systems. For all considered crystal classes, the entropy flux–heat flux relation was derived explicitly. Further, we demonstrate that for some crystal classes heat flux is nonzero even when temperature gradient vanishes (as stated by Eringen). The anisotropic functions, with respect to the symmetry groups of the crystal classes, were expressed in terms of isotropic functions. The proposed procedure is very general in the sense that it can be used with nonlinear constitutive relations as demonstrated here. The presented results confirm that the all crystal elastic bodies considered are hyperelastic.

Keywords Anisotropy · Constitutive models · Entropy flux · Heat flux · Isotropic functions · Symmetry groups

1 Introduction

One of the important problems in thermodynamics is the relationship between the entropy flux and the heat flux for phenomena far from equilibrium.
The entropy principle based on the Clausius–Duhem inequality

\[ \rho \dot{\eta} + \text{div} \frac{q}{\theta} - \rho \frac{r}{\theta} \geq 0, \]  

(1)

where \( \rho \) is density, \( \eta \) is the specific entropy density, \( q \) the heat flux and \( r \) the heat supply, has been widely adopted in the development of modern rational thermodynamics after the fundamental work of Coleman and Noll [1]. The main assumptions, motivated by the result of classical thermostatics, are that the entropy flux \( \Phi \) and the entropy supply \( s \) are proportional to the heat flux and the heat supply, respectively. Moreover, both constants of proportionality are assumed to be the reciprocal of the absolute temperature, i.e.,

\[ \Phi_k = \frac{1}{\theta} q_k, \quad s = \frac{1}{\theta} r. \]  

(2)

These main assumptions, while tacit in the classical theory of continuum mechanics, do not hold particularly well for materials in general. In fact, it is known that they are inconsistent with the kinetic theory of ideal gases and are also found to be inadequate to account for the thermodynamics of diffusion. Further, Sellitto et al. [2] demonstrated that the proportionality relations (2) do not hold for nonlocal heat transfer at nanoscale and provide an illustrative example of cylindrical nanodevice connected to a graphene layer.

There is an extended formulation of the second law of thermodynamics which has been applied to nonequilibrium thermodynamics by Serrin [3] and Silhavy [4] and summarized by Truesdell and Bharatha [5]. See also Muschik [6], Müller [7] and Domínguez-Cascante and Jou [8]. A comprehensive review of the related literature and detailed derivations can be found in Lebon et al. [9] and Jou et al. [10, 11].

The extended form of the second law, usually called the entropy inequality, seems to be the most general formulation of the continuous second law of thermodynamics proposed so far. In this theory, the assumptions given by Eq. (2) were abandoned and the entropy flux \( \Phi \) and the heat flux vector \( q \) are treated as independent constitutive quantities and hence leaving the entropy inequality in its general form

\[ \rho \dot{\eta} + \text{div} \Phi - \rho s \geq 0. \]  

(3)

Liu [12] proposed a method, reminiscent of the classical method of Lagrange multipliers, for expanding the inequality (3). Instead of this inequality restricting the solution of field equations, he considered solutions of an extended inequality which should hold for all fields. This can be done if one considers the field equations as constraints on solutions of the energy inequality.

Further, Liu [13] analyzed the thermodynamic theory of viscoelastic bodies and proved that for isotropic viscoelastic materials the results are identical to the classical results given by Eq. (2). In the same paper, he also proved that the body is hyperelastic because of the Lagrange multiplier \( \Lambda^c = \Lambda(\theta) \).

However, for anisotropic elastic materials in general, the validity of the classical entropy flux relation is yet to be demonstrated.
The first contribution in this direction has been given by Liu [14, 15], who proved by considering transversely isotropic elastic bodies and transversely isotropic rigid heat conductors that the classical entropy flux relation (2) need not be valid in general.

Three years later, Bargmann et al. [16] considered the energy influx–entropy influx relation in the Green–Naghdi type III theory of heat conduction and showed that the entropy influx and the energy influx are proportional via the absolute temperature if heat conduction is isotropic. Further, they demonstrated that influx proportionality cannot be postulated in general by giving counterexample of transversely isotropic conduction. Their proof is based on a representation formula for isotropic vector-valued mappings of two vector arguments where Lagrange multiplier is assumed to have the following general form: \( \Lambda = \Lambda(|u|, |v|, u \cdot v) \). Using Green–Naghdi, set of internal variables \( S\{\alpha, \dot{\alpha}, \nabla\alpha, \nabla\dot{\alpha}\} \) where \( \alpha \) is thermal displacement they showed, through an algebraic analysis, that the multiplier \( \Lambda = \Lambda(\alpha, \dot{\alpha}) \) is at least proportional to coldness (the inverse of absolute temperature and does not depend on the thermal displacement gradient \( \nabla\alpha \) nor on the temperature gradient \( \nabla\dot{\alpha} \)) for isotropic conduction.

Podio–Guidugli [17] considered energy and entropy inflows in the theory of heat conduction and demonstrated proportional via the absolute temperature for isotropic conduction using similar procedure.

We do not see the possibility for the Bargmann et al. procedure to be generalized and extended to conduction in continuum with other symmetry types.

In this paper, we investigate the functional dependence of the Lagrange multiplier conjugated to the energy balance equation \( \Lambda^\varepsilon = \Lambda(\theta) \), irrespective of whether the classical entropy flux relation is valid. This enables derivation of the entropy flux–heat flux relations for a number of crystal classes including transverse isotropy, orthotropy, triclinic systems, monoclinic systems and rhombic systems.

The paper is organized as follows: In Sect. 2, the basic ideas and formulas typically used in this field are given as a starting point of our investigation. In Sect. 3, the entropy flux relation for viscoelastic bodies and transverse isotropic elastic materials is reconsidered assuming the Lagrange multiplier dependency on temperature, i.e., \( \Lambda^\varepsilon = \Lambda(\theta) \). In Sect. 4, the procedure introduced in Sect. 3 is extended for the derivation of the entropy flux relation of anisotropic elastic materials defined by the crystal classes listed above. In Sect. 5, the entropy inequality for anisotropic bodies is examined further. Conclusions related to the outcome of this work are given in Sect. 6.

2 The Entropy Principle

In this section, the basic framework of the entropy principle for viscoelastic materials is presented. The balance laws of mass, linear momentum and energy can be stated in current configuration as:

\[
\begin{align*}
\dot{\rho} + \rho \text{div}\dot{x} &= 0, \\
\rho \dot{x} - \text{div}T &= \rho b, \\
\rho \dot{\varepsilon} + \text{div}\dot{q} - T : \text{grad}\dot{x} &= \rho r 
\end{align*}
\]
where $\mathbf{T}$ is the Cauchy stress tensor, $\mathbf{b}$ is external body force and $\mathbf{r}$ is external heat supply.

Note that for solid bodies, it is more convenient to use a referential description. Also, since constitutive relations do not depend on external supplies, it suffices to consider only supply-free bodies. Consequently, the balance laws can be rewritten as:

$$\rho = J^{-1} \rho_k,$$
$$\rho_k \dot{\mathbf{x}} - \text{div} \mathbf{T}_k = 0,$$
$$\rho_k \dot{\mathbf{e}} + \text{Div} \mathbf{q}_k - \mathbf{T}_k \cdot \dot{\mathbf{F}} = 0,$$

and the entropy inequality

$$\rho_k \dot{\eta} + \text{Div} \Phi_k \geq 0.$$

Here, the first Piola–Kirchhoff stress tensor $\mathbf{T}_k$, the material heat flux vector $\mathbf{q}_k$ and the material entropy flux vector $\Phi_k$ are related to the Cauchy stress tensor $\mathbf{T}$, the heat flux vector $\mathbf{q}$ and the entropy flux vector $\Phi$ by

$$\mathbf{T}_k = J \mathbf{F}^{-T}, \quad \mathbf{q}_k = J \mathbf{F}^{-1} \mathbf{q}, \quad \Phi_k = J \mathbf{F}^{-1} \Phi,$$

where $\mathbf{F}$ is the deformation gradient in referential coordinates and $J = |\text{det} \mathbf{F}|$. “Div” is the divergence operator with respect to the referential coordinates.

It is well known that the entropy principle imposes severe restrictions on constitutive functions and the exploitation of such restrictions based on the Clausius–Duhem inequality and is relatively easy. For elastic materials, in general, the thermodynamic restrictions can be easily obtained by the well-known Coleman–Noll procedure [1].

The derivation of the relation between the entropy flux and the heat flux based on the entropy principle, referred to as entropy flux relation, is a typical problem in this new theory.

Here, we outline the consideration for isotropic viscoelastic materials with isotropic elasticity as a special case within the framework of continuum mechanics. The thermodynamics of the continua sufficiently close to equilibrium so that the principle of equipresence can be used. Consequently, the local constitutive relations for viscoelastic materials can be written as functions of the state variables

$$(\mathbf{F}, \dot{\mathbf{F}}, \theta, \mathbf{g}_k),$$

i.e.,

$$\mathbf{T}_k = \hat{\mathbf{T}}_k (\mathbf{F}, \dot{\mathbf{F}}, \theta, \mathbf{g}_k),$$
$$\mathbf{q}_k = \hat{\mathbf{q}}_k (\mathbf{F}, \dot{\mathbf{F}}, \theta, \mathbf{g}_k),$$
$$\mathbf{\varepsilon} = \hat{\mathbf{\varepsilon}} (\mathbf{F}, \dot{\mathbf{F}}, \theta, \mathbf{g}_k),$$
$$\eta = \hat{\eta} (\mathbf{F}, \dot{\mathbf{F}}, \theta, \mathbf{g}_k),$$
$$\Phi_k = \hat{\Phi}_k (\mathbf{F}, \dot{\mathbf{F}}, \theta, \mathbf{g}_k),$$

(8)
where $\dot{F}$ is time derivative of the deformation gradient, $\varepsilon$ is the specific internal energy, $g_\kappa = \nabla \theta$ is temperature gradient, $\theta$ is an empirical temperature, which is some convenient measure of the hotness (or coldness) of the thermodynamic state. Note that the density field $\rho(X, t)$ is completely determined by the motion $x(X, t)$ and the density $\rho_\kappa(X)$ in the reference configuration. Therefore, the thermodynamic process is defined as the solution

$$\{x(X, t), \theta(X, t)\}$$

of the field equations (the balance laws of the linear momentum and energy) and integration of the constitutive relations for $T_\kappa, q_\kappa$ and $\varepsilon$.

The determination of the restrictions imposed on the constitutive functions by the entropy principle is one of the major objectives in modern continuum thermodynamics.

### 2.1 Method of Lagrange Multipliers

According to the entropy principle, there exist Lagrange multipliers $\Lambda^v$ conjugated to the momentum balance equation and $\Lambda^\varepsilon$ conjugated to the energy balance equation which depend on the state variables, such that the inequality

$$\rho_\kappa \dot{\eta} + \text{Div} \Phi_\kappa - \Lambda^v \cdot (\rho_\kappa \ddot{x} - \text{Div} T_\kappa) - \Lambda^\varepsilon (\rho_\kappa \dot{\varepsilon} + \text{Div} q_\kappa - T_\kappa \cdot \dot{F}) \geq 0$$

is valid under no additional constraints, i.e., valid for any field $x(X, t), \theta(X, t)$.

Further, we invoke the condition of material objectivity, which implies the following reduced constitutive equations for viscoelastic materials

$$T_\kappa = \hat{T}_\kappa (C, \dot{C}, \theta, g_\kappa),$$
$$q_\kappa = \hat{q}_\kappa (C, \dot{C}, \theta, g_\kappa),$$
$$\varepsilon = \hat{\varepsilon} (C, \dot{C}, \theta, g_\kappa),$$
$$\eta = \hat{\eta} (C, \dot{C}, \theta, g_\kappa),$$
$$\Phi_\kappa = \hat{\Phi}_\kappa (C, \dot{C}, \theta, g_\kappa),$$

where $C = F^T F$ is the right Cauchy–Green tensor.

Since the inequality (10) must hold for any $x(X, t)$ and $\theta(X, t)$, the values of $\{\theta, g_\kappa, C, \dot{C}\}$ and $\{\dot{\theta}, \ddot{x}, \dot{g}_\kappa, \dot{C}, \nabla g_\kappa, \nabla C, \nabla \dot{C}\}$ in (10) can have arbitrary values at any point and any instant.

First, note that (10) is linear with respect to $\ddot{x}$. Consequently, $\rho_\kappa \Lambda^v$ the coefficient of $\ddot{x}$ must be equal to zero, i.e.,

$$\Lambda^v = 0.$$  

Thus, (10) becomes

$$\rho_\kappa \dot{\eta} + \text{Div} \Phi_\kappa - \Lambda^\varepsilon \rho_\kappa \dot{\varepsilon} + \Lambda^\varepsilon \text{Div} q_\kappa - \Lambda^\varepsilon T_\kappa \cdot \dot{F} \geq 0$$
Next, we consider terms in
\[ \dot{\eta} - \Lambda^\varepsilon \dot{\varepsilon} = \left( \frac{\partial \eta}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta} \right) \dot{\theta} + \left( \frac{\partial \eta}{\partial g_\kappa} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial g_\kappa} \right) \cdot \dot{g}_\kappa \\
+ \left( \frac{\partial \eta}{\partial C} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial C} \right) \cdot \dot{C} + \left( \frac{\partial \eta}{\partial \dot{C}} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \dot{C}} \right) \cdot \ddot{C} \quad (14) \]

\[ \text{Div} \Phi_\kappa - \Lambda^\varepsilon \text{Div} q_\kappa = \left( \frac{\partial \Phi_\kappa}{\partial \theta} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial \theta} \right) \cdot g_\kappa + \left( \frac{\partial \Phi_\kappa}{\partial g_\kappa} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial g_\kappa} \right) \cdot \nabla g_\kappa \\
+ \left( \frac{\partial \Phi_\kappa}{\partial C} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial C} \right) \cdot \nabla C + \left( \frac{\partial \Phi_\kappa}{\partial \dot{C}} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial \dot{C}} \right) \cdot \nabla \dot{C} \quad (15) \]

Note that the term
\[ \left( \frac{\partial \Phi_\kappa}{\partial g_\kappa} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial g_\kappa} \right) \cdot \nabla g_\kappa \]
in component form reads as
\[ \left( \frac{\partial \Phi_\kappa}{\partial g_\kappa} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial g_\kappa} \right) \cdot \nabla g_\kappa = \left( \frac{\partial \Phi_\kappa}{\partial \theta, L} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial \theta, L} \right) \cdot \theta, L \kappa. \]

The other terms in the Eq. (15) have equivalent component forms.

After substituting (14) and (15) into (13), by inspection, we conclude that this inequality is also linear with respect to the following derivatives \( \{ \dot{\theta}, \dot{\bar{x}}, \dot{g}_\kappa, \ddot{C}, \nabla g_\kappa, \nabla C, \nabla \dot{C} \} \).

As the inequality must hold for arbitrary fields, we have eliminated the constraints imposed by the field equations. The coefficients of the above derivatives must vanish identically. Otherwise, we could choose the fields in such a way that one negative term would dominate all others and the inequality would be violated. Hence, we obtain the following equations

\[ \Lambda^v = 0 \]
\[ \frac{\partial \eta}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta} = 0 \]
\[ \frac{\partial \eta}{\partial g_\kappa} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial g_\kappa} = 0 \]
\[ \frac{\partial \eta}{\partial C} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial C} = 0 \]
\[ \left( \frac{\partial \Phi_\kappa}{\partial g_\kappa} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial g_\kappa} \right) \cdot \nabla g_\kappa = \left( \frac{\partial \Phi_\kappa}{\partial \theta, L} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial \theta, L} \right) \cdot \theta, L \kappa. \]
\[ \frac{\partial \Phi_\kappa}{\partial C} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial C} = 0 \]
\[ \frac{\partial \Phi_\kappa}{\partial \dot{C}} - \Lambda^\varepsilon \frac{\partial q_\kappa}{\partial \dot{C}} = 0 \quad (17) \]
Then, the entropy inequality (13) reduces to
\[
\left( \frac{\partial \Phi_k}{\partial \theta} - \Lambda^e \frac{\partial q_k}{\partial \theta} \right) \cdot g_k + \rho_k \left( \frac{\partial \eta}{\partial C} - \Lambda^e \frac{\partial \varepsilon}{\partial C} \right) \cdot \dot{\dot{C}} + \Lambda^e T_k \cdot \dot{F} \geq 0 \tag{18}
\]
Making use of second Piola–Kirchhoff tensor \( S_k = F^{-1} T_k = J F^{-1} T F^{-T} \) and the right Cauchy–Green tensor \( \dot{C} = \dot{F}^T F + F^T \dot{F} = 2(\ddot{F}^T F)_{\text{sym}} \) (which are symmetric tensors), the inequality (18) can be written in a more compact form as:
\[
\sigma = \left( \frac{\partial \Phi_k}{\partial \theta} - \Lambda^e \frac{\partial q_k}{\partial \theta} \right) \cdot g_k + \rho_k \left( \frac{\partial \eta}{\partial C} - \Lambda^e \frac{\partial \varepsilon}{\partial C} + \frac{1}{2 \rho_k} \Lambda^e S_k \right) \cdot \dot{C} \geq 0 \tag{19}
\]
where \( \sigma \) is entropy production density. Moreover, from (16) we obtain
\[
\frac{d \eta}{dt} - \Lambda^e \frac{d \varepsilon}{dt} = \left( \frac{\partial \eta}{\partial C} - \Lambda^e \frac{\partial \varepsilon}{\partial C} \right) \cdot \frac{d \dot{C}}{dt}
\]
\[
\frac{d \eta}{dt} = \Lambda^e \frac{d \varepsilon}{dt} + \left( \frac{\partial \eta}{\partial C} - \Lambda^e \frac{\partial \varepsilon}{\partial C} \right) \cdot \frac{d \dot{C}}{dt} \tag{20}
\]
which has the form of the thermostatic Gibbs relation.

3 Entropy Flux Relation for Viscoelastic Materials

For further evaluation of the consequences of the entropy principle, particularly in connection with relations (17), we invoke the material symmetry condition that has to be satisfied by \{\varepsilon, T_k, q_k, \Phi_k, \eta\} for isotropic viscoelastic bodies. For instance, this condition for heat flux can be expressed as:
\[
\dot{q}_k\left( QCQ^T, Q\dot{C}Q^T, \theta, Qg_k \right) = Q \dot{q}_k\left( C, \dot{C}, \theta, g_k \right), \forall Q \in O \tag{21}
\]
where \( O \) is the full orthogonal group. Note that \( \dot{q}_k \) is an isotropic vector-valued function of \{\( C, \dot{C}, \theta, g_k \)\} and that (21) imposes restriction on its form. After a lengthy calculation starting from (15), Liu [13] proved that the following entropy flux relation holds
\[
\Phi_k = \Lambda^e(C, \dot{C}, \theta, g_k)q_k \tag{22}
\]
Further, based on (22) and (17), I-Shih Liu concluded that \( \Lambda^e \) must be independent of \( C, \dot{C} \) and \( g_k \). Thus,
\[
\Lambda^e = \Lambda^e(\theta). \tag{23}
\]
Accordingly, (20) becomes
\[
\frac{d \eta}{dt} = \Lambda^e \frac{d \varepsilon}{dt} + \frac{\partial}{\partial C}(\eta - \Lambda^e \varepsilon) \cdot \frac{d \dot{C}}{dt}
\]
or

\[ \text{d} \eta = \Lambda^e \left( \text{d} \varepsilon - \frac{\partial \psi}{\partial \mathbf{C}} \cdot \text{d} \mathbf{C} \right) \]

where

\[ \psi = \varepsilon - \frac{\eta}{\Lambda^e} \]  

(24)

By comparison with the classical Gibbs relation in thermostatics, the function \( \Lambda^e \) can be identified as the reciprocal of the absolute temperature \( \theta \), i.e.,

\[ \Lambda^e = \frac{1}{\theta} \]  

(25)

which leads to the classical entropy flux relation (2).

Consequently, one can come to the conclusion that, following I-Shih Liu’s procedure for viscoelastic bodies outlined above, that for isotropic elastic materials with state variables (\( \mathbf{F}, \theta, \mathbf{g}_\kappa \)) the relation (25) holds.

### 3.1 Entropy Flux of Anisotropic Elastic Materials

In this subsection, the derivation of the relation between the entropy flux and the heat flux for anisotropic materials with state variables (\( \mathbf{F}, \theta, \mathbf{g}_\kappa \)) is considered. In this case, the requirements (16) and (17) reduce to (26) and (27), respectively.

\[ \frac{\partial \eta}{\partial \theta} - \Lambda^e \frac{\partial \varepsilon}{\partial \theta} = 0, \]

\[ \frac{\partial \eta}{\partial \mathbf{g}_\kappa} - \Lambda^e \frac{\partial \varepsilon}{\partial \mathbf{g}_\kappa} = 0, \]  

(26)

\[ \left( \frac{\partial \Phi_\kappa}{\partial \mathbf{g}_\kappa} - \Lambda^e \frac{\partial \mathbf{q}_\kappa}{\partial \mathbf{g}_\kappa} \right)_{\text{sym}} = 0, \]

\[ \frac{\partial \Phi_\kappa}{\partial \mathbf{C}} - \Lambda^e \frac{\partial \mathbf{q}_\kappa}{\partial \mathbf{C}} = 0. \]  

(27)

In addition, the material symmetry condition for anisotropic elastic bodies has to be satisfied by \( \{ \varepsilon, \mathbf{T}_\kappa, \mathbf{q}_\kappa, \Phi_\kappa, \eta \} \).

The first paper considering entropy flux for transversely isotropic elastic bodies, was published by Liu [14], which relies on his paper [18]. In this, anisotropic materials properties in preferential directions were characterized by a number of unit vectors \( \mathbf{m}_1, \ldots, \mathbf{m}_n \) and tensors \( \mathbf{M}_1, \ldots, \mathbf{M}_b \). Ig \( g \) is a group of transformations which preserve these characteristics, i.e.,

\[ g = \left\{ \mathbf{Q} \in G; \quad \mathbf{Q} \mathbf{m} = \mathbf{m}, \quad \mathbf{Q} \mathbf{M} \mathbf{Q}^T = \mathbf{M} \right\}, \]
where \( G \) is a subgroup of \( O \) the full orthogonal group, \( m = (m_1, \ldots, m_a) \) and \( M = (M_1, \ldots, M_b) \).

In other words, \( g \) is characterized by the set \((m, M)\) and the group \( G \in O \), i.e.,

\[
g = (G; m, M). \tag{28}
\]

**Theorem 1** A function \( f(v, A) \) is invariant to \( g \) if and only if it can be represented by

\[
f(v, A) = \hat{f}(v, A, m, M), \tag{29}
\]

where \( \hat{f}(v, A, m, M) \) is invariant relative to \( G \).

Here, \( v \) is a vector, \( A \) is a second-order tensor and \( f \) is either scalar-valued, vector-valued or tensor-valued function. Particularly, if \( \hat{f}(v, A, m, M) \) is an isotropic function then:

- for a scalar-valued function
  \[
  \hat{f}(Qv, QAQ^T, Qm, QMQ^T) = \hat{f}(v, A, m, M),
  \]

- for a vector-valued function
  \[
  Q\hat{f}(v, A, m, M) = \hat{f}(Qv, QAQ^T, Qm, QMQ^T),
  \]

- and for a tensor-valued function
  \[
  Q\hat{f}(v, A, m, M)Q^T = \hat{f}(Qv, QAQ^T, Qm, QMQ^T).
  \]

In the same paper, I-Shih Liu gives a list of 14 such groups \( g \) for some crystal classes. He uses the following notation:

- \( n_i, i = 1, 2, 3 \) where \( n_i \) are orthonormal vectors, i.e.,
  \[
  n_i \cdot n_j = \delta_{ij}. \tag{30}
  \]

\( N_i \) are skew-symmetric tensors defined by

\[
N_i = e_{ijk}n_j \otimes n_k, \quad i, j, k = 1, 2, 3. \tag{31}
\]

In order to write the exact form of the constitutive functions used in our further investigation, we need several functional relations particularly among \( n_i \) and \( N_i \). These basic relations are given in “Appendix.”

Liu [14] considered only two different classes of transversally isotropic bodies

\[
g_2 = (O; Qn_1 = n_1),
\]

\[
g_5 = \left( O; Qn_1 \otimes n_1 Q^T = n_1 \otimes n_1 \right).
\]
where \( \mathbf{n}_1 \) is the preferred direction of transverse isotropy.

In applying the isotropic representation of constitutive functions, instead of the Cauchy–Green strain tensor \( \mathbf{C} \), he used the Green–St. Venant strain tensor \( \mathbf{E} \), i.e.,

\[
\mathbf{E} = \frac{1}{2}(\mathbf{C} - \mathbf{I})
\]

which vanishes when there is no deformation and considers constitutive functions \( q_κ \) and \( \Phi_κ \) of \((\mathbf{E}, θ, \mathbf{g}_κ)\) up to bilinear terms in \( \mathbf{E} \) and \( \mathbf{g}_κ \), i.e.,

\[
\begin{align*}
q_κ &= (a_1 + a_2 \text{tr} \mathbf{E} + a_3 \mathbf{n} \cdot \mathbf{E} \mathbf{n})\mathbf{g}_κ + a_4 \mathbf{E} \mathbf{g}_κ + b_1 \mathbf{n} \otimes \mathbf{n} + c_1 \mathbf{n} \cdot \mathbf{E} \mathbf{n} + d_1 \\
\Phi_κ &= (β_1 + β_2 \text{tr} \mathbf{E} + β_3 \mathbf{n} \cdot \mathbf{E} \mathbf{n})\mathbf{g}_κ + β_4 \mathbf{n} \otimes \mathbf{n} + γ_1 \mathbf{n} \cdot \mathbf{E} \mathbf{n} + d_2
\end{align*}
\]

where all the material coefficients are functions of the temperature \( θ \) only.

For the class of transversally isotropic bodies defined by \( g_2 = (O; \mathbf{Qn}_1 = \mathbf{n}_1) \),

he was able to prove that \( Λ^ε \) is a function of the temperature only, i.e.,

\[
Λ^ε = Λ^ε(θ) = \frac{1}{θ}.
\]

Further, he obtained the entropy flux and the heat flux relation as:

\[
\Phi_κ = \frac{1}{θ} q_κ + k(θ)\mathbf{n}_1. \tag{32}
\]

Therefore, for this class of transversally isotropic bodies, the classical result does not hold in general.

For the class of transversally isotropic bodies defined by \( g_5 = (O; \mathbf{Qn}_1 \otimes \mathbf{n}_1 \mathbf{Q}^T = \mathbf{n}_1 \otimes \mathbf{n}_1) \),

he obtained

\[
Λ^ε = \frac{1}{θ}, \quad Φ_κ = \frac{1}{θ} q_κ, \tag{33}
\]

which is identical to the classical result (2).

For these cases, a functional form of \( Λ^ε \) had to be found first to determine the relation between entropy flux and heat flux. It appears that \( Λ^ε = Λ^ε(θ) \) holds in
all these cases, i.e., $\Lambda^\varepsilon = \Lambda^\varepsilon(\theta)$ is a necessary condition for the determination of a
relation between the entropy flux and the heat flux.

This is where we pose the question whether this is sufficient condition? Having this
in mind, we proceed first by re-examining the above cases.

This assumption differs substantially from Green and Laws [19], as well as from
Hutter [20] and Bargmann and Steinmann [21]. In Green and Laws [19], the entropy
flux and heat flux relationships are defined as $\Phi_\kappa = \frac{1}{\varphi} q_\kappa$, where $\varphi$ is a constitutive
function which reduces to the absolute temperature $\theta$ in equilibrium. Hutter [20]
postulated the classical entropy flux heat flux relation. In their contribution, Bargmann
and Steinmann [21] adopted the Green and Naghdi approach for non-classical theory
of thermos-elasticity for isotropic materials and to obtain the entropy flux–heat flux
relation (4).The consequence of the assumption that Lagrange multiplier conjugated
to the energy balance equation is function of temperature only $\Lambda^\varepsilon = \Lambda^\varepsilon(\theta)$.

Eringen stated [22] that “it is always possible to express the entropy change as a
sum of entropy flux and entropy source as”

$$\Phi = \frac{1}{\theta} q + \Phi_1$$  \hspace{1cm} (34)

where $\Phi_1$ is the entropy change due to all other effects except heat input.

In our consideration, we do not use Eringen’s postulate and do not make any assump-
tion about the entropy flux relation. The only assumption used in our derivation is that
Lagrange multiplier $\Lambda^\varepsilon$ is a function of temperature $\theta$ only, i.e., $\Lambda^\varepsilon = \Lambda^\varepsilon(\theta)$. The
implication of this assumption for isotropic viscoelastic bodies is considered first. In
this, the starting point is the set of Eq. (17) which are restated below

$$\left( \frac{\partial \Phi_{\kappa}}{\partial g_{\kappa}} - \Lambda^\varepsilon \frac{\partial q_{\kappa}}{\partial g_{\kappa}} \right)_{\text{sym}} = 0$$
$$\frac{\partial \Phi_{\kappa}}{\partial C} - \Lambda^\varepsilon \frac{\partial q_{\kappa}}{\partial C} = 0$$
$$\frac{\partial \Phi_{\kappa}}{\partial C} - \Lambda^\varepsilon \frac{\partial q_{\kappa}}{\partial C} = 0$$  \hspace{1cm} (35)

Let us introduce a new variable $k = \Phi_{\kappa} - \Lambda^\varepsilon q_{\kappa}$. Recall that $\Phi_{\kappa} = \hat{f}_{\kappa}(C, \dot{C}, \theta, g_{\kappa})$
and $q_{\kappa} = \hat{q}_{\kappa}(C, \dot{C}, \theta, g_{\kappa})$, consequently $k = \hat{k}(C, \dot{C}, \theta, g_{\kappa})$. Using $k$, Eq. (35) can
be written as:

$$\left( \frac{\partial k_{\kappa}}{\partial g_{\kappa}} \right)_{\text{sym}} = 0$$
$$\frac{\partial k_{\kappa}}{\partial C} = 0$$
$$\frac{\partial k_{\kappa}}{\partial C} = 0$$  \hspace{1cm} (36)
Thus, $\mathbf{k} = \dot{\mathbf{k}}(\theta, \mathbf{g}_\kappa)$ and the set of Eq. (36) reduces to

$$
\left( \frac{\partial \mathbf{k}}{\partial \mathbf{g}_\kappa} \right)_{\text{sym}} = 0
$$

(37)

For clarity reasons, the following few steps are written in index notation or component notation. Equation (37) when written in component form is

$$
\frac{\partial k_i}{\partial g_j} + \frac{\partial k_j}{\partial g_i} = 0
$$

where $k_i$ and $g_i$ are components of vectors $\mathbf{k}$ and $\mathbf{g}_\kappa$, respectively. Differentiation of (37) with respect to $\mathbf{g}_\kappa$ yields

$$
\frac{\partial^2 k_p}{\partial g_r \partial g_q} + \frac{\partial^2 k_q}{\partial g_r \partial g_p} = 0
$$

The remaining two relations obtained by cyclic index permutation are

$$
\frac{\partial^2 k_q}{\partial g_p \partial g_r} + \frac{\partial^2 k_r}{\partial g_p \partial g_q} = 0
$$

$$
\frac{\partial^2 k_r}{\partial g_q \partial g_p} + \frac{\partial^2 k_p}{\partial g_q \partial g_r} = 0
$$

From them, we have

$$
\frac{\partial^2 k_p}{\partial g_r \partial g_q} = 0
$$

The solution of this simple set of differential equations is

$$
k_p = A_{pq}(\theta)g_q + a_p(\theta), \quad A_{(pq)} = 0
$$

This solution can be rewritten, using symbolic notation, as:

$$
\mathbf{k}(\theta, \mathbf{g}_\kappa) = A(\theta)\mathbf{g}_\kappa + \mathbf{a}(\theta)
$$

(38)

where $A(\theta)$ is skew symmetric. Since we are dealing with isotropic viscoelastic bodies, $\mathbf{k}(\theta, \mathbf{g}_\kappa)$ must be a vector-valued isotropic function. Thus

$$
\mathbf{Qk}(\theta, \mathbf{g}_\kappa) = \mathbf{k}(\theta, \mathbf{Qg}_\kappa)
$$

(39)

must hold for all $\mathbf{Q} \in \mathcal{O}$ and an arbitrary $\mathbf{g}_\kappa$. Equivalently, (39) can be restated as:

$$
\mathbf{QA}(\theta)\mathbf{g}_\kappa + \mathbf{Qa}(\theta) = \mathbf{A}(\theta)\mathbf{Qg}_\kappa + \mathbf{a}(\theta)
$$

(40)

Particularly, for the case of $\mathbf{Q} = -\mathbf{I}$, it follows that $\mathbf{a}(\theta) = 0$ and consequently (40) reduces to

$$
\mathbf{QA}(\theta)\mathbf{g}_\kappa = \mathbf{A}(\theta)\mathbf{Qg}_\kappa
$$

(41)
which can be rewritten as:

\[ QA(\theta)Q^T Q_{g_k} = A(\theta)Q_{g_k} \]  

(42)

Since (42) must hold for all \( Q \in O \) and an arbitrary \( g_k \), we have that

\[ QA(\theta)Q^T = A(\theta) \]  

(43)

since \( A(\theta) \) is skew symmetric, only \( A(\theta) = 0 \) satisfies (43), and

\[ k = \Phi_k - \Lambda^\epsilon q_k = 0 \]  

(44)

This result is identical to Liu’s [13] for isotropic viscoelastic bodies, which validates the new procedure and led to its application to the anisotropic materials considered below. It is important to observe that the assumption \( \Lambda^\epsilon = \Lambda^\epsilon(\theta) \) significantly simplifies and shortens the procedure.

### 3.2 Entropy Flux Relation for Anisotropic Elastic Materials in General

This section considers anisotropic bodies characterized with

\[ g = \left\{ Q \in O; \ Qm = m, \ QMQ^T = M \right\} \]  

(45)

In other words, \( g \) comprises the set \( (m, M) \) and the group \( O \), i.e., \( g = (O; \ m, \ M) \). Consequently,

\[ k = \hat{k}(\theta, g_k, m, M) = A(\theta, m, M)g_k + a(\theta, m, M) \]  

(46)

is isotropic vector-valued function, i.e.,

\[ Qk(\theta, g_k, m, M) = k(\theta, Qg_k, Qm, QMQ^T) \]  

(47)

or

\[ QA(\theta, m, M)g_k + Qa(\theta, m, M) = A(\theta, Qm, QMQ^T)Qg_k + a(\theta, Qm, QMQ^T) \]  

(48)

which must hold for all \( Q \in O \) and arbitrary \( g_k \). Particularly, for \( g_k = 0 \), we have

\[ Qa(\theta, m, M) = a(\theta, Qm, QMQ^T) \]  

(49)

i.e., \( a(\theta, m, M) \) is vector-valued isotropic function of its arguments. Moreover,

\[ QA(\theta, m, M)g_k = A(\theta, Qm, QMQ^T)Qg_k \]  

(50)

or
\[
\mathbf{QA}(\theta, \mathbf{m}, \mathbb{M})\mathbf{Q}^T \mathbf{g}_\kappa = \mathbf{A}(\theta, \mathbf{Qm}, \mathbb{M}\mathbf{Q}^T)\mathbf{Q}_\kappa.
\]

This must hold for all \( \mathbf{Q} \in \mathcal{O} \), and hence
\[
\mathbf{QA}(\theta, \mathbf{m}, \mathbb{M})\mathbf{Q}^T = \mathbf{A}(\theta, \mathbf{m}, \mathbb{M})\mathbf{Q}^T = \mathbf{A}(\theta, \mathbf{Qm}, \mathbb{M}\mathbf{Q}^T),
\]
\[(51)\]
i.e., \( \mathbf{A}(\theta, \mathbf{m}, \mathbb{M}) \) is skew-symmetric tensor-valued isotropic function of its arguments.

For vector-valued and skew-symmetric tensor-valued isotropic functions in \( \mathbb{R}^3 \) see Smith [23] and Spencer [24]. All groups of crystal classes given by Liu [18] are considered below.

### 3.3 Transversally Isotropic Material Bodies

In this section, we consider transversely isotropic material bodies divided into four cases. The cases (a) characterized by \( g_2 = (\mathcal{O}; \mathbf{n}_1) \) and the case (b) characterized by \( g_5 = (\mathcal{O}; \mathbf{n}_1 \otimes \mathbf{n}_1) \) were selected in order to validate the proposed procedure against the results obtained by Liu [14] for the same materials. The results for the cases (c) characterized by \( g_1 = (\mathcal{O}; \mathbf{n}_1, \mathbf{N}_1) \) and (d) characterized \( g_1 = (\mathcal{O}; \mathbf{n}_1, \mathbf{N}_1) \) are new and, to the best of our knowledge, not available in the published literature.

(a) transversally isotropic bodies with group symmetry \( g_2 = (\mathcal{O}; \mathbf{n}_1) \).

In this case,
\[
\mathbf{k} = \mathbf{k}(\theta, \mathbf{g}_\kappa, \mathbf{n}_1) = \mathbf{A}(\theta, \mathbf{n}_1)\mathbf{g}_\kappa + \mathbf{a}(\theta, \mathbf{n}_1)
\]
\[(52)\]
where the following must hold
\[
\mathbf{Qa}(\theta, \mathbf{n}_1) = \mathbf{a}(\theta, \mathbf{Qn}_1),
\]
\[(53)\]
i.e., \( \mathbf{a}(\theta, \mathbf{n}_1) \) is vector-valued function which can be expressed as
\[
\mathbf{a}(\theta, \mathbf{n}_1) = \lambda(\theta)\mathbf{n}_1
\]
\[(54)\]
where \( \lambda(\theta) \) is an arbitrary scalar function. Further,
\[
\mathbf{QA}(\theta, \mathbf{n}_1)\mathbf{Q}^T = \mathbf{A}(\theta, \mathbf{Qn}_1)
\]
\[(55)\]
Thus, \( \mathbf{A}(\theta, \mathbf{n}_1) \) is skew-symmetric tensor-valued isotropic function. Consequently, \( \mathbf{A} = \mathbf{0} \) (see Smith [23]). In this case,
\[
\mathbf{k} = \Phi_\kappa - \Lambda^\kappa \mathbf{q}_\kappa = \lambda(\theta)\mathbf{n}_1.
\]
\[(56)\]
Moreover,
\[
\lambda(\theta) = (\Phi_\kappa - \Lambda^\kappa \mathbf{q}_\kappa)|_{\mathbb{C} = \mathbb{I}, \mathbf{g}_\kappa = \mathbf{0}} \cdot \mathbf{n}_1
\]
\[(57)\]
where $C = I$ implies that there is no deformation and $g_c = 0$ implies that there is no temperature gradient. The result (57) agrees with I-Shih Liu’s result for transversally isotropic bodies with group symmetry group $g_2$ [14].

(b) transversally isotropic bodies with group symmetry $g_5 = (O; n_1 \otimes n_1)$.

In this case,

$$k(\theta, n_1 \otimes n_1, g_c) = A(\theta, n_1 \otimes n_1) g_c + a(\theta, n_1 \otimes n_1)$$

(58)

where $a(\theta, n_1 \otimes n_1)$ and $A(\theta, n_1 \otimes n_1)$, as isotropic functions, must vanish, resulting in

$$k = \Phi - \Lambda^e q_k = 0.$$  

(59)

The result (59) agrees with I-Shih Liu’s result for transversally isotropic bodies with group symmetry group $g_5$ [14].

Therefore, for the above cases, we demonstrated that $\Lambda^e = \Lambda^e(\theta)$ is not only a necessary but also a sufficient condition to determine the entropy flux–heat flux relation.

To demonstrate the generality of the proposed procedure, we consider the other crystal classes for which representation of anisotropic invariants is given by Liu [18]. Note, in all these cases, representations of anisotropic invariant function are obtained using the tables for isotropic functions. This more general entropy principle delivers relations which are the same as those obtained by the Clausius–Duhem inequality and hold for all materials in classical thermodynamics. Heuristically, we do not see any physically based objection which would contradict the possibility that $\Lambda^e$ could be different to $\Lambda^e = \Lambda^e(\theta)$ for crystal classes from G3 to G14. It is also in accordance with assumption given by Hutter [25], p. 211, who demonstrated that $\Lambda^e(\theta)$ is independent of the material properties for the heat conducting compressible fluids.

Further, this could be related to the statement by Ingo Muller and Tommaso Ruggeri in relation to extended thermodynamics: “Physicists firmly believe that the differential equations of nature should be hyperbolic so as to exclude action at a distance. This incompatibility between the expectation of the physicist and the classical laws of thermodynamics has prompted the formulation of extended thermodynamics”.

In addition, we do not see any physical reason that $\Lambda^e$ would have a different form to $\Lambda^e = \Lambda^e(\theta)$ for these crystal classes.

The result for the following cases is new (to the best of our knowledge not available in the published literature).

(c) transversally isotropic bodies with group symmetry $g_1 = (O; n_1, N_1)$.

In this case,

$$k = \hat{k}(\theta, g_c, n_1, N_1) = A(\theta, n_1, N_1) g_c + a(\theta, n_1, N_1)$$

(60)
Here and in what follows, we use particularly the representation formulae \((2.41), (4.2), (4.3), (4.6), (4.7)\) given by Smith [23] (see also Liu [18], Wilmanski [26]) for vector-valued isotropic function and skew-symmetric tensor-valued function of their arguments. We strictly apply these formulae for the vector function \(a(\theta, \mathbf{n}_1, \mathbf{N}_1)\) and a skew-symmetric tensor-valued function \(A(\theta, \mathbf{n}_1, \mathbf{N}_1)\). Their scalar invariant functions are always functions of \(\theta\). Therefore, we must find the basis invariants of the set \((\mathbf{n}_1, \mathbf{N}_1)\). They are
\[
\begin{align*}
n_1 \cdot n_1 \\
\text{tr} \Lambda_1^n \\
n_1 \cdot N_1^2 n_1
\end{align*}
\] (61)
The generator of the set \((\mathbf{n}_1, \mathbf{N}_1)\) for \(a(\theta, \mathbf{n}_1 \otimes n_1)\) is \(n_1\), and consequently, \(a = \lambda(\theta)n_1\). The generator of the set \((\mathbf{n}_1, \mathbf{N}_1)\) for \(A(\theta, \mathbf{n}_1, \mathbf{N}_1)\) is \(N_1\) and, accordingly, \(A(\theta, \mathbf{n}_1, \mathbf{N}_1) = \mu(\theta)N_1\).
Thus,
\[
k = \Phi_\kappa - \Lambda^\kappa q_\kappa = -\mu(\theta)N_1 g_\kappa + \lambda(\theta)n_1
\]
\[
= \mu(\theta)n_1 \times g_\kappa + \lambda(\theta)n_1.
\] (62)
(d) transversally isotropic bodies with group symmetry \(g_3 = (O; N_1)\).
In this case,
\[
k = \Phi_\kappa - \Lambda^\kappa q_\kappa = \mu(\theta)n_1 \times g_\kappa
\] (63)
3.3.1 Orthotropic Material Bodies
This section considers anisotropic bodies characterized with group symmetry \(g_6 = (O; n_1 \otimes n_1, n_2 \otimes n_2)\). The basis of invariants for \((\theta, \mathbf{n}_1 \otimes n_1, \mathbf{n}_2 \otimes n_2)\) are functions only of \(\theta\) (see Smith [23] and the “Appendix”). There are no generators for \(a(\theta, \mathbf{n}_1 \otimes n_1, \mathbf{n}_2 \otimes n_2)\), i.e., \(a(\theta, \mathbf{n}_1 \otimes n_1, \mathbf{n}_2 \otimes n_2) = 0\) and \(A(\theta, \mathbf{n}_1 \otimes n_1, \mathbf{n}_2 \otimes n_2) = 0\).
Thus
\[
k = \Phi_\kappa - \Lambda^\kappa q_\kappa = 0
\] (64)
3.3.2 Triclinic System
(a) Predial class characterized with group symmetry \(g_7 = (O; n_1, n_2, n_3)\). For this class, there are no invariants of \((O; n_1, n_2, n_3)\). Generators for \(a(\theta, \mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3)\) are \(n_1, n_2\) and \(n_3\). Thus, \(a(\theta, n_1, n_2, n_3) = \lambda(\theta)n_1 + \mu(\theta)n_2 + \nu(\theta)n_3\). Generators for \(A(\theta, \mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3)\) are \(n_1 \times n_2 - n_2 \times n_1, n_2 \times n_3 - n_3 \times n_2\) and \(n_3 \times n_1 - n_1 \times n_3\). Thus,
\[
A(\theta, n_1, n_2, n_3) = -p(\theta)(n_1 \otimes n_2 - n_2 \otimes n_1)
\]
$$\begin{align*}
- q(\theta)(n_2 \otimes n_3 - n_3 \otimes n_2) - r(\theta)(n_3 \otimes n_1 - n_1 \otimes n_3) \\
= -p(\theta)N_3 - q(\theta)N_1 - r(\theta)N_2
\end{align*}$$

and consequently

$$\begin{align*}
k = \Phi_\kappa - \Lambda^\kappa q_\kappa &= [p(\theta)n_3 + q(\theta)n_1 + r(\theta)n_2] \times g_\kappa \\
&\quad + \lambda(\theta)n_3 + \mu(\theta)n_1 + v(\theta)n_2
\end{align*}$$

(65)

(b) Pinacoidal class characterized with group symmetry $g_8 = (O; N_1, N_2)$. For this class, there are no invariants and no generators for $a(\theta, N_1, N_2)$, i.e., $a = 0$. Generators for $A(\theta, N_1, N_2)$ are $N_1, N_2$ and $N_1N_2 - N_2N_1 = -N_3$. Thus

$$\begin{align*}
k &= \Phi_\kappa - \Lambda^\kappa q_\kappa = [-p(\theta)N_3 - q(\theta)N_1 - r(\theta)N_2]g_\kappa \\
&= [p(\theta)n_3 + q(\theta)n_1 + r(\theta)n_2] \times g_\kappa
\end{align*}$$

(66)

3.3.3 Monoclinic System

(a) Domatic class characterized with group symmetry $g_9 = (O; n_2, n_3)$. In the same way as in the case of the predial class, we obtain

$$\begin{align*}
k = \Phi_\kappa - \Lambda^\kappa q_\kappa &= [q(\theta)n_2 + r(\theta)n_3] \times g_\kappa + \lambda(\theta)n_2 + \mu(\theta)n_3
\end{align*}$$

(67)

(b) Sphenoidal class characterized with group symmetry $g_{10} = (O; n_1, n_2 \otimes n_2, N_1)$. For this class, there are no invariants for $a(\theta, n_1, n_2 \otimes n_2, N_1)$ and $A(\theta, n_1, n_2 \otimes n_2, N_1)$. Generator of $a(\theta, n_1, n_2 \otimes n_2, N_1)$ is $n_1$ and $a = \lambda(\theta)n_1$. Generator of $A(\theta, n_1, n_2 \otimes n_2, N_1)$ is $N_1$ and $A(\theta, n_1, n_2 \otimes n_2, N_1) = -\mu(\theta)N_1$. Therefore,

$$\begin{align*}
k &= \Phi_\kappa - \Lambda^\kappa q_\kappa = \mu(\theta)n_1 \times g_\kappa + \lambda(\theta)n_1.
\end{align*}$$

(68)

(c) Prismatic class characterized with group symmetry $g_{11} = (O; n_2 \otimes n_2, N_1)$. For this class, there are no invariants for $a(\theta, n_2 \otimes n_2, N_1)$ and $A(\theta, n_2 \otimes n_2, N_1)$. There are no generators of $a(\theta, n_2 \otimes n_2, N_1)$, thus, $a = 0$. Generator of $A(\theta, n_2 \otimes n_2, N_1)$ is $N_1$ and $A(\theta, n_2 \otimes n_2, N_1) = -\mu(\theta)N_1$. Therefore,

$$\begin{align*}
k &= \Phi_\kappa - \Lambda^\kappa q_\kappa = \mu(\theta)n_1 \times g_\kappa.
\end{align*}$$

(69)

3.3.4 Rhombic Systems

(a) Pyramidal class characterized with group symmetry $g_{12} = (O; n_1, n_2 \otimes n_2)$. For this class, there are no invariants of $a(O; n_1, n_2 \otimes n_2)$ and $A(O; n_1, n_2 \otimes n_2)$. Generator of $a(\theta, n_1, n_2 \otimes n_2)$ is $n_1$ and $a = \lambda(\theta)n_1$. There are no generators of $A(\theta, n_1, n_2 \otimes n_2)$, i.e., $A(O; n_1, n_2 \otimes n_2) = 0.$
Hence,
\[ k = \Phi_k - \Lambda^\varepsilon q_k = \lambda(\theta)n_1. \]  
(70)

(b) Dipyramidal class characterized with group symmetry \( g_{14} = g_6 = (O; n_2 \otimes n_2, n_3 \otimes n_3) \) and consequently
\[ k = \Phi_k - \Lambda^\varepsilon q_k = 0. \]  
(71)

4 The Entropy Inequality for Anisotropic Bodies

So far, we did not investigate the entropy inequality
\[ \sigma = \left( \frac{\partial \Phi_k}{\partial \theta} - \Lambda^\varepsilon \frac{\partial q_k}{\partial \theta} \right) \cdot g_k + \rho_k \left( \frac{\partial \eta}{\partial C} - \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial C} + \frac{1}{2\rho_k} \Lambda^\varepsilon S_k \right) \dot{C} \geq 0 \]  
(72)

for general anisotropic materials under the assumption that \( \Lambda^\varepsilon = \Lambda^\varepsilon(\theta) \). Making use of the free energy function \( \psi = \varepsilon - \theta \eta \), the expression for \( \sigma \) reduces to
\[ \sigma = \left( \frac{\partial \Phi_k}{\partial \theta} - \Lambda^\varepsilon \frac{\partial q_k}{\partial \theta} \right) \cdot g_k + \Lambda^\varepsilon \frac{S_k}{2} - 2\rho_k \frac{\partial \psi}{\partial C} \dot{C} \geq 0 \]  
(73)

which is linear in \( \dot{C} \). Thus,
\[ S_k = 2\rho_k \frac{\partial \psi}{\partial C} \]  
(74)

Equation (74) leads to the conclusion that all anisotropic elastic materials are hyperelastic as a consequence of \( \Lambda^\varepsilon(\theta) \), irrespective of whether the classical entropy flux relation is valid. The remaining inequality now reads
\[ \sigma = \left( \frac{\partial \Phi_k}{\partial \theta} - \Lambda^\varepsilon \frac{\partial q_k}{\partial \theta} \right) \cdot g_k \geq 0 \]  
(75)

or
\[ \sigma = \left( \frac{\partial k}{\partial \theta} + \frac{\partial \Lambda^\varepsilon}{\partial \theta} q_k \right) \cdot g_k \geq 0 \]  
(76)

where \( k = \Phi_k - \Lambda^\varepsilon q_k \). Now, from (46), we have
\[ \frac{\partial k}{\partial \theta} = \frac{\partial A(\theta, m, \mathfrak{M})}{\partial \theta} g_k + \frac{\partial a(\theta, m, \mathfrak{M})}{\partial \theta} \]  
(77)

Since \( A(\theta, m, \mathfrak{M}) \) is skew-symmetric \( g_k \cdot \frac{\partial A(\theta, m, \mathfrak{M})}{\partial \theta} g_k = 0 \), hence
\[ \frac{\partial k}{\partial \theta} \cdot g_k = \frac{\partial a(\theta, m, \mathfrak{M})}{\partial \theta} \cdot g_k \]  
(78)
Therefore (75) becomes

$$
\sigma = \left( \frac{\partial a(\theta, m, \mathcal{M})}{\partial \theta} - \frac{1}{\partial^2} q_k(C, \theta, g_k, m, \mathcal{M}) \right) \cdot g_k \geq 0 \quad (79)
$$

The nonnegative entropy production density $\sigma$ attains its minimum, which is in fact zero, when $g_k = 0$. A necessary condition for an extremum at $g_k = 0$ is

$$
\frac{\partial \sigma}{\partial g_k} \bigg|_{g_k = 0} = 0 \quad (80)
$$

or

$$
q_k(C, \theta, g_k = 0, m, \mathcal{M}) = \theta^2 \frac{\partial a(\theta, m, \mathcal{M})}{\partial \theta} \quad (81)
$$

at equilibrium.

Since Eq. (81) holds for all anisotropic elastic bodies, it can be used to define the heat flux vector at equilibrium for specific crystal classes. For instance, for transversally isotropic material bodies, considered by Liu [14], with the following group symmetries:

(a) $g_2 = (O; n_1)$ and $a(\theta, n_1) = \lambda(\theta)n_1$, where $\lambda(\theta)$ is an arbitrary scalar function, we have

$$
q_k(C, \theta, n_1, m, \mathcal{M}) = \theta^2 \frac{\partial \lambda}{\partial \theta} n_1 \quad (82)
$$

(b) $g_5 = (O; n_1 \otimes n_1)$

$$
q_k(C, \theta, 0, m, \mathcal{M}) = 0 \quad (83)
$$

And similarly, for other group symmetries investigated here, the following results hold:

$$
\begin{align*}
g_1 &= (O; n_1, N_1) : & q_k(C, \theta, 0, n_1, N_1) &= \theta^2 \frac{\partial \lambda}{\partial \theta} n_1 \\
g_2 &= (O; n_1) : & q_k(C, \theta, 0, n_1) &= \theta^2 \frac{\partial \lambda}{\partial \theta} n_1 \\
g_{10} &= (O; n_1, n_2 \otimes n_2, N_1) : & q_k(C, \theta, 0, n_1, n_2 \otimes n_2, N_1) &= \theta^2 \frac{\partial \lambda}{\partial \theta} n_1 \\
g_{12} &= (O; n_1, n_2 \otimes n_2) : & q_k(C, \theta, 0, n_1, n_2 \otimes n_2) &= \theta^2 \frac{\partial \lambda}{\partial \theta} n_1 \\
g_3 &= (O; N_1) : & q_k(C, \theta, 0, N_1) &= 0 \\
g_5 &= (O; n_1 \otimes n_1) : & q_k(C, \theta, 0, n_1 \otimes n_1) &= 0 \\
g_6 &= (O; n_1 \otimes n_1, n_2 \otimes n_2) : & q_k(C, \theta, 0, n_1 \otimes n_1, n_2 \otimes n_2) &= 0 \\
g_8 &= (O; N_1, N_2) : & q_k(C, \theta, 0, N_1, N_2) &= 0 \\
g_{11} &= (O; n_2 \otimes n_2, N_1) : & q_k(C, \theta, 0, n_2 \otimes n_2, N_1) &= 0 \\
g_{14} &= (O; n_2 \otimes n_2, n_3 \otimes n_3) : & q_k(C, \theta, 0, n_2 \otimes n_2, n_3 \otimes n_3) &= 0
\end{align*}
$$
Note, \( g_{14} = g_{6} \).

\[
g_7 = (O; \mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3) : \mathbf{q}_k(\mathbf{C}, \theta, 0, \mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3) = \frac{\mathrm{d} \mu}{\mathrm{d} \theta} \mathbf{n}_1 + \frac{\mathrm{d} v}{\mathrm{d} \theta} \mathbf{n}_2 + \frac{\mathrm{d} v}{\mathrm{d} \theta} \mathbf{n}_3
\]

\[
g_9 = (O; \mathbf{n}_2, \mathbf{n}_3) : \mathbf{q}_k(\mathbf{C}, \theta, 0, \mathbf{n}_2, \mathbf{n}_3) = \frac{\mathrm{d} \mu}{\mathrm{d} \theta} \mathbf{n}_2 + \frac{\mathrm{d} v}{\mathrm{d} \theta} \mathbf{n}_3
\]

(85)

A necessary condition that entropy production \( \sigma \) has minimum at \( \mathbf{g}_c = 0 \) is that the second derivative of \( \sigma \) with respect to \( \mathbf{g}_k \) be semi-positive, i.e.,

\[
\left. \frac{\partial^2 \sigma}{\partial g_i \partial g_j} \right|_{\mathbf{g}_c=0} \geq 0
\]

(86)

Note that \( \frac{\partial^2 \sigma}{\partial g_i \partial g_j} \) is a symmetric tensor. Using (76) and (79), it is easy to show that

\[
\left. \frac{\partial^2 \sigma}{\partial g_i \partial g_j} \right|_{\mathbf{g}_c=0} = 2 \left. \frac{\partial \Lambda^e}{\partial \theta} \frac{\partial q_i}{\partial g_j} \right|_{(i,j)\mathbf{g}_c=0} = -2 \left. \frac{1}{\theta^2} \left( \frac{\partial q_i}{\partial g_j} \right) \right|_{(i,j)\mathbf{g}_c=0} \geq 0
\]

having in mind that \( \Lambda^e = 1/\theta \).

Finally, (86) can be written as:

\[
\left. \left( \frac{\partial \mathbf{q}_k}{\partial \mathbf{g}_c} \right) \right|_{\text{sym}|\mathbf{g}_c=0} \leq 0
\]

(87)

which holds for all anisotropic elastic materials. The constraints that (87) imposes must be investigated for particular anisotropic materials. For example, for the transversely isotropic elastic materials where

\[
\mathbf{q}_k = a_0 \mathbf{g}_c + (b_0 + b_1 (\mathbf{n} \cdot \mathbf{g}_c)) \mathbf{n} + c_0 \mathbf{n} \times \mathbf{g}_c
\]

we have

\[
\left. \left( \frac{\partial \mathbf{q}_k}{\partial \mathbf{g}_c} \right) \right|_{\text{sym}|\mathbf{g}_c=0} = a_0 \mathbf{I} + b_1 \mathbf{n} \otimes \mathbf{n} \leq 0
\]

with the constraints

\[
a_0 \leq 0, \quad a_0 + b_1 \leq 0
\]

5 Conclusion

This paper revisits entropy flux and heat flux relations for isotropic and several anisotropic elastic materials. More specifically, we investigated the consequence of the assumption that Lagrange multiplier conjugated to the energy balance equation \( \Lambda^e = \Lambda(\theta) \) irrespective of validity of the classical entropy flux relation. This assumption is used to derive the relationship between the entropy flux and heat flux for all
isotropic elastic materials as well as for some crystal classes including transverse isotropy, orthotropy, triclinic systems and rhombic systems. First, we re-examined the entropy flux–heat flux relation for viscoelastic materials, isotropic elastic materials and transversely isotropic elastic bodies and demonstrated that our results agree with the results obtained by Liu [12–15, 27]. All these cases confirm that $\Lambda^e = \Lambda(\theta)$ is a necessary and sufficient condition for the determination of the entropy flux–heat flux relation.

Furthermore, we derived the entropy flux–heat flux relations, based on the assumption that $\Lambda^e = \Lambda(\theta)$, for all the following crystal classes: transverse isotropy, orthotropy, triclinic systems, monoclinic systems and rhombic systems for which representations of anisotropic functions with respect to their symmetry groups can be expressed in terms of isotropic functions. Our derivation is very general in the sense that the constitutive relations are nonlinear. One of our main results is the proof that all crystal elastic bodies, we considered, are hyperelastic. This represents a generalization of I-Shih Liu’s finding for transversely isotropic bodies, the only case he analyzed.

We would like to draw attention to the following three points:

(i) The vector function $a$ and skew-symmetric function $A$ are isotropic functions depending only on the set $(\theta, m, \mathbb{M})$ which simplifies the procedure.

(ii) Generally, the classical entropy flux–heat flux relation does not hold; it is true for all crystal classes investigated here except for $g_2, g_6 = g_{14}$.

(iii) The heat flux in the absence of a temperature gradient is not zero for all crystal classes. This confirms Eringen’s statement that $\Phi_1 = \frac{1}{\theta} q + \Phi_1$ where $\Phi_1$ is the entropy change due to all other effects except heat input.

We repeat that heuristically, we do not see any physically based objection which would contradict the possibility that $\Lambda^e$ could be different to $\Lambda^e = \Lambda^e(\theta)$ for crystal classes we considered. Of course, the assumption $\Lambda^e = \Lambda(\theta)$ and all our predictions have to be verified experimentally. This is a task for future research in collaboration with some experimentalists.

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**Appendix**

For orthonormal vectors $n_i \cdot n_j = \delta_{ij}$ and $N_i$ the skew-symmetric tensors defined by $N_i = e_{ijk}n_j \otimes n_k$, $i, j, k = 1, 2, 3$. it is easy to show that

$$n_i \otimes n_j = (n_i \otimes n_j)^n$$ for any natural number $n$,

$$N_i \mathbf{v} = -n_i \times \mathbf{v},$$

$$N_i N_j = n_i \otimes n_j - \delta_{ij} I,$$

$$N_i N_j \mathbf{v} = (n_i \cdot \mathbf{v}) n_j - \delta_{ij} \mathbf{v},$$

$$N_i^2 N_j = -\delta_{ij} N_i,$$
\[ \mathbf{w} \cdot \mathbf{N}_i \mathbf{v} = \mathbf{w} \cdot (\mathbf{v} \times \mathbf{n}_i), \]
\[ \mathbf{w} \cdot \mathbf{N}_i \mathbf{N}_j \mathbf{v} = (\mathbf{n}_i \cdot \mathbf{v})(\mathbf{n}_j \cdot \mathbf{v}) - \delta_{ij}(\mathbf{v} \cdot \mathbf{w}), \]
\[ \text{tr} \mathbf{N}_i = 0 \]
\[ \text{tr} \mathbf{N}_i \mathbf{N}_j = -2\delta_{ij} \]
\[ \mathbf{n}_i \otimes \mathbf{n}_j - \mathbf{n}_j \otimes \mathbf{n}_i = e_{ijk} \mathbf{N}_k, \]
\[ \mathbf{N}_i \mathbf{N}_j - \mathbf{N}_j \mathbf{N}_i = -e_{ijk} \mathbf{N}_k, \]

where \( \mathbf{v} \) and \( \mathbf{w} \) are arbitrary vectors.

References

1. B.D. Coleman, W. Noll, The thermodynamics of elastic materials with heat conduction and viscosity. Arch. Rational Mech. Anal. 13, 167–178 (1963)
2. A. Sellitto, V.A. Cimmelli, D. Jou, Entropy flux and anomalous axial heat transport at the nanoscale. Phys. Rev. B 87, 054302 (2013)
3. J. Serrin (ed.), New Perspectives in Thermodynamics (Springer, Berlin, 1986)
4. M. Silhavý, The Mechanics and Thermodynamics of Continuous Media (Springer, Berlin, 1997). ISBN 3-540-58378-5
5. C. Truesdell, S. Bharatha, The Concepts and Logics of Classical Thermodynamics as a Theory of Heat Engines (Springer, New York, 1977)
6. W. Muschik, Why so many “schools” of Themrodynamics?, Atti dell’Accademia Peloritana dei Pericolanti Classe di Scienze Fisiche. Mat. Nat. LXXXVI, CIS0801002 (2008)
7. I. Müller, On the entropy inequality. Arch. Ration. Mech. Anal. 26, 118–141 (1967)
8. R. Domínguez-Cascante, D. Jou, Entropy flux and Lagrange multipliers: information theory and thermodynamics. Open. Syst. Inf. Dyn. 5, 319–331 (1998)
9. G. Lebon, D. Jou, J. Casas-Vázquez, Understanding Non-equilibrium Thermodynamics (Springer, Berlin, 2008)
10. D. Jou, J. Casas-Vázquez, G. Lebon, Extended Irreversible Thermodynamics, 4th edn. (Springer, Berlin, 2010)
11. D. Jou, G. Lebon, M.S. Mongiovì, R. Peruzza, Entropy flux in non-equilibrium thermodynamics. Phys. A 338, 445–457 (2004)
12. I.-S. Liu, Method of Lagrange multipliers for exploitation of the entropy principle. Arch. Rational Mech. Anal. 46, 131–148 (1972)
13. I.-S. Liu, Entropy flux relation for viscoelastic bodies. J. Elasticity 90, 259–270 (2008)
14. I.-S. Liu, On entropy flux of transversely isotropic elastic bodies. J. Elast. 96, 97–104 (2009)
15. I.-S. Liu, Constitutive theory of anisotropic rigid heat conductors. J. Math. Phys. 50, 083506 (2009)
16. S. Bargmann, A. Antonio Favata, P. Podio-Guidugli, On energy and entropy influxes in the Green—Naghdi Type III theory of heat conduction. Proceedings of the Royal Society A 469, 21522013 (2013)
17. P. Podio-Guidugli, On energy and entropy inflows in the theory of heat conduction. Arch. Appl. Mech. 85, 347–353 (2015)
18. I.-S. Liu, On representation of anisotropic invariants. Int. J. Engng Sci 20, 1099–1109 (1982)
19. A.E. Green, N. Laws, On the Entropy Production Inequality. Arch. Ration. Mech. Anal. 45, 47–53 (1972)
20. K. Hutter, On thermodynamics and thermostatics of viscous thermoelastic solids in electromagnetic fields. Arch. Ration. Mech. Anal. 58, 339–386 (1975)
21. S. Bargmann, P. Steinmann, Classical results for a non-classical theory: remarks on thermodynamic relations in Green—Naghdi thermo-hyperelasticity. Continuum Mech. Thermodyn. 19, 59–66 (2007)
22. A.C. Eringen, Mechanics of Continua (Wiley, Hoboken, 1967)
23. G.F. Smith, On isotropic functions of symmetric tensors, skew-symmetric tensors and vectors. Int. J. Eng. Sci. 9, 899–916 (1971)
24. A.J.M. Spencer, in Continuum Physics, ed. by C. Eringen (Academic Press, New York, 1971)
25. K. Hutter, K. Johnk, *Continuum Methods of Physical Modelling, Continuum Mechanics, Dimensional Analysis, Turbulence* (Springer, Berlin, 2004)

26. K. Wilmanski, *Continuum Thermodynamics, Series on Advances in Mathematics for Applied Sciences*, vol. 77 (World Scientific Publishing Co., Pte. Ltd, Singapore, 2008)

27. I.-S. Liu, On entropy flux–heat flux relation in thermodynamic with Lagrange multipliers. *Continuum Mech Thermody.* 8, 247–256 (1996)

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