

A mixture of elastic materials with different constituent temperatures and internal constraints

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Abstract

A novel treatment of the 2nd Law of Thermodynamics and the development of general thermomechanical constraints are introduced for a mixture of two elastic materials in which the constituents may have different temperatures. First, a homothermal quasi-static process at a common mixture temperature is introduced. *Part I* of the 2nd Law of Thermodynamics is invoked to assert that the Clausius integrals are path-independent, which leads to a prescription, or an identification, of the partial entropy functions. Then, two assumptions are introduced that establish the values of the partial entropy functions for general processes, including those for which the constituent temperatures are not equal. Constitutive restrictions are derived for path-independent processes from the mixture energy equation, and further constitutive restrictions are derived for general processes upon invoking the Clausius–Duhem inequality as a statement of *Part II* of the 2nd Law of Thermodynamics. The complete set of constitutive restrictions are then shown to equal those derived by other authors, a result which supports the adopted assumptions concerning the partial entropy functions for general processes. Then, an internal constraint involving the deformation gradient tensors and the constituent temperatures is represented by a constraint manifold, and an internally constrained mixture of elastic materials is associated with each unique equivalence class of unconstrained mixtures. The examples of a mixture constrained to have a common temperature and a mixture constrained by temperature-dependent intrinsic compressibility are discussed.

1. Introduction

Theories for mixtures that allow different constituent temperatures were developed and studied by various authors in the 1960s and 1970s, including Eringen and Ingram [1], Steel [2], Bowen and Garcia [3], Dunwoody and Müller [4], and Craine et al. [5]. In [1–5], the constituent entropy was introduced as a primitive variable and constitutive restrictions were derived from an entropy inequality. Those treatments of the thermodynamics of mixtures follow the approach first presented by Coleman and Noll [6], which is widely used in many areas of continuum thermodynamics. However, the validity of introducing the entropy as a primitive variable was questioned by Rivlin [7,8] and Day [9], both of whom advocated the identification of a thermomechanical process that leads to a prescription for the entropy. In a mathematically rigorous fashion, Coleman and Owen [10] established the existence of the entropy function for several classes of materials, but they did not study mixtures.

Krishnaswamy and Batra [11] were the first authors to extend the ideas of Rivlin [7,8] to mixtures. In [11], a special process was identified that was assumed to be path-independent and which led to a prescription for the partial entropy in a mixture of an elastic solid and a viscous fluid *at a common temperature*. Using this approach, one obtains the identification of a series of experiments that, if performed, allows the measurement of the partial entropy function. Consequently, this approach is physically appealing for understanding the thermodynamics of mixtures. In the first part of this paper I extend the theory of Krishnaswamy and Batra [11] to a mixture of two elastic materials with different constituent temperatures. This is done by using the framework for mixtures with different constituent temperatures presented by Craine et al. [5], so that the results of this paper can be compared with theories that view the partial entropy as a primitive variable. After the constitutive restrictions are obtained through this new approach, it is shown that the constitutive restrictions are the same as those derived in [5].

The form of the stress tensor in an internally constrained elastic material can be obtained only after introducing additional assumptions beyond those inherent in the theory of unconstrained elastic materials. The first general theory of internally constrained elastic materials with an explicitly stated assumption appears to have been presented by Adkins [12]. Adkins [12] assumed that the stress could be expressed as an additive decomposition of two terms: a determinate stress and a symmetric indeterminate stress, for which the stress power vanishes. This approach was further developed by Truesdell and Noll [13] for simple materials. Green et al. [14] developed the first general theory of thermomechanical constraints. Additional treatments of thermomechanical constraints have appeared in many papers, e.g., see [15–18]. Casey and Krishnaswamy [19] developed a new approach to internally constrained thermoelastic materials; the method of Casey and Krishnaswamy [19] was extended to mixtures of elastic materials at a common temperature by Klisch [20]. A general internal constraint was introduced in [20]; this constraint involved both deformation gradient tensors and the common mixture temperature. This approach was motivated by the constraint of intrinsic incompressibility first proposed by Mills [21] and studied by other authors, including Craine [22], Bowen [23], Rajagopal and Tao [24], and Atkin and Craine [25]. As with incompressible elasticity, the introduction of this constraint makes it possible to obtain solutions to a wider variety of boundary-value problems. In particular, the intrinsic incompressibility constraint has been used in mixture models of biological tissues including articular

cartilage [26,27] and the intervertebral disc [28]. In the second part of this paper, the approach of [20] is extended to a mixture with different constituent temperatures.

Preliminaries for a mixture of two elastic materials with different constituent temperatures using the basic equations of Craine et al. [5] are given in Section 2. The identification of a path-independent process, a prescription for the partial entropy, and constitutive restrictions are obtained in Section 3, which concludes with an analysis that shows that the results agree with those derived in [5]. An internal constraint involving the deformation gradient tensors and the constituent temperatures is represented by a constraint manifold in Section 4, and an equivalence class of unconstrained mixtures is associated with the constraint. A definition of a constrained mixture is presented in Section 5. Two important examples are presented in Section 6: a mixture constrained to have a common mixture temperature and a mixture constrained by temperature-dependent intrinsic compressibility.

2. Preliminaries

In this section, the basic definitions and equations presented by Craine et al. [5] are specialized to a mixture of two elastic materials with different constituent temperatures. We consider a mixture \mathcal{C} of two elastic materials \mathcal{C}^α , with the superscript $\alpha = 1, 2$ being used to designate each constituent (the summation convention is not used on α). A material particle of \mathcal{C}^α occupies a position \mathbf{X}^α in a fixed reference configuration \mathcal{K}_0 and a position \mathbf{x}^α in a present configuration \mathcal{K} . It is assumed that there exists one particle of each \mathcal{C}^α at each point \mathbf{x} in the mixture such that $\mathbf{x} = \mathbf{x}^1 = \mathbf{x}^2$. The motion and temperature histories of \mathcal{C}^α are defined by sufficiently smooth mappings

$$\mathbf{x}^\alpha = \boldsymbol{\chi}^\alpha(\mathbf{X}^\alpha, t), \quad \theta^\alpha = \hat{\theta}^\alpha(\mathbf{X}^\alpha, t). \quad (2.1)$$

The pair $\{\boldsymbol{\chi}^\alpha, \hat{\theta}^\alpha\}$ is referred to as a process for \mathcal{C}^α . We will assume that $\theta^1 = \theta^2$ in the reference configuration \mathcal{K}_0 .

The density ρ^α of \mathcal{C}^α is considered to be the average mass density of \mathcal{C}^α over a small mixture volume. The density of the mixture is defined as

$$\rho = \sum_{\alpha=1}^2 \rho^\alpha. \quad (2.2)$$

The velocity of \mathcal{C}^α is

$$\mathbf{v}^\alpha = \frac{d^\alpha}{dt} \boldsymbol{\chi}^\alpha(\mathbf{X}^\alpha, t), \quad (2.3)$$

where the material time derivative $d^\alpha(\cdot)/dt$ following the motion of \mathcal{C}^α is given for scalar or vector functions $\zeta(\mathbf{x}, t)$ and $\mathbf{w}(\mathbf{x}, t)$ by

$$\frac{d^\alpha \zeta}{dt} = \frac{\partial \zeta}{\partial t} + (\text{grad } \zeta) \cdot \mathbf{v}^\alpha, \quad \frac{d^\alpha \mathbf{w}}{dt} = \frac{\partial \mathbf{w}}{\partial t} + (\text{grad } \mathbf{w}) \mathbf{v}^\alpha. \quad (2.4)$$

The material time derivative $d(\cdot)/dt$ following the mean mixture motion is defined as

$$\frac{d\zeta}{dt} = \frac{\partial \zeta}{\partial t} + (\text{grad } \zeta) \cdot \mathbf{v}, \quad \frac{d\mathbf{w}}{dt} = \frac{\partial \mathbf{w}}{\partial t} + (\text{grad } \mathbf{w}) \mathbf{v}, \quad (2.5)$$

where the mean, or barycentric, velocity \mathbf{v} is

$$\rho \mathbf{v} = \sum_{\alpha=1}^2 \rho^\alpha \mathbf{v}^\alpha. \quad (2.6)$$

The diffusion velocity \mathbf{u}^α and the relative velocity \mathbf{a}^α are

$$\mathbf{u}^\alpha = \mathbf{v}^\alpha - \mathbf{v}, \quad \mathbf{a}^\alpha = \mathbf{v}^\alpha - \mathbf{v}^2. \quad (2.7)$$

From (2.4), (2.5) and (2.7) we obtain the following useful relationships:

$$\begin{aligned} \frac{d^\alpha \zeta}{dt} &= \frac{d^\beta \zeta}{dt} + (\text{grad } \zeta) \cdot (\mathbf{v}^\alpha - \mathbf{v}^\beta) = \frac{d\zeta}{dt} + (\text{grad } \zeta) \cdot \mathbf{u}^\alpha, \\ \frac{d^\alpha \mathbf{w}}{dt} &= \frac{d^\beta \mathbf{w}}{dt} + (\text{grad } \mathbf{w})(\mathbf{v}^\alpha - \mathbf{v}^\beta) = \frac{d\mathbf{w}}{dt} + (\text{grad } \mathbf{w}) \mathbf{u}^\alpha. \end{aligned} \quad (2.8)$$

For each \mathcal{C}^α , the deformation gradient tensor is

$$\mathbf{F}^\alpha = \frac{\partial \boldsymbol{\chi}^\alpha(\mathbf{X}^\alpha, t)}{\partial \mathbf{X}^\alpha}, \quad (2.9)$$

where

$$\mathbf{J}^\alpha = \det \mathbf{F}^\alpha > 0. \quad (2.10)$$

The velocity gradient tensor, the rate of deformation tensor, and the spin tensor are

$$\mathbf{L}^\alpha = \frac{\partial \mathbf{v}^\alpha}{\partial \mathbf{x}}, \quad \mathbf{D}^\alpha = \frac{1}{2}(\mathbf{L}^\alpha + \mathbf{L}^{\alpha T}), \quad \mathbf{W}^\alpha = \frac{1}{2}(\mathbf{L}^\alpha - \mathbf{L}^{\alpha T}), \quad (2.11)$$

respectively, where the superscript T denotes the transpose operator.

The spatial forms of the balance of mass, linear momentum, angular momentum, and energy equations for \mathcal{C}^α take the form ¹

¹ The balance equations in this section are obtained from [5] after omitting the terms due to mass exchange.

$$\frac{d^\alpha \rho^\alpha}{dt} + \rho^\alpha \operatorname{div} \mathbf{v}^\alpha = 0, \quad (2.12)$$

$$\rho^\alpha \frac{d^\alpha \mathbf{v}^\alpha}{dt} = \operatorname{div} \mathbf{T}^\alpha - \boldsymbol{\mu}^\alpha + \rho^\alpha \mathbf{b}^\alpha, \quad (2.13)$$

$$\frac{1}{2} (\mathbf{T}^\alpha - \mathbf{T}^{\alpha T}) = \mathbf{T}_{\text{skew}}^\alpha = -\boldsymbol{\lambda}^\alpha, \quad (2.14)$$

$$\rho^\alpha \frac{d^\alpha \varepsilon^\alpha}{dt} = \rho^\alpha r^\alpha - \operatorname{div} \mathbf{q}^\alpha + \beta^\alpha + \mathbf{T}^\alpha \cdot \mathbf{D}^\alpha, \quad (2.15)$$

where \mathbf{T}^α is the partial Cauchy stress tensor, $\boldsymbol{\mu}^\alpha$ is the diffusive force, \mathbf{b}^α is the partial external body force, $\boldsymbol{\lambda}^\alpha$ is the internal body couple, ε^α is the partial internal energy, r^α is the partial external heat supply, \mathbf{q}^α is the partial heat flux, and β^α is the internal energy supply. The energy equations (2.15) will be used in Section 3 when invoking *Part I* of the 2nd Law of Thermodynamics.

The balance of momentum for the mixture requires that

$$\sum_{\alpha=1}^2 \boldsymbol{\mu}^\alpha = \mathbf{0}. \quad (2.16)$$

The balance of angular momentum for the mixture requires that

$$\sum_{\alpha=1}^2 \boldsymbol{\lambda}^\alpha = \mathbf{0}, \quad (2.17)$$

so that the total stress in the mixture is symmetric, i.e.,

$$\mathbf{T} = \sum_{\alpha=1}^2 \mathbf{T}^\alpha = \mathbf{T}^T. \quad (2.18)$$

The balance of energy for the mixture requires that

$$\sum_{\alpha=1}^2 (\beta^\alpha - \boldsymbol{\mu}^\alpha \cdot \mathbf{v}^\alpha + \boldsymbol{\lambda}^\alpha \cdot \mathbf{W}^\alpha) = 0, \quad (2.19)$$

which can be written in the form

$$\sum_{\alpha=1}^2 \Theta^\alpha = 0, \quad (2.20)$$

where

$$\Theta^\alpha = \beta^\alpha - \boldsymbol{\mu}^\alpha \cdot (\mathbf{v}^\alpha - \mathbf{v}^2) - \mathbf{T}_{\text{skew}}^\alpha \cdot (\mathbf{W}^\alpha - \mathbf{W}^2). \quad (2.21)$$

We now derive an alternative expression for the mixture energy balance, which will be used for studying the consequences of the 2nd Law. Using (2.20) and (2.21), we write the energy equation for \mathcal{C}^α (2.15) in the alternative form

$$\rho^\alpha \frac{d^\alpha \varepsilon^\alpha}{dt} = \rho^\alpha r^\alpha - \operatorname{div} \mathbf{q}^\alpha + \Theta^\alpha + \boldsymbol{\mu}^\alpha \cdot (\mathbf{v}^\alpha - \mathbf{v}^2) + \mathbf{T}^\alpha \cdot \mathbf{D}^\alpha + \mathbf{T}_{\text{skew}}^\alpha \cdot (\mathbf{W}^\alpha - \mathbf{W}^2). \quad (2.22)$$

Partial Helmholtz free energy functions ψ^α are introduced as

$$\psi^\alpha = \varepsilon^\alpha - \eta^\alpha \theta^\alpha, \quad (2.23)$$

where η^α is the partial entropy, for which a prescription will be given in Section 3. The mixture Helmholtz free energy function ψ is defined as

$$\rho \psi = \sum_{\alpha=1}^2 \frac{\rho^\alpha \psi^\alpha}{\theta^\alpha}. \quad (2.24)$$

Without loss of generality, the partial stresses and diffusive forces can be written as

$$\mathbf{T}^\alpha = \theta^\alpha \phi^\alpha \mathbf{I} + \bar{\mathbf{T}}^\alpha, \quad \boldsymbol{\mu}^\alpha = \theta^\alpha \operatorname{grad} \phi^\alpha + \bar{\boldsymbol{\mu}}^\alpha, \quad (2.25)$$

where

$$\phi^\alpha = \rho^\alpha \left(\frac{\psi^\alpha}{\theta^\alpha} - \psi \right), \quad \sum_{\alpha=1}^2 \phi^\alpha = 0, \quad (2.26)$$

and the parts of the partial stresses and diffusive forces in which ϕ^α appears do not contribute to the balance equations. Following [5] we make the additional definitions

$$\eta^{*\alpha} = \eta^\alpha + \frac{\psi^\alpha}{\theta^\alpha}, \quad \mathbf{q}^{*\alpha} = \mathbf{q}^\alpha + \rho^\alpha \theta^\alpha \mathbf{u}^\alpha \eta^{*\alpha}, \quad (2.27)$$

and

$$T^\alpha = \frac{1}{\theta^\alpha}, \quad \Delta = T^1 - T^2, \quad (2.28)$$

where T^α is often called the *coldness* of \mathcal{C}^α . The balance of energy for the mixture is obtained by adding (2.22) for each \mathcal{C}^α and using (2.7)₂, (2.11), (2.20), and (2.23)–(2.28):²

² This is the only major equation presented in this section that does not appear in [5]. Note that the terms involving ϕ^α in the partial stresses and diffusive forces (2.25) do not contribute to the mixture energy balance (2.29).

$$\begin{aligned}
& -\rho \frac{d\psi}{dt} + \sum_{\alpha=1}^2 \frac{\rho^\alpha \eta^{*\alpha}}{T^\alpha} \frac{dT^\alpha}{dt} + \Theta^1 \Delta + \sum_{\alpha=1}^2 \rho^\alpha T^\alpha \left(-\frac{1}{T^\alpha} \frac{d^\alpha \eta^\alpha}{dt} + r^\alpha \right) + \sum_{\alpha=1}^2 T^\alpha (\bar{\boldsymbol{\mu}}^\alpha \cdot \mathbf{a}^\alpha + \bar{\mathbf{T}}^\alpha \cdot \mathbf{L}^\alpha) \\
& - \sum_{\alpha=1}^2 [T^\alpha \operatorname{div} \mathbf{q}^{*\alpha} - \operatorname{div}(\rho^\alpha \mathbf{u}^\alpha \eta^{*\alpha})] = 0.
\end{aligned} \tag{2.29}$$

The Clausius–Duhem inequality is

$$\sum_{\alpha=1}^2 \left[\rho^\alpha \frac{d^\alpha \eta^\alpha}{dt} - \frac{\rho^\alpha r^\alpha}{\theta^\alpha} + \operatorname{div} \left(\frac{\mathbf{q}^\alpha}{\theta^\alpha} \right) \right] \geq 0. \tag{2.30}$$

Using (2.23), (2.24) and (2.27)–(2.29), (2.30) becomes³

$$-\rho \frac{d\psi}{dt} + \sum_{\alpha=1}^2 \frac{\rho^\alpha \eta^{*\alpha}}{T^\alpha} \frac{dT^\alpha}{dt} + \Theta^1 \Delta + \sum_{\alpha=1}^2 T^\alpha (\bar{\boldsymbol{\mu}}^\alpha \cdot \mathbf{a}^\alpha + \bar{\mathbf{T}}^\alpha \cdot \mathbf{L}^\alpha) + \sum_{\alpha=1}^2 \mathbf{q}^{*\alpha} \cdot \operatorname{grad} T^\alpha \geq 0, \tag{2.31}$$

which will be invoked in Section 3 as a statement of *Part II* of the 2nd Law of Thermodynamics.

A superposed rigid-body motion of the mixture is defined by

$$\boldsymbol{\chi}^{\alpha+}(\mathbf{X}^\alpha, t^+) = \mathbf{Q}(t) \boldsymbol{\chi}^\alpha(\mathbf{X}^\alpha, t) + \mathbf{c}(t), \quad t^+ = t + c, \tag{2.32}$$

where $\mathbf{Q}(t)$ is a proper-orthogonal second-order tensor, $\mathbf{c}(t)$ is a vector, and c is a constant. The quantities $(\mathbf{Q}(t), \mathbf{c}(t), c)$ for each \mathcal{C}^α are equal. Under a superposed rigid-body motion of an unconstrained mixture at fixed temperatures, it can be shown that the following kinematic quantities transform as:

$$\begin{aligned}
\mathbf{F}^{\alpha+} &= \mathbf{Q} \mathbf{F}^\alpha, \quad \mathbf{J}^{\alpha+} = \mathbf{J}^\alpha, \quad \mathbf{D}^{\alpha+} = \mathbf{Q} \mathbf{D}^\alpha \mathbf{Q}^\top, \\
\rho^{\alpha+} &= \rho^\alpha, \quad \mathbf{a}^{\alpha+} = \mathbf{a}^\alpha, \quad \mathbf{W}^{\alpha+} = \frac{d^\alpha \mathbf{Q}}{dt} \mathbf{Q}^\top + \mathbf{Q} \mathbf{W}^\alpha \mathbf{Q}^\top,
\end{aligned} \tag{2.33}$$

while it is assumed that

$$\mathbf{T}^{\alpha+} = \mathbf{Q} \mathbf{T}^\alpha \mathbf{Q}^\top, \quad \boldsymbol{\mu}^{\alpha+} = \mathbf{Q} \boldsymbol{\mu}^\alpha, \quad \mathbf{q}^{\alpha+} = \mathbf{Q} \mathbf{q}^\alpha, \quad \beta^{\alpha+} = \beta^\alpha, \quad \varepsilon^{\alpha+} = \varepsilon^\alpha. \tag{2.34}$$

From (2.15), (2.21), (2.28)₂, and (2.33) and (2.34) it can be concluded that

$$r^{\alpha+} = r^\alpha, \quad \Theta^{\alpha+} = \Theta^\alpha, \quad \Delta^+ = \Delta. \tag{2.35}$$

³ This inequality is equal to a result (Eq. 5.23) in [5] with the mass exchange terms set to zero.

3. Entropy and restrictions on constitutive equations

The approach taken in this paper to develop a prescription for the partial entropy generalizes that of Krishnaswamy and Batra [11] to a mixture with different constituent temperatures. In particular, those authors applied an approach advocated for materials with memory [7–9] and thermoelastic materials [19] to a mixture of an elastic solid and a viscous fluid with a common temperature. In this paper, a homothermal quasi-static process at a common mixture temperature is introduced and *Part I* of the 2nd Law of Thermodynamics is invoked. This assumption immediately leads to a prescription for the partial entropy function for processes at a common mixture temperature. In order to define the entropy function for general processes, e.g., when the constituents have different temperatures, two important assumptions are made. Then, restrictions on the constitutive equations are derived from the mixture energy equation for path-independent processes. Further restrictions are derived for general processes from the Clausius–Duhem inequality, which is invoked as a statement of *Part II* of the 2nd Law of Thermodynamics. Finally, the constitutive results are compared, and shown to equal, those derived by Craine et al. [5], which lends support to the two assumptions made regarding the entropy function for general processes.

For a mixture of two elastic materials, we adopt the notation

$$\mathbf{\Omega} = \{\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^2\}, \quad (3.1)$$

where $\mathbf{G}^\alpha = \text{Grad } \mathbf{F}^\alpha$; $\mathbf{\Omega}$ can be considered to be a point in a 73-dimensional Euclidean space \mathcal{R}^{73} . Without loss of generality, we take

$$\varepsilon^\alpha = \hat{\varepsilon}^\alpha(\mathbf{\Omega}, \mathbf{a}^1, \Delta) = {}_o\hat{\varepsilon}^\alpha(\mathbf{\Omega}) + {}_e\hat{\varepsilon}^\alpha(\mathbf{\Omega}, \mathbf{a}^1, \Delta), \quad (3.2)$$

$$\mathbf{T}^\alpha = \hat{\mathbf{T}}^\alpha(\mathbf{\Omega}, \mathbf{a}^1, \Delta) = {}_o\hat{\mathbf{T}}^\alpha(\mathbf{\Omega}) + {}_e\hat{\mathbf{T}}^\alpha(\mathbf{\Omega}, \mathbf{a}^1, \Delta), \quad (3.3)$$

where

$${}_o\hat{\varepsilon}^\alpha(\mathbf{\Omega}) = \hat{\varepsilon}^\alpha(\mathbf{\Omega}, \mathbf{0}, 0), \quad {}_e\hat{\varepsilon}^\alpha(\mathbf{\Omega}, \mathbf{0}, 0) = 0, \quad (3.4)$$

$${}_o\hat{\mathbf{T}}^\alpha(\mathbf{\Omega}) = \hat{\mathbf{T}}^\alpha(\mathbf{\Omega}, \mathbf{0}, 0), \quad {}_e\hat{\mathbf{T}}^\alpha(\mathbf{\Omega}, \mathbf{0}, 0) = \mathbf{0}. \quad (3.5)$$

Further, it is assumed that

$$\mathbf{q}^\alpha = \hat{\mathbf{q}}^\alpha(\mathbf{\Omega}, \Delta, \mathbf{g}^1, \mathbf{g}^2), \quad \hat{\mathbf{q}}^\alpha(\mathbf{\Omega}, 0, \mathbf{0}, \mathbf{0}) = \mathbf{0}, \quad (3.6)$$

where $\mathbf{g}^\alpha = \text{grad } T^\alpha$. We require that $\varepsilon^\alpha(\mathbf{I}, \mathbf{I}, \mathbf{0}, \mathbf{0}, T_0, \mathbf{0}, 0) = 0$, where T_0 is the common mixture coldness in the reference configuration \mathcal{K}_0 . A path \mathcal{P} in the space \mathcal{R}^{73} is parameterized by a real-valued function $\delta(t)$ as

$$\mathcal{P}(\delta) = \{\mathbf{F}^1(\delta), \mathbf{F}^2(\delta), \mathbf{G}^1(\delta), \mathbf{G}^2(\delta), T^2(\delta)\}, \quad (3.7)$$

where $\delta_1 \leq \delta \leq \delta_2$. A homothermal quasi-static process at a common mixture temperature is defined to be the limit of homothermal processes at a common mixture temperature:

$$\mathbf{g}^\alpha = \mathbf{0}, \quad \Delta = 0, \quad \dot{\delta} = \frac{d\delta}{dt} > 0, \quad \dot{\delta} \rightarrow 0. \quad (3.8)$$

By defining

$$\mathbf{v}_*^\alpha = \frac{d^\alpha}{d\delta} \chi^\alpha(\mathbf{X}^\alpha, t) \quad (3.9)$$

and using \mathbf{v}_*^α in place of \mathbf{v}^α in (2.6), (2.7) and (2.11) we obtain definitions for the quantities \mathbf{v}_* , \mathbf{u}_*^α , \mathbf{a}_*^1 , \mathbf{L}_*^α , and \mathbf{D}_*^α so that

$$\mathbf{v}^\alpha = \mathbf{v}_*^\alpha \dot{\delta}, \quad \mathbf{v} = \mathbf{v}_* \dot{\delta}, \quad \mathbf{u}^\alpha = \mathbf{u}_*^\alpha \dot{\delta}, \quad \mathbf{a}^1 = \mathbf{a}_*^1 \dot{\delta}, \quad \mathbf{L}^\alpha = \mathbf{L}_*^\alpha \dot{\delta}, \quad \mathbf{D}^\alpha = \mathbf{D}_*^\alpha \dot{\delta}. \quad (3.10)$$

Therefore, in a homothermal quasi-static process at a common mixture temperature $\mathbf{v}^\alpha \rightarrow \mathbf{0}$, $\mathbf{v} \rightarrow \mathbf{0}$, $\mathbf{u}^\alpha \rightarrow \mathbf{0}$, $\mathbf{a}^1 \rightarrow \mathbf{0}$, $\mathbf{L}^\alpha \rightarrow \mathbf{0}$, and $\mathbf{D}^\alpha \rightarrow \mathbf{0}$. Finally, for such processes it is assumed that

$$\beta^\alpha \rightarrow 0, \quad r^\alpha \rightarrow 0 \quad (3.11)$$

and

$$\beta^\alpha / \dot{\delta} \rightarrow 0, \quad r^\alpha / \dot{\delta} \rightarrow r_{\text{lim}}^\alpha, \quad (3.12)$$

where r_{lim}^α remains finite. Hence, the energy equation (2.15) for \mathcal{C}^α can be written in rate-independent form for a homothermal quasi-static process at a common mixture temperature as

$$\rho^\alpha \frac{d^\alpha \hat{\varepsilon}^\alpha(\boldsymbol{\Omega}, \mathbf{0}, 0)}{d\delta} = \rho^\alpha r_{\text{lim}}^\alpha + \hat{\mathbf{T}}^\alpha(\boldsymbol{\Omega}, \mathbf{0}, 0) \cdot \mathbf{D}_*^\alpha \quad (3.13)$$

or, using (3.4) and (3.5), as

$$T^\alpha \rho^\alpha r_{\text{lim}}^\alpha = T^\alpha \left(\rho^\alpha \frac{d^\alpha \hat{\varepsilon}^\alpha}{d\delta} - \hat{\mathbf{T}}^\alpha \cdot \mathbf{D}_*^\alpha \right), \quad (3.14)$$

when $T^1 = T^2$.

Before invoking the 2nd Law of Thermodynamics, it is important to clarify how the paths $\mathcal{P}(\delta)$ in the space \mathcal{R}^{73} are defined.⁴ The assumption of the existence of a path-independent process is stated pointwise for some time interval $[t^1, t^2]$; due to the presence of two material points \mathbf{X}^1 of \mathcal{C}^1 and \mathbf{X}^2 of \mathcal{C}^2 at each spatial point \mathbf{x} in the mixture, this becomes non-trivial. For any process, the vectors $\boldsymbol{\Omega}(\delta(t^*))$, $t^* \in [t^1, t^2]$, defined for the material points \mathbf{X}^1 and \mathbf{X}^2 may generate distinct paths in the space \mathcal{R}^{73} . For example, following the material point \mathbf{X}^1 , at each time t^* the vector $\boldsymbol{\Omega}(\delta^1(t^*))$ is defined by evaluating \mathbf{F}^1 and \mathbf{G}^1 for the material point \mathbf{X}^1 that exists at the spatial point \mathbf{x} at t^* , and evaluating \mathbf{F}^2 and \mathbf{G}^2 for the material point \mathbf{X}^2 that exists at the same spatial point \mathbf{x} at t^* .

⁴ Prashanth Vijalapura (U.C. Berkeley) offered this clarification upon reading an earlier version of this paper.

Thus, by evaluating $\mathbf{\Omega}(\delta^1(t^*))$ for all $t^* \in [t^1, t^2]$, a path $\mathcal{P}_{\mathbf{X}^1}(\delta^1)$ is generated by following \mathbf{X}^1 . Likewise, a path $\mathcal{P}_{\mathbf{X}^2}(\delta^2)$ is generated by following \mathbf{X}^2 .

Therefore, consider paths $\mathcal{P}_{\mathbf{X}^1}(\delta^1)$ and $\mathcal{P}_{\mathbf{X}^2}(\delta^2)$ corresponding to homothermal quasi-static processes at a common mixture temperature for which the collection of vectors $\mathbf{\Omega}(\delta^\alpha(t))$ are defined for \mathbf{X}^1 and \mathbf{X}^2 , respectively. Now, *Part I* of the 2nd Law of Thermodynamics is invoked to assert that the Clausius integrals given by

$$\mathcal{J}^\alpha = \int_{\delta_1^\alpha}^{\delta_2^\alpha} T^\alpha \rho^\alpha r_{\text{lim}}^\alpha d\delta^\alpha = \int_{\delta_1^\alpha}^{\delta_2^\alpha} T^\alpha \left(\rho^\alpha \frac{d^\alpha \hat{\mathbf{e}}^\alpha}{d\delta^\alpha} - \hat{\mathbf{T}}^\alpha \cdot \mathbf{D}_*^\alpha \right) d\delta^\alpha \quad (3.15)$$

are path-independent. This furnishes a partial entropy function $\eta^\alpha = \hat{\eta}^\alpha(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^\alpha)$ such that for all homothermal quasi-static processes

$$\frac{d^\alpha \eta^\alpha}{d\delta^\alpha} = T^\alpha r_{\text{lim}}^\alpha, \quad (3.16)$$

when $T^1 = T^2$. The arbitrary constant of integration in the partial entropy is fixed by requiring $\eta^\alpha(\mathbf{I}, \mathbf{I}, \mathbf{0}, \mathbf{0}, T_0) = 0$.

Finally, we make two additional assumptions for general processes, in which T^1 may not be equal to T^2 :⁵

1. each partial entropy function $\eta^\alpha = \hat{\eta}^\alpha(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^\alpha)$ is independent of $\mathbf{a}^1, \mathbf{g}^\alpha$, and Δ ;
2. each partial entropy function $\eta^\alpha = \hat{\eta}^\alpha(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^\alpha)$ is defined through (3.16) for the corresponding homothermal quasi-static process at a common mixture temperature equal to $\theta^\alpha = 1/T^\alpha$.

In other words, for a general process in which $T^1 \neq T^2$, $\eta^1 = \hat{\eta}^1(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^1)$ is prescribed by considering a homothermal quasi-static process when the common mixture temperature is equal to $\theta^1 = 1/T^1$ while $\eta^2 = \hat{\eta}^2(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^2)$ is prescribed by considering a different homothermal quasi-static process when the common mixture temperature is equal to $\theta^2 = 1/T^2$. Thus, we obtain

$$\eta^1 = \hat{\eta}^1(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^1), \quad \eta^2 = \hat{\eta}^2(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^2) \quad (3.17)$$

for all processes. From (2.27) and (3.17) we obtain⁶

$$\eta^{*\alpha} = \hat{\eta}^\alpha(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^\alpha) + T^\alpha \hat{\psi}^\alpha(\mathbf{F}^1, \mathbf{F}^2, \mathbf{G}^1, \mathbf{G}^2, T^2, \Delta). \quad (3.18)$$

To develop restrictions on the constitutive equations, we recall (2.27), (3.6)₂, and (3.10) and write the mixture energy equation (2.29) as follows for a homothermal quasi-static process at a common mixture temperature:

⁵ These two assumptions are the crucial generalization of the procedure outlined in [11] to a mixture with different constituent temperatures. It will be seen that, with these assumptions, the final constitutive restrictions obtained from the 2nd Law are the same as those derived in [5].

⁶ Thus, although the partial entropy functions (3.17) depend only on their respective temperatures, the modified entropy functions (3.18) may depend on both temperatures.

$$\begin{aligned}
& -\rho \frac{d\psi}{d\delta} \dot{\delta} + \sum_{\alpha=1}^2 \frac{\rho^\alpha \eta^{*\alpha}}{T^2} \frac{dT^2}{d\delta} \dot{\delta} + \sum_{\alpha=1}^2 \left(-\rho^\alpha \frac{d^\alpha \eta^\alpha}{d\delta} \dot{\delta} + \rho^\alpha r^\alpha T^2 \right) + T^2 \left({}_o\bar{\boldsymbol{\mu}}^1 \cdot \mathbf{a}_*^1 + {}_o\bar{\mathbf{T}}^1 \cdot \mathbf{L}_*^1 + {}_o\bar{\mathbf{T}}^2 \cdot \mathbf{L}_*^2 \right) \dot{\delta} \\
& - \sum_{\alpha=1}^2 \left[T^\alpha \operatorname{div} \left(\frac{\rho^\alpha \mathbf{u}_*^\alpha \dot{\delta} \eta^{*\alpha}}{T^\alpha} \right) - \operatorname{div}(\rho^\alpha \mathbf{u}_*^\alpha \dot{\delta} \eta^{*\alpha}) \right] = 0.
\end{aligned} \tag{3.19}$$

It is apparent that the last summation term in (3.19) vanishes because, for a homothermal process, $\operatorname{grad} T^\alpha$ vanishes. We define, as in (3.2)–(3.5),

$$\psi = \hat{\psi}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta) = {}_o\hat{\psi}(\boldsymbol{\Omega}) + {}_e\hat{\psi}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta), \tag{3.20}$$

$$\bar{\boldsymbol{\mu}}^\alpha = \bar{\boldsymbol{\mu}}^\alpha(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta) = {}_o\bar{\boldsymbol{\mu}}^\alpha(\boldsymbol{\Omega}) + {}_e\bar{\boldsymbol{\mu}}^\alpha(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta), \tag{3.21}$$

$$\bar{\mathbf{T}}^\alpha = \bar{\mathbf{T}}^\alpha(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta) = {}_o\bar{\mathbf{T}}^\alpha(\boldsymbol{\Omega}) + {}_e\bar{\mathbf{T}}^\alpha(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta), \tag{3.22}$$

$$\Theta = \hat{\Theta}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta) = {}_o\hat{\Theta}(\boldsymbol{\Omega}) + {}_e\hat{\Theta}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta). \tag{3.23}$$

From (2.14), (2.19), (2.21), and (3.11)₁ we obtain

$${}_o\hat{\Theta}(\boldsymbol{\Omega}) = 0 \Rightarrow \Theta = \hat{\Theta}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta) = {}_e\hat{\Theta}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta). \tag{3.24}$$

Using (3.12)₂ and (3.16), the mixture energy equation (3.19) can be written for a homothermal quasi-static process at a common mixture temperature as

$$-\rho \frac{d_o\hat{\psi}}{d\delta} + \frac{\rho(\eta + {}_o\hat{\psi})}{T^2} \frac{dT^2}{d\delta} + T^2 \left({}_o\bar{\boldsymbol{\mu}}^1 \cdot \mathbf{a}_*^1 + {}_o\bar{\mathbf{T}}^1 \cdot \mathbf{L}_*^1 + {}_o\bar{\mathbf{T}}^2 \cdot \mathbf{L}_*^2 \right) = 0, \tag{3.25}$$

where the second term in (3.25) was obtained by recalling (2.24), (2.27)₁, (3.20), and defining

$$\rho\eta = \sum_{\alpha=1}^2 \rho^\alpha \eta^\alpha. \tag{3.26}$$

Eq. (3.25) will be referred to as the Gibbs equation for a mixture of elastic materials. Because the partial internal energies and the partial entropies vanish in the reference configuration \mathcal{K}_0 , (2.23) and (2.24) lead to the result $\psi(\mathbf{I}, \mathbf{I}, \mathbf{0}, \mathbf{0}, T_0, \mathbf{0}, 0) = 0$. Using (3.1), (3.20), and the chain rule, (3.25) can be written as

$$\begin{aligned}
& \left(\frac{\rho(\eta + {}_o\hat{\psi})}{T^2} - \rho \frac{\partial {}_o\hat{\psi}}{\partial T^2} \right) \frac{dT^2}{d\delta} + T^2 {}_o\bar{\boldsymbol{\mu}}^1 \cdot \mathbf{a}_*^1 + \sum_{\alpha=1}^2 \left(\rho \frac{\partial {}_o\hat{\psi}}{\partial \mathbf{F}^\alpha} \operatorname{grad} \mathbf{F}^\alpha \cdot \mathbf{u}_*^\alpha \right) \\
& + \sum_{\alpha=1}^2 \left(T^\alpha {}_o\bar{\mathbf{T}}^\alpha - \rho \frac{\partial {}_o\hat{\psi}}{\partial \mathbf{F}^\alpha} \mathbf{F}^{\alpha T} \right) \cdot \mathbf{L}_*^\alpha - \sum_{\alpha=1}^2 \rho \frac{\partial {}_o\hat{\psi}}{\partial \mathbf{G}^\alpha} \cdot \left(\frac{d^\alpha \mathbf{G}^\alpha}{d\delta} - \operatorname{grad} \mathbf{G}^\alpha[\mathbf{u}_*^\alpha] \right) = 0,
\end{aligned} \tag{3.27}$$

where the notation $(\partial_{\circ}\hat{\psi}/\partial\mathbf{F}^{\alpha})\mathbf{grad}\mathbf{F}^{\alpha}$ has the component form $(\partial_{\circ}\hat{\psi}/\partial F_{jA}^{\alpha})F_{jA,i}^{\alpha}$ and $\mathbf{grad}\mathbf{G}^{\alpha}[\mathbf{u}_*^{\alpha}]$ has the component form $\mathbf{G}_{iAB,j}^{\alpha}\mathbf{u}_{*j}^{\alpha}$. Using arguments that have become standard, the following constitutive results are deduced from (3.27):

$$\frac{\rho(\eta + \circ\hat{\psi})}{T^2} = \rho \frac{\partial_{\circ}\hat{\psi}}{\partial T^2}, \quad (3.28)$$

$$\circ\bar{\mathbf{T}}^{\alpha} = \frac{\rho}{T^2} \frac{\partial_{\circ}\hat{\psi}}{\partial \mathbf{F}^{\alpha}} \mathbf{F}^{\alpha\top}, \quad (3.29)$$

$$\circ\bar{\boldsymbol{\mu}}^1 = \frac{1}{T^2} \left(-\rho^2 \frac{\partial_{\circ}\hat{\psi}}{\partial \mathbf{F}^1} \mathbf{grad}\mathbf{F}^1 + \rho^1 \frac{\partial_{\circ}\hat{\psi}}{\partial \mathbf{F}^2} \mathbf{grad}\mathbf{F}^2 \right), \quad (3.30)$$

$$\frac{\partial_{\circ}\hat{\psi}}{\partial \mathbf{G}^{\alpha}} = \mathbf{0}. \quad (3.31)$$

These equations also hold for arbitrary processes because none of the variables that appear in (3.28)–(3.31) depend on either \mathbf{a}^1 , Δ , or \mathbf{g}^{α} . We remark that (3.29) and (3.30) agree with Eqs. (6.12) and (6.13) of [5] while (3.31) agrees with a result that is discussed in p. 180 of [5]. It will be shown from (3.28) and a result obtained below that our partial entropy restriction agrees with Eq. (6.9) of [5].

Also, the partial stresses (3.29) and diffusive forces (3.30) can be written in terms of the constituent free energy functions. To do this, we introduce the additive decomposition for each partial free energy function

$$\psi^{\alpha} = \hat{\psi}^{\alpha}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta) = \circ\hat{\psi}^{\alpha}(\boldsymbol{\Omega}) + \circ\hat{\psi}^{\alpha}(\boldsymbol{\Omega}, \mathbf{a}^1, \Delta). \quad (3.32)$$

From (2.24), (3.20), and (3.32) the mixture free energy function for path-independent processes becomes

$$\rho \circ\hat{\psi} = T^2 \sum_{\alpha=1}^2 \rho^{\alpha} \circ\hat{\psi}^{\alpha}. \quad (3.33)$$

Consequently, (3.29) and (3.30) may be expressed as

$$\circ\bar{\mathbf{T}}^{\alpha} = \sum_{\beta=1}^2 \rho^{\beta} \frac{\partial_{\circ}\hat{\psi}^{\beta}}{\partial \mathbf{F}^{\alpha}} \mathbf{F}^{\alpha\top}, \quad (3.34)$$

$$\circ\bar{\boldsymbol{\mu}}^1 = \rho^1 \frac{\partial_{\circ}\hat{\psi}^1}{\partial \mathbf{F}^2} \mathbf{grad}\mathbf{F}^2 - \rho^2 \frac{\partial_{\circ}\hat{\psi}^2}{\partial \mathbf{F}^1} \mathbf{grad}\mathbf{F}^1, \quad (3.35)$$

which agree with (6.16) and (6.17) of [5].

To obtain further restrictions on the constitutive equations, the Clausius–Duhem inequality is invoked as a statement of *Part II* of the 2nd Law of Thermodynamics for general processes. Recalling (2.8), (3.1), (3.20)–(3.24), and (3.28)–(3.31) the Clausius–Duhem inequality (2.31) becomes

$$\begin{aligned}
& \left(-\rho \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^1} \mathbf{F}^{1\text{T}} + T^2 {}_e \bar{\mathbf{T}}^1 + \Delta_o \bar{\mathbf{T}}^1 + \Delta_e \bar{\mathbf{T}}^1 \right) \cdot \mathbf{L}^1 + \left(-\rho \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^2} \mathbf{F}^{2\text{T}} + T^2 {}_e \bar{\mathbf{T}}^2 \right) \cdot \mathbf{L}^2 \\
& + \left(\rho^2 \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^1} \text{grad } \mathbf{F}^1 - \rho^1 \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^2} \text{grad } \mathbf{F}^2 + T^2 {}_e \bar{\boldsymbol{\mu}}^1 + \Delta_o \bar{\boldsymbol{\mu}}^1 + \Delta_e \bar{\boldsymbol{\mu}}^1 \right) \cdot \mathbf{a}^1 \\
& + \left(\frac{\sum_{\alpha=1}^2 \rho^\alpha T^\alpha {}_e \hat{\psi}^\alpha}{T^2} - \frac{\rho^1 \eta^{*1}}{T^2} - \rho \frac{\partial_e \hat{\psi}}{\partial T^2} + \frac{\rho^1 \eta^{*1}}{T^1} \right) \frac{dT^2}{dt} + \left(\frac{\rho^1 \eta^{*1}}{T^1} - \rho \frac{\partial_e \hat{\psi}}{\partial \Delta} \right) \frac{d\Delta}{dt} + {}_e \Theta^1 \Delta \\
& - \rho \frac{\partial_e \hat{\psi}}{\partial \mathbf{a}^1} \frac{d\mathbf{a}^1}{dt} - \rho \sum_{\alpha=1}^2 \frac{\partial_e \hat{\psi}}{\partial \mathbf{G}^\alpha} \cdot \left(\frac{d^\alpha \mathbf{G}^\alpha}{dt} - \text{grad } \mathbf{G}^\alpha [\mathbf{u}^\alpha] \right) + \sum_{\alpha=1}^2 \mathbf{q}^{*\alpha} \cdot \text{grad } T^\alpha \geq 0. \tag{3.36}
\end{aligned}$$

Using arguments that have become standard, we obtain from (3.36) the additional restrictions

$$-\frac{\rho^1 \eta^{*1}}{T^2} + \frac{\rho^1 \eta^{*1}}{T^1} + \frac{\sum_{\alpha=1}^2 \rho^\alpha T^\alpha {}_e \hat{\psi}^\alpha}{T^2} = \rho \frac{\partial_e \hat{\psi}}{\partial T^2}, \tag{3.37}$$

$$\frac{\rho^1 \eta^{*1}}{T^1} = \rho \frac{\partial_e \hat{\psi}}{\partial \Delta}, \tag{3.38}$$

$$\frac{\partial_e \hat{\psi}}{\partial \mathbf{a}^1} = \mathbf{0}, \tag{3.39}$$

$$\frac{\partial_e \hat{\psi}}{\partial \mathbf{G}^\alpha} = \mathbf{0}, \tag{3.40}$$

and the residual inequality

$$R \geq 0, \tag{3.41}$$

where ⁷

⁷ This residual inequality does not appear in [5].

$$\begin{aligned}
R = & \left(-\rho \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^1} \mathbf{F}^{1T} + T^2 {}_e\bar{\mathbf{T}}^1 + \Delta_o \bar{\mathbf{T}}^1 + \Delta_e \bar{\mathbf{T}}^1 \right) \cdot \mathbf{L}^1 + \left(-\rho \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^2} \mathbf{F}^{2T} + T^2 {}_e\bar{\mathbf{T}}^2 \right) \cdot \mathbf{L}^2 \\
& + \left(\rho^2 \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^1} \text{grad} \mathbf{F}^1 - \rho^1 \frac{\partial_e \hat{\psi}}{\partial \mathbf{F}^2} \text{grad} \mathbf{F}^2 + T^2 {}_e\bar{\boldsymbol{\mu}}^1 + \Delta_o \bar{\boldsymbol{\mu}}^1 + \Delta_e \bar{\boldsymbol{\mu}}^1 \right) \cdot \mathbf{a}^1 + {}_e\Theta^1 \Delta + \sum_{\alpha=1}^2 \mathbf{q}^{*\alpha} \cdot \text{grad} T^\alpha.
\end{aligned} \tag{3.42}$$

This residual inequality reduces to that presented in [11] when the possible processes are restricted to those for which there exist a common mixture temperature, since ${}_e\hat{\psi} = 0$ when $\Delta = 0$.

Using (3.20), (3.31), (3.39), and (3.40), the Helmholtz free energy function becomes

$$\psi = \hat{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^2, \Delta) = {}_o\hat{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^2) + {}_e\hat{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^2, \Delta). \tag{3.43}$$

Upon adding (3.37) and (3.38) we obtain

$$\frac{\rho^1 \eta^{*1}}{T^2} = \rho \left(-\frac{\partial_e \hat{\psi}}{\partial T^2} + \frac{\partial_e \hat{\psi}}{\partial \Delta} \right) + \frac{\sum_{\alpha=1}^2 \rho^\alpha T^\alpha {}_e\hat{\psi}^\alpha}{T^2}. \tag{3.44}$$

The results (3.39) and (3.40) (and consequently (3.43)) agree with those derived in [5]; thus, it remains to show that the restrictions (3.28), (3.37), and (3.38) for the partial entropies agree with those presented in [5]. To see this, we first define

$$\psi = \bar{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^1, T^2) = {}_o\bar{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^2) + {}_e\bar{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^1, T^2). \tag{3.45}$$

Comparison of (3.45) with (3.43) shows that

$${}_o\bar{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^2) = {}_o\hat{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^2), \quad {}_e\bar{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^1, T^2) = {}_e\hat{\psi}(\mathbf{F}^1, \mathbf{F}^2, T^2, T^1 - T^2). \tag{3.46}$$

From (3.44)–(3.46), we obtain

$$\frac{\partial_o \bar{\psi}}{\partial T^2} = \frac{\partial_o \hat{\psi}}{\partial T^2}, \tag{3.47}$$

$$\frac{\partial \hat{\psi}}{\partial T^2} = \frac{\partial_o \hat{\psi}}{\partial T^2} + \frac{\partial_e \hat{\psi}}{\partial T^2}, \tag{3.48}$$

$$\frac{\partial_e \bar{\psi}}{\partial T^2} = \frac{\partial_e \hat{\psi}}{\partial T^2} + \frac{\partial_e \hat{\psi}}{\partial \Delta} \frac{\partial \Delta}{\partial T^2} = \frac{\partial_e \hat{\psi}}{\partial T^2} - \frac{\partial_e \hat{\psi}}{\partial \Delta}, \tag{3.49}$$

$$\frac{\partial_e \bar{\psi}}{\partial T^1} = \frac{\partial_e \hat{\psi}}{\partial \Delta} \frac{\partial \Delta}{\partial T^1} = \frac{\partial_e \hat{\psi}}{\partial \Delta}. \tag{3.50}$$

From (2.24), (2.27)₁, (3.26), and (3.28) we have

$$\frac{\rho(\eta + {}_o\hat{\psi})}{T^2} = \frac{\sum_{\alpha=1}^2(\rho^\alpha\eta^{*\alpha} - \rho^\alpha T^\alpha {}_e\hat{\psi}^\alpha)}{T^2} = \rho \frac{\partial_o\hat{\psi}}{\partial T^2}. \quad (3.51)$$

Using (3.44) and (3.47)–(3.50) we obtain from (3.51)

$$\begin{aligned} \rho^2\eta^{*2} &= -\rho^1\eta^{*1} + \rho T^2 \left(\frac{\partial\hat{\psi}}{\partial T^2} - \frac{\partial_e\hat{\psi}}{\partial T^2} \right) + \sum_{\alpha=1}^2 \rho^\alpha T^\alpha {}_e\hat{\psi}^\alpha \\ &= -\rho T^2 \left(-\frac{\partial_e\hat{\psi}}{\partial T^2} + \frac{\partial_e\hat{\psi}}{\partial \Delta} \right) - \sum_{\alpha=1}^2 \rho^\alpha T^\alpha {}_e\hat{\psi}^\alpha + \rho T^2 \left(\frac{\partial\hat{\psi}}{\partial T^2} - \frac{\partial_e\hat{\psi}}{\partial T^2} \right) + \sum_{\alpha=1}^2 \rho^\alpha T^\alpha {}_e\hat{\psi}^\alpha \\ &= -\rho T^2 \left(-\frac{\partial_e\bar{\psi}}{\partial T^2} - \frac{\partial_e\hat{\psi}}{\partial \Delta} + \frac{\partial_e\hat{\psi}}{\partial \Delta} \right) + \rho T^2 \left(\frac{\partial\hat{\psi}}{\partial T^2} - \frac{\partial_e\hat{\psi}}{\partial T^2} \right) \\ &= \rho T^2 \left(\frac{\partial\hat{\psi}}{\partial T^2} + \frac{\partial_e\bar{\psi}}{\partial T^2} - \frac{\partial_e\hat{\psi}}{\partial T^2} \right) = \rho T^2 \left(\frac{\partial_o\hat{\psi}}{\partial T^2} + \frac{\partial_e\hat{\psi}}{\partial T^2} + \frac{\partial_e\bar{\psi}}{\partial T^2} - \frac{\partial_e\hat{\psi}}{\partial T^2} \right) \\ &= \rho T^2 \left(\frac{\partial_o\hat{\psi}}{\partial T^2} + \frac{\partial_e\bar{\psi}}{\partial T^2} \right) \end{aligned} \quad (3.52)$$

so that, using (3.45) and (3.47),

$$\rho^2\eta^{*2} = \rho T^2 \frac{\partial\bar{\psi}}{\partial T^2}. \quad (3.53)$$

Finally, using (3.38) and (3.50) we obtain

$$\frac{\rho^1\eta^{*1}}{T^1} = \rho \frac{\partial_e\hat{\psi}}{\partial \Delta} = \rho \frac{\partial_e\bar{\psi}}{\partial T^1}, \quad (3.54)$$

so that, using (3.45),

$$\rho^1\eta^{*1} = \rho T^1 \frac{\partial\bar{\psi}}{\partial T^1}. \quad (3.55)$$

Eqs. (3.53) and (3.55) are equal to (6.9) of [5].

In summary, the constitutive restrictions were first obtained from the mixture energy equation for path-independent processes, and further restrictions were obtained from the Clausius–Duhem inequality for general processes. These constitutive restrictions equal those of Craine et al. [5] even though in [5] all restrictions were obtained from the Clausius–Duhem inequality after introducing the partial entropy as a primitive variable. There is one important difference between the results of the present paper and those of [5]: even though the modified entropy functions (3.53) and (3.55) may depend on both temperatures and agree with those of [5], we have the additional

“restriction” that the partial entropy functions η^α depend only on their respective constituent temperatures, due to the nature of the entropy prescriptions (3.17).

4. Equivalence classes

In mixture theory, Mills [21] and other authors [22–25] have studied the special constraint of intrinsic incompressibility, which simultaneously restricts the possible values of the constituent densities. For a mixture of two elastic materials, this mechanical constraint can be expressed in terms of the deformation gradient tensors of both constituents. Here, we wish to consider more general thermomechanical constraints, so that the constraint of Mills [21] can be extended to include temperature-dependent incompressibility, as proposed by Trapp [29] for thermoelastic materials. Furthermore, the results obtained for a mixture constrained to have a common temperature will be compared to those obtained for the special case of a common mixture temperature.

Consider a thermomechanical internal constraint of the form

$$\phi(\mathbf{F}^1, \mathbf{F}^2, T^2, \Delta) = 0, \quad (4.1)$$

where ϕ is a sufficiently smooth scalar-valued function defined for the subset of the 20-dimensional space \mathcal{E} for which $\det \mathbf{F}^\alpha > 0$, $T^2 > 0$, and $T^1 = \Delta + T^2 > 0$. We assume that the 20-dimensional vector

$$\left(\frac{\partial \phi}{\partial \mathbf{F}^1}, \frac{\partial \phi}{\partial \mathbf{F}^2}, \frac{\partial \phi}{\partial T^2}, \frac{\partial \phi}{\partial \Delta} \right) \neq \mathbf{0}$$

so that (4.1) defines a fixed 19-dimensional hypersurface $\mathcal{S} \subset \mathcal{E}$ referred to as the *constraint manifold*. Furthermore, we assume that ϕ remains invariant under superposed rigid-body motions of the mixture at fixed constituent temperatures so that (4.1) can be written in the objective form

$$\hat{\phi}(\mathbf{C}^1, \mathbf{F}^{1T} \mathbf{F}^2, T^2, \Delta) = 0, \quad (4.2)$$

where $\mathbf{C}^\alpha = \mathbf{F}^{\alpha T} \mathbf{F}^\alpha$. Although (4.2) may be more convenient for representing some types of internal constraints, in the present paper the development will proceed with the more primitive form given by (4.1).

Klisch [20] has discussed how a mixture process that satisfies (4.1) may generate different paths on \mathcal{S} . In particular, the vectors $(\mathbf{F}^1(t), \mathbf{F}^2(t), T^2(t), \Delta(t))$ defined for \mathbf{X}^1 , \mathbf{X}^2 , and \mathbf{x} generate paths $\mathcal{C}_{\mathbf{X}^1}$, $\mathcal{C}_{\mathbf{X}^2}$, and $\mathcal{C}_{\mathbf{x}}$, respectively, on \mathcal{S} . Furthermore, a tangent vector to $\mathcal{C}_{\mathbf{X}^1}$ on \mathcal{S} is defined using the material time derivative $d^1(\cdot)/dt$ following \mathcal{C}^1 . In a similar fashion, the tangent vector to $\mathcal{C}_{\mathbf{X}^2}$ on \mathcal{S} is defined using the material time derivative $d^2(\cdot)/dt$ following \mathcal{C}^2 while a tangent vector to $\mathcal{C}_{\mathbf{x}}$ on \mathcal{S} is defined using the partial time derivative $\partial(\cdot)/\partial t$.

Therefore, the constraint (4.1) can be considered while one of three points are held fixed: (i) a material point \mathbf{X}^1 ; (ii) a material point \mathbf{X}^2 ; or (iii) the spatial point \mathbf{x} which is simultaneously occupied by \mathbf{X}^1 and \mathbf{X}^2 at time t . A normal to \mathcal{S} is given by

$$\mathbf{n} = \left(\frac{\partial \phi}{\partial \mathbf{F}^1}, \frac{\partial \phi}{\partial \mathbf{F}^2}, \frac{\partial \phi}{\partial T^2}, \frac{\partial \phi}{\partial \Delta} \right) \quad (4.3)$$

for all three cases (i)–(iii). Tangents to the curves $\mathcal{C}_{\mathbf{x}^1}$, $\mathcal{C}_{\mathbf{x}^2}$, and $\mathcal{C}_{\mathbf{x}}$ corresponding to the three cases (i)–(iii) are given by

$$\begin{aligned} \mathbf{t}_{\mathbf{x}^1} &= \left(\frac{d^1 \mathbf{F}^1}{dt}, \frac{d^1 \mathbf{F}^2}{dt}, \frac{d^1 T^2}{dt}, \frac{d^1 \Delta}{dt} \right), \\ \mathbf{t}_{\mathbf{x}^2} &= \left(\frac{d^2 \mathbf{F}^1}{dt}, \frac{d^2 \mathbf{F}^2}{dt}, \frac{d^2 T^2}{dt}, \frac{d^2 \Delta}{dt} \right), \\ \mathbf{t}_{\mathbf{x}} &= \left(\frac{\partial \mathbf{F}^1}{\partial t}, \frac{\partial \mathbf{F}^2}{\partial t}, \frac{\partial T^2}{\partial t}, \frac{\partial \Delta}{\partial t} \right). \end{aligned} \quad (4.4)$$

Hence, for any process satisfying the constraint (4.1) it is necessary that

$$\begin{aligned} \mathbf{n} \cdot \mathbf{t}_{\mathbf{x}^1} &= \frac{\partial \phi}{\partial \mathbf{F}^1} \cdot \frac{d^1 \mathbf{F}^1}{dt} + \frac{\partial \phi}{\partial \mathbf{F}^2} \cdot \frac{d^1 \mathbf{F}^2}{dt} + \frac{\partial \phi}{\partial T^2} \frac{d^1 T^2}{dt} + \frac{\partial \phi}{\partial \Delta} \frac{d^1 \Delta}{dt} = 0, \\ \mathbf{n} \cdot \mathbf{t}_{\mathbf{x}^2} &= \frac{\partial \phi}{\partial \mathbf{F}^1} \cdot \frac{d^2 \mathbf{F}^1}{dt} + \frac{\partial \phi}{\partial \mathbf{F}^2} \cdot \frac{d^2 \mathbf{F}^2}{dt} + \frac{\partial \phi}{\partial T^2} \frac{d^2 T^2}{dt} + \frac{\partial \phi}{\partial \Delta} \frac{d^2 \Delta}{dt} = 0, \\ \mathbf{n} \cdot \mathbf{t}_{\mathbf{x}} &= \frac{\partial \phi}{\partial \mathbf{F}^1} \cdot \frac{\partial \mathbf{F}^1}{\partial t} + \frac{\partial \phi}{\partial \mathbf{F}^2} \cdot \frac{\partial \mathbf{F}^2}{\partial t} + \frac{\partial \phi}{\partial T^2} \frac{\partial T^2}{\partial t} + \frac{\partial \phi}{\partial \Delta} \frac{\partial \Delta}{\partial t} = 0 \end{aligned} \quad (4.5)$$

for the three cases (i)–(iii). Recalling

$$\frac{d^\alpha \mathbf{F}^\alpha}{dt} = \mathbf{L}^\alpha \mathbf{F}^\alpha, \quad (4.6)$$

(2.4)₂, and (2.8)₂, the constraint equations (4.5) can be written as

$$\begin{aligned} \mathbf{n} \cdot \mathbf{t}_{\mathbf{x}^1} &= \frac{\partial \phi}{\partial \mathbf{F}^1} \cdot \mathbf{L}^1 \mathbf{F}^1 + \frac{\partial \phi}{\partial \mathbf{F}^2} \cdot (\mathbf{L}^2 \mathbf{F}^2 + \mathbf{grad} \mathbf{F}^2[\mathbf{a}^1]) + \frac{\partial \phi}{\partial T^2} \left(\frac{dT^2}{dt} + \mathbf{grad} T^2 \cdot \mathbf{u}^1 \right) \\ &\quad + \frac{\partial \phi}{\partial \Delta} \left(\frac{d\Delta}{dt} + \mathbf{grad} \Delta \cdot \mathbf{u}^1 \right) = 0, \\ \mathbf{n} \cdot \mathbf{t}_{\mathbf{x}^2} &= \frac{\partial \phi}{\partial \mathbf{F}^1} \cdot (\mathbf{L}^1 \mathbf{F}^1 - \mathbf{grad} \mathbf{F}^1[\mathbf{a}^1]) + \frac{\partial \phi}{\partial \mathbf{F}^2} \cdot \mathbf{L}^2 \mathbf{F}^2 + \frac{\partial \phi}{\partial T^2} \left(\frac{dT^2}{dt} + \mathbf{grad} T^2 \cdot \mathbf{u}^2 \right) \\ &\quad + \frac{\partial \phi}{\partial \Delta} \left(\frac{d\Delta}{dt} + \mathbf{grad} \Delta \cdot \mathbf{u}^2 \right) = 0, \\ \mathbf{n} \cdot \mathbf{t}_{\mathbf{x}} &= \frac{\partial \phi}{\partial \mathbf{F}^1} \cdot (\mathbf{L}^1 \mathbf{F}^1 - \mathbf{grad} \mathbf{F}^1[\mathbf{v}^1]) + \frac{\partial \phi}{\partial \mathbf{F}^2} \cdot (\mathbf{L}^2 \mathbf{F}^2 - \mathbf{grad} \mathbf{F}^2[\mathbf{v}^2]) + \frac{\partial \phi}{\partial T^2} \left(\frac{dT^2}{dt} - \mathbf{grad} T^2 \cdot \mathbf{v} \right) \\ &\quad + \frac{\partial \phi}{\partial \Delta} \left(\frac{d\Delta}{dt} - \mathbf{grad} \Delta \cdot \mathbf{v} \right) = 0, \end{aligned} \quad (4.7)$$

where the notation $\text{grad } \mathbf{F}^\alpha[\mathbf{a}]$ has the component form $F_{iA,k}^\alpha a_k$. The middle terms of the constraint equations (4.7) can also be shown to be equal since (4.1) implies

$$\text{grad } \phi = \frac{\partial \phi}{\partial \mathbf{x}} = \frac{\partial \phi}{\partial \mathbf{F}^1} \text{grad } \mathbf{F}^1 + \frac{\partial \phi}{\partial \mathbf{F}^2} \text{grad } \mathbf{F}^2 + \frac{\partial \phi}{\partial T^2} \text{grad } T^2 + \frac{\partial \phi}{\partial \Delta} \text{grad } \Delta = \mathbf{0}. \quad (4.8)$$

Although the three tangents (4.4) are, in general, not equal at a time t during a given process, the relation (4.8) ensures that they all lie in the tangent space to a point on \mathcal{S} . The development of constrained mixtures will proceed with case (ii) (i.e., holding \mathbf{X}^2 fixed) represented by (4.7)₂. Also, it is assumed that the constraint is satisfied in the reference configuration:⁸

$$\phi(\mathbf{I}, \mathbf{I}, T_0, 0) = 0. \quad (4.9)$$

To define an equivalence class associated with the constraint, consider two mixtures of elastic materials, m_1 and m_2 , which have common values of partial densities in the reference configuration \mathcal{H}_0 . These mixtures can be considered as elements of the set \mathcal{M} of all unconstrained mixtures, which are infinite in number. An equivalence relation associated with the constraint (4.1) is defined as:

Definition 1. The mixture m_1 is equivalent to the mixture m_2 ($m_1 \sim m_2$) if and only if

(i) $\psi_{m_1}^\alpha = \psi_{m_2}^\alpha$ ($\Rightarrow \psi_{m_1} = \psi_{m_2}$);

(ii) $\mathbf{q}_{m_1}^\alpha = \mathbf{q}_{m_2}^\alpha$, ${}^e \bar{\boldsymbol{\mu}}_{m_1}^1 = {}^e \bar{\boldsymbol{\mu}}_{m_2}^1$, ${}^e \bar{\mathbf{T}}_{m_1}^\alpha = {}^e \bar{\mathbf{T}}_{m_2}^\alpha$, $\Theta_{m_1}^1 = \Theta_{m_2}^1$

for all $(\mathbf{F}^1, \mathbf{F}^2, T^2, \Delta) \in \mathcal{S}$ and for all $(\mathbf{G}^1, \mathbf{G}^2, \mathbf{a}^1, \mathbf{g}^1, \mathbf{g}^2)$.

This equivalence relation partitions the set \mathcal{M} into disjoint subsets whose union is \mathcal{M} . The disjoint subsets are equivalence classes denoted by $M(m) = \{n \in \mathcal{M} : n \sim m\}$.

To derive relationships among the constitutive restrictions for two equivalent mixtures m_1 and m_2 , parts (i) and (ii) of Definition 1 will be used with the Clausius–Duhem inequality (2.31) invoked for m_2 .⁹ If $m_1 \sim m_2$, then ψ_{m_1} and ψ_{m_2} match on \mathcal{S} and using Definition 1 we have

$$\frac{d\psi_{m_1}}{dt} = \frac{d\psi_{m_2}}{dt}, \quad (4.10)$$

when m_1 and m_2 are undergoing processes that satisfy the constraint. Introducing (4.10) and (4.7)₂ multiplied by a Lagrange multiplier λ into the Clausius–Duhem inequality (2.31) invoked for m_2 and recalling (3.28)–(3.30), (3.37), and (3.38) evaluated for m_1 we obtain

⁸ To be consistent with the development in Section 3, we assume that the constraint allows $\Delta = 0$ so that a reference configuration with a common mixture temperature may be chosen.

⁹ For a mixture at a common mixture temperature, Klisch [20] applied Definition 1 in two parts; in particular, part (i) of Definition 1 was used with the Gibbs equation. However, we cannot use this approach in the present paper as the internal constraint (4.1) depends on the temperature difference while the Gibbs equation (3.25) is developed for a process in which the temperature difference is zero.

$$\begin{aligned}
\circ\bar{\mathbf{T}}_{m_2}^\alpha &= \circ\bar{\mathbf{T}}_{m_1}^\alpha + \lambda \frac{\partial \phi}{\partial \mathbf{F}^\alpha} \mathbf{F}^{\alpha\top}, \\
\circ\bar{\boldsymbol{\mu}}_{m_2}^1 &= \circ\bar{\boldsymbol{\mu}}_{m_1}^1 - \lambda \frac{\partial \phi}{\partial \mathbf{F}^1} \text{grad } \mathbf{F}^1, \\
\frac{\rho^1 \eta_{m_2}^{*1}}{T^1} &= \frac{\rho^1 \eta_{m_1}^{*1}}{T^1} + \lambda \frac{\partial \phi}{\partial \Delta}, \\
\frac{\rho^2 \eta_{m_2}^{*2}}{T^2} &= \frac{\rho^2 \eta_{m_1}^{*2}}{T^2} + \lambda \left(\frac{\partial \phi}{\partial T^2} - \frac{\partial \phi}{\partial \Delta} \right)
\end{aligned} \tag{4.11}$$

for any two mixtures $m_1, m_2 \in M(m)$ which are undergoing processes which satisfy the constraint (4.1). In addition, there is the residual inequality

$$R_{m_1} + \left(\frac{\rho^1 \eta_{m_2}^{*1}}{T^1} - \frac{\rho^1 \eta_{m_1}^{*1}}{T^1} \right) \mathbf{a}^1 \cdot \mathbf{g}^1 \geq 0 \tag{4.12}$$

for any two mixtures $m_1, m_2 \in M(m)$ which are undergoing processes which satisfy the constraint (4.1), where R_{m_1} is obtained by evaluating (3.42) for m_1 .

Upon repeating the analysis with (4.7)₁ corresponding to holding \mathbf{X}^1 fixed, it can be shown that (4.11) and (4.12) are recovered. However, we can express (4.11)₂ and (4.12) in the alternative and equal forms

$$\circ\bar{\boldsymbol{\mu}}_{m_2}^1 = \circ\bar{\boldsymbol{\mu}}_{m_1}^1 + \lambda \frac{\partial \phi}{\partial \mathbf{F}^2} \text{grad } \mathbf{F}^2 \tag{4.13}$$

and

$$R_{m_1} - \left(\frac{\rho^2 \eta_{m_2}^{*2}}{T^2} - \frac{\rho^2 \eta_{m_1}^{*2}}{T^2} \right) \mathbf{a}^1 \cdot \mathbf{g}^2 \geq 0. \tag{4.14}$$

Similarly, by repeating the analysis with (4.7)₃ corresponding to holding \mathbf{x} fixed, it can be shown that (4.11) and (4.12) are recovered. It should be pointed out that in [20], three different residual inequalities were obtained for internally constrained mixtures of elastic materials with a common mixture temperature. Thus, we have shown in the present paper that by generalizing the approach of [20] for a mixture of elastic materials with different temperatures, the same restrictions (4.11) and (4.12) are recovered regardless of whether \mathbf{X}^1 , \mathbf{X}^2 , or \mathbf{x} is held fixed.

5. Constrained mixtures of elastic materials

The above development for unconstrained mixtures of elastic materials leads to the following definition of a constrained mixture of elastic materials:

Definition 2. A constrained mixture of elastic materials with different constituent temperatures m' associated with an equivalence class $M(n)$ is a mixture for which:

- (i) the possible processes are those and only those which satisfy the constraint (4.1);
- (ii) m' can possess the values of the quantities $(\psi^\alpha, \mathbf{q}^\alpha, {}_o\bar{\boldsymbol{\mu}}^1, {}_e\bar{\boldsymbol{\mu}}^1, {}_o\bar{\mathbf{T}}^\alpha, {}_e\bar{\mathbf{T}}^\alpha, \eta^\alpha, \Theta^1)$ of any $m \in M(n)$ when m undergoes a process satisfying the constraint;
- (iii) m' can only possess values of the quantities $(\psi^\alpha, \mathbf{q}^\alpha, {}_o\bar{\boldsymbol{\mu}}^1, {}_e\bar{\boldsymbol{\mu}}^1, {}_o\bar{\mathbf{T}}^\alpha, {}_e\bar{\mathbf{T}}^\alpha, \eta^\alpha, \Theta^1)$ that are possible for any $m \in M(n)$ when m undergoes a process satisfying the constraint.

From this definition, it is clear that the union of all equivalence classes associated with the constraint will generate the set of all constrained mixtures \mathcal{M}' associated with the constraint.

Consider any constrained mixture $m' \in \mathcal{M}'$ that is associated with an equivalence class $M(n)$. For any process which satisfies the constraint, m' possesses values of $(\psi_{m'}^\alpha, \mathbf{q}_{m'}^\alpha, {}_e\bar{\boldsymbol{\mu}}_{m'}^1, {}_e\bar{\mathbf{T}}_{m'}^\alpha, \Theta_{m'}^1)$ which are the common values of all elements in $M(n)$. Because m' can possess values of $({}_o\bar{\boldsymbol{\mu}}_{m'}^1, {}_o\bar{\mathbf{T}}_{m'}^\alpha, \eta_{m'}^\alpha)$ of any element in $M(n)$, from (4.11) it is evident that ¹⁰

$$\begin{aligned}
{}_o\bar{\mathbf{T}}_{m'}^\alpha &= {}_o\bar{\mathbf{T}}_m^\alpha + \lambda \frac{\partial \phi}{\partial \mathbf{F}^\alpha} \mathbf{F}^{\alpha\top}, \\
{}_o\bar{\boldsymbol{\mu}}_{m'}^1 &= {}_o\bar{\boldsymbol{\mu}}_m^1 - \lambda \frac{\partial \phi}{\partial \mathbf{F}^1} \text{grad } \mathbf{F}^1, \\
\frac{\rho^1 \eta_{m'}^{*1}}{T^1} &= \frac{\rho^1 \eta_m^{*1}}{T^1} + \lambda \frac{\partial \phi}{\partial \Delta}, \\
\frac{\rho^2 \eta_{m'}^{*2}}{T^2} &= \frac{\rho^2 \eta_m^{*2}}{T^2} + \lambda \left(\frac{\partial \phi}{\partial T^2} - \frac{\partial \phi}{\partial \Delta} \right)
\end{aligned} \tag{5.1}$$

on \mathcal{S} for any element $m \in M(n)$ undergoing the same process as m' . Also, from (4.12) it is evident that

$$R_{m'} + \left(\frac{\rho^1 \eta_{m'}^{*1}}{T^1} - \frac{\rho^1 \eta_m^{*1}}{T^1} \right) \mathbf{a}^1 \cdot \mathbf{g}^1 \geq 0 \tag{5.2}$$

on \mathcal{S} for any element $m \in M(n)$ undergoing the same process as m' , where $R_{m'}$ is obtained by evaluating (3.42) for m' . Upon repeating the analysis using conditions (4.7)₁ and (4.7)₃ corresponding to holding \mathbf{X}^1 and \mathbf{x} fixed, respectively, we obtain the same restrictions (5.1) and (5.2). Recalling (2.27)₁ and noting that $\psi_{m'}^\alpha = \psi_m^\alpha$ on \mathcal{S} , (5.1)_{3,4} and (5.2) may be written as

$$\begin{aligned}
\frac{\rho^1 \eta_{m'}^1}{T^1} &= \frac{\rho^1 \eta_m^1}{T^1} + \lambda \frac{\partial \phi}{\partial \Delta}, \\
\frac{\rho^2 \eta_{m'}^2}{T^2} &= \frac{\rho^2 \eta_m^2}{T^2} + \lambda \left(\frac{\partial \phi}{\partial T^2} - \frac{\partial \phi}{\partial \Delta} \right),
\end{aligned} \tag{5.3}$$

¹⁰ These results are obtained from (4.11) and (4.12) by specifying $m_1 = m'$, $m_2 = m$, and replacing λ with $-\lambda$.

and

$$R_{m'} + \left(\frac{\rho^1 \eta_{m'}^1}{T^1} - \frac{\rho^1 \eta_m^1}{T^1} \right) \mathbf{a}^1 \cdot \mathbf{g}^1 \geq 0. \quad (5.4)$$

By defining two constrained mixtures to be identical if the quantities $(\psi_m^\alpha, \mathbf{q}_m^\alpha, {}_e\bar{\boldsymbol{\mu}}_m^1, {}_e\bar{\mathbf{T}}_m^\alpha, \Theta_m^1)$ are equal, then it can be seen that there exists a one-to-one relationship between equivalence classes of unconstrained mixtures and constrained mixtures. Furthermore, a constrained mixture m' can be constructed from a corresponding unconstrained mixture m by evaluating the quantities $(\psi_m^\alpha, \mathbf{q}_m^\alpha, {}_e\bar{\boldsymbol{\mu}}_m^1, {}_e\bar{\mathbf{T}}_m^\alpha, \Theta_m^1)$ for m on the constraint manifold \mathcal{S} , and noting that the quantities $({}_o\bar{\boldsymbol{\mu}}_{m'}^1, {}_o\bar{\mathbf{T}}_{m'}^\alpha, \eta_{m'}^\alpha)$ are specified by (5.1)_{1,2} and (5.3) where $({}_o\bar{\boldsymbol{\mu}}_m^1, {}_o\bar{\mathbf{T}}_m^\alpha, \eta_m^\alpha)$ are evaluated on \mathcal{S} .

6. Examples

Example 1. Consider a mixture constrained to have equal constituent temperatures. Thus, the constraint (4.1) becomes

$$\phi(\Delta) = \Delta = 0, \quad \frac{\partial \phi}{\partial \Delta} = 1. \quad (6.1)$$

Letting $T^1 = T^2 = T$, from (5.1)_{1,2} and (5.3) we obtain

$$\begin{aligned} {}_o\bar{\mathbf{T}}_{m'}^\alpha &= {}_o\bar{\mathbf{T}}_m^\alpha, \\ {}_o\bar{\boldsymbol{\mu}}_{m'}^1 &= {}_o\bar{\boldsymbol{\mu}}_m^1, \\ \frac{\rho^1 \eta_{m'}^1}{T} &= \frac{\rho^1 \eta_m^1}{T} + \lambda, \\ \frac{\rho^2 \eta_{m'}^2}{T} &= \frac{\rho^2 \eta_m^2}{T} - \lambda, \end{aligned} \quad (6.2)$$

while the residual inequality (5.4) reduces to

$$R_{m'} + \lambda \mathbf{a}^1 \cdot \text{grad } T \geq 0. \quad (6.3)$$

Upon adding (6.2)_{3,4} we find

$$\rho \eta_{m'} = \sum_{\alpha=1}^2 \rho^\alpha \eta_{m'}^\alpha = \sum_{\alpha=1}^2 \rho^\alpha \eta_m^\alpha = \rho \eta_m. \quad (6.4)$$

Thus, although (6.2)_{3,4} reveals that there is an indeterminacy in each partial entropy, (6.4) shows that the mixture entropy defined by (3.26) is determinate.

For a mixture constrained by (6.1), we wish to compare the constitutive restrictions for the mixture entropy (3.28) and the residual inequality (6.3) to earlier results obtained for the special case where it is assumed that there exists a common mixture temperature. We introduce

$$\begin{aligned}\rho\tilde{\psi} &= \sum_{\alpha=1}^2 \rho^\alpha \psi^\alpha, & \tilde{\phi}^\alpha &= \rho^\alpha (\psi^\alpha - \tilde{\psi}), & \mathbf{T}^\alpha &= \tilde{\phi}^\alpha \mathbf{I} + \tilde{\mathbf{T}}^\alpha, \\ \boldsymbol{\mu}^1 &= \text{grad } \tilde{\phi}^1 + \tilde{\boldsymbol{\mu}}^1, & \tilde{\mathbf{q}}^* &= \mathbf{q} + \sum_{\alpha=1}^2 \rho^\alpha \eta^\alpha \theta \mathbf{u}^\alpha, & \mathbf{q} &= \sum_{\alpha=1}^2 \mathbf{q}^\alpha.\end{aligned}\tag{6.5}$$

Because the mixture is constrained by (6.1) to have a common mixture temperature, recalling (3.20) and (3.43) we note that

$$\epsilon\psi_{m'} = 0, \quad \frac{\partial \epsilon\psi_{m'}}{\partial \mathbf{F}^\alpha} = \mathbf{0}, \quad \frac{\partial \epsilon\psi_{m'}}{\partial T^2} = 0,\tag{6.6}$$

whereas, in general,

$$\frac{\partial \epsilon\psi_{m'}}{\partial \Delta} \neq 0.\tag{6.7}$$

It can then be shown that (3.28) takes the form

$$\eta = -\frac{\partial \tilde{\psi}}{\partial \theta},\tag{6.8}$$

which agrees with classical results. Furthermore, the residual inequality (6.3) reduces to

$$\sum_{\alpha=1}^2 \epsilon \tilde{\mathbf{T}}_{m'}^\alpha \cdot \mathbf{L}^\alpha + \epsilon \tilde{\boldsymbol{\mu}}_{m'} \cdot \mathbf{a}^1 - \frac{\mathbf{q}_{m'}^* \cdot \text{grad } \theta}{\theta} + \frac{\lambda \mathbf{a}^1 \cdot \text{grad } \theta}{\theta} \geq 0,\tag{6.9}$$

which, using (6.2)_{3,4}, can be written in the alternative and equivalent forms

$$\begin{aligned}\sum_{\alpha=1}^2 \epsilon \tilde{\mathbf{T}}_{m'}^\alpha \cdot \mathbf{L}^\alpha + \epsilon \tilde{\boldsymbol{\mu}}_{m'} \cdot \mathbf{a}^1 - \frac{\mathbf{q}_{m'}^* \cdot \text{grad } \theta}{\theta} + (\rho^1 \eta_{m'}^1 - \rho^1 \eta_m^1) \mathbf{a}^1 \cdot \text{grad } \theta &\geq 0, \\ \sum_{\alpha=1}^2 \epsilon \tilde{\mathbf{T}}_{m'}^\alpha \cdot \mathbf{L}^\alpha + \epsilon \tilde{\boldsymbol{\mu}}_{m'} \cdot \mathbf{a}^1 - \frac{\mathbf{q}_{m'}^* \cdot \text{grad } \theta}{\theta} - (\rho^2 \eta_{m'}^2 - \rho^2 \eta_m^2) \mathbf{a}^1 \cdot \text{grad } \theta &\geq 0, \\ \sum_{\alpha=1}^2 \epsilon \tilde{\mathbf{T}}_{m'}^\alpha \cdot \mathbf{L}^\alpha + \epsilon \tilde{\boldsymbol{\mu}}_{m'} \cdot \mathbf{a}^1 - \frac{\mathbf{q}_{m'}^* \cdot \text{grad } \theta}{\theta} + \sum_{\alpha=1}^2 (\rho^\alpha \eta_{m'}^\alpha - \rho^\alpha \eta_m^\alpha) \mathbf{v}^\alpha \cdot \text{grad } \theta &\geq 0.\end{aligned}\tag{6.10}$$

The three equivalent inequalities (6.10) are the same as those derived by Klisch [20] for a constrained mixture of elastic materials at a common mixture temperature.

Example 2. The second example we wish to consider is that of temperature-dependent intrinsic incompressibility. A commonly used constraint in the theory of mixtures is that of intrinsic

incompressibility first proposed by Mills [21] and studied by other authors [22–25]. Each constituent \mathcal{C}^α is assumed to be separable from the others with constant (true) density $\rho^{\alpha\text{T}}$ defined as the mass of \mathcal{C}^α per unit volume of \mathcal{C}^α . Upon addition in forming the mixture, it is assumed that the volumes of \mathcal{C}^α add to form the volume of the mixture. With these assumptions, Mills [20] derived an equation that is a special form of the general internal constraint represented by (4.1):

$$\frac{\rho^1}{\rho^{1\text{T}}} + \frac{\rho^2}{\rho^{2\text{T}}} = 1. \quad (6.11)$$

Using the local form of the continuity equation, $\rho^\alpha J^\alpha = \rho_0^\alpha$, (6.11) can be written as

$$\frac{\rho_0^1}{\rho^{1\text{T}} \det \mathbf{F}^1} + \frac{\rho_0^2}{\rho^{2\text{T}} \det \mathbf{F}^2} - 1 = 0. \quad (6.12)$$

Following Trapp [29] who proposed the internal constraint of temperature-dependent compressibility for thermoelastic materials, we generalize (6.12) as follows:

$$\frac{f^1(\Delta + T^2)\rho_0^1}{\rho^{1\text{T}} \det \mathbf{F}^1} + \frac{f^2(T^2)\rho_0^2}{\rho^{2\text{T}} \det \mathbf{F}^2} - 1 = 0, \quad f^1(T_0) = f^2(T_0) = 1. \quad (6.13)$$

Recalling

$$\frac{\partial \det \mathbf{F}^\alpha}{\partial \mathbf{F}^\alpha} = (\det \mathbf{F}^\alpha) \mathbf{F}^{\alpha-\text{T}}, \quad (6.14)$$

Eqs. (5.1) become ¹¹

$$\begin{aligned} \circ \bar{\mathbf{T}}_{m'}^\alpha &= \circ \bar{\mathbf{T}}_m^\alpha - \lambda f^\alpha \frac{\rho^\alpha}{\rho^{\alpha\text{T}}} \mathbf{I}, \\ \circ \bar{\boldsymbol{\mu}}_{m'} &= \circ \bar{\boldsymbol{\mu}}_m - \lambda f^1 \frac{\text{grad } \rho^1}{\rho^{1\text{T}}}, \\ \frac{\rho^1 \eta_{m'}^1}{T^1} &= \frac{\rho^1 \eta_m^1}{T^1} + \lambda \frac{\rho^1}{\rho^{1\text{T}}} \frac{\partial f^1}{\partial \Delta}, \\ \frac{\rho^2 \eta_{m'}^2}{T^2} &= \frac{\rho^2 \eta_m^2}{T^2} + \lambda \left(\frac{\rho^1}{\rho^{1\text{T}}} \left[\frac{\partial f^1}{\partial T^2} - \frac{\partial f^1}{\partial \Delta} \right] + \frac{\rho^2}{\rho^{2\text{T}}} \frac{\partial f^2}{\partial T^2} \right). \end{aligned} \quad (6.15)$$

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¹¹ In deriving (6.15)₂, it was assumed that $\text{grad } \rho_0^1 = 0$. Klisch [20] has discussed two ways that (6.15) may be obtained without making this assumption.

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