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A thermodynamic Approach to Rate Equations in Continuum Physics

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Abstract: The paper addresses the formulation of rate equations, via objective time derivatives, within continuum physics. The concept of objectivity is reviewed and distinction is made with material frame-indifference whose meaning is restricted to the invariance of the balance equations relative to Galilean frames. Objective time derivatives are defined to leave the tensor character of the appropriate field invariant within the set of Euclidean frames. Rate equations are required to involve objective time derivatives and to be consistent with the second law of thermodynamics. Here the general structure of objective time derivatives is established and the known derivatives of the physical literature are shown to be particular cases. Next, to fix ideas, a rate equation is considered for the model of heat conduction via a generalization of the Maxwell-Cattaneo equation with higher-order gradients as in the Guyer-Krumhansl equation. The thermodynamic restrictions are investigated and the expected effects, of the selected derivative of the heat flux, on the stress tensor are derived.

Key words: Objective derivatives, rate equations, thermodynamic consistency.

1 Introduction

Evolution (or rate) equations are commonly used for modelling material behaviours such as memory and/or delay effects. Usually they are expressed by relating the time derivative of proper fields to a set of state variables. As any constitutive equation, rate equations are required to comply with the principles of continuum physics and hence with objectivity (frame indifference) and consistency with the second law of thermodynamics. In this sense we need to clarify the general structure of objective time derivatives and to investigate how to establish the compatibility, of the whole set of constitutive equations, with the second law of thermodynamics.

The physical literature shows a number of contexts where the mathematical modeling is based on rate equations. Rheological models motivate rate equations for the stress tensor $\boldsymbol{T}$ in terms of the infinitesimal strain $\boldsymbol{E}$ or the stretching $\boldsymbol{D}$ in the form [1]

$$\tau\dot{\mathbf{T}} + \mathbf{T} = k\mathbf{E}$$

$$\tau\dot{\mathbf{T}} + \mathbf{T} = k_1\mathbf{E} + k_2\dot{\mathbf{E}}$$

$$\tau\dot{\mathbf{T}} + \mathbf{T} = 2\mathrm{u}\big(\mathbf{D} + \xi\dot{\mathbf{D}}\big)$$

the superposed dot denoting the total (or material) time derivative. These equations are referred to as Maxwell model, standard or Wiechert model, and Jeffreys model. They are examples of rate equations of the form

$$\dot{\mathbf{T}} = \hat{\mathbf{T}}(\mathbf{T}, \mathbf{E}, \dots)$$

the dots representing additional variables.

In nonequilibrium thermodynamics the evolution of appropriate fields is governed by rate equations. Perhaps the best known rate equation in thermodynamics is the Maxwell-Cattaneo equation for the heat flux $\mathbf{q}$,

$$\tau\dot{\mathbf{q}} + \mathbf{q} = -\kappa\mathbf{g} \tag{1}$$

where $\mathbf{g}$ is the temperature gradient [2].

The evolution of the polarization $\mathbf{P}$ in ferroelectrets and that of the magnetization $\mathbf{M}$ in ferromagnets is described by a variety of rate equations. For instance, the well known Landau-Lifshitz-Gilbert equation describes the evolution of $\mathbf{M}$ in the form [3]

$$\dot{\mathbf{M}} = -\gamma\mathbf{M}\times\mathbf{H}_{\mathrm{eff}} - \lambda\mathbf{M}\times(\mathbf{M}\times\mathbf{H}_{\mathrm{eff}})$$

where $\mathbf{H}_{\mathrm{eff}}$ is the effective magnetic field.

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A drawback of these equations is that the time derivative is not objective (or frame indifferent) [4]. Since these equations are considered as physically sound, it is natural to ask about the improvements of the time derivative so that the resulting equations prove to be objective. A further question arises about the thermodynamic consistency of the (objective) rate equations [5]. Both objectivity of the rate equations and compatibility with thermodynamics are the subject of this paper.

First the concept of objectivity is reviewed and distinction is made with material frame-indifference whose meaning is restricted to the invariance of the balance equations relative to Galilean frames. Next the general structure of objective time derivatives is established and the known derivatives of the literature are shown to be particular cases.

Owing to the kinematical fields occurring in the time derivative, the chosen time derivative may induce effects on the constitutive equation for the stress tensor. For definiteness, in this paper we address attention to a generalization of Eq. (1) with higher order gradients as in the Guyer-Krumhansl equation [6]. The thermodynamic restrictions are investigated and the expected effects, of the selected derivative of q, on the stress tensor are derived.

Notation. We consider a body occupying a time-dependent three-dimensional region $\mathcal{R}_t$. The points of the body are labelled by their position vector **X** in a reference configuration $\mathcal{R}$ while x = X(X, t) is the position vector of **X** in $\mathcal{R}_t$, at time t. Throughout we use Cartesian components. We denote by **F** the deformation gradient, relative to $\mathcal{R}$, $F_{iK} = \partial \mathrm{x}_K \mathrm{x}_i$, and by $\mathbf{C} = \mathbf{F}^T\mathbf{F}$ the Cauchy-Green tensor, the superscript T meaning transpose. Moreover, **v** is the velocity, **L** is the velocity gradient, $L_{i\mathrm{j}} = \partial_{x\mathrm{j}} v_i$, **D** is the stretching tensor and **W** is the spin tensor so that **L** = **D** + **W**. Also, ∇ is the gradient in the current configuration. We let θ be the absolute temperature and g = $\nabla\theta$ is the temperature gradient. Also, Sym is the set of symmetric tensors. For any vector, **u** say, $\mathbf{u}^2$ stands for the inner product $\mathbf{u} \cdot \mathbf{u}$.

2. Objectivity and Material Frame-Indifference

It is asserted as a fundamental principle of classical physics that material properties are independent of the frame of reference or observer. Often, in the literature, this principle is referred to as the principle of material frame-indifference[1] ([7], §19) though objectivity and material frame-indifference are regarded as synonyms.

Earlier Noll [8] used the term *principle of objectivity* to express that processes related by a change of frame must be compatible with the same constitutive equation. Accordingly, the material properties of a body should not depend on the observer, no matter how he moves. In Ref. [7] (§19) the statement is referred to as *principle of material frame indifference*. Seemingly it was Truesdell that preferred the use of frame indifference in that observer might be easily misinterpreted whereas frame of reference is a much better term [9].

Let $\mathcal{F}$, $\mathcal{F}^*$ be two frames of reference. The position vectors $\mathbf{x}$ and $\mathbf{x}^*$ of a point, relative to $\mathcal{F}$ and $\mathcal{F}^*$, are related by the Euclidean transformation[1] (see [7], §19)

$$\mathbf{x}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{x} \tag{2}$$

where $\mathbf{c}(t)$ is an arbitrary vector-valued function of $t \in \mathbb{R}$ while $\mathbf{Q}(t)$ is a proper orthogonal tensor function, det **Q** = 1. Hence **Q** represents a rotation. Galilean frames are related by a linear function $\mathbf{c}(t)$ and a constant rotation **Q**.

Conceptually it seems convenient to have two concepts at our disposal by letting objectivity and material frame-indifference be two distinct concepts. This view is not new in the literature (see, e.g., [10, 11]) and is made formal as follows.

The balance equations are invariant relative to Galilean frames and hence the material properties should be the same in all of the set of Galilean frames. Accordingly we expect that, e.g., stress and heat flux

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[1] For simplicity we let $t^* = t$.

are frame independent within the set of Galilean frames but they might be frame dependent relative to the set of non-inertial (Euclidean) frames. This point is investigated, e.g., in Ref. [12] within a kinetic theory approach and the conclusion is that stress and heat flux are frame dependent because the corresponding relations contain the spin tensor **W**.

Since the material properties may be affected by the motion of the body, it seems natural to assume that *material properties are independent of the frame of reference within the set of Galilean frames*. This might be the content of material frame-indifference.

We then confine objectivity to the constitutive equations viewed as the mathematical description of material behaviour. As a statement of the principle of objectivity we assume that *the constitutive equations are form-invariant for any change of frame*. To make it formal the content of objectivity, we let $\mathcal{F}$, $\mathcal{F}^*$ be Euclidean frames related by Eq. (2). The vector **u** and the tensors **T**, **K** are transformed into

$$\mathbf{u}^* = \mathbf{Q}\mathbf{u},\ \mathbf{T}^* = \mathbf{Q}\mathbf{T}\mathbf{Q}^T,\ \mathbf{K}^* = \mathbf{Q}\mathbf{K}\mathbf{Q}^T$$

while scalars, say ϕ, remain unchanged. If $\hat{\mathbf{T}}(\phi, \mathbf{u}, \mathbf{K})$ is the constitutive equation for **T** the objectivity requires that

$$\mathbf{T}^* = \mathbf{Q}\hat{\mathbf{T}}(\phi, \mathbf{u}, \mathbf{K})\mathbf{Q}^T = \hat{\mathbf{T}}(\phi, \mathbf{Q}\mathbf{u}, \mathbf{Q}\mathbf{K}\mathbf{Q}^T) = \hat{\mathbf{T}}(\phi^*, \mathbf{u}^*, \mathbf{K}^*)$$

and the like for vector functions, for any proper orthogonal tensor function $\mathbf{Q}(t)$.

If both objectivity and material frame-indifference are related to Euclidean frames then we might find that some material properties are objective but frame-dependent [13].

3. Objective Time Derivatives

For any function f ($\mathbf{X}$, t), where $\mathbf{X} \in \mathcal{R}$ and $t \in \mathbb{R}$, we let

$$\dot{f} = \partial_t f(\mathbf{X}, t).$$

If, instead, $f = \hat{f}(\mathbf{x}, t), \mathbf{x} \in \mathcal{R}_t$, then

$$\dot{f} = \partial_t \hat{f} + \mathbf{v} \cdot \nabla \hat{f}\,.$$

Throughout a superposed dot denotes the material time derivative, that is the derivative with **X** fixed.

We denote by $\boldsymbol{\Omega}$ the spin tensor associated with **Q**,

$$\boldsymbol{\Omega} : \dot{\mathbf{Q}}\mathbf{Q}^T = -\boldsymbol{\Omega}^T.$$

Let **K** be any tensor. The values $\mathbf{K}^*$ in $\mathcal{F}^*$ and **K** in $\mathcal{F}$ are related by

$$\mathbf{K}^* = \mathbf{Q}\mathbf{K}\mathbf{Q}^T.$$

We let $\mathbf{K} = \mathbf{K}(\mathbf{X}, t)$, $(\mathbf{X}, t) \in \mathcal{R} \times \mathbb{R}$, so that

$$\dot{\overline{\mathbf{K}^*}} = \boldsymbol{\Omega}\mathbf{K}^* + \mathbf{K}^*\boldsymbol{\Omega}^T + \mathbf{Q}\dot{\mathbf{K}}\mathbf{Q}^T.$$

Accordingly $\dot{\mathbf{K}}$ is not a tensor relative to Euclidean frames. Likewise, if **u** is a vector function, on $\mathcal{R} \times \mathbb{R}$, then

$$\mathbf{u}^* = \mathbf{Q}\mathbf{u}$$

and hence

$$\dot{\overline{\mathbf{u}^*}} = \boldsymbol{\Omega}\mathbf{u}^* + \mathbf{Q}\dot{\mathbf{u}}.$$

A derivation [14, 15] ∂ of a vector algebra $\mathcal{V}$, over $\mathbb{R}$, is a rule $\partial : \mathcal{V} \to \mathcal{V}$ such that, for every **u**, $\mathbf{w} \in \mathcal{V}$ and $\alpha, \beta \in \mathbb{R}$,

$$\partial(\alpha\mathbf{u} + \beta\mathbf{w}) = \alpha\partial\mathbf{u} + \beta\partial\mathbf{w},$$
$$\partial(\mathbf{u} \otimes \mathbf{w}) = (\partial\mathbf{u}) \otimes \mathbf{w} + \mathbf{u} \otimes (\partial\mathbf{w}).$$

These conditions are referred to as the linearity and the Leibnitz rule.

For any vector **u** the derivative $\partial\mathbf{u}$ is taken in the form

$$\partial\mathbf{u} = \dot{\mathbf{u}} - \mathbf{A}\mathbf{u} \tag{3}$$

where $\mathbf{A} : \mathcal{V} \to \mathcal{V}$ is a function on $\mathcal{R} \times \mathbb{R}$. Accordingly,

$$\partial(\mathbf{u} \otimes \mathbf{w}) = (\partial\mathbf{u}) \otimes \mathbf{w} + \mathbf{u} \otimes (\partial\mathbf{w}) = (\dot{\mathbf{u}} - \mathbf{A}\mathbf{u}) \otimes \mathbf{w} + \mathbf{u} \otimes (\dot{\mathbf{w}} - \mathrm{A}\mathbf{w}).$$

A derivative $\partial\mathbf{u}$ is *objective* if, under the change of frame $\mathcal{F} \to \mathcal{F}^*$ of Eq. (2), it is

$$\mathbf{Q}\partial\mathbf{u} = (\partial\mathbf{u})^* = \partial(\mathbf{u}^*) = \partial(\mathbf{Q}\mathbf{u})\,, \mathbf{u} \in \mathcal{V}\,.$$

The following statement characterizes the set of functions A guaranteeing the objectivity of Eq. (3).

Proposition 1. *The derivative (3) of a vector* **u** *is objective if and only if*

$$\mathbf{A}^* = \mathbf{Q}\mathbf{A}\mathbf{Q}^T + \boldsymbol{\Omega} \tag{4}$$

Proof. If $\partial\mathbf{u} = \dot{\mathbf{u}} - \mathbf{A}\mathbf{u}$ then objectivity requires that

$$\dot{\overline{\mathbf{Q}\mathbf{u}}} - \mathbf{A}^*\mathbf{Q}\mathbf{u} = \partial\mathbf{u}^* = (\partial\mathbf{u})^* = \mathbf{Q}(\dot{\mathbf{u}} - \mathbf{A}\mathbf{u}).$$

Hence we have

$$\dot{\mathbf{Q}}\mathbf{u} - \mathbf{A}^*\,\mathbf{Q}\mathbf{u} = -\mathbf{Q}\mathbf{A}\mathbf{u}\,.$$

The arbitrariness of **u** implies that

$$\mathbf{A}^*\mathbf{Q} = \mathbf{QA} + \dot{\mathbf{Q}}.$$

Right multiplication by $\mathbf{Q}^T$ gives Eq. (4). Conversely, by Eq. (4),

$$\dot{\overline{\mathbf{u}^*}} - \mathbf{A}^*\mathbf{u}^* = \dot{\overline{\mathbf{Qu}}} - \mathbf{QAQ}^T\mathbf{Qu} - \mathbf{\Omega Qu} = \mathbf{Q}(\dot{\mathbf{u}} - \mathbf{Au})$$

whence the conclusion $\partial(\mathbf{u}^*) = (\partial\mathbf{u})^*$. □

We now examine the derivative of a dyadic product $\mathbf{u} \otimes \mathbf{w}$,

$$\partial(\mathbf{u} \otimes \mathbf{v}) = (\dot{\mathbf{u}} - \mathbf{Au}) \otimes \mathbf{w} + \mathbf{u} \otimes (\dot{\mathbf{w}} - \mathbf{Aw}). \quad (5)$$

Proposition 2. *The derivative (5) is objective if and only if (4) holds.*

Proof. The objectivity requirement

$$[\partial(\mathbf{u} \otimes \mathbf{w})]^* = \partial(\mathbf{u}^* \otimes \mathbf{w}^*) \quad (6)$$

gives

$$\mathbf{Q}(\dot{\mathbf{u}} - \mathbf{Au}) \otimes \mathbf{Qw} + \mathbf{Qu} \otimes \mathbf{Q}(\dot{\mathbf{w}} - \mathbf{Aw}) = \left(\dot{\overline{\mathbf{Qu}}} - \mathbf{A}^*\mathbf{Qu}\right) \otimes \mathbf{Qw} + \mathbf{Qu} \otimes \left(\dot{\overline{\mathbf{Qw}}} - \mathbf{A}^*\mathbf{Qw}\right)$$

whence

$$\left[\dot{\mathbf{Q}}\mathbf{u} - \mathbf{A}^*\mathbf{Qu} + \mathbf{QAu}\right] \otimes \mathbf{Qw} + \mathbf{Qu} \otimes \left[\dot{\mathbf{Q}}\mathbf{w} - \mathbf{A}^*\mathbf{Qw} + \mathbf{QAw}\right] = 0.$$

By the arbitrariness of **u** and **w** this condition holds if

$$\dot{\mathbf{Q}}\mathbf{u} - \mathbf{A}^*\mathbf{Qu} + \mathbf{QAu} = 0,$$

whence Eq. (4) follows. Conversely, if Eq. (4) holds then the objectivity requirement (6) is satisfied. □

The derivation of a tensor **K** is defined by generalizing the particular case $\mathbf{K} = \mathbf{u} \otimes \mathbf{w}$. Since

$$\mathbf{Au} \otimes \mathbf{w} + \mathbf{u} \otimes \mathbf{Aw} = \mathbf{A}(\mathbf{u} \otimes \mathbf{w}) + (\mathbf{u} \otimes \mathbf{w})\mathbf{A}^T$$

then we let

$$\partial\mathbf{K} = \dot{\mathbf{K}} - \mathbf{AK} - \mathbf{KA}^T. \quad (7)$$

A direct check proves the following.

Proposition 3. *If* **A** *satisfies (4) then the derivative (7) is objective.*

Proof. We have to show that $(\partial\mathbf{K})^* = \partial(\mathbf{K}^*)$. Since

$$\partial(\mathbf{K}^*) = \dot{\overline{\mathbf{K}^*}} - \mathbf{A}^*\mathbf{K}^* - \mathbf{K}^*\mathbf{A}^{*T} = \dot{\overline{\mathbf{QKQ}^T}} - \mathbf{QAKQ}^T - \mathbf{\Omega QKQ}^T - \mathbf{QKA}^T\mathbf{Q}^T - \mathbf{QKQ}^T\mathbf{\Omega}^T$$

then

$$\partial(\mathbf{K}^*) = \mathbf{Q}(\dot{\mathbf{K}} - \mathbf{AK} - \mathbf{KA}^T)\mathbf{Q}^T + (\dot{\mathbf{Q}} - \mathbf{\Omega Q})\mathbf{KQ}^T + \mathbf{QK}(\dot{\mathbf{Q}}^T - \mathbf{Q}^T\mathbf{\Omega}^T) = \mathbf{Q}(\partial\mathbf{K})\mathbf{Q}^T.$$

Hence

$$\partial(\mathbf{K}^*) = (\partial\mathbf{K})^*. \qquad □$$

It is worth pointing out that the derivatives

$$\partial\mathbf{u} = \dot{\mathbf{u}} - \mathbf{A}_1\mathbf{u}, \ \partial\mathbf{K} = \dot{\mathbf{K}} - \mathbf{A}_2\mathbf{K} - \mathbf{KA}_3^T,$$

with $\mathbf{A}_i$, i = 1, 2, 3, subject to

$$\mathbf{A}_i^* = \mathbf{QA}_i\mathbf{Q}^T + \mathbf{\Omega},$$

are objective. The proof parallels the steps of Propositions 1 to 3 and shows that $\mathbf{A}_1$, $\mathbf{A}_2$, $\mathbf{A}_3$ need not be related to each other. Now, while known derivatives involve $\mathbf{A}_2 = \mathbf{A}_3$, we will see that the Truesdell derivative is such that $\mathbf{A}_1 \neq \mathbf{A}_2 = \mathbf{A}_3$.

If $\mathbf{A}_1$ and $\mathbf{A}_2$ satisfy (4) then

$$(\mathbf{A}_1 + \mathbf{A}_2)^* = \mathbf{Q}(\mathbf{A}_1 + \mathbf{A}_2)\mathbf{Q}^T + 2\mathbf{\Omega}$$

and hence $\mathbf{A}_1 + \mathbf{A}_2$ does not satisfy (4). Instead, the following statement provides a generalization of the structure of objective time derivatives via an appropriate splitting of **A**.

Proposition 4. *If* $\widetilde{\mathbf{A}}$ *satisfies the transformation law (4) and* $\widetilde{\mathbf{B}}$ *is any tensor, that is*

$$\widetilde{\mathbf{A}}^* = \mathbf{Q}\widetilde{\mathbf{A}}\mathbf{Q}^T + \mathbf{\Omega}, \quad \widetilde{\mathbf{B}}^* = \mathbf{Q}\widetilde{\mathbf{B}}\mathbf{Q}^T,$$

then

$$\mathbf{A} = \widetilde{\mathbf{A}} + \widetilde{\mathbf{B}} \quad (8)$$

too satisfies (4) and the derivatives

$$\partial\mathbf{K} = \dot{\mathbf{K}} - \mathbf{AK} - \mathbf{KA}^T, \ \partial\mathbf{u} = \dot{\mathbf{u}} - \mathbf{Au} \quad (9)$$

are objective.

Proof. By definition

$$\mathbf{A}^* = (\widetilde{\mathbf{A}} + \widetilde{\mathbf{B}})^* = \widetilde{\mathbf{A}}^* + \widetilde{\mathbf{B}}^* = \mathbf{Q}\widetilde{\mathbf{A}}\mathbf{Q}^T + \mathbf{\Omega} + \mathbf{Q}\widetilde{\mathbf{B}}\mathbf{Q}^T = \mathbf{Q}(\widetilde{\mathbf{A}} + \widetilde{\mathbf{B}})\mathbf{Q}^T + \mathbf{\Omega} = \mathbf{QAQ}^T$$

and hence **A** satisfies (4). Consequently, by Propositions 1 and 3 the derivatives (9), subject to $\mathbf{A} = \widetilde{\mathbf{A}} + \widetilde{\mathbf{B}}$, are objective. □

4. Objective Derivatives in Continuum Physics

By Proposition 4, any function **A**, on $\mathcal{R} \times \mathbb{R}$, possibly in the form $\mathbf{A} = \widetilde{\mathbf{A}} + \widetilde{\mathbf{B}}$, that transforms to $\mathbf{A}^*$ according to (4) determines an objective time derivative. We then look for physically remarkable objective time derivatives characterized by $\mathbf{A}$ subject to (4).

It is known (see, e.g., [4], §20.3) that the velocity gradient $\mathbf{L}$ transforms according to (4),

$$\mathbf{L}^* = \mathbf{Q}\mathbf{L}\mathbf{Q}^T + \mathbf{\Omega}.$$

It follows that

$$\mathbf{W}^* = \mathbf{Q}\mathbf{W}\mathbf{Q}^T + \mathbf{\Omega}, \quad \mathbf{D}^* = \mathbf{Q}\mathbf{D}\mathbf{Q}^T.$$

Hence $\mathbf{A} = \mathbf{W}$ satisfies (4) whereas $\mathbf{D}$ is a tensor (relative to the change $\mathcal{F} \to \mathcal{F}^*$).

Now let $\mathbf{Q} = \mathbf{R}$ be the rotation provided by the polar decomposition theorem so that

$$\mathbf{R} = \mathbf{F}\mathbf{U}^{-1}, \ \mathbf{U}^2 = \mathbf{F}^T\mathbf{F}.$$

Since $\mathbf{F}^* = \mathbf{Q}\mathbf{F}$ and $\mathbf{U}$ is invariant, $\mathbf{U}^* = \mathbf{U}$, then

$$\mathbf{R}^* = \mathbf{F}^*\mathbf{U}^{-1} = \mathbf{Q}\mathbf{F}\mathbf{U}^{-1} = \mathbf{Q}\mathbf{R}.$$

Hence it follows

$$\dot{\overline{\mathbf{R}^*}}\,\mathbf{R}^{*T} = \dot{\mathbf{Q}}\mathbf{R}\mathbf{R}^T\mathbf{Q}^T + \mathbf{Q}\dot{\mathbf{R}}\mathbf{R}^T\mathbf{Q}^T = \mathbf{\Omega} + \mathbf{Q}\dot{\mathbf{R}}\mathbf{R}^T\mathbf{Q}^T.$$

As a consequence $\mathbf{A} = \dot{\mathbf{R}}\mathbf{R}^T$ satisfies (4). To save writing we let $\mathbf{Z} := \dot{\mathbf{R}}\mathbf{R}^T$ be the spin tensor associated with $\mathbf{R}$.

Remarkable examples of $\widetilde{\mathbf{A}}$ and $\widetilde{\mathbf{B}}$ are $\widetilde{\mathbf{A}} = \mathbf{W}$, $\mathbf{Z}$ and $\widetilde{\mathbf{B}} = \mathbf{D}, (\nabla \cdot \mathbf{v})\mathbf{1}$. Hence

$$\mathbf{A} = \mathbf{W} + \lambda\mathbf{D} + \upsilon(\nabla \cdot \mathbf{v})\mathbf{1},$$
$$\mathbf{A} = \mathbf{Z} + \lambda\mathbf{D} + \upsilon(\nabla \cdot \mathbf{v})\mathbf{1},$$

where λ and υ are real-valued invariants, satisfy (8). By Proposition 3 it follows that the derivatives (9) with $\mathbf{A} = \mathbf{W}$, $\mathbf{A} = \mathbf{Z}$, $\mathbf{A} = \mathbf{W} - \mathbf{D} - (\nabla \cdot \mathbf{v})\mathbf{1}$, and $\mathbf{A} = \mathbf{L}$ are objective. Indeed, they are known derivatives in the literature and referred to as the corotational or Jaumann-Zaremba derivative [7],

$$\overset{\circ}{\mathbf{K}} := \dot{\mathbf{K}} - \mathbf{W}\mathbf{K} - \mathbf{K}\mathbf{W}^T,$$

the Green-Naghdi derivative [16],

$$\overset{\odot}{\mathbf{K}} := \dot{\mathbf{K}} - \mathbf{Z}\mathbf{K} - \mathbf{K}\mathbf{Z}^T,$$

the Cotter-Rivlin derivative [4],

$$\overset{\triangle}{\mathbf{K}} := \dot{\mathbf{K}} - \mathbf{W}\mathbf{K} - \mathbf{K}\mathbf{W}^T + \mathbf{D}\mathbf{K} + \mathbf{K}\mathbf{D},$$

and the Oldroyd derivative [17],

$$\overset{\diamond}{\mathbf{K}} := \dot{\mathbf{K}} - \mathbf{L}\mathbf{K} - \mathbf{K}\mathbf{L}^T.$$

Within the modelling of monatomic gases, Muller and Ruggeri [17] consider the derivative

$$\dot{\mathbf{u}} - \mathbf{W}\mathbf{u} + \mathbf{D}\mathbf{u}$$

for $\mathbf{u} = \mathbf{q}/\rho$. This amounts to considering the derivative

$$\dot{\mathbf{q}} - \mathbf{W}\mathbf{q} + \mathbf{D}\mathbf{q} + (\nabla \cdot \mathbf{v})\mathbf{q}$$

for the heat flux $\mathbf{q}$. As Muller and Ruggeri point out, the derivative is objective. Indeed, we observe that the derivative of $\mathbf{u} = \mathbf{q}/\rho$ is just the Cotter-Rivlin derivative whereas

$$\overset{\oslash}{\mathbf{q}} := \dot{\mathbf{q}} - \mathbf{W}\mathbf{q} + \mathbf{D}\mathbf{q} + (\nabla \cdot \mathbf{v})\mathbf{q} \tag{10}$$

is a further derivative that corresponds to $\mathbf{A} = \mathbf{W} - \mathbf{D} - (\nabla \cdot \mathbf{v})\mathbf{1}$ [18].

The Truesdell derivative for tensors and vectors [19],

$$\overset{\square}{\mathbf{K}} := \dot{\mathbf{K}} - \mathbf{L}\mathbf{K} - \mathbf{K}\mathbf{L}^T + (\nabla \cdot \mathbf{v})\mathbf{K},$$
$$\overset{\square}{\mathbf{u}} := \dot{\mathbf{u}} - \mathbf{L}\mathbf{u} + (\nabla \cdot \mathbf{v})\mathbf{u}$$

corresponds to selecting $\mathbf{A} = \mathbf{W} + \mathbf{D} - \frac{1}{2}(\nabla \cdot \mathbf{v})\mathbf{1}$ and $\mathbf{A} = \mathbf{W} + \mathbf{D} - (\nabla \cdot \mathbf{v})\mathbf{1}$, respectively.

If $\mathbf{K}$, and analogously $\mathbf{u}$, is given in the Eulerian description then

$$\overset{\diamond}{\mathbf{K}} := \partial_t\mathbf{K} + \mathbf{v} \cdot \nabla\mathbf{K} - \mathbf{L}\mathbf{K} - \mathbf{K}\mathbf{L}^T.$$

Since

$$\mathcal{L}_{\mathbf{v}}\mathbf{K} = \mathbf{v} \cdot \nabla\mathbf{K} - \mathbf{L}\mathbf{K} - \mathbf{K}\mathbf{L}^T$$

is the Lie derivative of $\mathbf{K}$ with respect to the vector field $\mathbf{v}$ [20] then we see that the Oldroyd derivative differs from the Lie derivative $\mathcal{L}_{\mathbf{v}}\mathbf{K}$ by the partial time derivative $\partial_t\mathbf{K}$. That is why sometimes $\overset{\diamond}{\mathbf{K}}$ is referred to as Lie-Oldroyd derivative. If $\mathbf{K}$ is a tensor density then, apart from $\partial_t\mathbf{K}$, the Lie derivative takes the form of the Truesdell derivative $\overset{\square}{\mathbf{K}}$ [21].

There is an obvious equivalence between rate equations with different objective time derivatives. To fix ideas, let

$$\overset{\circ}{\mathbf{K}} = \hat{\mathbf{K}}(\mathbf{K}, \theta, \rho) \tag{11}$$

be the rate equation of $\mathbf{K}$. Since

$$\overset{\diamond}{\mathbf{K}} = \overset{\circ}{\mathbf{K}} - \mathbf{D}\mathbf{K} - \mathbf{K}\mathbf{D}$$

Then

$$\overset{\diamond}{\mathrm{K}} := \widehat{\mathbf{K}}(\mathbf{K}, \theta, \rho) - \mathbf{DK} - \mathbf{KD}$$

is equivalent to Eq. (11). In the following thermodynamic analysis it is understood that we examine inequivalent rate equations.

We now consider the time derivatives, occurring in the continuum physics literature, for an objective vector $\mathbf{u}$ and an objective tensor $\mathbf{K}$. They are denoted and represented as follows.

	Derivative of vectors	Derivative of tensors
Jaumann-Zaremba	$\overset{\circ}{\mathbf{u}} = \dot{\mathbf{u}} - \mathbf{Wu}$	$\overset{\circ}{\mathbf{K}} = \dot{\mathbf{K}} - \mathbf{WK} - \mathbf{KW}^T$
Green-Naghdi	$\overset{\odot}{\mathbf{u}} = \dot{\mathbf{u}} - \mathbf{Zu}$	$\overset{\odot}{\mathbf{K}} = \dot{\mathbf{K}} - \mathbf{ZK} - \mathbf{KZ}^T$
Cotter-Rivlin	$\overset{\triangle}{\mathbf{u}} = \dot{\mathbf{u}} + \mathbf{L}^T\mathbf{u}$	$\overset{\triangle}{\mathbf{K}} = \dot{\mathbf{K}} + \mathbf{L}^T\mathbf{K} + \mathbf{KL}$
Oldroyd	$\overset{\triangledown}{\mathbf{u}} = \dot{\mathbf{u}} - \mathbf{Lu}$	$\overset{\triangledown}{\mathbf{K}} = \dot{\mathbf{K}} - \mathbf{LK} - \mathbf{KL}^T$
Truesdell	$\overset{\square}{\mathbf{u}} = \dot{\mathbf{u}} - \mathbf{Lu} + (\nabla \cdot \mathbf{v})\mathbf{u}$	$\overset{\square}{\mathbf{K}} = \dot{\mathbf{K}} - \mathbf{LK} - \mathbf{KL}^T + (\nabla \cdot \mathbf{v})\mathbf{K}$

In view of Proposition 4, we recognize that the given derivatives are objective in that they are associated with $\widetilde{\mathbf{A}}$ and $\widetilde{\mathbf{B}}$ as shown in the following table.

	Derivative of vectors	Derivative of tensors
Jaumann-Zaremba	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = \mathbf{0}$	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = \mathbf{0}$
Green-Naghdi	$\widetilde{\mathbf{A}} = \widehat{\mathbf{\Omega}},\ \widetilde{\mathbf{B}} = \mathbf{0}$	$\widetilde{\mathbf{A}} = \widehat{\mathbf{\Omega}},\ \widetilde{\mathbf{B}} = \mathbf{0}$
Cotter-Rivlin	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = -\mathbf{D}$	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = -\mathbf{D}$
Oldroyd	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = \mathbf{D}$	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = \mathbf{D}$
Truesdell	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = \mathbf{D} - (\nabla \cdot \mathbf{v})\mathbf{1}$	$\widetilde{\mathbf{A}} = \mathbf{W},\ \widetilde{\mathbf{B}} = \mathbf{D} - \frac{1}{2}(\nabla \cdot \mathbf{v})\mathbf{1}$

The principle of objectivity requires that the time derivatives within constitutive equations, and hence in the rate equations, have to be objective. It is then natural to wonder which derivative is the appropriate one for the constitutive equations at hand.

Answers to this question arise by framing the whole model of the pertinent material in a thermodynamic scheme where all of the set of constitutive equations comply with the second law of thermodynamics. Indeed, as we see in a moment, different objective time derivatives in the rate equations induce significant terms on the other constitutive equations especially in the one of the stress tensors.

5. Entropy Inequality and Second Law

Let ε be the energy density (per unit mass) and ρ the mass density. The balance of energy is written in the form

$$\rho\dot{\varepsilon} = \mathbf{T} \cdot \mathbf{D} - \nabla \cdot \mathbf{q} + \rho r \tag{12}$$

with r being the heat supply. Let η be the entropy density. Let ϕ be the entropy flux so that the entropy inequality is expressed as

$$\rho\dot{\eta} + \nabla \cdot \phi - \frac{\rho r}{\theta} \geq 0.$$

For technical convenience let

$$\phi = \frac{\mathbf{q}}{\theta} + \mathbf{k}$$

$\mathbf{k}$ being regarded as the extra-entropy flux. Hence we can write the entropy inequality in the form

$$\rho\theta\dot{\eta} + \nabla \cdot \mathbf{q} - \rho r - \frac{1}{\theta}\mathbf{q} \cdot \mathbf{g} + \theta\nabla \cdot \mathbf{k} \geq 0.$$

Substitution of $\nabla \cdot \mathbf{q} - \rho r$ from (12) and use of the Helmholtz free energy density $\psi = \varepsilon - \theta\eta$ allow the entropy inequality to be written in the form

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \mathbf{T} \cdot \mathbf{D} - \frac{1}{\theta}\mathbf{q} \cdot \mathbf{g} + \theta\nabla \cdot \mathbf{k} \geq 0 \tag{13}$$

The second law is stated by saying that inequality (13) has to hold for any thermodynamic process compatible with the balance equations (mass, momentum, and energy).

6. Constitutive Equations for Thermoelastic Solids

To give evidence to the different consequences, on the constitutive model, of the choice of the objective time derivative we look at a generalized thermoelastic solid where the heat flux is governed by a rate equation of the Guyer-Krumhansl type. To see the different consequences we examine the rate equation in a form that comprises the known derivatives occurring in the literature.

Eq. (1) is generalized by letting $\mathbf{q}$ be governed by

$$\tau\partial\mathbf{q} + \mathbf{q} = -\kappa\mathbf{g} + \alpha(\triangle\,\mathbf{q} + 2\nabla\nabla\cdot\mathbf{q}) \quad (14)$$

where $\partial\mathbf{q}$ denotes the chosen time derivative. For generality we let

$$\partial\mathbf{q} = \dot{\mathbf{q}} - \mathbf{W}\mathbf{q} + \mathrm{u}\mathbf{D}\mathbf{q} + v(\nabla\cdot\mathbf{v})\mathbf{q}.$$

The derivatives provided in §3 are obtained with appropriate values of the parameters u, v or, for the Green-Naghdi derivative, by replacing $\mathbf{W}$ with $\mathbf{Z}$ and letting $u=0$, $v=0$.

Based on Eq. (14) we model a generalized thermoelastic solid by letting

$$\Gamma = (\mathbf{F},\theta,\mathbf{g},\mathbf{q},\nabla\mathbf{q},\nabla\nabla\mathbf{q})$$

be the set of state variables. Hence we let ψ, η, and $\mathbf{T}$ be functions of Γ, ψ being differentiable, while $\mathbf{q}$ satisfies the rate Eq. (14).

Some restrictions follow at once from the objectivity requirements. The invariance of the free energy ψ under the change of frame (2) implies that

$$\psi(\mathbf{F},\theta,\mathbf{g},\mathbf{q},\nabla\mathbf{q},\nabla\nabla\mathbf{q})$$
$$= \psi\big(\mathbf{QF},\theta,\mathbf{Qg},\mathbf{Qq},(\mathbf{Q}\nabla)(\mathbf{Qq}),(\mathbf{Q}\nabla)(\mathbf{Q}\nabla)(\mathbf{Qq})\big).$$

Owing to the polar decomposition, $\mathbf{F}=\mathbf{RU}$, letting $\mathbf{Q}=\mathbf{R}^T$ we find

$$\psi(\mathbf{F},\theta,\mathbf{g},\mathbf{q},\nabla\mathbf{q},\nabla\nabla\mathbf{q}) =$$
$$\psi\big(\mathbf{U},\theta,\mathbf{R}^T\mathbf{g},\mathbf{R}^T\mathbf{q},(\mathbf{R}^T\nabla)(\mathbf{R}^T\mathbf{q}),(\mathbf{R}^T\nabla)(\mathbf{R}^T\nabla)(\mathbf{R}^T\mathbf{q})\big).$$

for any rotation $\mathbf{R}$. Accordingly we let ψ depend on $\mathbf{F}$ only through $\mathbf{U}$ and hence through $\mathbf{C}$. Moreover we let ψ depend on $\mathbf{g}$, $\mathbf{q}$, $\nabla\mathbf{q},\nabla\nabla\mathbf{q}$ via invariants under the change of frame. With this in mind we let

$$\psi = \psi(\mathbf{C},\theta,\mathbf{g},\mathbf{q},\nabla\mathbf{q},\nabla\nabla\mathbf{q}).$$

6.1 Thermodynamic Restrictions

We now examine the thermodynamic restrictions placed by the second law on the constitutive functions ψ, η, and $\mathbf{T}$. Upon evaluation of ψ and substitution in Eq. (13) we have

$$-\rho\Big(\partial_{\mathbf{C}}\psi\cdot\dot{\mathbf{C}} + \partial_\theta\psi\dot\theta + \partial_{\mathbf{g}}\psi\cdot\dot{\mathbf{g}} + \partial_{\mathbf{q}}\psi\cdot\dot{\mathbf{q}}$$
$$+ \partial_{\nabla\mathbf{q}}\psi\cdot\overline{\nabla\mathbf{q}}^{\boldsymbol{\cdot}} + \partial_{\nabla\nabla\mathbf{q}}\psi\cdot\overline{\nabla\nabla\mathbf{q}}^{\boldsymbol{\cdot}}\Big)$$
$$-\rho\eta\dot\theta + \mathbf{T}\cdot\mathbf{D} - \frac{1}{\theta}\mathbf{q}\cdot\mathbf{g} + \theta\nabla\cdot\mathbf{k} \ge 0 \quad (15)$$

The term $\overline{\nabla\nabla\mathbf{q}}^{\boldsymbol{\cdot}}$ comprises $\nabla\nabla\dot{\mathbf{q}}$ and hence, in view of Eq. (14), gives fourth-order gradients of $\mathbf{q}$. Likewise $\overline{\nabla\mathbf{q}}^{\boldsymbol{\cdot}}$ comprises $\nabla\dot{\mathbf{q}}$ and hence gives third-order gradients of $\mathbf{q}$. The arbitrariness and the linearity of these terms imply that

$$\partial_{\nabla\nabla\mathbf{q}}\psi = 0, \quad \partial_{\nabla\mathbf{q}}\psi = 0.$$

Moreover the arbitrariness and the linearity of $\dot\theta$, $\dot{\mathbf{g}}$ in Eq. (15) imply that

$$\eta = -\partial_\theta\psi, \quad \partial_{\mathbf{g}}\psi = 0.$$

Now observe

$$\dot{\mathbf{C}} = 2\mathbf{F}^T\mathbf{DF}$$

and then

$$\partial_{\mathbf{C}}\psi\cdot\dot{\mathbf{C}} = 2(\mathbf{F}\partial_{\mathbf{C}}\psi\mathbf{F}^T)\cdot\mathbf{D}.$$

Upon dividing by θ we can write the remaining inequality in the form

$$\frac{1}{\theta}(\mathbf{T} - 2\rho\mathbf{F}\partial_{\mathbf{C}}\psi\mathbf{F}^T)\cdot\mathbf{D} - \frac{\rho}{\theta}\partial_{\mathbf{q}}\psi\cdot\dot{\mathbf{q}}$$
$$-\frac{1}{\theta^2}\mathbf{q}\cdot\mathbf{g} + \nabla\cdot\mathbf{k} \ge 0 \quad (16)$$

Let

$$\mathbf{p} = -\frac{\rho}{\theta}\partial_{\mathbf{q}}\psi.$$

By Eq. (14) we find

$$\mathbf{p}\cdot\dot{\mathbf{q}} = \mathbf{p}\cdot\Big[\mathbf{Wq} - u\mathbf{Dq} - v(\nabla\cdot\mathbf{v})\mathbf{q} - \frac{1}{\tau}\mathbf{q} - \frac{\kappa}{\tau}\mathbf{g}$$
$$+\frac{\alpha}{\tau}(\triangle\,\mathbf{q} + 2\nabla\nabla\cdot\mathbf{q})\Big] =$$
$$\mathbf{p}\otimes\mathbf{q}\cdot[\mathbf{W} - u\mathbf{D} - v\mathrm{tr}\mathbf{D}\mathbf{1}] - \frac{1}{\tau}\mathbf{p}\cdot\mathbf{q}$$
$$-\frac{\kappa}{\tau}\mathbf{p}\cdot\mathbf{g} + \frac{\alpha}{\tau}\mathbf{p}\cdot(\triangle\,\mathbf{q} + 2\nabla\nabla\cdot\mathbf{q}).$$

Owing to the form of inequality (16), we have to investigate the possible definiteness of $(\alpha/\tau)\mathbf{p} \cdot (\triangle\, \mathbf{q} + 2\nabla\nabla \cdot \mathbf{q})$ within a divergence term. Assume

$$\frac{\alpha}{\tau}\mathbf{p} = -\gamma\mathbf{q} \tag{17}$$

γ being a parameter, and observe

$$-\gamma\mathbf{q} \cdot \triangle\, \mathbf{q} = -\nabla \cdot \left(\frac{1}{2}\gamma\nabla\mathbf{q}^2\right) + \gamma(\nabla\mathbf{q}) \cdot (\nabla\mathbf{q}),$$

$$-\gamma\mathbf{q} \cdot (\nabla\nabla \cdot \mathbf{q}) = -\nabla \cdot (\gamma\mathbf{q}\nabla \cdot \mathbf{q}) + \gamma(\nabla \cdot \mathbf{q})^2.$$

We can then write inequality (16) in the form

$$\begin{aligned}\frac{1}{\theta}\Big(\mathbf{T} - 2\rho\mathbf{F}\partial_{\mathrm{C}}\psi\mathbf{F}^T + \frac{u\rho}{\theta}\partial_{\mathbf{q}}\psi \otimes \mathbf{q} + \frac{v\rho}{\theta}\partial_{\mathbf{q}} \cdot \mathbf{q}1\Big)&\\ \cdot \mathbf{D} - \frac{\rho}{\theta}\partial_{\mathbf{q}}\psi \otimes \mathbf{q} \cdot \mathbf{W} + \frac{\rho}{\theta\tau}\partial_{\mathbf{q}}\psi \cdot \mathbf{q}&\\ + \left(\frac{\rho\kappa}{\theta\tau}\partial_{\mathbf{q}}\psi - \frac{1}{\theta^2}\mathbf{q}\right) \cdot \mathbf{g}&\\ + \nabla \cdot \left(\mathbf{k} - \frac{1}{2}\gamma\nabla\mathbf{q}^2 - \gamma\mathbf{q}\nabla \cdot \mathbf{q}\right)&\\ + \gamma[(\nabla \cdot \mathbf{q})^2 + (\nabla\mathbf{q}) \cdot (\nabla\mathbf{q})] \geq 0&\end{aligned}$$

Accordingly we let

$$\mathbf{k} = \tfrac{1}{2}\gamma\nabla\mathbf{q}^2 + \gamma\mathbf{q}\nabla \cdot \mathbf{q}. \tag{18}$$

The linearity and the arbitrariness of $\mathbf{W}$, $\mathbf{D}$, $\mathbf{g}$ imply that

$$\partial_{\mathbf{q}}\psi \otimes \mathbf{q} \in \mathrm{Sym}, \tag{19}$$

$$\mathbf{T} = 2\rho\mathbf{F}\partial_{\mathrm{C}}\psi\mathbf{F}^T - \frac{u\rho}{\theta}\partial_{\mathbf{q}}\psi \otimes \mathbf{q} - \frac{v\rho}{\theta}\partial_{\mathbf{q}}\psi \cdot \mathbf{q}\mathbf{1},$$

$$\partial_{\mathbf{q}}\psi = \frac{\tau}{\rho\theta\kappa}\mathbf{q}. \tag{20}$$

Since ψ is independent of $\nabla \mathrm{q}$ the remaining inequality splits into the two conditions

$$\partial_{\mathbf{q}}\psi \cdot \mathbf{q} \geq 0, \tag{21}$$

$$\gamma[(\nabla \cdot \mathbf{q})^2 + (\nabla\mathbf{q}) \cdot (\nabla\mathbf{q})] \geq 0. \tag{22}$$

Incidentally, by Eq. (22) it follows that $\gamma \geq 0$. The result (18), subject to $\gamma \geq 0$, coincides with the entropy flux determined in Ref. [22]. Moreover, the assumption (17) is consistent with Eq. (20) provided

$$\alpha = \gamma\kappa\theta^2$$

We know that ρ, θ, τ are positive-valued. Hence substitution of Eq. (20) in Eq. (21) results in

$$\tfrac{1}{\kappa}\mathbf{q}^2 \geq 0.$$

This implies the expected condition that the conductivity κ is positive.

Now, Eq. (20) shows that (19) holds identically. Moreover a direct integration of Eq. (20) provides the free energy ψ in the form

$$\psi = \Psi(\mathbf{C}, \theta) + \frac{\tau}{2\rho\theta\kappa}\mathbf{q}^2. \tag{23}$$

By replacing $\partial_{\mathbf{q}}\psi$ we find that $\mathbf{T}$ takes the form

$$\mathbf{T} = 2\rho\mathbf{F}\partial_{\mathrm{C}}\psi\mathbf{F}^T - \frac{u\tau}{\kappa\theta^2}\mathbf{q} \otimes \mathbf{q} - \frac{v\tau}{\kappa\theta^2}\mathbf{q}^2\mathbf{1}. \tag{24}$$

Some comments on Eq. (24) are in order. The stress $\mathbf{T}$ is the sum of the (formally) elastic term $2\rho\mathbf{F}\partial_{\mathrm{C}}\psi\mathbf{F}^T$ and

$$-\frac{u\tau}{\kappa\theta^2}\mathbf{q} \otimes \mathbf{q} - \frac{v\tau}{\kappa\theta^2}\mathbf{q}^2\mathbf{1}. \tag{25}$$

The additional terms (25) are nonzero with the Cotter-Rivlin derivative $(u = -1,\ v = 0)$, the Oldroyd derivative $(u = 1,\ v = 0)$, and the Truesdell derivative $(u = 1,\ v = -1)$. Instead they vanish if the Jaumann-Zaremba derivative and the Green-Naghdi derivatives are involved. Yet, also with these derivatives we can have a dependence of $\mathbf{T}$ on $\mathbf{q}^2$. To fix ideas, let $\tau/\rho\kappa$ depend on the mass density ρ, say

$$\frac{\tau}{\rho\kappa} = f\,(\theta, \rho).$$

Now,

$$\rho = \frac{\rho_R}{d^{1/2}},$$

where ρ_R is the mass density in the reference configuration and $d = \det\mathbf{C}$. Since $\partial_{\mathbf{C}}d = d\mathbf{C}^{-1}$ then we find that

$$\partial_{\mathbf{C}}\frac{\tau}{2\rho\theta\kappa}\mathbf{q}^2 = -\frac{\rho}{4\theta}\partial_\rho f\mathbf{q}^2\mathbf{C}^{-1}.$$

Since $\mathbf{F}\mathbf{C}^{-1}\mathbf{F}^T = 1$ we obtain

$$2\rho\mathbf{F}\partial_{\mathrm{C}}\psi\mathbf{F}^T = 2\rho\mathbf{F}\partial_{\mathbf{C}}\Psi\mathbf{F}^T - \frac{\rho^2}{2\theta}\partial_\rho f\mathbf{q}^2\mathbf{1}.$$

If, further, τ/κ is independent of ρ then $\partial_\rho f = -\tau/\kappa\,\rho^2$ and

$$2\rho\mathbf{F}\partial_{\mathbf{C}}\psi\mathbf{F}^{T} = 2\rho\mathbf{F}\partial_{\mathbf{C}}\Psi\mathbf{F}^{T} + \frac{\tau}{2\theta\kappa}\mathbf{q}^{2}\mathbf{1}.$$

It is worth remarking that the results so derived hold formally unchanged if $\mathbf{W}$ in the chosen derivative is replaced with $\mathbf{Z} = \dot{\mathbf{R}}\mathbf{R}^{T}$ in that the only feature of $\mathbf{W}$ used in the thermodynamic analysis is the skew-symmetry.

7. Conclusions

The paper deals with the formulation of rate equations within continuum physics. Two main results emerge from the present developments.

Rate equations have to involve objective time derivatives and the general structure of objective time derivatives is given by Eq. (3) where the linear operator *A* satisfies the transformation law

$$\mathbf{A}^{*} = \mathbf{Q}\mathbf{A}\mathbf{Q}^{T} + \dot{\mathbf{Q}}\mathbf{Q}^{T}$$

$\mathbf{Q}$ being the time dependent rotation between the corresponding Euclidean frames $\mathcal{F}$ and $\mathcal{F}^{*}$. As expected, the familiar objective time derivatives, appeared in the literature, turn out to be particular cases with $\mathbf{A}$ taking the forms given in §4.

As any constitutive equation, rate equations are required to be consistent with thermodynamics. To fix ideas, here a rate equation for the heat flux is considered with non-local properties as in the Guyer-Krumhansl equation and with a general objective derivative of the form

$$\partial\mathbf{q} = \dot{\mathbf{q}} - \mathbf{W}\mathbf{q} + u\mathbf{D}\mathbf{q} + \lambda(\mathrm{tr}\mathbf{D})\mathbf{q}$$

for the heat flux $\mathbf{q}$. The thermodynamic consistency holds if the stress tensor is affected by a dependence on q as is shown by Eq. (24).

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