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Second Law Constraints on the Dynamics of a Mixture of Two Fluids at Different Temperatures

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Abstract: Constitutive laws for multi-component fluids (MCF) is one of the thorniest problems in science. Two questions explored here are: how to ensure that these relations reduce to accepted forms when all but one of the constituents vanishes; and what constraints does the Second Law impose on the dynamics of viscous fluids at different temperatures? The analysis suggests an alternative to the metaphysical principles for MCF proposed by Truesdell [1].

Keywords: entropy; Second Law; mixture theory; constitutive theory; metaphysical principles; ontology

1. Introduction

The theoretical paradigm for multi-component materials is generally taken as Truesdell's [1] three metaphysical principles:

1. All properties of the mixture must be mathematical consequences of the properties of the constituents.
2. So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.
3. The motion of the mixture is governed by the same equations as is a single body.

Despite their broad scope, these metaphysical principles do not cover a number of issues in mixture theory. Subsequently, several additional principles have been proposed. See Massoudi [2] for a timely

and succinct summary. Two are of particular relevance here. The first is the Green and Adkins [3] “reduction” principle:

“Also, in the absence of one fluid the constitutive equation for the other must reduce to the usual one for that fluid alone.”

In distinction to Truesdell’s principles, which stress generality, the later principle is a fundamental constraint on constitutive equations not unlike material frame indifference. As Green and Adkins did not provide guidance on implementation of this principle, it has had little impact in the development of constitutive theories of MCF to date.

Massoudi [2] applied this principle in a study of a mixture of two Navier–Stokes fluids. After an intricate analysis of ways to implement the principle, he arrived at the “limiting” assumption:

“It indicates that the limiting case(s) or in the absence of one component, we expect the governing equations and the constitutive relations(s) to reduce to their appropriate form(s) for the single component.”

Based on this, he developed a general weighting function for the material properties in the constitutive equations for the viscous stresses with this property. The simplest form of the weighting function is

$$f(\phi) = \phi(1 - \phi)$$

where ϕ is the volume fraction of one of the two constituents.

At this point it is appropriate to consider the use of volume fractions as the basis for weighting functions in the constitutive equations for the stresses. As noted by Massoudi [2], volume fraction models are common in mixture studies. For example, Hansen [4] developed a consistent theory based on mixture velocities obtained by volume averaged constituents. Nevertheless it is not at all obvious why volume fractions are appropriate for stresses. After all, they arise from surface tractions, which suggests that area fractions would be more appropriate. However, Hansen *et al.* [5] showed that partial stresses based on volume fractions is consistent with classical statistical mechanics. They also argue from stereological considerations that there is no difference between volume and area fractions in randomly distributed mixtures. These considerations validate the use of volume fraction mixture stresses here.

Massoudi’s analysis [2] was restricted to the mixture of two Navier–Stokes fluids at a common temperature, although it was clear he expected it to have general applicability. One purpose of this communication is to demonstrate this applicability. To this end it is postulated that the reduction principle is fundamental and thus applicable to the constitutive equations of any MCF. Below this principle is called the Green–Atkins–Massoudi or GAM reduction principle.

The second concern here is the third metaphysical principle. This principle is used to constrain the constituent interaction terms so that when summed over all constituents they equal zero. The resulting “mixture balance equations” formally resemble those of a single constituent. Perhaps this principle was motivated by Truesdell’s ontological question “how does a mixture know it is a mixture?” In any event the principle has caused some angst in the literature often associated with the appearance of a “diffusion” stress associated with the “peculiar” velocities in the mixture momentum balance equations and in formulations of constitutive equations. After a detailed comparison of classical mixture and kinetic theory, Hansen *et al.* [5] offered a revised third metaphysical principle:

“The motion of the mixture is governed by the sum of the constituent balance equations. Furthermore, the equations of a single continuum must be recovered as a special case of the mixture relations.”

The overarching issue raised by these considerations is the efficacy of the third metaphysical principle in constraining the physics demanded by the second principle. Three specific questions are posed here:

1. Under what conditions do the constitutive balance equations reduce to those of a single constituent?
2. Is the third principle compatible with the Second Law in all cases?
3. What are alternatives to the metaphysical principles?

These questions are addressed with a two fluid model with different temperatures. As noted by Ruggeri and Lou [6], most studies consider a common temperature for both constituents even though there are many examples where this is clearly not the case. In fact the only recent papers we are aware of that address multi-temperature mixtures of fluids are the above citation along with Ruggeri and Simić [7,8] and Gouin and Ruggeri [9]. Ruggeri and Lou [6] note that one motivation for single temperature models is to avoid difficulties in measuring constituent temperatures. It has also been argued that multi-temperature mixtures quickly reach a thermal equilibrium state characterized by a common temperature, or that a mixture dependent conductivity can account for variable temperatures in mixtures. Of course both possibilities are true in many cases. However, thermally stratified fluids such as the ocean or atmosphere demonstrate that thermal equilibrium is not always achieved and that mixture dependent conductivities may be difficult to characterize. In any event the possibility of multi-temperature mixtures was recognized as early as in [1] and many of the early theoretical papers allowed for this. Thus there is precedent for considering this model.

The rest of this report is organized as follows. The next section reviews the basic equations of mass, momentum, energy conservation, and entropy tendency for MCF. Section 3 specifies linear constitutive equations for the heat flux, interaction forces, and the viscous stresses for a mixture of two Navier Stokes fluids at different temperatures. In Section 4 these equations are assessed for conformance with the Second Law. This establishes constraints on the phenomenological coefficients that conflict with third principle when the constituents have distinct temperatures. The last section discusses the results and proposes an alternative to Truesdell’s metaphysical principles.

2. Formulation

The starting points for the analysis are the local balances of mass, momentum, energy, and entropy for each constituent. Following Truesdell [1] and Rajagopal and Tao [10], these are well known to be

$$\begin{aligned}
 D^\alpha \rho^\alpha + \rho^\alpha v_{j,j}^\alpha &= \tilde{c}^\alpha \\
 \rho^\alpha D^\alpha v_i^\alpha &= \sigma_{ji,j}^\alpha + \rho^\alpha b_i^\alpha + \tilde{m}_i^\alpha \\
 \sigma_{ji}^\alpha - \sigma_{ij}^\alpha &= \tilde{M}_{ji}^\alpha \\
 \rho^\alpha D^\alpha \varepsilon^\alpha &= \sigma_{ji}^\alpha v_{i,j}^\alpha - q_{j,j}^\alpha + \rho^\alpha r^\alpha + \tilde{\varepsilon}^\alpha \\
 \rho^\alpha D^\alpha \eta^\alpha &= \rho^\alpha r^\alpha / \theta^\alpha - (q_j^\alpha / \theta^\alpha)_{,j} + \tilde{\eta}^\alpha
 \end{aligned} \tag{1}$$

Here Greek superscripts denote individual mixture constituents, D^α is the material derivative following constituent α and $(\)_{,j} = \partial(\) / \partial x_j$. The dependent variables in (1) are generally standard: ρ^α , v_j^α , σ_{ji}^α , ε^α , θ^α , and η^α are, respectively, the partial density, velocity, partial stress, internal energy, temperature, and entropy of α . The prescribed forcing terms $\rho^\alpha b_i^\alpha$, q_j^α , and r^α are force per unit volume, heat flux, and net radiation exchange for α . Finally the $\tilde{(\)}$ terms account for internal sources of appropriate quantities arising from interactions between the constituents. Application of Truesdell’s third metaphysical principal requires these terms to satisfy

$$\sum_\alpha \tilde{c}^\alpha = \sum_\alpha (\tilde{m}_i^\alpha + \tilde{c}^\alpha v_i^\alpha) = \sum_\alpha \tilde{M}_{ji}^\alpha = \sum_\alpha [\tilde{\varepsilon}^\alpha + \tilde{m}_j^\alpha v_j^\alpha + \tilde{c}^\alpha (\varepsilon^\alpha + \kappa^\alpha)] = 0 \tag{2}$$

Here κ^α is the kinetic energy per unit mass of the α constituent. Chemical reactions between constituents is not considered so hereafter $\tilde{c}^\alpha = 0$. Finally, it is stipulated that the Second Law of Thermodynamics requires

$$\sum_\alpha \tilde{\eta}^\alpha \geq 0 \tag{3}$$

Following Coleman and Noll [11] and Müller [12] r^α is eliminated between between the last two equations in (1) to yield

$$\tilde{\eta}^\alpha = (\theta^\alpha)^{-1} [\rho^\alpha (\theta^\alpha D^\alpha \eta^\alpha - D^\alpha \varepsilon^\alpha) - (\theta^\alpha)^{-1} q_j^\alpha \theta_{,j}^\alpha + \sigma_{ji}^\alpha v_{i,j}^\alpha + \tilde{\varepsilon}^\alpha] \tag{4}$$

Inserting the Helmholtz free energy $\psi^\alpha = \varepsilon^\alpha - \theta^\alpha \eta^\alpha$ into (4) gives the Clausius–Duhem relation

$$\tilde{\eta}^\alpha = (\theta^\alpha)^{-1} [\sigma_{ji}^\alpha v_{i,j}^\alpha + \tilde{\varepsilon}^\alpha - q_j^\alpha \theta_{,j}^\alpha (\theta^\alpha)^{-1} - \rho^\alpha (D^\alpha \psi^\alpha + \eta^\alpha D^\alpha \theta^\alpha)] \tag{5}$$

Obviously (3) requires the sum of the right hand side of (5) to be nonnegative. The large number of terms in this sum present possibilities that some negative terms may be negated by larger positive terms. Considerable simplification is achieved if the constituent temperatures are the same, *i.e.*, $\theta^\alpha = \theta$. Then from (3) and (4) $\sum_\alpha \tilde{\eta} \geq 0$ implies $\sum_\alpha \tilde{\eta} \theta \geq 0$. Obviously this is not generally true if the constituent temperatures are different and some of the terms on the right hand side are negative. As discussed below this fact has deep implications for the foundations of mixture theory.

The primary interest here is on irreversible processes for the case where $\tilde{c}^\alpha = 0$. Then

$$\sum_\alpha (\theta^\alpha)^{-1} [\sigma_{ji}^\alpha v_{i,j}^\alpha - (\theta^\alpha)^{-1} q_j^\alpha \theta_{,j}^\alpha - \tilde{m}_j^\alpha v_j^\alpha - \rho^\alpha (D^\alpha \psi^\alpha + \eta^\alpha D^\alpha \theta^\alpha)] \geq 0 \tag{6}$$

In arriving at (6) use was made of $\sum_\alpha (\tilde{\varepsilon}^\alpha + \tilde{m}_j^\alpha v_j^\alpha) = 0$ from (2). The latter equation implies that the internal friction generated by the velocity differences between constituents is a possible source of internal energy.

It is customary to divide the terms in (6) into forces and fluxes. In the Eringen [13] (p. 50) classification the fluxes are q_j^α , \tilde{m}_i^α , σ_{ji}^α and $\rho^\alpha \eta^\alpha$, while $\rho^\alpha D^\alpha \psi^\alpha$ is confined to reversible processes. The fluxes are expressed in terms of the forces θ_{ij}^α , $v_{i,j}^\alpha$, $v_i^\alpha - v_i^\beta$ through constitutive equations. Relations for the first three listed fluxes are developed in the next section. A thermodynamic constitutive equation for $\rho^\alpha \eta^\alpha$ for multi-temperature mixtures is not as clear cut, and is not considered here. The only work I am aware of that addresses this in a serious fashion is Gouin and Ruggeri [9], Ruggeri and Simić [7,8], and Ruggeri and Lou [6]. Two important ideas have emerged from their studies. One is a precise definition of the equilibrium or average temperature based on requirement that the internal energy of the mixture reduce to the form for a single constituent medium. The other is the issue of measurement of temperature in a multi-temperature mixture. Theorists have generally neglected the question of what exactly do measurements of temperature, or other constituent properties for that matter, mean. These papers provide a quantitative paradigm for constituent temperatures.

Nevertheless including their ideas in this report is deferred. Their theory is based on developing constitutive relations for the internal energy rather than the Clausius–Duhem equation inequality. Moreover, for consistency with the development here their approach would have to be modified to account for the GAM principle. Addressing these issues would expand significantly the scope of this effort while not directly addressing the three questions listed in the previous section. The focus here then is on constraints imposed by the Second Law (4) on the phenomenological coefficients that appear in the constitutive equations for the first three terms in (6). No matter what arises from the internal energy or Helmholtz free energy these terms must be nonnegative.

3. Constitutive Theory for a Mixture of Two Fluids

The essential issues can be demonstrated with linear constitutive equations as one does not expect more realistic nonlinear constitutive equations to obviate the essential conclusions. Following Kuiken [14] central symmetry and material invariance requires that the constitutive equations for q_j^α and \tilde{m}_i^α be functions of just the vectors θ_i^α and $v_i^\alpha - v_i^\beta$. Similarly σ_{ij}^α depends on the symmetric part of the constituent velocity gradients and the difference between the spin tensors of the two constituents. No effort is made to depict the functional dependence of material parameters on θ^α or ρ^α .

There is extensive literature on constitutive equations for multi-component materials. Massoudi [2,15–17] provides extensive critiques of much of this work. There is also substantial literature on multi-temperature elastic mixtures. See, for example, Bowen and Garcia [18], Bowen [19], Iesan [20], and Klisch [21]. However, they provide little guidance for the irreversible processes considered here. The only recent work on multi-temperature fluid mixtures is by Ruggeri and colleagues cited earlier. The approach taken here differs from all of these studies in that the constitutive models adhere to the GAM principle.

The subsequent analysis is streamlined by using the canonical representation of second order tensors as sums of isotropic, deviatoric, and skew symmetric components. Thus, the velocity gradient of constituent α in a two component mixture is

$$v_{i,j}^\alpha = (d^\alpha/3) \delta_{ij} + \hat{d}_{ij}^\alpha + w_{[ij]}^\alpha \quad (7)$$

with

$$\begin{aligned}
 d^\alpha &= v_{j,j}^\alpha \\
 \hat{d}_{ij}^\alpha &= (v_{i,j}^\alpha + v_{j,i}^\alpha) / 2 - (d^\alpha / 3) \delta_{ij} \\
 w_{[ij]}^\alpha &= (v_{i,j}^\alpha - v_{j,i}^\alpha) / 2
 \end{aligned}
 \tag{8}$$

These last three objects are recognized as the divergence, deviatoric rate of strain tensor, and the spin tensor. From (7) and (8), it is easy to establish

$$v_{i,j}^\alpha v_{i,j}^\beta = d^\alpha d^\beta / 3 + \hat{d}_{ij}^\alpha \hat{d}_{ij}^\beta + w_{[ij]}^\alpha w_{[ij]}^\beta
 \tag{9}$$

As noted in the Introduction Massoudi [2] analyzed several constitutive models for a mixture of two Navier–Stokes fluids and found that none of the standard models obeyed the GAM principle “... in the absence of one fluid the constitutive equation for the other must reduce to the usual one for that fluid alone.” To satisfy this principle, he hypothesized

$$\sigma_{ji}^\alpha = \phi^\alpha \left[\lambda_{\alpha\alpha} d^\alpha \delta_{ji} + 2\mu_{\alpha\alpha} \hat{d}_{ji}^\alpha + \phi^\beta \left(\lambda_{\alpha\beta} d^\beta \delta_{ji} + 2\mu_{\alpha\beta} \hat{d}_{ji}^\beta \right) + \nu_{\alpha\beta} \phi^\beta \left(w_{[ij]}^\alpha - w_{[ij]}^\beta \right) \right]
 \tag{10}$$

In (10) $\alpha, \beta = 1, 2; \alpha \neq \beta$; and the volume fractions satisfy $\sum_\alpha \phi^\alpha = 1$. When adjusted for the definitions given in (8) the phenomenological coefficients λ and μ in (10) are the same as given by Massoudi [2]. He considered a uniform temperature in the mixture and required $\sum_\alpha \tilde{M}_{ji}^\alpha = 0$, which resulted in $\nu_{\alpha\beta} = \nu_{\beta\alpha} = \nu$. However, as shown later, this conflicts with the Second Law when the constituents have different temperatures. Consequently the general version of (10) is retained. Nevertheless, in accordance with GAM, if the volume fraction of one of the two constituents goes to zero, this term will vanish. Finally note that only dissipative and irreversible processes are considered in (10) so constituent partial pressures are omitted.

Now consider the constitutive equations for the constituent heat fluxes q_j^α and the internal momentum source \tilde{m}_i . As with the stresses, attention is focused on linear approximations. The simplest available frame indifferent variables are the temperature gradients $\theta_{,j}^\alpha$ and the constituent velocity differences or diffusion velocity $v_i^\alpha - v_i^\beta = u_i^{\alpha\beta}$. Truesdell [22] has an enlightening discussion on the role and history of $u_i^{\alpha\beta}$ in constitutive equations of this sort. Also, since the constituents may be at different temperatures a general version of Fourier’s heat conduction law is assumed here.

Application of GAM gives

$$\begin{aligned}
 q_j^\alpha &= -\phi^\alpha \left(k_{\alpha\alpha} \theta_{,j}^\alpha + \phi^\beta k_{\alpha\beta} \theta_{,j}^\beta + \phi^\beta h_{\alpha\beta} u_j^{\alpha\beta} \right) \\
 \tilde{m}_j^\alpha &= -\phi^\alpha \phi^\beta \left(l_{\alpha\beta} u_j^{\alpha\beta} + \sum_{\gamma=1}^2 r_{\alpha\beta\gamma} \theta_{,j}^\gamma \right)
 \end{aligned}
 \tag{11}$$

as in (10) $\alpha, \beta = 1, 2$ and $\alpha \neq \beta$. The first of (11) is consistent with Gidaspow [23] and also extends the constitutive theory of Massoudi [17] to include distinct constituent temperature. Moreover, it reduces to Fourier’s law when either constituent vanishes. The second of (11) extends the work of Massoudi [16] to include the effect of constituent temperature gradients.

Truesdell’s third principle, as expressed by (2), imposes constraints on some the coefficients in (10) and (11). The complete list is:

$$\begin{aligned}
 \nu_{\alpha\beta} &= \nu_{\beta\alpha} \\
 h_{\alpha\beta} &= h_{\beta\alpha} \\
 l_{\alpha\beta} &= l_{\beta\alpha} \\
 r_{\alpha\beta\gamma} &= -r_{\beta\alpha\gamma}
 \end{aligned}
 \tag{12}$$

I refer to these as dynamical constraints since they apply to the fundamental balance equations for each of the constituents. However, as shown in the next section (12) conflicts with constraints imposed by the Second Law for a mixture of two fluids at different temperatures. Hence the dilemma: one may accept (2), in which case positive entropy production cannot be ensured; or one may accept the Second Law, in which case (2) is not always be satisfied. Consequently (12) is not imposed at this stage.

4. Entropy Production

This section determines the restrictions imposed on the phenomenological coefficients in (10) and (11) by (6). The theory developed by Klika and Maršík [24] in a study of the entropy production by mechanical loading in the presence of chemical reactions applies directly here as well. Since the coefficient matrices in (10) and (11) are symmetric, they can be replaced by diagonal matrices whose values are the eigenvalues of the original matrices. Second Law constraints are imposed by requiring that the diagonal elements be non-negative. Since the largest matrices considered here are of order three, the eigenvalues are well known and the problem is reduced to ensuring they are non-negative. The notation, and perhaps the physics, is simplified if the constituent “coldness” $\mathcal{C}_\alpha = (\theta^\alpha)^{-1}$ is used below instead of temperature.

The tensor and vector constraints are considered separately. For the former

$$\sum_{\alpha} \mathcal{C}_\alpha \sigma_{ji}^{\alpha} v_{i,j}^{\alpha} \geq 0
 \tag{13}$$

When (10) is inserted into this equation it is readily seen that it reduces to quadratic forms in d^α , \hat{d}_{ij}^α , and w_{ij}^α . Since the latter are independent kinematic quantities, motions where just one of these quantities is non-zero are conceivable. Hence each of the three quadratic forms are required to be non-negative. Obviously this strict constraint requires any combination kinematic quantities to be non-negative as well.

Consider first the d^α terms. The quadratic form is

$$\mathcal{F}_\lambda = \begin{bmatrix} d^1 & d^2 \end{bmatrix} \begin{bmatrix} \phi^1 \lambda_{11} \mathcal{C}_1 & \phi^1 \phi^2 (\lambda_{12} \mathcal{C}_1 + \lambda_{21} \mathcal{C}_2) / 2 \\ \phi^1 \phi^2 (\lambda_{12} \mathcal{C}_1 + \lambda_{21} \mathcal{C}_2) / 2 & \phi^2 \lambda_{22} \mathcal{C}_2 \end{bmatrix} \begin{bmatrix} d^1 \\ d^2 \end{bmatrix}
 \tag{14}$$

The eigenvalue equation for a second order symmetric matrix **A** is

$$\gamma^2 - \gamma \text{tr}(\mathbf{A}) + \det(\mathbf{A}) = 0$$

The roots of this equation are non-negative when $\text{tr}(\mathbf{A}) \geq 0$ and $\det(\mathbf{A}) \geq 0$. When applied to (14) this gives

$$\begin{aligned}
 \phi^1 \lambda_{11} \mathcal{C}_1, \phi^2 \lambda_{22} \mathcal{C}_2 &\geq 0 \\
 \lambda_{11} \lambda_{22} \mathcal{C}_1 \mathcal{C}_2 &\geq (\phi^1 \phi^2 / 4) (\lambda_{12} \mathcal{C}_1 + \lambda_{21} \mathcal{C}_2)^2
 \end{aligned}
 \tag{15}$$

The same grouping applies to the \hat{d}_{ij}^α terms. This results in

$$\begin{aligned} \phi^1 \mu_{11} C_1, \phi^2 \mu_{22} C_2 &\geq 0 \\ \mu_{11} \mu_{22} C_1 C_2 &\geq (\phi^1 \phi^2 / 4) (\mu_{12} C_1 + \mu_{21} C_2)^2 \end{aligned} \tag{16}$$

After accounting for the differences in definitions and the presence of volume fractions and distinct constituent temperatures, these are identical to results first reported by Atkin and Craine [25].

Consider now the $w_{[ij]}^\alpha$ terms in (13)

$$\sum C_\alpha \sigma_{ji}^\alpha w_{[ij]}^\alpha = \phi^1 \phi^2 \begin{bmatrix} w_{[ij]}^1 & w_{[ij]}^2 \end{bmatrix} \begin{bmatrix} \nu_{12} C_1 & -(\nu_{12} C_1 + \nu_{21} C_2) / 2 \\ -(\nu_{12} C_1 + \nu_{21} C_2) / 2 & \nu_{21} C_2 \end{bmatrix} \begin{bmatrix} w_{[ij]}^1 \\ w_{[ij]}^2 \end{bmatrix} \tag{17}$$

For the eigenvalues of coefficient matrix to be non-negative it is necessary that the determinant vanish. Thus

$$\nu_{12} C_1 = \nu_{21} C_2 \geq 0 \tag{18}$$

Note that this reduces to $\nu_{12} = \nu_{21}$ only if $C_1 = C_2$. Then $\nu_{12} = \nu_{21} \geq 0$ in accordance with Atkin and Craine [25]. What does this imply about $\tilde{M}_{ji}^\alpha = 2\phi^\alpha \phi^\beta \nu_{\alpha\beta} (w_{ij}^\alpha - w_{ij}^\beta)$? In the general case of non-uniform constituent temperatures, the Second Law requirement $\sum C_\alpha \sigma_{ji}^\alpha w_{[ij]}^\alpha \geq 0$ and the dynamic hypothesis $\sum_\alpha \tilde{M}_{ji}^\alpha = 0$ cannot both be satisfied.

Now focus attention on $-\sum_\alpha C_\alpha [C_\alpha q_j^k \theta_{,j}^\alpha + \tilde{m}_j^\alpha v_j^\alpha]$. The goal is to reduce this term to a quadratic in the objective variables $\theta_{,j}^\alpha$ and $u_j^{\alpha\beta}$. Of course gradients of C_α could replace the gradients of θ^α but there is no advantage to this in the subsequent analysis.

The reduction to a quadratic form is not straightforward because of the product of \tilde{m}_j^α and v_j^α , the latter variable not being objective. However, if

$$\begin{aligned} l_{\alpha\beta} C_\alpha &= l_{\beta\alpha} C_\beta \\ r_{\alpha\beta\gamma} C_\gamma &= -r_{\beta\alpha\gamma} C_\gamma \end{aligned} \tag{19}$$

then

$$\sum_\alpha \tilde{m}_j^\alpha v_j^\alpha C_\alpha = \phi^1 \phi^2 [l_{\beta\gamma} C_\beta u_j^{12} u_j^{12} + (r_{121} \theta_{,j}^1 C_1 - r_{212} \theta_{,j}^2 C_2) u_j^{12}] \tag{20}$$

Equation (19) reduces to the dynamic constraints given by (12) only when $C_\alpha = C_\beta$.

Using (19) the vector components of (6) become

$$\sum_\alpha C_\alpha [C_\alpha q_j^\alpha \theta_{,j}^\alpha + \tilde{m}_j^\alpha v_j^\alpha] = [\theta_{,j}^1, \theta_{,j}^2, u_j^{12}] \begin{bmatrix} \Gamma_{11} & \Gamma_{12} & \Gamma_{13} \\ \Gamma_{12} & \Gamma_{22} & \Gamma_{23} \\ \Gamma_{13} & \Gamma_{23} & \Gamma_{33} \end{bmatrix} \begin{bmatrix} \theta_{,j}^1 \\ \theta_{,j}^2 \\ u_j^{12} \end{bmatrix} \tag{21}$$

Here

$$\begin{aligned} \Gamma_{11} &= \phi^1 k_{11} C_1^2 \\ \Gamma_{12} &= (\phi^1 \phi^2 / 2) (k_{12} C_1^2 + k_{21} C_2^2) \\ \Gamma_{13} &= (\phi^1 \phi^2 / 2) (h_{12} C_1^2 + r_{121} C_1) \\ \Gamma_{22} &= \phi^2 k_{22} C_2^2 \\ \Gamma_{23} &= -(\phi^1 \phi^2 / 2) (h_{21} C_2^2 + r_{212} C_2) \\ \Gamma_{33} &= \phi^1 \phi^2 l_{12} C_1 = \phi^1 \phi^2 l_{21} C_2 \end{aligned} \tag{22}$$

Non-negative entropy production requires the Γ matrix in (21) to be non-negative definite. The resulting eigenvalue equation is

$$\gamma^3 - \gamma^2 \text{tr}(\Gamma) + \gamma \Sigma(\Gamma) - \det(\Gamma) = 0$$

with $\Sigma(\Gamma)$ the sum of the three principal minors. The strictest requirements for the roots to be non-negative are $\text{tr}(\Gamma) \geq 0$, $\Sigma(\Gamma) \geq 0$, and $\det(\Gamma) \geq 0$. Thus for $\text{tr}(\Gamma) \geq 0$

$$\begin{aligned} k_{11} C_1^2, k_{22} C_2^2 &\geq 0 \\ \Gamma_{33} &\geq 0 \end{aligned} \tag{23}$$

$\Sigma(\Gamma) \geq 0$ gives

$$\begin{aligned} k_{11} k_{22} C_1^2 C_2^2 &\geq (\phi^1 \phi^2 / 4) (k_{12} C_1^2 + k_{21} C_2^2)^2 \\ k_{11} l_{12} C_1 &\geq (\phi^2 / 4) (h_{12} C_1 + r_{121})^2 \\ k_{22} l_{21} C_2 &\geq (\phi^1 / 4) (h_{21} C_2 + r_{212})^2 \end{aligned} \tag{24}$$

Finally, the requirement

$$\det(\Gamma) \geq 0 \tag{25}$$

appears to be a new constraint on the phenomenological coefficients in (11).

The dynamic constraints (12) provide considerable simplification when $\theta^1 = \theta^2 = \theta = C^{-1}$. Setting $r_{12\gamma} = -r_{21\gamma} = r$ and $l_{12} = l_{21} = l$ it follows that

$$\begin{aligned} \phi^1 k_{11} + \phi^2 k_{22} + \phi^1 \phi^2 (k_{12} + k_{21}) &\geq 0 \\ l &\geq 0 \\ l [\phi^1 k_{11} + \phi^2 k_{22} + \phi^1 \phi^2 (k_{12} + k_{21})] C^2 + (\phi^1 \phi^2 / 4) [(h_{12} - h_{21}) C + r]^2 &\geq 0 \end{aligned} \tag{26}$$

Observe that the cross terms considered in the entropy inequalities have a symmetry property that is not present in the constitutive equations. For example, in the shear deformation, the cross terms in (10) were given as μ_{12} and μ_{21} , but in the entropy inequality only the sum of these terms, weighted by the coldness of the respective constituent, survives as is seen in (15), (16), and (24). Now Kirwan *et al.* [26] argued that any dissipative phenomenological parameters that do not appear in entropy inequalities have no physical meaning. Although that study was not concerned with different constituent temperatures the fundamental idea is applicable here as well.

To see this, consider two rheological experiments performed on MCF that are identical in every respect except that in one experiment the components are at different temperatures while in the other experiment the component temperatures are the same. In the second case Kirwan *et al.* [26] would argue that since only $\mu_{12} + \mu_{21}$, for example, entered into the entropy inequality, then it would be appropriate to replace the two coefficients in the constitutive equations by a single coefficient, say $\mu_S/2$. This reduces the number of coefficients by one. And since the MCF are identical the same condition could just as well be applied to the first experiment. This thought experiment suggests

$$\begin{aligned} \lambda_{12} &= \lambda_{21} \\ \mu_{12} &= \mu_{21} \\ k_{12} &= k_{21} \end{aligned} \tag{27}$$

From the discussion above it seems that this argument does not apply to the interaction coefficients $h_{\alpha\beta}$, $l_{\alpha\beta}$, and $r_{\alpha\beta\gamma}$.

5. Discussion

Linear constitutive equations for the viscous stress, heat flux, and internal energy source based on GAM were developed for a mixture of two Navier–Stokes fluids at different temperatures. GAM ensured that these equations reduced to the appropriate form for a Navier–Stokes fluid when the volume fraction of either constituent vanished. The resultant constitutive equations were used to calculate the entropy production and the results were consistent with the previous analyses with two exceptions. One was that the cross terms automatically vanished when the volume fraction of either constituent vanished. The other difference was the peculiar effect distinct constituent temperatures had on entropy production. For this situation the internal source terms could not satisfy both positive entropy production and the requirement imposed by Truesdell’s third principle that they vanish when summed over all constituents.

As noted earlier Green and Adkins [3], Hansen [4], Hansen *et al.* [5] and more recently Massoudi [2] proposed other metaphysical principles. It is appropriate then to reassess Truesdell’s three principles. The first principle is a truism that applies to all theories and thus offers no specific insight to MCF. On the other hand GAM seems to be an attractive modification of Truesdell’s second principle, Hansen *et al.* [5] offered an alternative to his third principle, and Kirwan *et al.* [26] suggested a way to reduce the number of coefficients in constitutive theories for MCF. In view of this it seems appropriate to reassess these three metaphysical principles. To codify these ideas I propose:

- The constituent balance equations for mass, linear and angular momentum, and internal energy must account for all interactions between the constituents in accordance with the general principles of physics. They must reduce to the balance equations for a pristine medium when all but one of the constituents vanishes.
- The evolution of MCF is determined by the simultaneous solution of the coupled balance equations for each of the constituents.
- All phenomenological coefficients must be constrained by the Second Law applied to the sum of all the constituents. Any coefficient not so constrained has no effect in the dynamical evolution of MCF.

It is stressed that these principles do not appeal to “mixture balance equations”. Instead, they are motivated by the ontological question “how does a constituent know it is in an MCF?” These new principles offer guidance on the formulation of constitutive theories for MCF that are in strict accordance with the Second Law. Moreover, they are consistent with previous studies that focused on uniform constituent temperatures.

It is worth noting that the three revised metaphysical principles given above provide guidance to generalize (10) and (11) to an MCF composed of N constituents. These equations can be compactly stated as

$$\begin{aligned}
\sigma_{ji}^{\alpha} &= \phi^{\alpha} \left(\lambda_{\alpha\alpha} d^{\alpha} \delta_{ji} + 2\mu_{\alpha\alpha} \hat{d}_{ji}^{\alpha} \right) + \\
&\quad \phi^{\alpha} \sum_{\beta \neq \alpha} \phi^{\beta} \left[\left(\lambda_{\alpha\beta} d^{\beta} \delta_{ji} + 2\mu_{\alpha\beta} \hat{d}_{ji}^{\beta} \right) + \nu_{\beta\alpha} \left(w_{[ij]}^{\alpha} - w_{[ij]}^{\beta} \right) \right] \\
q_j^{\alpha} &= -\phi^{\alpha} \left[k_{\alpha\alpha} \theta_{,j}^{\alpha} + \sum_{\beta \neq \alpha} \phi^{\beta} k_{\alpha\beta} \theta_{,j}^{\beta} + \sum_{\beta \neq \alpha} \phi^{\beta} h_{\beta\alpha} \left(v_j^{\alpha} - v_i^{\beta} \right) \right] \\
\tilde{m}_j^{\alpha} &= -\phi^{\alpha} \sum_{\beta \neq \alpha} \phi^{\beta} \left[l_{\beta\alpha} \left(v_j^{\alpha} - v_j^{\beta} \right) + \sum_{\gamma=1}^N r_{\alpha\beta\gamma} \theta_{,j}^{\gamma} \right]
\end{aligned} \tag{28}$$

The Second Law imposes inequality constraints that are straightforward extensions of (15), (18), (19), (23), and (24). At the same time the third metaphysical principle provides restrictions on the number of independent coefficients that are straightforward extensions of (12) and (27).

In closing it is noted that constitutive equations based on the three metaphysical principles proposed above provide guidance for rheological experiments on MCF. The principal coefficients $\lambda_{\alpha\alpha}$, $\mu_{\alpha\alpha}$, and $k_{\alpha\alpha}$ are the values determined from pristine conditions. These values are simply diluted by the appropriate specific volumes when the constituents appear in MCF.

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