

CONSTITUTIVE EQUATIONS FOR MULTIPHASE MIXTURES OF FLUIDS

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Abstract—Constitutive equations for a multiphase mixture of fluids are presented. The mixture is assumed to consist of a single non-uniform temperature and no phase change is allowed. The theory is based on the conservation and balance equations of multiphase mixtures proposed by Dobran, and the constitutive assumption allows for the effects of temperature gradient, density gradients, velocity gradients, velocities and accelerations. A linearized form of the constitutive equations is presented for an arbitrary number of phases, and restrictions on the constitutive assumption are investigated by the second law of thermodynamics. The theory yielded a significant number of results and they are compared with previous investigations.

1. INTRODUCTION

In the *theory of multiphase mixtures*, the term phase denotes a portion of matter with a smoothly varying chemical composition and physical properties, and the phases are distinguished from one another by the well-defined boundary surfaces. When the interfacial area of the multiphase mixture is reduced to zero, this mixture is modeled by the *theory of mixtures*. It is important to carefully distinguish these two mixtures, since the latter theory has achieved considerable maturity principally through the works of Truesdell (1969), Eringen & Ingram (1965), Mueller (1968) and Bowen (1973).

The theory of multiphase mixtures has not yet achieved a recognized status. This is principally because (1) no universal accord exists as to what constitutes a complete set of conservation and balance equations, and (2) the constitutive equations have not been rigorously studied.

The existing theories of multiphase mixtures are of two varieties: (1) those that were constructed by utilizing an averaging approach, and (2) those that were postulated. The former theories are due to Drew (1971), Ishii (1975), Delhay & Achard (1977), Nigmatulin (1979) and Dobran (1982a). The postulated multiphase field equations are due to Goodman & Cowin (1972), Drumheller & Bedford (1980) and by Passman *et al.* (1983). The detailed discussions of various formulations were performed by Dobran (1982a, 1983) and by Bedford & Drumheller (1983). The theory of multiphase mixtures formulated by Dobran (1982a) has the following features: (1) it is motivated by the volume averaging approach of the macroscopic conservation laws of each phase; (2) it is given a rigorous mathematical structure; and (3) it is consistent with the theory of mixtures when the interfacial area is reduced to zero. In such a theory of multiphase mixtures, all phases of the mixture exist at each point of space, and *each phase* is described by the conservation laws of mass, and balance equations of linear momentum, angular momentum, energy and entropy. The interaction between the phases is accounted by the interphase mass, momentum, energy and entropy supplies, and the effect of the finite interfacial area or microstructural characteristics of the mixture can be taken into consideration in the theory through the non-local effect in the constitutive equations or through an explicit assumption of the microstructure in the supply or interaction terms.

Constitutive equations for multiphase mixtures have not been extensively studied in the past. Ishii (1975), Drew (1976) and Drew & Lahey (1979) have taken important steps toward the construction of a theory of constitutive equations for a 2-phase fluid mixture but they did not systematically utilize the second law of thermodynamics to restrict the form of these equations. An approach to where the second law of thermodynamics is

utilized to restrict the form of the constitutive equations is that of Drumheller & Bedford (1980). Their theory of constitutive equations is based on (1) the second law of thermodynamics for the mixture as a whole, and (2) on the conservation and balance equations of immiscible mixtures which were derived using the "Hamilton's extended variational formulation". The validity of the second law of thermodynamics for only the mixture is not consistent with the volume averaging formulation of the conservation and balance equations of Dobran (1982a) as well as with the time averaging formulation of Ishii (1975), since these formulations require the second law of thermodynamics for each phase. As discussed by Dobran (1982a), Drumheller & Bedford's (1980) equations are also special, since they have a built-in *a priori* constitutive assumption of the virtual mass and expansion-contraction effects and rest upon the premise of a variational principle whose validity is not altogether clear. Nevertheless, this variational approach yields constitutive equations for the microstructural characteristics of the mixture and the results of the theory agree with the selected special cases. Drumheller & Bedford restricted the constitutive equations by utilizing an entropy balance equation for the mixture as a whole and invoked the principle of immiscibility for the free energy or Helmholtz potential whereby the free energy of phase α is assumed to depend only on the independent variables associated with this phase. Passman *et al.* (1983), by extending on the work of Goodman & Cowin (1972), also utilized the entropy balance equation for the mixture as a whole to restrict the constitutive equations and invoked the principle of immiscibility or phase separation for the free energy. Their postulated field equations not only contain the effects of microstructure of the mixture but include also separate balance equations for these microstructural characteristics. Dobran (1982a) showed that the field equations based on the averaging procedures also contain the microstructural characteristics of the mixture in the supply or interaction terms for each phase as well as for the mixture as a whole. In the postulated theories of Drumheller & Bedford and Passman *et al.* there are no source terms in the linear momentum, angular momentum and entropy balance equations for the mixture as a whole as in the averaged theories, and, therefore, no recognition is made in these theories for the microstructural characteristics of the mixture that can affect the motion of the mixture as a whole. Since the postulated field equations described above also assume explicit forms of the microstructure of the mixture, it appears that these equations have already a built-in constitutive assumption. Consequently, when additional assumptions on the constitutive equations are made it is difficult to judge their adequacy in modeling the physical phenomena. What is needed, clearly, is not only an extensive test of any theory with the experimental data, but also a clear delineation between the multiphase field equations and constitutive equations.

It is clear from the above discussion that the constitutive equations for multiphase mixtures have not been adequately studied. The principal reason for this is that the proposed theories of multiphase mixtures are not complete, and many of them are not given a sufficient mathematical structure which is indispensable for the proper study of constitutive equations. The objective of this paper is to study the constitutive equations for multiphase mixtures utilizing the conservation and balance equations of Dobran (1982a), since this formulation appears to be more satisfactory than formulations presented in some other investigations (Dobran 1982a, 1983).

The conservation and balance equations for multiphase mixtures are summarized in section 2. In section 3 a single temperature dispersed mixture without the phase change is selected for analysis, and the second law of thermodynamics for each phase is used to derive restrictions on the constitutive assumption. In section 3.4 the mixture is assumed to consist of fluids only, and in section 4, the linearized constitutive equations are derived. The discussion of results and comparison of these results with existing formulations is carried out in section 5.

Notation

A direct notation is utilized in this paper, and the space is the 3-dimensional Euclidean space E^3 with the Cartesian coordinate system. Vectors and vector fields are denoted by the Latin bold-faced miniscules: \mathbf{a} , \mathbf{b} , \mathbf{x} , ... Second order tensors are viewed as linear transformations in E^3 , and are denoted by Latin bold-faced majuscules: \mathbf{A} , \mathbf{B} , \mathbf{T} , ... (except \mathbf{X} which is a vector of the reference position of the material body point). The product of two linear transformations is a linear transformation, $\mathbf{AB} = \mathbf{C}$, and the product of a linear transformation and a vector is a vector, $\mathbf{x} = \mathbf{T}\mathbf{u}$. \mathbf{T}^T is the transpose of \mathbf{T} , \mathbf{T}^{-1} is the inverse of \mathbf{T} , $\det \mathbf{T}$ is the determinant of \mathbf{T} , and the contraction of \mathbf{T} is its trace $\text{tr } \mathbf{T}$. The divergence operator is denoted by $\nabla \cdot$, ∇a is the gradient of a , and the gradient of a vector field \mathbf{b} is the linear transformation $\nabla \mathbf{b}$. \mathbf{I} is the unit linear transformation. The tensor product of two vectors \mathbf{a} and \mathbf{b} is denoted by $\mathbf{a} \otimes \mathbf{b}$ and is identified as a linear transformation.

The basis in E^3 is denoted by the Cartesian triad of unit vectors $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$. The tensorial indices are denoted by the italic light-faced miniscules: i, j, \dots , and majuscules: I, J, \dots , and the summation convention always applies to them. The Greek light-faced symbols $\alpha, \beta, \sigma, \delta$ always occur as subscripts or superscripts and denote the phases of the multiphase mixture: $\alpha, \beta, \sigma, \delta = 1, \dots, \gamma$. The sum of phases ($\alpha = 1$, to $\alpha = \gamma$) is always denoted explicitly by the summation symbol \sum_{α}^{γ} . Other symbols are defined in the text when they first appear.

2. CONSERVATION LAWS FOR THE MULTIPHASE MIXTURES

In this section, I will summarize the conservation laws for multiphase mixtures which are proposed by Dobran (1982a). This formulation utilizes the volume averaging approach where \mathcal{V} is the arbitrary averaging volume which contains all phases of the multiphase mixture and \mathcal{V}_{α} is the volume of phase α in \mathcal{V} at any instant of time. The volume-averaged quantity of the field F_{α} is defined by

$$\langle F_{\alpha} \rangle \equiv \frac{1}{\mathcal{V}_{\alpha}} \int_{\mathcal{V}_{\alpha}} F_{\alpha} d\mathcal{V}_{\alpha},$$

and the (partial) density of phase α is defined as

$$\bar{\rho}_{\alpha} \equiv \frac{\mathcal{V}_{\alpha}}{\mathcal{V}} \langle \rho_{\alpha} \rangle.$$

The density-weighted average of a physical property H_{α} will be denoted by \bar{H}_{α} , whereas the partial quantity of a physical variable G_{α} will be denoted by \bar{G}_{α} , i.e.

$$\bar{H}_{\alpha} \equiv \frac{\langle \rho_{\alpha} H_{\alpha} \rangle}{\langle \rho_{\alpha} \rangle} = \frac{1}{\bar{\rho}_{\alpha}} \frac{\mathcal{V}_{\alpha}}{\mathcal{V}} \langle \rho_{\alpha} H_{\alpha} \rangle$$

$$\bar{G}_{\alpha} \equiv \frac{\mathcal{V}_{\alpha}}{\mathcal{V}} \langle G_{\alpha} \rangle$$

$$\bar{G}_{\alpha} \equiv \langle G_{\alpha} \rangle.$$

2.1 Kinematics

The multiphase mixture consists of γ diffusing bodies (phases) \mathcal{B}_{α} , $\alpha = 1, \dots, \gamma$, and each \mathcal{B}_{α} consists of *body points* or particles X_{α} . The position \mathbf{x} in E^3 of the body points X_{α} is represented by the *configuration* χ_{α} of \mathcal{B}_{α} , i.e.

$$\mathbf{x} = \chi_{\alpha}(X_{\alpha}, t). \tag{2.1}$$

To each \mathcal{B}_α is assigned a *reference configuration* κ_α at time $t_0 < t$, and the place of the particle X_α in κ_α is given by the following expression:

$$\mathbf{X}_\alpha = \kappa_\alpha(X_\alpha, t_0). \quad [2.2]$$

Combining [2.1] and [2.2] we have

$$\mathbf{x} = \chi_\alpha(\kappa_\alpha^{-1}(\mathbf{X}_\alpha, t_0), t) \equiv \chi_{\alpha\kappa}(\mathbf{X}_\alpha, t), \quad [2.3]$$

where $\chi_{\alpha\kappa}$ is the *deformation function* of \mathcal{B}_α .

For each phase α and at each time t , the expression [2.3] is assumed invertible, $\mathbf{X}_\alpha = \chi_{\alpha\kappa}^{-1}(\mathbf{x}, t)$, and $\chi_{\alpha\kappa}$ and $\chi_{\alpha\kappa}^{-1}$ are assumed twice differentiable. The spatial coordinates will be denoted by the lower case italic indices, $\mathbf{x} = x_i \mathbf{e}_i$, and the material coordinates will be expressed by the upper case italic indices, $\mathbf{X}_\alpha = X_{\alpha I} \mathbf{e}_I$, where $\mathbf{e}_i \cdot \mathbf{e}_k = \delta_{ik}$ and $\mathbf{e}_I \cdot \mathbf{e}_K = \delta_{IK}$ are the Kronecker deltas.

The velocity and acceleration of a body point or particle X_α are, respectively,

$$\tilde{\mathbf{v}}_\alpha = \frac{\partial \chi_{\alpha\kappa}(\mathbf{X}_\alpha, t)}{\partial t}, \quad \tilde{\mathbf{a}}_\alpha = \frac{\partial^2 \chi_{\alpha\kappa}(\mathbf{X}_\alpha, t)}{\partial t^2}. \quad [2.4]$$

The deformation gradient and its inverse for the phase α are the linear transformations defined by the following expressions:

$$\begin{aligned} \mathbf{F}_\alpha &= \text{GRAD } \chi_{\alpha\kappa}(\mathbf{X}_\alpha, t), & F_{\alpha k I} &= \frac{\partial x_k}{\partial X_{\alpha I}}, \\ \mathbf{F}_\alpha^{-1} &= \mathcal{V} \chi_{\alpha\kappa}^{-1}(\mathbf{x}, t), & F_{\alpha I k}^{-1} &= \frac{\partial X_{\alpha I}}{\partial x_k}, \end{aligned} \quad [2.5]$$

where GRAD is the gradient with respect to the material coordinates, and the *velocity gradient* of phase α is defined as follows:

$$\mathbf{L}_\alpha \equiv \mathcal{V} \tilde{\mathbf{v}}_\alpha(\mathbf{x}, t) = \dot{\mathbf{F}}_\alpha \mathbf{F}_\alpha^{-1}, \quad L_{\alpha ij} = \frac{\partial \tilde{v}_{\alpha i}}{\partial x_j}. \quad [2.6]$$

The *density of mixture*, ρ , and the center of mass *velocity of mixture*, \mathbf{v} , are defined, respectively, as

$$\rho = \sum_\alpha \bar{\rho}_\alpha, \quad \rho \mathbf{v} = \sum_\alpha \bar{\rho}_\alpha \tilde{\mathbf{v}}_\alpha, \quad [2.7]$$

where $\bar{\rho}_\alpha$ is the partial density of phase α and is defined above. In the 2-phase literature, it is a common practice to express $\bar{\rho}_\alpha$ in terms of the void fraction for phase α and the true density of the same phase. In this paper, I will, however, not utilize this approach, for it adds nothing to the theory. In the discussion of section 5, I will have more to say about this point.

The *diffusion velocity* is the difference between the phase velocity and the mixture velocity, i.e.

$$\mathbf{u}_\alpha = \tilde{\mathbf{v}}_\alpha - \mathbf{v}. \quad [2.8]$$

If we let Γ be a differentiable function of \mathbf{x} and t , then the time derivative “following” the α th phase (material derivative for phase α) and the time derivative “following” the mixture (material derivative for the mixture) are, respectively,

$$\dot{\Gamma} = \frac{\partial \Gamma}{\partial t} + (\nabla \Gamma) \tilde{\mathbf{v}}_\alpha, \quad \dot{\Gamma} = \frac{\partial \Gamma}{\partial t} + (\nabla \Gamma) \mathbf{v}, \quad [2.9]$$

and thus

$$\dot{\Gamma} - \dot{\Gamma} = (\nabla \Gamma) \mathbf{u}_\alpha, \quad [2.10]$$

where [2.8] was used. If $\rho \Gamma \equiv \sum_\alpha \bar{\rho}_\alpha \tilde{\Gamma}_\alpha$, then it follows that

$$\rho \dot{\Gamma} = \sum_\alpha \left[\bar{\rho}_\alpha \dot{\tilde{\Gamma}}_\alpha - \nabla \cdot \bar{\rho}_\alpha \tilde{\Gamma}_\alpha \mathbf{u}_\alpha + \left(\frac{\partial \bar{\rho}_\alpha}{\partial t} + \nabla \cdot \bar{\rho}_\alpha \tilde{\mathbf{v}}_\alpha \right) \tilde{\Gamma}_\alpha - \left(\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} \right) \Gamma \right]. \quad [2.11]$$

The above identities are due to Truesdell & Toupin (1960).

2.2 Conservation of mass

The conservation of mass equations for the phase α and for the mixture are, respectively,

$$\dot{\bar{\rho}}_\alpha + \bar{\rho}_\alpha \nabla \cdot \tilde{\mathbf{v}}_\alpha = \hat{c}_\alpha \quad \dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0, \quad [2.12]$$

where \hat{c}_α is the mass supply for phase α (the rate of phase change or the rate of chemical reaction per unit volume of the mixture). The compatibility condition on \hat{c}_α between [2.12]₁ and [2.12]₂ is:

$$\sum_\alpha \hat{c}_\alpha = 0. \quad [2.13]$$

2.3 Balance of the linear momentum

The balance of linear momentum for the phase α and for the mixture are expressed by the following equations:

$$\begin{aligned} \bar{\rho}_\alpha \dot{\tilde{\mathbf{v}}}_\alpha &= \nabla \cdot \tilde{\mathbf{T}}_\alpha + \bar{\rho}_\alpha \tilde{\mathbf{b}}_\alpha + \hat{\mathbf{p}}_\alpha \\ \rho \dot{\mathbf{v}} &= \nabla \cdot \mathbf{T} + \rho \mathbf{b} + \hat{\mathbf{p}}_m. \end{aligned} \quad [2.14]$$

In [2.14]₁, $\tilde{\mathbf{T}}_\alpha$ is the (partial) stress tensor, $\tilde{\mathbf{b}}_\alpha$ is the external body force, and $\hat{\mathbf{p}}_\alpha$ is the momentum supply or source for phase α . The mixture stress tensor \mathbf{T} , body force \mathbf{b} , and momentum supply $\hat{\mathbf{p}}_m$ in [2.14]₂ are defined, respectively, as follows:

$$\begin{aligned} \mathbf{T} &\equiv \sum_\alpha (\tilde{\mathbf{T}}_\alpha - \bar{\rho}_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha) \\ \rho \mathbf{b} &\equiv \sum_\alpha \bar{\rho}_\alpha \tilde{\mathbf{b}}_\alpha \\ \hat{\mathbf{p}}_m &\equiv \sum_\alpha (\hat{c}_\alpha \mathbf{u}_\alpha + \hat{\mathbf{p}}_\alpha). \end{aligned} \quad [2.15]$$

The momentum supply vector for the mixture $\hat{\mathbf{p}}_m$ arises due to both the interfacial forces (surface tension) and the non-local material response (see Dobran 1982a) which can be thought as representing the microstructural characteristics of the mixture. When these effects are absent $\hat{\mathbf{p}}_m = \mathbf{0}$.

2.4 Balance of the angular momentum

When there are no body couples and couple stresses acting on the mixture, the balance of the angular momentum for the phase α and for the mixture is reflected in the nonsymmetry of stress tensors, i.e.

$$\hat{\mathbf{M}}_\alpha \equiv \mathbf{T}_\alpha - \mathbf{T}_\alpha^T \quad [2.16]$$

$$\hat{\mathbf{M}}_m \equiv \sum_\alpha \hat{\mathbf{M}}_\alpha = \mathbf{T} - \mathbf{T}^T,$$

and $\hat{\mathbf{M}}_m = \mathbf{0}$ for a mixture with negligible interfacial forces and with the absence of non-local effects.

2.5 Balance of energy

The energy equations for the phase α and for the mixture are, respectively,

$$\begin{aligned} \bar{\rho}_\alpha \tilde{\epsilon}_\alpha &= \text{tr}(\mathbf{T}_\alpha^T \nabla \tilde{\mathbf{v}}_\alpha) - \nabla \cdot \bar{\mathbf{q}}_\alpha + \bar{\rho}_\alpha \tilde{r}_\alpha + \hat{\epsilon}_\alpha \\ \rho \dot{\epsilon} &= \text{tr}(\mathbf{T}^T \nabla \mathbf{v}) - \nabla \cdot \mathbf{q} + \rho r + (\hat{\epsilon}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m), \end{aligned} \quad [2.17]$$

where $\tilde{\epsilon}_\alpha$ is the internal energy, $\bar{\mathbf{q}}_\alpha$ is the heat flux vector, \tilde{r}_α is the heat generation rate and $\hat{\epsilon}_\alpha$ is the energy supply or source for phase α . The mixture properties ϵ , r , \mathbf{q} and $(\hat{\epsilon}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m)$ in [2.17]₂ are defined as follows:

$$\begin{aligned} \rho \epsilon &\equiv \sum_\alpha \left[\bar{\rho}_\alpha \tilde{\epsilon}_\alpha + \frac{1}{2} \bar{\rho}_\alpha \mathbf{u}_\alpha \cdot \mathbf{u}_\alpha \right] \\ \rho r &\equiv \sum_\alpha [\bar{\rho}_\alpha \tilde{r}_\alpha + \bar{\rho}_\alpha \tilde{\mathbf{b}}_\alpha \cdot \mathbf{u}_\alpha] \\ \mathbf{q} &\equiv \sum_\alpha \left[\bar{\mathbf{q}}_\alpha - \mathbf{T}_\alpha^T \mathbf{u}_\alpha + \bar{\rho}_\alpha \tilde{\epsilon}_\alpha \mathbf{u}_\alpha + \frac{1}{2} \bar{\rho}_\alpha (\mathbf{u}_\alpha \cdot \mathbf{u}_\alpha) \mathbf{u}_\alpha \right] \\ \hat{\epsilon}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m &\equiv \sum_\alpha \left[\hat{\epsilon}_\alpha + \mathbf{u}_\alpha \cdot \hat{\mathbf{p}}_\alpha + \hat{c}_\alpha \left(\tilde{\epsilon}_\alpha + \frac{1}{2} \mathbf{u}_\alpha \cdot \mathbf{u}_\alpha \right) \right]. \end{aligned} \quad [2.18]$$

For a mixture with negligible interfacial forces and with the absence of non-local effects $\hat{\epsilon}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m = 0$.

2.6 The second law of thermodynamics

The second laws of thermodynamics for the phase α and for the mixture are expressed by the following equations:

$$\begin{aligned} \bar{\rho}_\alpha \hat{s}_\alpha + \nabla \cdot \left(\frac{\bar{\mathbf{q}}_\alpha}{\bar{\theta}_\alpha} \right) - \frac{\bar{\rho}_\alpha \tilde{r}_\alpha}{\bar{\theta}_\alpha} + \hat{c}_\alpha \hat{s}_\alpha + \hat{s}_\alpha = \bar{\rho}_\alpha \tilde{\xi}_\alpha \geq 0 \\ \rho \hat{s} + \nabla \cdot \sum_\alpha \left(\frac{\bar{\mathbf{q}}_\alpha}{\bar{\theta}_\alpha} + \bar{\rho}_\alpha \tilde{s}_\alpha \mathbf{u}_\alpha \right) - \sum_\alpha \frac{\bar{\rho}_\alpha \tilde{r}_\alpha}{\bar{\theta}_\alpha} + \hat{s}_m = \rho \xi \geq 0. \end{aligned} \quad [2.19]$$

In [2.19]₁, \tilde{s}_α is the entropy, $\bar{\theta}_\alpha$ is the temperature, \hat{s}_α is the entropy supply or source, and $\tilde{\xi}_\alpha$ is the entropy production rate of phase α . The mixture entropy, entropy production rate, and entropy supply in [2.19]₂ are defined respectively as follows:

$$\begin{aligned} \rho s &\equiv \sum_\alpha \bar{\rho}_\alpha \tilde{s}_\alpha \\ \rho \xi &\equiv \sum_\alpha \bar{\rho}_\alpha \tilde{\xi}_\alpha \\ \hat{s}_m &\equiv \sum_\alpha \hat{s}_\alpha. \end{aligned} \tag{2.20}$$

The conservation laws in the theory of multiphase mixtures summarized above differ from the conservation laws in the theory of mixtures with a negligible interfacial area in two important ways. First, in the former theory, the mixture source terms $\hat{\mathbf{p}}_m, \hat{\mathbf{M}}_m, \hat{e}_m$ and \hat{s}_m do not vanish since they are a consequence of the interfacial forces (surface tension) and of the non-local material response. It is this mechanism of the non-local material response in which the size of the averaging volume \mathcal{V} is buried, and the constitutive assumption should, therefore, account for the size of \mathcal{V} . The second important difference lies in the second law of thermodynamics. In the theory of multiphase mixtures, it is plausible to have a second law of thermodynamics for each phase, while in the theory of mixtures, only the second law of thermodynamics for the mixture as a whole gives the equilibrium results which are consistent with the classical equilibrium thermodynamics (Bowen 1973).

3. SINGLE TEMPERATURE MULTIPHASE MIXTURE WITHOUT THE PHASE CHANGE

In a multiphase mixture each phase can be assigned a unique temperature; however, in this paper a mixture of a single $\bar{\theta}_\alpha = \theta$, but nonuniform temperature, and without the possibility of undergoing a phase change, $\hat{c}_\alpha = 0$, will be considered. This special mixture is of significant practical interest nevertheless, and the basic concepts which are involved in the construction of constitutive equations for this simple mixture carry over to more general situations. Later on in this section an additional assumption is made that the mixture consists of fluids.

3.1 The thermodynamic process for the mixture

Before defining the thermodynamic process for multiphase mixture, it is useful to recast the second law of thermodynamics [2.19]₁ into a more convenient form.

Eliminating the heat generation rate \tilde{r}_α in the entropy inequality [2.19]₁ by using the energy equation [2.17]₁, and setting $\bar{\theta}_\alpha = \theta$ and $\hat{c}_\alpha = 0$, yields the following equation:

$$\bar{\rho}_\alpha (\hat{s}_\alpha \theta - \tilde{\xi}_\alpha) + \text{tr}(\mathbf{T}_\alpha^T \mathbf{V} \tilde{\mathbf{v}}_\alpha) - \frac{\bar{\mathbf{q}}_\alpha \cdot \mathbf{V} \theta}{\theta} + \hat{e}_\alpha + \theta \hat{s}_\alpha = \bar{\rho}_\alpha \tilde{\xi}_\alpha \theta \geq 0. \tag{3.1}$$

Equation [3.1] is further reduced by using the definitions of Helmholtz potential $\tilde{\psi}_\alpha$, chemical potential tensor $\tilde{\mathbf{K}}_\alpha$, potential Ψ_α , i.e.

$$\begin{aligned} \tilde{\psi}_\alpha &\equiv \tilde{e}_\alpha - \theta \tilde{s}_\alpha \\ \tilde{\mathbf{K}}_\alpha &\equiv \tilde{\psi}_\alpha \mathbf{I} - \frac{1}{\bar{\rho}_\alpha} \mathbf{T}_\alpha^T \\ \Psi_\alpha &\equiv \bar{\rho}_\alpha \tilde{\psi}_\alpha, \end{aligned} \tag{3.2}$$

and eliminating $\hat{\theta}$ using [2.11] with $\tilde{F}_\alpha = \theta$. Thus

$$-\Psi_\alpha - \bar{\rho}_\alpha \tilde{s}_\alpha \theta - \text{tr}(\bar{\rho}_\alpha \tilde{\mathbf{K}}_\alpha \nabla \tilde{\mathbf{v}}_\alpha) - \frac{\nabla \theta}{\theta} \cdot \mathbf{h}_\alpha - \mathbf{u}_\alpha \cdot \hat{\mathbf{p}}_\alpha + \hat{R}_\alpha \geq 0, \quad [3.3]$$

where

$$\begin{aligned} \mathbf{h}_\alpha &\equiv \bar{\mathbf{q}}_\alpha \tilde{s}_\alpha \theta \mathbf{u}_\alpha \\ \hat{R}_\alpha &\equiv \hat{e}_\alpha + \mathbf{u}_\alpha \cdot \hat{\mathbf{p}}_\alpha + \theta \hat{s}_\alpha. \end{aligned} \quad [3.4]$$

The variable \hat{R}_α is introduced for convenience. Its interesting properties are summarized in section 3.4.

The second law of thermodynamics for the multiphase *mixture* is obtained by summing up α in [3.3], i.e.

$$-\sum_\alpha \Psi_\alpha - \sum_\alpha \bar{\rho}_\alpha \tilde{s}_\alpha \theta - \text{tr} \left\{ \sum_\alpha \bar{\rho}_\alpha \tilde{\mathbf{K}}_\alpha \nabla \tilde{\mathbf{v}}_\alpha \right\} - \frac{\nabla \theta}{\theta} \cdot \sum_\alpha \mathbf{h}_\alpha - \sum_\alpha \mathbf{u}_\alpha \cdot \hat{\mathbf{p}}_\alpha + \hat{R}_m \geq 0. \quad [3.5]$$

The mixture source term

$$\hat{R}_m = \sum_\alpha \hat{R}_\alpha = \hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m + \theta \hat{s}_m \quad [3.6]$$

follows from [3.4]₂, [2.18]₄ and [2.20]₃. Equation [3.5] can be also obtained from [2.19]₂ and it is useful to study constitutive equations which are only restricted by the second law of thermodynamics for the mixture.

Setting $\hat{c}_\alpha = 0$ in [2.12]₁, the conservation of mass equation for phase α can be integrated to yield

$$\bar{\rho}_\alpha \det \mathbf{F}_\alpha = \bar{\rho}_{\alpha\kappa}, \quad [3.7]$$

where $\bar{\rho}_{\alpha\kappa}$ is the density of phase α in the reference configuration and it is assumed to be known. The density $\bar{\rho}_\alpha$ is thus determined from the knowledge of the deformation gradient \mathbf{F}_α .

The final set of equations which are utilized in this article to study the constitutive equations are the conservation of mass equation [3.7], linear momentum equation [2.14]₁, angular momentum equation [2.16]₁, energy equation [2.17]₂, and the second law of thermodynamics equation [3.3]. Since all the phases of the mixture have an identical temperature, there is no need to use the phasic energy equation [2.17]₁.

The *thermodynamic process* (Coleman & Noll 1963; Dobran 1982a) for the multiphase mixture of a single temperature and without the phase change is defined by $\mathbf{x} = \chi_{\alpha\kappa}(\mathbf{X}_\alpha, t)$ and by the following fields which depend on \mathbf{x} and t :

$$\bar{\rho}_\alpha, \mathbf{T}_\alpha, \tilde{\mathbf{b}}_\alpha, \hat{\mathbf{p}}_\alpha, \hat{\mathbf{M}}_\alpha, \tilde{e}_\alpha, r, \bar{\mathbf{q}}_\alpha, \tilde{s}_\alpha, \hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m, \theta \text{ and } \hat{R}_\alpha \quad [3.8]$$

for $\alpha = 1, \dots, \gamma$. Furthermore, to define such a thermodynamic process, it is *sufficient* to assign the constitutive equations for

$$\mathbf{T}_\alpha, \hat{\mathbf{p}}_\alpha, \hat{\mathbf{M}}_\alpha, \tilde{e}_\alpha, \bar{\mathbf{q}}_\alpha, \hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m, \tilde{s}_\alpha \text{ and } \hat{R}_\alpha \quad [3.9]$$

for $\alpha = 1, \dots, \gamma$, at \mathbf{X}_α by the *history* of the fields $\mathbf{x} = \chi_{\beta\kappa}(\mathbf{X}_\beta, t)$ and $\theta(\mathbf{x}, t)$. The remaining

fields $\bar{\rho}_\alpha$, $\bar{\mathbf{b}}_\alpha$ and r in the list [3.8] are determined from the conservation laws [3.7], [2.14]₁ and [2.17]₂, respectively. The entropy inequality [3.3] is utilized to place a restriction on the constitutive assumption.

Notice that $\hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m$ in [2.17]₂ is only restricted by the compatibility condition [3.6], and if $\hat{s}_m = 0$, then $\hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m = \sum_\alpha \hat{R}_\alpha$ and there is no need to specify the constitutive equation for it.

Using [3.2]₁, [3.2]₃ and [3.4]₁, we can replace the constitutive equations [3.9] by the following equivalent set:

$$\Psi_\alpha, \tilde{s}_\alpha, \hat{\mathbf{T}}_\alpha, \hat{\mathbf{M}}_\alpha, \hat{\mathbf{p}}_\alpha, \hat{\mathbf{h}}_\alpha, \hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m \text{ and } \hat{R}_\alpha. \tag{3.10}$$

Note that although $\hat{\mathbf{T}}_\alpha^T$ can be calculated from $\hat{\mathbf{T}}_\alpha$, the reason for including $\hat{\mathbf{M}}_\alpha$ (or $\hat{\mathbf{T}}_\alpha^T$) in the above list of constitutive equations is that the entropy equation [3.3] contains this variable (after eliminating $\hat{\mathbf{K}}_\alpha$ by [3.2]₃ and [2.16]₁) and, therefore, it places a restriction on its possible form.

3.2 The constitutive assumption

The constitutive assumption relates the thermodynamical state of the body \mathcal{B}_α to its thermokinetic state defined by $\chi_{\beta\kappa}(\mathbf{X}_\beta, t)$ and $\theta(\mathbf{x}, t)$, $\beta = 1, \dots, \gamma$, at the present time as well as with the past history of the body.

The constitutive equations for multiphase mixtures are expected to be of greater complexity than the constitutive equations for the mixture with a negligible interfacial area due to the microstructural characteristics of the mixture. The finite interfacial area also introduces non-local material response into the theory, and the size of the averaging volume should, therefore, be accounted for within the constitutive assumption through this non-local representation. It is through such a mechanism that it should be possible to construct constitutive equations for different classes of mixtures. Clearly, this is an ambitious task which is well worth pursuing.

In the present paper, the multiphase mixture is assumed to be represented by the constitutive assumption of the following form:

$$(\Psi_\alpha, \tilde{s}_\alpha, \hat{\mathbf{T}}_\alpha, \hat{\mathbf{M}}_\alpha, \hat{\mathbf{p}}_\alpha, \hat{\mathbf{h}}_\alpha, \hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m, \hat{R}_\alpha) = f(\theta, \nabla\theta, \mathbf{F}_\beta, \hat{\mathbf{F}}_\beta, \text{GRAD } \mathbf{F}_\beta, \tilde{\mathbf{v}}_\beta, \hat{\tilde{\mathbf{v}}}_\beta). \tag{3.11}$$

In the notation of [3.11] each constitutive variable of the phase α , $\alpha = 1, \dots, \gamma$, depends on all other variables in the functional expression f . For example,

$$\Psi_\alpha = \Psi_\alpha(\theta, \nabla\theta, \mathbf{F}_1, \dots, \mathbf{F}_\gamma, \hat{\mathbf{F}}_1, \dots, \hat{\mathbf{F}}_\gamma, \text{GRAD } \mathbf{F}_1, \dots, \text{GRAD } \mathbf{F}_\gamma, \tilde{\mathbf{v}}_1, \dots, \tilde{\mathbf{v}}_\gamma, \hat{\tilde{\mathbf{v}}}_1, \dots, \hat{\tilde{\mathbf{v}}}_\gamma), \quad \alpha = 1, \dots, \gamma. \tag{3.12}$$

The constitutive assumption [3.11] allows for heat conduction, $\nabla\theta$; for viscous effects, $\hat{\mathbf{F}}_\beta$; for density gradients, $\text{GRAD } \mathbf{F}_\beta$; for viscous drag, $\tilde{\mathbf{v}}_\beta$; and for the virtual mass effects, $\hat{\tilde{\mathbf{v}}}_\beta$. It excludes the propagation of thermal waves (the absence of $\hat{\theta}$), memory effects, and nonlocal material response. The included independent variables in the constitutive assumption are expected to yield constitutive equations of wide range of applicability. Equation [3.11] also satisfies the following five constitutive principles but not the sixth:

- (1) Causality
- (2) Determinism
- (3) Equipresence
- (4) Material uniformity and homogeneity
- (5) Local action
- (6) Objectivity or material frame indifference

The principle of determinism requires that the past determines the future, and the principle of causality demands that the past history of the body determines all the conditions in the body at the present time. The principle of equipresence requires that there should be *non a priori* reason for discriminating any kinematical variable which enters into the different response functionals f in [3.11]. The material uniformity and homogeneity implies that there is a reference configuration for each body such that the response functionals are the same for all particles X_α of the body \mathcal{B}_α . The principle of local action states that the response of a particle X_α is determined if the conditions are known in a small neighborhood of X_α . In multiphase mixtures, the principle of local action is probably only valid for the *dispersed* mixtures. (The validity of the principle of the local action is equivalent to the neglect of the non-local material response.)

A general discussion of the restrictions imposed by the principle of objectivity or the principle of the material frame indifference on the conservation equations of section 2, and on the constitutive assumption [3.11], is presented by Dobran (1982a). Here, I will highlight only the main issues.

For the phase α , the principle of objectivity is stated as follows: Given a deformation function $\chi_{\alpha\kappa}(\mathbf{X}_\alpha, t)$, the change of frame ϕ in E^3 to a frame ϕ^* in E^3 is expressed by the following equation:†

$$\chi_{\alpha\kappa}^*(\mathbf{X}_\alpha, t) = \mathbf{c}(t) + \mathbf{Q}(t)\chi_{\alpha\kappa}(\mathbf{X}_\alpha, t), \quad [3.13]$$

where $\mathbf{c}(t)$ is an arbitrary time-dependent translation vector, and $\mathbf{Q}(t)$ is a time-dependent orthogonal linear transformation which represents the rigid body rotation, i.e.

$$\mathbf{Q}(t)\mathbf{Q}(t)^T = \mathbf{I}. \quad [3.14]$$

Under the change of frame [3.13], the defining properties of objective scalars, vectors and second order tensors are as follows:

$$\begin{aligned} f^*(\mathbf{x}^*, t) &= f(\mathbf{x}, t) \\ \mathbf{y}^*(\mathbf{x}^*, t) &= \mathbf{Q}(t)\mathbf{y}(\mathbf{x}, t) \\ \mathbf{M}^*(\mathbf{x}^*, t) &= \mathbf{Q}(t)\mathbf{M}(\mathbf{x}, t)\mathbf{Q}(t)^T. \end{aligned} \quad [3.15]$$

Using [3.13]–[3.15] in [3.11], Dobran (1982a) showed that the material frame indifferent form of the constitutive assumption is as follows:

$$\begin{aligned} &\left(\Psi_\alpha, \tilde{s}_\alpha, \mathbf{T}_\alpha, \hat{\mathbf{M}}_\alpha, \hat{\mathbf{p}}_\alpha, \hat{\mathbf{h}}_\alpha, \hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m - \frac{1}{2} \text{tr}(\hat{\mathbf{M}}_m \mathbf{W}_\gamma), \hat{R}_\alpha - \frac{1}{2} \text{tr}(\hat{\mathbf{M}}_\alpha \mathbf{W}_\gamma) \right) \\ &= f^\circ(\theta, \nabla\theta, \mathbf{F}_\beta, \mathbf{D}_\beta, \mathbf{W}_\beta - \mathbf{W}_\gamma, \text{GRAD } \mathbf{F}_\beta, \tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma, \dot{\tilde{\mathbf{v}}}_\beta - \dot{\tilde{\mathbf{v}}}_\gamma - 2\mathbf{W}_\gamma(\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma)), \end{aligned} \quad [3.16]$$

and thus satisfies all six constitutive principles enumerated above. In [3.16], \mathbf{D}_β is the symmetric and \mathbf{W}_β is the antisymmetric part of the velocity gradient, i.e.

$$\begin{aligned} \mathbf{L}_\beta &= \mathbf{D}_\beta + \mathbf{W}_\beta \\ \mathbf{D}_\beta &= \frac{1}{2}(\mathbf{L}_\beta + \mathbf{L}_\beta^T) \\ \mathbf{W}_\beta &= \frac{1}{2}(\mathbf{L}_\beta - \mathbf{L}_\beta^T). \end{aligned} \quad [3.17]$$

†Without the loss of generality the origin of time in the frames ϕ and ϕ^* is here taken to be the same.

3.3 Restrictions imposed on the constitutive assumption by the second law of thermodynamics, and the equilibrium state for the mixture

The restrictions imposed by the second law of thermodynamics [3.3] on the constitutive assumption [3.16] is obtained by substituting into [3.3] the material derivative of Ψ_α from [3.12]. Using the identities [2.9] and [2.10], we have from [3.12] that

$$\begin{aligned}
 \dot{\Psi}_\alpha &= \frac{\partial \Psi_\alpha}{\partial \theta} (\dot{\theta} + \nabla \theta \cdot \mathbf{u}_\alpha) + \frac{\partial \Psi_\alpha}{\partial \nabla \theta} \cdot [(\nabla \theta) + (\nabla(\nabla \theta))\mathbf{u}_\alpha] \\
 &+ \sum_\beta \left[\text{tr} \left\{ \left(\frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\beta} \right)^T [\dot{\mathbf{F}}_\beta + \mathbf{G}_\beta \mathbf{F}_\beta^{-1} \cdot (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta)] \right\} \right. \\
 &+ \text{tr} \left\{ \left(\frac{\partial \Psi_\alpha}{\partial \dot{\mathbf{F}}_\beta} \right)^T [\dot{\tilde{\mathbf{F}}}_\beta + \dot{\mathbf{G}}_\beta \mathbf{F}_\beta^{-1} \cdot (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta)] \right\} \\
 &+ C \left\{ \left(\frac{\partial \Psi_\alpha}{\partial \mathbf{G}_\beta} \right) \otimes [\dot{\mathbf{G}}_\beta + (\text{GRAD } \mathbf{G}_\beta) \mathbf{F}_\beta^{-1} \cdot (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta)] \right\} \\
 &\left. + \left(\frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} \right) \cdot [\dot{\tilde{\mathbf{v}}}_\beta + \dot{\mathbf{F}}_\beta \mathbf{F}_\beta^{-1} \cdot (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta)] + \left(\frac{\partial \Psi_\alpha}{\partial \tilde{\dot{\mathbf{v}}}_\beta} \right) \cdot [\dot{\tilde{\dot{\mathbf{v}}}}_\beta + \dot{\tilde{\mathbf{F}}}_\beta \mathbf{F}_\beta^{-1} \cdot (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta)] \right], \tag{3.18}
 \end{aligned}$$

where

$$\mathbf{G}_\beta \equiv \text{GRAD } \mathbf{F}_\beta,$$

and

$$C\{\mathbf{A} \otimes \mathbf{B}\} \equiv A_{ij} B_{ij}$$

denotes the contraction of a fourth order tensor. Substituting [3.18] into [3.3] and rearranging, the second law of thermodynamics for phase α becomes

$$\begin{aligned}
 & - \left(\frac{\partial \Psi_\alpha}{\partial \theta} + \bar{\rho}_\alpha \tilde{s}_\alpha \right) \dot{\theta} - \left(\frac{\partial \Psi_\alpha}{\partial \nabla \theta} \right) \cdot (\nabla \theta) - \sum_\beta \left(\frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} \right) \cdot \tilde{\dot{\mathbf{v}}}_\beta - \sum_\beta \left(\frac{\partial \Psi_\alpha}{\partial \tilde{\dot{\mathbf{v}}}_\beta} \right) \cdot \tilde{\dot{\dot{\mathbf{v}}}}_\beta - \frac{\nabla \theta}{\theta} \cdot \left(\mathbf{h}_\alpha + \theta \frac{\partial \Psi_\alpha}{\partial \theta} \mathbf{u}_\alpha \right) \\
 & - \text{tr} \left\{ \bar{\rho}_\alpha \mathbf{F}_\alpha^{-1} \dot{\mathbf{K}}_\alpha \dot{\mathbf{F}}_\alpha \right\} - \sum_\beta \text{tr} \left\{ \mathbf{F}_\beta^{-1} \left[\mathbf{F}_\beta \left(\frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\beta} \right)^T \right. \right. \\
 & \left. \left. + (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \otimes \frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} \right] \dot{\mathbf{F}}_\beta \right\} - \sum_\beta C \left(\frac{\partial \Psi_\alpha}{\partial \mathbf{G}_\beta} \otimes \dot{\mathbf{G}}_\beta \right) \\
 & - \frac{\partial \Psi_\alpha}{\partial \nabla \theta} \cdot [(\nabla(\nabla \theta))\mathbf{u}_\alpha] - \mathbf{u}_\alpha \cdot \hat{\mathbf{p}}_\alpha + \hat{R}_\alpha - \sum_\beta \text{tr} \left\{ \mathbf{F}_\beta^{-1} \left[\mathbf{F}_\beta \left(\frac{\partial \Psi_\alpha}{\partial \dot{\mathbf{F}}_\beta} \right)^T + (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \otimes \frac{\partial \Psi_\alpha}{\partial \tilde{\dot{\mathbf{v}}}_\beta} \right] \dot{\tilde{\mathbf{F}}}_\beta \right\} \\
 & - \sum_\beta (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \cdot \left\{ \mathbf{F}_\beta^{-1T} \left(\frac{\partial \Psi_\alpha}{\partial \dot{\mathbf{F}}_\beta} [\dot{\mathbf{G}}_\beta] \right) \right\} - \sum_\beta (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \cdot \left\{ \mathbf{F}_\beta^{-1T} \frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\beta} [\mathbf{G}_\beta] \right\} \\
 & - \sum_\beta (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \cdot \left\{ \mathbf{F}_\beta^{-1T} \left(\frac{\partial \Psi_\alpha}{\partial \mathbf{G}_\beta} [\text{GRAD } \mathbf{G}_\beta] \right) \right\} \geq 0, \tag{3.19}
 \end{aligned}$$

where

$$\frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\beta} [\mathbf{G}_\beta] \equiv \frac{\partial \Psi_\alpha}{\partial F_{\beta k k, l}} F_{\beta k k, l}$$

is the I th component of a vector, and

$$C\left(\frac{\partial \Psi_\alpha}{\partial \mathbf{G}_\beta} \otimes \dot{\mathbf{G}}_\beta\right) \equiv \frac{\partial \Psi_\alpha}{\partial F_{\beta k K, I}} \hat{F}_{\beta k K, I}.$$

The necessary and sufficient conditions for the inequality [3.19] to be satisfied for arbitrary variations of nonindependent variables $\hat{\theta}$, $(\nabla\theta)$, $\tilde{\mathbf{v}}_\beta$, $\nabla(\nabla\theta)$, $\tilde{\mathbf{F}}_\beta$, $\dot{\mathbf{G}}_\beta$ and GRAD \mathbf{G}_β are:

$$\begin{aligned} \frac{\partial \Psi_\alpha}{\partial \theta} + \tilde{\rho}_\alpha \tilde{s}_\alpha &= 0, & \frac{\partial \Psi_\alpha}{\partial \nabla\theta} &= \mathbf{0} \\ \frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} &= \mathbf{0}, & \frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{F}}_\beta} &= \mathbf{O}, & \frac{\partial \Psi_\alpha}{\partial \mathbf{G}_\beta} &= \mathbf{O}, \end{aligned} \tag{3.20}$$

and thus

$$\Psi_\alpha = \Psi_\alpha(\theta, \mathbf{F}_\beta, \tilde{\mathbf{v}}_\beta). \tag{3.21}$$

The conditions [3.20] reduce the second law of thermodynamics [3.19] to the following form:

$$\begin{aligned} & - \sum_\beta \frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} \cdot \tilde{\mathbf{v}}_\beta - \frac{\nabla\theta}{\theta} \cdot \left(\tilde{\mathbf{h}}_\alpha + \theta \frac{\partial \Psi_\alpha}{\partial \theta} \mathbf{u}_\alpha \right) - tr \{ \tilde{\rho}_\alpha \mathbf{F}_\alpha^{-1} \tilde{\mathbf{K}}_\alpha \dot{\mathbf{F}}_\alpha \} - \mathbf{u}_\alpha \cdot \hat{\mathbf{p}}_\alpha + \hat{R}_\alpha \\ & - \sum_\beta tr \left\{ \mathbf{F}_\beta^{-1} \left[\mathbf{F}_\beta \left(\frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\beta} \right)^T + (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \otimes \frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} \right] \dot{\mathbf{F}}_\beta \right\} - \sum_\beta (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \cdot \left\{ \mathbf{F}_\beta^{-1T} \frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\beta} [\mathbf{G}_\beta] \right\} \\ & = \phi_\alpha(\theta, \nabla\theta, \mathbf{F}_\beta, \dot{\mathbf{F}}_\beta, \mathbf{G}_\beta, \tilde{\mathbf{v}}_\beta, \dot{\tilde{\mathbf{v}}}_\beta) \geq 0. \end{aligned} \tag{3.22}$$

Again, no confusion should arise in the notation of [3.22] for ϕ_α which is similar to the notation of Ψ_α in [3.12].

The Helmholtz potential Ψ_α in [3.21] has interesting properties when the constitutive assumption [3.11] is relaxed as it is shown below.

Case	Constitutive assumption	Ψ_α (from [3.20] and [3.22])
A	[3.11]	$\Psi_\alpha(\theta, \mathbf{F}_\beta, \tilde{\mathbf{v}}_\beta)$
B	[3.11] with $\dot{\mathbf{F}}_\beta = \mathbf{O}$, $\tilde{\mathbf{v}}_\beta = \mathbf{0}$, $\tilde{\mathbf{v}}_\beta = \mathbf{v}$	$\Psi_\alpha(\theta, \mathbf{F}_\alpha, \mathbf{v})$
C	[3.11] with $\mathbf{G}_\beta = \mathbf{O}$, $\tilde{\mathbf{v}}_\beta = \mathbf{0}$, $\tilde{\mathbf{v}}_\beta = \mathbf{v}$	$\Psi_\alpha(\theta, \mathbf{F}_\alpha, \mathbf{v})$
D	[3.11] with $\dot{\mathbf{F}}_\beta = \mathbf{O}$, $\mathbf{G}_\beta = \mathbf{O}$, $\tilde{\mathbf{v}}_\beta = \mathbf{0}$, $\tilde{\mathbf{v}}_\beta = \mathbf{v}$	$\Psi_\alpha(\theta, \mathbf{F}_\alpha, \mathbf{v})$

The case B above illustrates that when viscous, acceleration, and relative velocity effects are ignored in the constitutive assumption, then the Helmholtz potential for phase α depends only on the temperature and deformation gradient from the same phase since the dependence of Ψ_α on the velocity \mathbf{v} is not possible as it is shown in [3.16], and there is no need to exclude the dependence on \mathbf{G}_α in order for the phase to be in an equilibrium.

The equilibrium state for the multiphase mixture is defined to be that state for which:

- (1) The entropy inequality [3.22] becomes an equality.
- (2) $\nabla\theta = \mathbf{o}$ (no temperature gradient), $\dot{\mathbf{F}}_\beta = \mathbf{O}$ (no viscous effects), $\tilde{\mathbf{v}}_\beta = \mathbf{v}$ (no diffusion effects), $\tilde{\dot{\mathbf{v}}}_\beta = \mathbf{o}$ (no acceleration effects); $\beta = 1, \dots, \gamma$.

From [3.22] it then follows that

$$\phi_\alpha(\theta, \nabla\theta = \mathbf{o}, \mathbf{F}_\beta, \dot{\mathbf{F}}_\beta = \mathbf{O}, \mathbf{G}_\beta, \tilde{\mathbf{v}}_\beta = \mathbf{v}, \tilde{\dot{\mathbf{v}}}_\beta = \mathbf{o}) \equiv \hat{R}_\alpha^\circ = 0. \quad [3.23]$$

The above definition of the equilibrium state is consistent with the definition in the equilibrium thermodynamics, since in such a state no possibility exists for the temperature gradient, viscous effects, and diffusion effects. A mixture with these properties is by no means an ideal mixture.

To examine the equilibrium state properties of the multiphase mixture in more detail, it is useful to utilize a method which is similar to Bowen (1973). For this purpose let λ be a parameter. Set $\nabla\theta = \lambda \mathbf{a}$, $\dot{\mathbf{F}}_\beta = \lambda \mathbf{A}_\beta$, $\tilde{\mathbf{v}}_\beta = \mathbf{v} + \lambda \mathbf{d}_\beta$, $\tilde{\dot{\mathbf{v}}}_\beta = \lambda \mathbf{t}_\beta$, and substitute into [3.22]. Taking the account of [3.21], the result is as follows:

$$\begin{aligned} & - \sum_\beta \frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta)}{\partial \tilde{\mathbf{v}}_\beta} \cdot \lambda \mathbf{t}_\beta \\ & - \frac{\lambda \mathbf{a}}{\theta} \cdot \left[\hat{\mathbf{h}}_\alpha(\theta, \lambda \mathbf{a}, \mathbf{F}_\beta, \lambda \mathbf{A}_\beta, \mathbf{G}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta, \lambda \mathbf{t}_\beta) + \theta \frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta)}{\partial \theta} \lambda \mathbf{d}_\beta \right] \\ & - \text{tr} \left\{ \bar{\rho}_\alpha \mathbf{F}_\alpha^{-1} \hat{\mathbf{K}}_\alpha(\theta, \lambda \mathbf{a}, \mathbf{F}_\beta, \lambda \mathbf{A}_\beta, \mathbf{G}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta, \lambda \mathbf{t}_\beta) \lambda \mathbf{A}_\alpha \right\} \\ & - \lambda \mathbf{d}_\alpha \cdot \hat{\mathbf{p}}_\alpha(\theta, \lambda \mathbf{a}, \mathbf{F}_\beta, \lambda \mathbf{A}_\beta, \mathbf{G}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta, \lambda \mathbf{t}_\beta) \\ & + \hat{R}_\alpha(\theta, \lambda \mathbf{a}, \mathbf{F}_\beta, \lambda \mathbf{A}_\beta, \mathbf{G}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta, \lambda \mathbf{t}_\beta) \\ & - \sum_\beta \text{tr} \left\{ \mathbf{F}_\beta^{-1} \left[\mathbf{F}_\beta \left(\frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta)}{\partial \mathbf{F}_\beta} \right)^T + \lambda (\mathbf{d}_\alpha - \mathbf{d}_\beta) \otimes \frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta)}{\partial \tilde{\mathbf{v}}_\beta} \right] \lambda \mathbf{A}_\beta \right\} \\ & - \sum_\beta \lambda (\mathbf{d}_\alpha - \mathbf{d}_\beta) \cdot \left\{ \mathbf{F}_\beta^{-1T} \frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta)}{\partial \mathbf{F}_\beta} [\mathbf{G}_\beta] \right\} \\ & = \phi_\alpha(\theta, \lambda \mathbf{a}, \mathbf{F}_\beta, \lambda \mathbf{A}_\beta, \mathbf{G}_\beta, \mathbf{v} + \lambda \mathbf{d}_\beta, \lambda \mathbf{t}_\beta) \geq 0. \end{aligned} \quad [3.24]$$

Since $\phi_\alpha \geq 0$, and $\phi_\alpha = 0$ in the equilibrium state (*cit.* [3.23]), it follows from [3.24] that the stability conditions of the equilibrium state are:

$$\left. \frac{d\phi_\alpha}{d\lambda} \right|_{\lambda=0} = 0, \quad \left. \frac{d^2\phi_\alpha}{d\lambda^2} \right|_{\lambda=0} > 0. \quad [3.25]$$

Carrying out the operation [3.25]₁ in [3.24] and requiring the arbitrariness of \mathbf{a} , \mathbf{A}_β , \mathbf{d}_β and \mathbf{t}_β for $\beta = 1, \dots, \gamma$, we find the following sought-for equilibrium state properties:

$$\begin{aligned} & \frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\beta, \mathbf{v})}{\partial \tilde{\mathbf{v}}_\beta} = \mathbf{o}, \quad \hat{\mathbf{h}}_\alpha(\theta, \mathbf{o}, \mathbf{F}_\beta, \mathbf{O}, \mathbf{G}_\beta, \mathbf{v}, \mathbf{o}) = \mathbf{o} \\ & \frac{d\hat{R}_\alpha(\theta, \mathbf{o}, \mathbf{F}_\beta, \mathbf{O}, \mathbf{G}_\beta, \mathbf{v}, \mathbf{o})}{d\lambda} = \mathbf{o}, \quad \frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\beta, \mathbf{v})}{\partial \mathbf{F}_\beta} = \mathbf{O} \quad \text{for } \alpha \neq \beta, \\ & \bar{\rho}_\alpha \hat{\mathbf{K}}_\alpha(\theta, \mathbf{o}, \mathbf{F}_\beta, \mathbf{O}, \mathbf{G}_\beta, \mathbf{v}, \mathbf{o}) = -\mathbf{F}_\alpha \left(\frac{\partial \Psi_\alpha(\theta, \mathbf{F}_\alpha, \mathbf{v})}{\partial \mathbf{F}_\alpha} \right)^T, \\ & \hat{\mathbf{p}}_\alpha(\theta, \mathbf{o}, \mathbf{F}_\beta, \mathbf{O}, \mathbf{G}_\beta, \mathbf{v}, \mathbf{o}) = \mathbf{o}. \end{aligned} \quad [3.26]$$

Further stability results of the equilibrium state can be obtained by examining the condition [3.25]₂. This, however, will not be pursued in this article. Notice that the results [3.26] are not presented in the frame indifferent form. When this is achieved, no dependence on the velocity \mathbf{v} is possible (*cit.* [3.16]).

The development of the constitutive equations so far is not restricted to either fluids or solids. My objective in the remaining part of this paper is to specialize further development of the constitutive equations to a multiphase mixture of *fluids*.

3.4 Multiphase mixture of fluids

For a mixture of fluids, Cross (1973) demonstrated that a function of $(\mathbf{F}_\beta, \hat{\mathbf{F}}_\beta, \mathbf{G}_\beta)$ can be replaced by the one of $(\bar{\rho}_\beta, \mathbf{L}_\beta, \nabla \bar{\rho}_\beta)$. Mathematically, this replacement has to do with the invariance of the response functionals in the constitutive assumption under a material symmetry transformation. Physically, this means that the response of the fluid to a given deformation history is the same when starting from any two configurations with the same density. This, clearly, can be looked upon as the definition of isotropic fluids, and the constitutive assumption [3.16] under these conditions, is reduced to

$$\begin{aligned} & \left(\Psi_\alpha, \tilde{s}_\alpha, \mathbf{T}_\alpha, \hat{\mathbf{M}}_\alpha, \hat{\mathbf{p}}_\alpha, \hat{\mathbf{h}}_\alpha, \hat{e}_m - \mathbf{v} \cdot \hat{\mathbf{p}}_m - \frac{1}{2} \text{tr}(\hat{\mathbf{M}}_m \mathbf{W}_\gamma), \hat{R}_\alpha - \frac{1}{2} \text{tr}(\hat{\mathbf{M}}_\alpha \mathbf{W}_\gamma) \right) \\ & = f^A(\theta, \nabla \theta, \bar{\rho}_\beta, \mathbf{D}_\beta, \mathbf{W}_\beta - \mathbf{W}_\gamma, \nabla \bar{\rho}_\beta, \tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma, \tilde{\hat{\mathbf{v}}}_\beta - \tilde{\hat{\mathbf{v}}}_\gamma - 2\mathbf{W}_\gamma(\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma)). \end{aligned} \tag{3.27}$$

Utilizing the identity (Truesdell & Toupin 1960)

$$\frac{\partial(\det \mathbf{F}_\alpha)}{\partial \mathbf{F}_\alpha} = (\det \mathbf{F}_\alpha) \mathbf{F}_\alpha^{-1T}, \tag{3.28}$$

and the conservation of mass equation [3.7], we can easily derive the following useful results:

$$\begin{aligned} \frac{\partial}{\partial \mathbf{F}_\alpha} &= -\bar{\rho}_\alpha \mathbf{F}_\alpha^{-1T} \frac{\partial}{\partial \bar{\rho}_\alpha} \\ \frac{\partial \bar{\rho}_\alpha}{\partial x_k} &= -\bar{\rho}_\alpha F_{\alpha l}^{-1} G_{\alpha l k} F_{\alpha k k}, \end{aligned} \tag{3.29}$$

and it, therefore, follows that

$$\mathbf{F}_\beta^{-1T} \frac{\partial \Psi_\alpha}{\partial \mathbf{F}_\beta} [\mathbf{G}_\beta] = \frac{\partial \Psi_\alpha}{\partial \bar{\rho}_\beta} \nabla \bar{\rho}_\beta. \tag{3.30}$$

Equations [3.29], [3.30], [2.6] and [3.17] reduce the second law of thermodynamics [3.22] to the following form:

$$\begin{aligned} & - \sum_\beta \frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} \cdot \tilde{\mathbf{v}}_\beta - \frac{\nabla \theta}{\theta} \cdot \left(\hat{\mathbf{h}}_\alpha + \theta \frac{\partial \Psi_\alpha}{\partial \theta} \mathbf{u}_\alpha \right) - \text{tr} \{ \bar{\rho}_\alpha \hat{\mathbf{K}}_\alpha (\mathbf{D}_\alpha + \mathbf{W}_\alpha) \} - \mathbf{u}_\alpha \cdot \hat{\mathbf{p}}_\alpha + \hat{R}_\alpha \\ & - \sum_\beta \text{tr} \left\{ \left[-\bar{\rho}_\beta \frac{\partial \Psi_\alpha}{\partial \bar{\rho}_\beta} \mathbf{I} + (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \otimes \frac{\partial \Psi_\alpha}{\partial \tilde{\mathbf{v}}_\beta} \right] (\mathbf{D}_\beta + \mathbf{W}_\beta) \right\} - \sum_\beta (\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta) \cdot (\nabla \bar{\rho}_\beta) \frac{\partial \Psi_\alpha}{\partial \bar{\rho}_\beta} = \phi_\alpha \geq 0. \end{aligned} \tag{3.31}$$

We will return to this equation in the next section where the constitutive equations are studied in detail.

The independent variables in the equilibrium state properties [3.23] and [3.26] follow the order in the constitutive assumption [3.11]. When the order of the independent variables in the constitutive assumption [3.27] is utilized instead, these equilibrium state properties become

$$\begin{aligned}
 \bar{\mathbf{h}}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\beta, \mathbf{O}, \mathbf{O}, \nabla \bar{\rho}_\beta, \mathbf{o}, \mathbf{o}) &= \mathbf{o} \\
 \bar{\mathbf{p}}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\beta, \mathbf{O}, \mathbf{O}, \nabla \bar{\rho}_\beta, \mathbf{o}, \mathbf{o}) &= \mathbf{o} \\
 \bar{\mathbf{K}}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\beta, \mathbf{O}, \mathbf{O}, \nabla \bar{\rho}_\beta, \mathbf{o}, \mathbf{o}) &= \frac{\partial \Psi_\alpha(\theta, \bar{\rho}_\alpha)}{\partial \bar{\rho}_\alpha} \mathbf{I} \\
 \bar{\mathbf{R}}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\beta, \mathbf{O}, \mathbf{O}, \nabla \bar{\rho}_\beta, \mathbf{o}, \mathbf{o}) &= \mathbf{o}.
 \end{aligned} \tag{3.32}$$

The variable $\bar{\mathbf{R}}_\alpha$ defined by [3.4]₂ has interesting properties. From [3.6], [3.26]₃, [3.31] and [3.32]₄ it follows that it is a positive semidefinite function and vanishes in the equilibrium state.

The chemical or Gibbs' potential $\bar{\mu}_\alpha$ in the present theory is defined from [3.32]₃, i.e.

$$\bar{\mu}_\alpha \mathbf{I} \equiv \bar{\mathbf{K}}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\beta, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) \tag{3.33}$$

where it was used the fact that $\bar{\mathbf{K}}_\alpha$ in equilibrium is independent of $\nabla \bar{\rho}_\beta$ (*cit.* [3.32]₃). Combining [3.33] with [3.2] results in the following equation:

$$\bar{\rho}_\alpha \bar{\mu}_\alpha = \bar{\rho}_\alpha \bar{\psi}_\alpha(\theta, \bar{\rho}_\alpha) + \bar{\pi}_\alpha, \tag{3.34}$$

where the (partial) pressure of phase α is defined as follows:

$$\bar{\pi}_\alpha \mathbf{I} \equiv -\bar{\mathbf{T}}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\beta, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}). \tag{3.35}$$

Combining [3.2]₃, [3.32]₃, [3.33] and [3.34] yields:

$$\bar{\pi}_\alpha = \bar{\rho}_\alpha^2 \frac{\partial \bar{\psi}_\alpha(\theta, \bar{\rho}_\alpha)}{\partial \bar{\rho}_\alpha}, \tag{3.36}$$

and using this equation and equation [3.20]₁, the differential of Helmholtz potential $\bar{\psi}_\alpha(\theta, \bar{\rho}_\alpha)$ becomes

$$d\bar{\psi}_\alpha(\theta, \bar{\rho}_\alpha) = -\bar{s}_\alpha d\theta + \frac{\bar{\pi}_\alpha}{\bar{\rho}_\alpha^2} d\bar{\rho}_\alpha. \tag{3.37}$$

Considering also the differential of [3.2]₁ and utilizing [3.37] we obtain

$$d\bar{\epsilon}_\alpha(\bar{s}_\alpha, \bar{\rho}_\alpha) = \theta d\bar{s}_\alpha + \frac{\bar{\pi}_\alpha}{\bar{\rho}_\alpha^2} d\bar{\rho}_\alpha. \tag{3.38}$$

Similarly, from [3.34] and [3.37] the differential of Gibbs potential $\bar{\mu}_\alpha$ is

$$d\bar{\mu}_\alpha(\theta, \bar{\pi}_\alpha) = -\bar{s}_\alpha d\theta + \frac{1}{\bar{\rho}_\alpha} d\bar{\pi}_\alpha. \tag{3.39}$$

In the equilibrium state, the momentum equation of phase α [2.14]₁ is reduced to

$$-\nabla \bar{\pi}_\alpha + \bar{\rho}_\alpha \tilde{\mathbf{b}}_\alpha = \mathbf{0}, \quad [3.40]$$

where [3.32]₂ was used. The pressure gradient can be eliminated in this equation by utilizing [3.34], [3.2]₁, [3.38] and by noting that $\nabla \theta = \mathbf{0}$ in the equilibrium state, i.e.

$$-\nabla \tilde{\mu}_\alpha + \tilde{\mathbf{b}}_\alpha = \mathbf{0}. \quad [3.41]$$

This result shows that the chemical potential is not a constant in the presence of body forces, and that

$$\tilde{\mu}_1 = \dots = \tilde{\mu}_\gamma = \text{const.} \quad [3.42]$$

if and only if there are no body forces acting on the multiphase mixture.

4. LINEARIZED CONSTITUTIVE EQUATIONS

In this section, a linearized analysis of the constitutive equations for multiphase mixtures is presented. Even though the linearized equations have a restricted validity, their form is already sufficiently complex (see below), and in many instances of the practical interest, the computational restrictions dictate their linearity and simplicity. The form of the constitutive equations is not arbitrary since they must satisfy the second law of thermodynamics [3.22]. The linearized constitutive equations are presented for (1) a multiphase mixture of an arbitrary number of phases, (2) for a multiphase mixture of highly dispersed fluids, and (3) the coefficients which multiply the independent variables in these equations are studied for a mixture of two phases.

4.1 Linearized analysis

Linearization will be carried out about an equilibrium state with the properties $\nabla \theta = \mathbf{0}$, $\mathbf{D}_\beta = \mathbf{0}$, $\mathbf{W}_\beta = \mathbf{0}$, $\nabla \bar{\rho}_\beta = \mathbf{0}$, $\tilde{\mathbf{v}}_\beta = \mathbf{v}$ and $\hat{\tilde{\mathbf{v}}}_\beta = \mathbf{0}$. It is noticed that this equilibrium state is more restrictive than the equilibrium state of section 3.3 in that it also assumes that $\nabla \bar{\rho}_\beta = \mathbf{0}$. This state will be called the *reduced equilibrium state*.

In the linearized analysis all second and higher order terms of the independent variables in the constitutive assumption [3.27] are neglected. A measure which relates the deviation from the reduced equilibrium state can be defined through a quantity which is defined as follows:

$$\begin{aligned} \epsilon^2 \equiv & c_1 \nabla \theta \cdot \nabla \theta + \sum_{\beta}^{\gamma} c_{2\beta} \text{tr}(\mathbf{D}_\beta \mathbf{D}_\beta) + \sum_{\beta}^{\gamma-1} c_{3\beta} \text{tr}[(\mathbf{W}_\beta - \mathbf{W}_\gamma)(\mathbf{W}_\beta - \mathbf{W}_\gamma)] \\ & + \sum_{\beta}^{\gamma} c_{4\beta} \nabla \bar{\rho}_\beta \cdot \nabla \bar{\rho}_\beta + \sum_{\beta}^{\gamma-1} c_{5\beta} (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) \cdot (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) + \sum_{\beta}^{\gamma-1} c_{6\beta} (\hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma) \cdot (\hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma). \end{aligned} \quad [4.1]$$

When $\epsilon = 0$, [4.1] implies that $\nabla \theta = \mathbf{0}$, $\nabla \bar{\rho}_\beta = \mathbf{0}$, $\tilde{\mathbf{v}}_\beta = \mathbf{v}$, $\hat{\tilde{\mathbf{v}}}_\beta = \mathbf{0}$, $\mathbf{D}_\beta = \mathbf{0}$, and $\mathbf{W}_\beta = \mathbf{0}$ for $\beta = 1, \dots, \gamma$. Given an integer n , let the function of $(\nabla \theta, \mathbf{D}_\beta, \mathbf{W}_\beta - \mathbf{W}_\gamma, \nabla \bar{\rho}_\beta, \tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma, \hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma)$ be denoted by $O(\epsilon^n)$ with the property that $\|O(\epsilon^n)\| < M\epsilon^n$ as $\epsilon \rightarrow 0$, where $\|\dots\|$ is the Euclidean norm, M is a positive constant, and $\epsilon < 1$. $\epsilon < 1$ implies that temperature gradients, viscous effects, density gradients, diffusion of species, and acceleration effects are small. The coefficients $c_1, c_{2\beta}, c_{3\beta}, c_{4\beta}, c_{5\beta}$ and $c_{6\beta}$ in [4.1] are suitable reference variables which allow ϵ to be expressed in a nondimensional form.

To obtain the constitutive equations, the variables on the left side of [3.27] are

expanded in a Taylor series about the reduced equilibrium state in terms of the independent constitutive variables on the right side of [3.27]. Considering first the heat flux vector field \mathbf{h}_α , we have:

$$\begin{aligned}
& \mathbf{h}_\alpha(\theta, \nabla\theta, \bar{\rho}_\sigma, \mathbf{D}_\sigma, \mathbf{W}_\sigma - \mathbf{W}_\gamma, \nabla\bar{\rho}_\sigma, \tilde{\mathbf{v}}_\sigma - \tilde{\mathbf{v}}_\gamma, \hat{\tilde{\mathbf{v}}}_\sigma - \hat{\tilde{\mathbf{v}}}_\gamma - 2\mathbf{W}_\gamma(\tilde{\mathbf{v}}_\sigma - \tilde{\mathbf{v}}_\gamma)) \\
&= \mathbf{h}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) + \frac{\partial \mathbf{h}_\alpha}{\partial \nabla\theta}(\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o})\nabla\theta \\
&+ \sum_{\beta}^{\gamma} \left(\frac{\partial \mathbf{h}_\alpha}{\partial \mathbf{D}_\beta} \right) (\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) \mathbf{D}_\beta \\
&+ \sum_{\beta}^{\gamma-1} \frac{\partial \mathbf{h}_\alpha}{\partial (\mathbf{W}_\beta - \mathbf{W}_\gamma)} (\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) (\mathbf{W}_\beta - \mathbf{W}_\gamma) \\
&+ \sum_{\beta}^{\gamma} \left(\frac{\partial \mathbf{h}_\alpha}{\partial \nabla\bar{\rho}_\beta} \right) (\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) \nabla\bar{\rho}_\beta + \sum_{\beta}^{\gamma-1} \left(\frac{\partial \mathbf{h}_\alpha}{\partial (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma)} \right) (\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) \\
&+ \sum_{\beta}^{\gamma-1} \left(\frac{\partial \mathbf{h}_\alpha}{\partial (\hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma - 2\mathbf{W}_\gamma(\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma))} \right) (\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) (\hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma) + \mathbf{o}(\epsilon^2) \quad [4.2]
\end{aligned}$$

Note that (1) the first and fifth terms on the right side of [4.2] are equal to \mathbf{o} because of [3.32]₁, and (2) the function f^d in [3.27] is *isotropic*. Since odd order isotropic tensors change signs in an improper orthogonal transformation (Spencer 1971), all odd order tensors in [4.2] must vanish, i.e. $\partial \mathbf{h}_\alpha / \partial \mathbf{D}_\beta = \mathbf{O}$, $\partial \mathbf{h}_\alpha / \partial (\mathbf{W}_\beta - \mathbf{W}_\gamma) = \mathbf{O}$, and the even order isotropic tensors must have the following representation:

$$\begin{aligned}
& (\partial \mathbf{h}_\alpha / \partial \nabla\theta)(\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) = -\kappa_\alpha(\theta, \bar{\rho}_\sigma) \mathbf{I} \\
& (\partial \mathbf{h}_\alpha / \partial (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma))(\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) = -\zeta_{\alpha\beta}(\theta, \bar{\rho}_\sigma) \mathbf{I} \quad [4.3] \\
& (\partial \mathbf{h}_\alpha / \partial (\hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma - 2\mathbf{W}_\gamma(\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma)))(\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) = -\nu_{\alpha\beta}(\theta, \bar{\rho}_\sigma) \mathbf{I}.
\end{aligned}$$

Taking account of the above conditions, [4.2] is reduced to

$$\mathbf{h}_\alpha = -\kappa_\alpha(\theta, \bar{\rho}_\sigma) \nabla\theta - \sum_{\beta}^{\gamma-1} \zeta_{\alpha\beta}(\theta, \bar{\rho}_\sigma) (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) - \sum_{\beta}^{\gamma-1} \nu_{\alpha\beta}(\theta, \bar{\rho}_\sigma) (\hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma) + \mathbf{o}(\epsilon^2), \quad [4.4]$$

where it is understood that $\kappa_\alpha(\theta, \bar{\rho}_\sigma) = \kappa_\alpha(\theta, \bar{\rho}_1, \dots, \bar{\rho}_\gamma)$, and similarly for $\zeta_{\alpha\beta}$, $\nu_{\alpha\beta}$, and for all other coefficients in the constitutive equations below.

A similar analysis which gives [4.4] also gives the momentum supply for phase α

$$\hat{\mathbf{p}}_\alpha = -\gamma_\alpha(\theta, \bar{\rho}_\sigma) \nabla\theta - \sum_{\beta}^{\gamma-1} \xi_{\alpha\beta}(\theta, \bar{\rho}_\sigma) (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) - \sum_{\beta}^{\gamma-1} \Delta_{\alpha\beta}(\theta, \bar{\rho}_\sigma) (\hat{\tilde{\mathbf{v}}}_\beta - \hat{\tilde{\mathbf{v}}}_\gamma) + \mathbf{o}(\epsilon^2), \quad [4.5]$$

where [3.32]₂ was used.

The chemical potential tensor $\tilde{\mathbf{K}}_\alpha$ appears in the entropy inequality [3.31] and it is, therefore, natural to obtain a constitutive equation for it and replace the stress tensor $\tilde{\mathbf{T}}_\alpha$ and the Helmholtz potential Ψ_α in [3.27] by a new set $\bar{\rho}_\alpha \tilde{\mathbf{K}}_\alpha$ and Ψ_α . The new set of variables is equivalent to the original set as can be seen from [3.2]₂. Expanding $\bar{\rho}_\alpha \tilde{\mathbf{K}}_\alpha$ in series and using the fact that it is a second order isotropic tensor, its representation is as follows:

$$\begin{aligned}
\bar{\rho}_\alpha \tilde{\mathbf{K}}_\alpha &= \bar{\rho}_\alpha \tilde{\mathbf{K}}_\alpha(\theta, \mathbf{o}, \bar{\rho}_\sigma, \mathbf{O}, \mathbf{O}, \mathbf{o}, \mathbf{o}, \mathbf{o}) - \sum_{\beta}^{\gamma} [\lambda_{\alpha\beta}(\theta, \bar{\rho}_\sigma) (tr \mathbf{D}_\beta) \mathbf{I} + 2\mu_{\alpha\beta}(\theta, \bar{\rho}_\sigma) \mathbf{D}_\beta] \\
&+ 2 \sum_{\beta}^{\gamma-1} \varphi_{\alpha\beta}(\theta, \bar{\rho}_\sigma) (\mathbf{W}_\beta - \mathbf{W}_\gamma) + \mathbf{O}(\epsilon^2). \quad [4.6]
\end{aligned}$$

Using [2.16]₁, [3.2]₂ and [4.6], the angular momentum supply for phase α becomes

$$\hat{\mathbf{M}}_\alpha = \mathbf{T}_\alpha - \mathbf{T}_\alpha^T = \bar{\rho}_\alpha \bar{\mathbf{K}}_\alpha - \bar{\rho}_\alpha \bar{\mathbf{K}}_\alpha^T = 4 \sum_{\beta}^{\gamma-1} \varphi_{\alpha\beta}(\theta, \bar{\rho}_\sigma)(\mathbf{W}_\beta - \mathbf{W}_\gamma) + \mathbf{O}(\epsilon^2). \quad [4.7]$$

The representation of Ψ_α and $\hat{\mathbf{R}}_\alpha$ is needed within an order of ϵ^2 . This is clear from [3.31] if the left side of this inequality is to have a representation within an $\mathbf{O}(\epsilon^3)$. Taking into account that (1) $\Psi_\alpha = \Psi_\alpha(\theta, \bar{\rho}_\beta, \tilde{\mathbf{v}}_\beta, -\tilde{\mathbf{v}}_\gamma)$ in a frame indifferent form, (2) $\Psi_\alpha = \Psi_\alpha(\theta, \bar{\rho}_\alpha)$ in the reduced equilibrium state, and (3) the fact that Ψ_α has an isotropic tensor representation, we have

$$\Psi_\alpha = \Psi_\alpha(\theta, \bar{\rho}_\alpha) + \sum_{\beta \leq \delta, \delta}^{\gamma-1} \eta_{\beta\delta}^\alpha(\theta, \bar{\rho}_\sigma)(\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) \cdot (\tilde{\mathbf{v}}_\delta - \tilde{\mathbf{v}}_\gamma) + \mathbf{O}(\epsilon^3). \quad [4.8]$$

and thus

$$\frac{\partial \Psi_\alpha}{\partial \bar{\rho}_\beta} = \mathbf{O}(\epsilon^2) \quad \text{for} \quad \alpha \neq \beta.$$

The representation of the entropy supply $\hat{\mathbf{R}}_\alpha$ in [3.27] in terms of vectors and tensors is as follows (see also Truesdell & Noll (1965) for the representation theorems):

$$\begin{aligned} \hat{\mathbf{R}}_\alpha - \frac{1}{2} \text{tr}(\hat{\mathbf{M}}_\alpha \mathbf{W}_\gamma) &= \sum_{\beta}^{\gamma} \omega_{0,\beta}^\alpha(\text{tr} \mathbf{D}_\beta) + \sum_{\beta \leq \delta, \delta}^{\gamma} \omega_{1,\beta\delta}^\alpha(\text{tr} \mathbf{D}_\beta \mathbf{D}_\delta) + \sum_{\beta \leq \delta, \delta}^{\gamma} \omega_{2,\beta\delta}^\alpha(\text{tr} \mathbf{D}_\beta)(\text{tr} \mathbf{D}_\delta) \\ &+ \sum_{\beta \leq \delta, \delta}^{\gamma-1} \omega_{3,\beta\delta}^\alpha \text{tr}[(\mathbf{W}_\beta - \mathbf{W}_\gamma)(\mathbf{W}_\delta - \mathbf{W}_\gamma)] \\ &+ \omega_0^\alpha \nabla \theta \cdot \nabla \theta + \nabla \theta \cdot \sum_{\beta}^{\gamma} \omega_{4,\beta}^\alpha \nabla \bar{\rho}_\beta + \nabla \theta \cdot \sum_{\beta}^{\gamma-1} \omega_{5,\beta}^\alpha (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) \\ &+ \nabla \theta \cdot \sum_{\beta}^{\gamma-1} \omega_{6,\beta}^\alpha (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) + \sum_{\beta \leq \delta, \delta}^{\gamma} \omega_{7,\beta\delta}^\alpha \nabla \bar{\rho}_\beta \cdot \nabla \bar{\rho}_\delta + \sum_{\beta}^{\gamma} \sum_{\delta}^{\gamma-1} \omega_{8,\beta\delta}^\alpha \nabla \bar{\rho}_\beta \cdot (\tilde{\mathbf{v}}_\delta - \tilde{\mathbf{v}}_\gamma) \\ &+ \sum_{\beta}^{\gamma} \sum_{\delta}^{\gamma-1} \omega_{9,\beta\delta}^\alpha \nabla \bar{\rho}_\beta \cdot (\tilde{\mathbf{v}}_\delta - \tilde{\mathbf{v}}_\gamma) + \sum_{\beta \leq \delta, \delta}^{\gamma-1} \omega_{10,\beta\delta}^\alpha (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) \cdot (\tilde{\mathbf{v}}_\delta - \tilde{\mathbf{v}}_\gamma) \\ &+ \sum_{\beta, \delta}^{\gamma-1} \omega_{11,\beta\delta}^\alpha (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) \cdot (\tilde{\mathbf{v}}_\delta - \tilde{\mathbf{v}}_\gamma) + \sum_{\beta \leq \delta, \delta}^{\gamma-1} \omega_{12,\beta\delta}^\alpha (\tilde{\mathbf{v}}_\beta - \tilde{\mathbf{v}}_\gamma) \cdot (\tilde{\mathbf{v}}_\delta - \tilde{\mathbf{v}}_\gamma) + \mathbf{O}(\epsilon^3), \quad [4.9] \end{aligned}$$

where the coefficients ω depend on θ and $\bar{\rho}_\sigma$, $\sigma = 1, \dots, \gamma$.

Before studying the restrictions on the coefficients which appear in [4.4]–[4.9] with the second law of thermodynamics, let us obtain the constitutive equations for stress tensors, entropy, heat flux vectors and energy.

Eliminating the chemical potential tensor between [3.2]₂ and [4.6], and using [3.32]₃, [3.34] and [4.8], the stress tensor for phase α becomes

$$\mathbf{T}_\alpha = -\bar{\pi}_\alpha \mathbf{I} + \sum_{\beta}^{\gamma} [\lambda_{\alpha\beta}(\text{tr} \mathbf{D}_\beta) \mathbf{I} + 2\mu_{\alpha\beta} \mathbf{D}_\beta] + 2 \sum_{\beta}^{\gamma-1} \varphi_{\alpha\beta}(\mathbf{W}_\beta - \mathbf{W}_\gamma) + \mathbf{O}(\epsilon^2), \quad [4.10]$$

and from [2.15]₁, the stress tensor for the multiphase mixture is expressed by the following

equation:

$$\mathbf{T} = -\left(\sum_{\beta}^{\gamma} \bar{\pi}_{\alpha}\right) \mathbf{I} + \sum_{\beta}^{\gamma} \left[\left(\sum_{\alpha}^{\gamma} \lambda_{\alpha\beta}\right) (\text{tr } \mathbf{D}_{\beta}) \mathbf{I} + 2\left(\sum_{\alpha}^{\gamma} \mu_{\alpha\beta}\right) \mathbf{D}_{\beta} \right] + 2 \sum_{\beta}^{\gamma-1} \left(\sum_{\alpha}^{\gamma} \varphi_{\alpha\beta}\right) (\mathbf{W}_{\beta} - \mathbf{W}_{\gamma}) + \mathbf{O}(\epsilon^2) \quad [4.11]$$

From [3.20],

$$\tilde{s}_{\alpha} = -\frac{1}{\bar{\rho}_{\alpha}} \frac{\partial \Psi_{\alpha}(\theta, \bar{\rho}_{\alpha}, \tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma})}{\partial \theta},$$

and utilizing [4.8], the entropy of phase α is

$$\tilde{s}_{\alpha} = -\frac{1}{\bar{\rho}_{\alpha}} \frac{\partial \Psi_{\alpha}(\theta, \bar{\rho}_{\alpha})}{\partial \theta} + O(\epsilon^2). \quad [4.12]$$

Substituting this expression and [4.4] into [3.4], the heat flux vector for phase α is obtained, i.e.

$$\bar{\mathbf{q}}_{\alpha} = -\kappa_{\alpha} \nabla \theta - \sum_{\beta}^{\gamma-1} \zeta_{\alpha\beta} (\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma}) - \sum_{\beta}^{\gamma-1} \nu_{\alpha\beta} (\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma}) - \bar{\rho}_{\alpha} \tilde{s}_{\alpha} \theta \mathbf{u}_{\alpha} + \mathbf{o}(\epsilon^2) \quad [4.13]$$

The internal energy of phase α is obtained by substituting [4.8] and [4.12] into [3.2], i.e.

$$\tilde{\epsilon}_{\alpha} = \tilde{\psi}_{\alpha}(\theta, \bar{\rho}_{\alpha}) - \theta \frac{\partial \Psi_{\alpha}(\theta, \bar{\rho}_{\alpha})}{\partial \theta} + O(\epsilon^2) = \tilde{\epsilon}_{\alpha}(\theta, \bar{\rho}_{\alpha}) + O(\epsilon^2). \quad [4.14]$$

This result is important since it implies that the internal energy of phase α is to a first order approximation equal to the internal energy of the same phase in the equilibrium state. The energy of multiphase mixture is obtained from [4.14] and [2.18]. The result is:

$$\rho \epsilon = \sum_{\alpha}^{\gamma} \bar{\rho}_{\alpha} \tilde{\epsilon}_{\alpha}(\theta, \bar{\rho}_{\alpha}) + o(\epsilon^2). \quad [4.15]$$

The heat flux vector for a mixture follows from [2.18], [4.10], [4.13], [4.14], [3.34] and [3.2], i.e.

$$\mathbf{q} = -\left(\sum_{\alpha}^{\gamma} \kappa_{\alpha}\right) \nabla \theta - \sum_{\beta}^{\gamma-1} \left(\sum_{\alpha}^{\gamma} \zeta_{\alpha\beta}\right) (\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma}) - \sum_{\beta}^{\gamma-1} \left(\sum_{\alpha}^{\gamma} \nu_{\alpha\beta}\right) (\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma}) + \sum_{\alpha}^{\gamma} \bar{\rho}_{\alpha} \tilde{\mu}_{\alpha} \mathbf{u}_{\alpha} + \mathbf{o}(\epsilon^2). \quad [4.16]$$

4.2 Restrictions imposed on the linearized constitutive equations by a mixture of highly dispersed fluids and by the second law of thermodynamics

I will define a *highly dispersed multiphase mixture* by the following two characteristics:

(1) Absence of non-local effects.

(2) The interfacial area is negligible.

It then follows from Dobran (1982a) that the momentum supply for the mixture $\hat{\mathbf{p}}_m = \mathbf{o}$, the angular momentum supply for the mixture $\hat{\mathbf{M}}_m = \mathbf{O}$, the energy supply for the mixture $\hat{\epsilon}_m = o$, and the entropy supply for the mixture $\hat{s}_m = o$. The above definition of a highly dispersed mixture requires, for example, that the number of bubbles in a fluid volume approaches zero or a constant as their size (diameter) approaches zero. This definition, then, corresponds to the void fraction of the dispersed phase approaching zero.

Substituting [4.7] into [2.16]₂ and requiring that $\hat{\mathbf{M}}_m = \mathbf{O}$ we obtain

$$\sum_{\alpha}^{\gamma} \varphi_{\alpha\beta} = 0; \quad \beta = 1, \dots, \gamma - 1. \quad [4.17]$$

Similarly, using [4.5] in [2.15]₃, with $\hat{\mathbf{p}}_m = \mathbf{o}$, and [4.9] in [3.6] with $\hat{\mathbf{R}}_m = 0$, we have:

$$\begin{aligned} \sum_{\alpha}^{\gamma} \gamma_{\alpha} &= \sum_{\alpha}^{\gamma} \xi_{\alpha\beta} = \sum_{\alpha}^{\gamma} \Delta_{\alpha\beta} = 0; \quad \beta = 1, \dots, \gamma - 1 \\ \sum_{\alpha}^{\gamma} \omega_0^{\alpha} &= 0 \\ \sum_{\alpha}^{\gamma} \omega_{\delta, \beta}^{\alpha} &= \sum_{\alpha}^{\gamma} \omega_{4, \beta}^{\alpha} = 0; \quad \beta = 1, \dots, \gamma \\ \sum_{\alpha}^{\gamma} \omega_{8, \beta\delta}^{\alpha} &= \sum_{\alpha}^{\gamma} \omega_{9, \beta\delta} = 0; \quad \beta = 1, \dots, \gamma; \quad \delta = 1, \dots, \gamma - 1 \\ \sum_{\alpha}^{\gamma} \omega_{3, \beta\delta}^{\alpha} &= \sum_{\alpha}^{\gamma} \omega_{10, \beta\delta}^{\alpha} = \sum_{\alpha}^{\gamma} \omega_{12, \beta\delta}^{\alpha} = 0; \quad \beta \leq \delta = 1, \dots, \gamma - 1 \\ \sum_{\alpha}^{\gamma} \omega_{1, \beta\delta}^{\alpha} &= \sum_{\alpha}^{\gamma} \omega_{2, \beta\delta}^{\alpha} = \sum_{\alpha}^{\gamma} \omega_{7, \beta\delta}^{\alpha} = 0; \quad \beta \leq \delta = 1, \dots, \gamma \\ \sum_{\alpha}^{\gamma} \omega_{11, \beta\delta}^{\alpha} &= 0; \quad \beta = 1, \dots, \gamma - 1; \quad \delta = 1, \dots, \gamma - 1 \\ \sum_{\alpha}^{\gamma} \omega_{5, \beta}^{\alpha} &= \sum_{\alpha}^{\gamma} \omega_{6, \beta}^{\alpha} = 0; \quad \beta = 1, \dots, \gamma - 1. \end{aligned} \quad [4.18]$$

For the 2-phase mixture, the coefficients in [4.17] and [4.18] are reduced to the following form:

$$\begin{aligned} \varphi_{11} + \varphi_{21} &= 0, & \gamma_1 + \gamma_2 &= 0, \\ \xi_{11} + \xi_{21} &= 0, & \Delta_{11} + \Delta_{21} &= 0, & \omega_0^1 + \omega_0^2 &= 0, \\ \omega_{11, 11}^1 + \omega_{11, 11}^2 &= 0, & \omega_{0, 1}^1 + \omega_{0, 1}^2 &= 0, & \omega_{0, 2}^1 + \omega_{0, 2}^2 &= 0, \\ \omega_{4, 1}^1 + \omega_{4, 1}^2 &= 0, & \omega_{4, 2}^1 + \omega_{4, 2}^2 &= 0, & \omega_{8, 11}^1 + \omega_{8, 11}^2 &= 0, \\ \omega_{8, 21}^1 + \omega_{8, 21}^2 &= 0, & \omega_{9, 11}^1 + \omega_{9, 11}^2 &= 0, & \omega_{9, 21}^1 + \omega_{9, 21}^2 &= 0, \\ \omega_{3, 11}^1 + \omega_{3, 11}^2 &= 0, & \omega_{10, 11}^1 + \omega_{10, 11}^2 &= 0, & \omega_{12, 11}^1 + \omega_{12, 11}^2 &= 0, \\ \omega_{1, 11}^1 + \omega_{1, 11}^2 &= 0, & \omega_{1, 12}^1 + \omega_{1, 12}^2 &= 0, & \omega_{1, 22}^1 + \omega_{1, 22}^2 &= 0, \\ \omega_{2, 11}^1 + \omega_{2, 11}^2 &= 0, & \omega_{2, 12}^1 + \omega_{2, 12}^2 &= 0, & \omega_{2, 22}^1 + \omega_{2, 22}^2 &= 0, \\ \omega_{7, 11}^1 + \omega_{7, 11}^2 &= 0, & \omega_{7, 12}^1 + \omega_{7, 12}^2 &= 0, & \omega_{7, 22}^1 + \omega_{7, 22}^2 &= 0, \\ \omega_{5, 1}^1 + \omega_{5, 1}^2 &= 0, & \omega_{6, 1}^1 + \omega_{6, 1}^2 &= 0. \end{aligned} \quad [4.19]$$

The 56 coefficients for the 2-phase dispersed mixture are related by the 28 equations in [4.19]. However, not all of the remaining 28 coefficients are independent, since the second law of thermodynamics [3.31] introduces additional restrictions. These restrictions are obtained by substituting the constitutive equations [4.4]–[4.9] into [3.31] and requiring that

this inequality be satisfied for all variations of the independent variables in the constitutive assumption [3.27]. The details of this analysis are presented in appendix A, and the desired *necessary* conditions (which are also *sufficient* if $O(\epsilon^3) = 0$ in [A1]) are expressed by [A4], [A6], [A8], [A10] and [A15]. These conditions and other consequences of the present theory are discussed in the next section.

5. DISCUSSION

Constitutive equations for multiphase mixtures have not been systematically studied in the past. Notable attempts have been those of Ishii (1975), Drew (1976), Drew & Lahey (1979), Drumheller & Bedford (1980) and Passman *et al.* (1983).

Ishii obtained the constitutive equations for stress tensors and heat flux vectors by time averaging of the local constitutive equations of each phase. The time-averaged form of these equations are then expressed in terms of transport coefficients and independent time-averaged kinematical and thermal variables. In this approach, important information is lost, since the principle of equipresence of the constitutive equations is *a priori* compromised. Drew and Drew & Lahey adopted a postulatory approach which is guided by the principle of objectivity in the constitutive assumption and they utilized Cauchy's representation theorem for isotropic tensors to obtain the form of some constitutive equations (for momentum supply and stress tensor). Drew (1976) also proposed that the 2-phase mixture should be governed by the principle of phase separation and by the principle of local dependence on dispersed phase variables. The former principle states that the bulk phase variables ($\bar{\mathbf{h}}_\alpha$, $\bar{\mathbf{T}}_\alpha$, $\bar{\mathbf{q}}_\alpha$, etc.) should depend only on the variables from the same phase, while the interphase variables ($\hat{\mathbf{p}}_\alpha$, $\hat{\epsilon}_\alpha$, etc.) should depend on the variables from all other phases. The principle of local dependence on dispersed phase variables of Drew states that the gradients of dispersed phase variables should be omitted from the constitutive equations. Both of these principles are very restrictive and they might only be correct in some special circumstances. It will be shown below that the principle of phase separation in the present theory is likely to be correct for some constitutive equations close to the equilibrium state.

The variational formulation of Drumheller & Bedford (1980) yields, in addition to the equation of motion of each phase, the balance equations for microstructural properties of the constituents. For two-phase bubbly flows these equations yield the Rayleigh-Plesset equation for the dilatational motion of a bubble (Plesset & Prosperetti 1977). Similar result for the bubble motion was obtained by Passman, Nunziato & Walsh (1983) from their postulated balance equations of microstructural characteristics of the mixture (balance of the equilibrated force). Drumheller & Bedford also studied the equilibrium state constitutive equations for immiscible or multiphase mixtures by: (1) using a variational formulation; (2) using the second law of thermodynamics or balance of the entropy equation for the mixture as a whole with the absence of entropy source term ($\hat{s}_m = 0$ in [2.19]₂); (3) assuming that the principle of phase separation applies to the Helmholtz potential; (4) assuming that the independent variables in the constitutive assumption are both partial and true densities; and (5) that the volume fractions form a constraint condition in the variational formulation ($\sum_\alpha \mathcal{V}_\alpha / \mathcal{V} = 1$). Their equilibrium results for the heat flux vector $\bar{\mathbf{q}}_\alpha$, momentum supply $\hat{\mathbf{p}}_\alpha$, and energy supply $\hat{\epsilon}_\alpha$ agree with the present results [3.32]. However, their result that $\mu_1 = \dots = \mu_l$ is in variance with the equilibrium thermodynamics when the body forces are included in the theory (*cit.* [3.41]). For fluid mixtures, Drumheller & Bedford found that the Helmholtz potential of each phase depends on the true density and temperature of the same phase. While this result is physically appealing, it does rest on the assumptions enumerated above where some of them are open to criticism (Dobran 1982a). An immiscible mixture of two incompressible fluids was also

studied by Sampaio & Williams (1979) using an entropy balance equation for each constituent with the entropy interaction or supply term between the constituents absent (this would correspond to $\hat{s}_\alpha = 0$ in the present theory). Their constitutive assumption for the mixture of two constituents involves $\mathbf{v}_1 - \mathbf{v}_2$, $\nabla \mathbf{v}_1$, $\nabla \mathbf{v}_2$, $\mathcal{V}_1/\mathcal{V}$, θ , $\nabla(\mathcal{V}_1/\mathcal{V})$, and $\nabla\theta$. The results of Sampaio & Williams for the Helmholtz potential give $\psi_\alpha = \psi_\alpha(\theta, \mathcal{V}_\alpha/\mathcal{V})$ which is in close accord with the present result of $\tilde{\psi}_\alpha = \tilde{\psi}_\alpha(\theta, \bar{\rho}_\alpha)$ when the true densities are assumed to be constant (note that $\bar{\rho}_\alpha = \bar{\rho}_\alpha \mathcal{V}_\alpha/\mathcal{V}$, where $\bar{\rho}_\alpha$ is the true density).

Passman *et al.* (1983) utilizing the Goodman & Cowin's (1972) field equations of multiphase mixtures utilized: (1) the entropy balance equation for the mixture as a whole; (2) separate balance equations describing the microstructural characteristics of the mixture; and (3) the principle of phase separation (similar to that of Drew (1976) discussed above) to study the constitutive equations of fluid mixtures. Denoting by \mathcal{S}_α an array of independent variables for the use in the constitutive equations,

$$\mathcal{S}_\alpha = (\bar{\rho}_\alpha, \theta_\alpha, \mathcal{V}_\alpha/\mathcal{V}, \nabla(\mathcal{V}_\alpha/\mathcal{V}), \mathbf{u}_\alpha, (\mathcal{V}_\alpha/\mathcal{V}), \mathbf{D}_\alpha, \nabla\theta_\alpha), \quad \alpha = 1, \dots, \gamma \quad [5.1]$$

and by using the above assumptions and the procedure followed in this paper to obtain restrictions from the entropy balance equation, Passman, Nunziato & Walsh obtained the following results:

$$\begin{aligned} \tilde{\psi}_\alpha &= \tilde{\psi}_\alpha(\bar{\rho}_\alpha, \theta_\alpha, \mathcal{V}_\alpha/\mathcal{V}, \nabla(\mathcal{V}_\alpha/\mathcal{V})) \\ \hat{s}_\alpha &= -\frac{\partial \tilde{\psi}_\alpha}{\partial \theta_\alpha}, \quad \bar{\pi}_\alpha = \bar{\rho}_\alpha^2 \frac{\partial \tilde{\psi}_\alpha}{\partial \bar{\rho}_\alpha}. \end{aligned} \quad [5.2]$$

Clearly, the results for \hat{s}_α and $\bar{\pi}_\alpha$ retain the features of classical thermodynamics. The free energy or Helmholtz potential, $\tilde{\psi}_\alpha$, depends, however, on both the volume fraction $\mathcal{V}_\alpha/\mathcal{V}$ and its gradient in addition to the true density $\bar{\rho}_\alpha$ and temperature θ_α (in classical thermodynamics the free energy would have the form $\tilde{\psi}_\alpha = \tilde{\psi}_\alpha(\theta, \bar{\rho}_\alpha)$). This dependence is to be contrasted with the results of the present analysis as expressed by [3.36] and [3.37] where $\tilde{\psi}_\alpha = \tilde{\psi}_\alpha(\theta, \bar{\rho}_\alpha)$.

The equilibrium state properties of the present theory were presented in section 3.4. Of particular interest in this theory is that the (partial) pressure $\bar{\pi}_\alpha$ and (partial) density $\bar{\rho}_\alpha$ enter into the theory instead of "true" pressure and "true" density. The reason for this is that the conservation and balance equations of section 2 contain these partial variables (notice that true densities do not enter into the governing field equations), and to include into the constitutive assumption [3.11] the variables such as volumetric fractions and "true" densities does not appear reasonable, since the only permissible kinematic variables which can enter into the constitutive assumption are those which are contained in the conservation and balance equations. In the postulated theories of multiphase mixtures discussed above, the volumetric fractions and true densities are included as the independent variables in the constitutive equations because of the presence of additional balance equations expressing the microstructural characteristics of the mixture. The conservation, balance and constitutive equations presented in the paper yield a closed system of equations since the coefficients γ_α , $\xi_{\alpha\beta}$, $\Delta_{\alpha\beta}$, $\varphi_{\alpha\beta}$, $\lambda_{\alpha\beta}$, $\mu_{\alpha\beta}$, κ_α , $\zeta_{\alpha\beta}$ and $\nu_{\alpha\beta}$ for $\alpha, \beta = 1, \dots, \gamma$ depend on θ , $\bar{\rho}_1, \dots, \bar{\rho}_\gamma$. As discussed in more detail by Dobran (1983), the theory constructed in this manner requires also the knowledge of the fundamental equation such as $\tilde{\psi}_\alpha(\theta, \bar{\rho}_\alpha)$ which unfortunately is not known to a significant degree. Since the fundamental equations of Passman *et al.* (1983), and Drumheller & Bedford (1980) as well, are also not known to a significant degree, it is, therefore, not clear at the present time whether the microstructural characteristics of multiphase mixtures should be modeled through the constitutive equations or through the additional balance equations.

The constitutive equation [4.5] for the momentum supply of phase α accounts for three effects. The term $\sum_{\beta}^{\gamma-1} \xi_{\alpha\beta}(\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma})$ accounts for the viscous drag and diffusion of phases, whereas the term $\sum_{\beta}^{\gamma-1} \Delta_{\alpha\beta}(\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma})$ accounts for the virtual mass effect. Although the difference in accelerations $(\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma})$ is not frame indifferent (*cit.* [3.27]), this form is nevertheless correctly represented in [4.5] in the linear approximation. The temperature gradient term in the momentum supply is the *Soret* effect, and it accounts for the diffusion of phases because of the temperature gradient. Its form in [4.5] is similar as in a single phase mixture of different constituents. From [A.15]₂ for a 2-phase mixture, it is sufficient (and also necessary if $\omega_{10,11}^{\alpha} = 0$) that $\xi_{11} \geq 0$ and $\xi_{21} \leq 0$ (compare this result with [5.8] below). The values of γ_2 and $\Delta_{\alpha\beta}$ are restricted by [A15]₆ and [A15]₇. If, however, the heat flux vector [4.13] excludes the dependence on $\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma}$ (i.e. $\zeta_{\alpha\beta} = 0$), and if in [4.9] $\omega_{\xi,\beta}^{\alpha} = 0$, then from [A15]₆ it is sufficient that

$$\left(\frac{\partial \Psi_{\alpha}(\theta, \bar{\rho}_{\alpha})}{\partial \theta} - \gamma_{\alpha} \right) = 0. \quad [5.3]$$

Using [4.12], for $\alpha = 1$ it is obtained that

$$\gamma_1 = \bar{\rho}_1 \frac{\partial \tilde{\Psi}_1(\theta, \bar{\rho}_1)}{\partial \theta} = -\bar{\rho}_1 \tilde{s}_1, \quad [5.4]$$

and for $\alpha = 2$

$$\gamma_2 = \bar{\rho}_2 \frac{\partial \tilde{\Psi}_2(\theta, \bar{\rho}_2)}{\partial \theta} = -\bar{\rho}_2 \tilde{s}_2. \quad [5.5]$$

Equation [A.15]₇, with $\omega_{11,11}^{\alpha} = 0$, yields as a sufficient condition that

$$\Delta_{\alpha 1} \left(\delta_{\alpha 1} - \frac{\bar{\rho}_1}{\rho} \right) = 2\eta_{11}^{\alpha}. \quad [5.6]$$

From a physical point of view it should be permissible to argue that the effect of diffusion of phases is to increase their free energies. In [4.8] therefore, $\eta_{\beta\beta}^{\alpha} \geq 0$ and the following conditions must be true:

$$\Delta_{11} \geq 0, \quad \Delta_{21} \leq 0. \quad [5.7]$$

The first condition is consistent with the result [5.9] discussed below. It should be noted, however, that by excluding the dependence of heat flux vector on $\tilde{\mathbf{v}}_{\beta} - \tilde{\mathbf{v}}_{\gamma}$ is probably not very realistic.

Anderson & Jackson (1967), Ishii & Zuber (1979) and Drew & Lahey (1979) have proposed the momentum supplies which are similar to [4.5]. In addition to the presence of viscous drag and virtual mass effects in the momentum supply expression, Anderson and Jackson also argue the presence of the buoyancy term in this expression. The buoyancy effect is proportional to the density gradient, and the theory presented in this paper allows for this effect through the term $\nabla \bar{\rho}_{\beta}$ in the constitutive assumption [3.27]. In the linear approximation of the momentum supply [4.5], no dependence on the density gradients arises. The buoyancy effect in [4.5] would arise if we were to study the constitutive equations using the second law of thermodynamics for the mixture and not for each phase as I have used above. (I leave to the reader to prove this result.) The second law of

thermodynamics for only the mixture is, however, not restrictive enough as it is discussed by Dobran (1982a). The virtual mass effect in $\hat{\mathbf{p}}_\alpha$ proposed by Drew & Lahey (1969) depends on the difference of mixed accelerations $(\partial \tilde{\mathbf{v}}_\alpha / \partial t + (\nabla \tilde{\mathbf{v}}_\alpha) \tilde{\mathbf{v}}_\beta - \partial \tilde{\mathbf{v}}_\beta / \partial t - (\nabla \tilde{\mathbf{v}}_\beta) \tilde{\mathbf{v}}_\alpha)$ and not on $\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta$. Their reasoning for choosing the difference of mixed acceleration is that it is frame indifferent while $\tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta$ is not. To me, the mixed accelerations are physically not very meaningful, and it is for this reason that the constitutive assumption [3.27] contains only the "true" accelerations $\tilde{\mathbf{a}}_\alpha$. In the linear approximation, the coefficients γ_α , $\xi_{\alpha\beta}$ and $\Delta_{\alpha\beta}$ in [4.5] depend only on the temperature and densities. When, however, we consider the complete representation of $\hat{\mathbf{p}}_\alpha$ in terms of its independent variables in [3.27] by using the Cauchy's Representation Theorem (Truesdell & Noll 1965), then the coefficients in [4.5] would also depend on the invariants of tensors in this representation. For example, for a 2-phase dispersed mixture Ishii & Zuber (1979) consider

$$\xi_{dd} = \frac{3}{8} \alpha_d \bar{\rho}_c \frac{C_D}{r_d} |\mathbf{v}_d - \mathbf{v}_c|, \quad [5.8]$$

where the subscripts c and d refer to continuous and dispersed phases respectively (i.e. $\alpha = d$ and $\gamma = c$ in [4.5]), $\bar{\rho}_c$ is the true density, α_d is the void fraction, r_d is the effective radius of the dispersed phase, $C_D = C_d(2\bar{\rho}_c r_d |\mathbf{v}_d - \mathbf{v}_c| / \mu_c, \alpha_d)$ is the drag coefficient, and μ_c is the viscosity. It is clear from [5.8] that the representation of $\xi_{\alpha\beta}$ in [4.5] in terms of the temperature and densities of phases is, in general, not adequate. But if we admit its dependence on the invariants of the variables in the constitutive assumption other than the temperature and densities, then we should also admit higher order approximations of $\hat{\mathbf{p}}_\alpha$ in [4.5]. Drew & Lahey (1979) discuss these second order contributions to $\hat{\mathbf{p}}_\alpha$ which clearly belong to the theory of non-linear constitutive equations for multiphase mixtures. The virtual mass coefficient Δ_{dd} for small α_d is given by Drew and Lahey as

$$\Delta_{dd} = \alpha_d \rho_c C_{VM}(\alpha_d), \quad [5.9]$$

where $C_{VM} \approx 0.1-0.5$.

The constitutive equation [4.13] for the heat flux vector of phase α contains the expected terms. The first term which is proportional to the temperature gradient is the *Fourier* effect, and from [A15]_i it is sufficient (and also necessary if $\omega_0^\alpha = 0$) that $\kappa_\alpha \geq 0$. The term in [4.13] which is proportional to the difference in velocities is the *Dufour* effect and it accounts for the heat flux which results from the diffusion of phases. The heat flux terms in [4.13] which are proportional to the differences in accelerations arise due to the non-uniform accelerations and velocity fields of the phases, and are probably not very significant when compared to the temperature gradient term. $\zeta_{\alpha 1}$ are restricted by [A15]₆ (it is sufficient that $\zeta_{\alpha 1} \geq 0$), while $v_{\alpha 1}$ are not restricted by any of the inequalities in [A15].

A constitutive equation for the heat flux vector was also proposed by Ishii (1975). He time-averaged the local form of the Fourier law for each phase and obtained two contributions to the heat flux vector: one which is proportional to the temperature gradient, and the other which is proportional to the concentration gradient which Ishii attributes to the Dufour effect. While such an interpretation of the Dufour effect is possible, the interpretation in this article is consistent with the interpretation in the theory of mixtures with negligible interfacial area (Bowen 1973).

The constitutive equation for the stress tensor of phase α is expressed by [4.10], and its 2-phase coefficients $\lambda_{\alpha\beta}$, $\mu_{\alpha\beta}$ and $\varphi_{\alpha\beta}$ are restricted by [A6], [A8] and [A10]. As it can be

†The densities in this article can be identified with true densities and void fractions in 2-phase literature by noting that $\bar{\rho}_c = \alpha_c \rho_c$, $\bar{\rho}_d = \alpha_d \rho_d$, $\alpha_d + \alpha_c = 1$, where ρ_c and ρ_d are true densities of the continuous and dispersed phases, respectively.

seen from [4.10], the principle of phase separation of Drew (1976) does not necessarily apply within the framework of the present theory. Very close to the equilibrium state [3.23], where it is possible to argue that the supply \hat{K}_α is equal to zero, [4.9], [A6], [A8] and [A10] give:

$$\begin{aligned} \lambda_{11} + \frac{2}{3}\mu_{11} &\geq 0, & \lambda_{22} + \frac{2}{3}\mu_{22} &\geq 0, \\ \lambda_{12} + \frac{2}{3}\mu_{12} &= 0, & \lambda_{21} + \frac{2}{3}\mu_{21} &= 0, \\ \mu_{11} &\geq 0, & \mu_{22} &\geq 0, & \mu_{12} = \mu_{21} &= 0, \\ \varphi_{11} &\geq 0, & \varphi_{12} &\leq 0, & -4\varphi_{11}\varphi_{12} &\geq (\varphi_{11} - \varphi_{12})^2. \end{aligned} \tag{5.10}$$

From [5.10]_{3,4,7} it, therefore, follows that $\lambda_{12} = \lambda_{21} = 0$, and from [4.10] the stress tensors for a 2-phase mixture become

$$\begin{aligned} \mathbf{T}_1 &= -\bar{\pi}_1\mathbf{I} + \lambda_{11}(tr \mathbf{D}_1)\mathbf{I} + 2\mu_{11}\mathbf{D}_1 + 2\varphi_{11}(\mathbf{W}_1 - \mathbf{W}_2) + \mathbf{O}(\epsilon^2) \\ \mathbf{T}_2 &= -\bar{\pi}_2\mathbf{I} + \lambda_{22}(tr \mathbf{D}_2)\mathbf{I} + 2\mu_{22}\mathbf{D}_2 + 2\varphi_{21}(\mathbf{W}_1 - \mathbf{W}_2) + \mathbf{O}(\epsilon^2). \end{aligned} \tag{5.11}$$

By the definition in section 4.2, the highly dispersed mixture is characterized by a vanishing angular momentum tensor $\hat{\mathbf{M}}_m$ or by the condition [4.19]₁. In this case, we have in [5.11] that $\varphi_{21} = -\varphi_{11}$. If \mathbf{T}_α is symmetric, then from [4.7] it follows that $\hat{\mathbf{M}}_\alpha = \mathbf{O}$ or $\varphi_{11} = 0$ and $\varphi_{21} = 0$.

The present theory yields, therefore, the simple results

$$\begin{aligned} \mathbf{T}_1 &= -\bar{\pi}_1\mathbf{I} + \lambda_{11}(tr \mathbf{D}_1)\mathbf{I} + 2\mu_{11}\mathbf{D}_1 + \mathbf{O}(\epsilon^2) \\ \mathbf{T}_2 &= -\bar{\pi}_2\mathbf{I} + \lambda_{22}(tr \mathbf{D}_2)\mathbf{I} + 2\mu_{22}\mathbf{D}_2 + \mathbf{O}(\epsilon^2) \end{aligned} \tag{5.12}$$

if (1) \mathbf{T}_α are symmetric, and (2) $\hat{K}_\alpha = 0$. Drew's (1976) constitutive equations for stress tensors are similar to [5.12] and for the continuous and dispersed phases he assumes respectively that

$$\begin{aligned} \mathbf{T}_c &= (1 - \alpha_d)[-p\mathbf{I} + \lambda E(\alpha_d)(tr \mathbf{D}_c)\mathbf{I} + \mu D(\alpha_d)\mathbf{D}_c] \\ \mathbf{T}_d &= -p\alpha_d\mathbf{I}, \end{aligned} \tag{5.13}$$

where α_d is the void fraction of dispersed phase and p is the pressure. Comparing [5.12] with [5.13], we have $\bar{\pi}_c = (1 - \alpha_d)p$, $\bar{\pi}_d = \alpha_d p$, $\lambda_{cc} = (1 - \alpha_d)\lambda E(\alpha_d)$, $2\mu_{cc} = (1 - \alpha_d)\mu D(\alpha_d)$, and $\lambda_{dd} = \mu_{dd} = 0$. Notice that the coefficients in [5.12] depend on the equilibrium state properties (θ , $\bar{\rho}_c = (1 - \alpha_d)\bar{\rho}_c$, and $\bar{\rho}_d = \alpha_d\bar{\rho}_d$) and thus there is some truth in [5.13] that the coefficients E and D depend on α_d , as assumed by Drew. Comparing the present results with the 2-phase stress tensors of Ishii (1975) is not straightforward unless the present results are also time-averaged. If, however, the turbulent contributions are neglected in the model of Ishii, then his stress tensors are similar to [5.12] with $\bar{\pi}_1 = \alpha_1 p_1$, $tr \mathbf{D}_1 = 0$,[†] $\mu_{11} = \alpha_1 \mu_1$, $\alpha_1 = \mathcal{V}_1/\mathcal{V}$, and similarly for phase 2.

It is clear from the above discussion that the constitutive equations for stress tensors in the present theory are very general, and whether or not the full generality of [4.10] is

[†]Ishii assumes that the 2-phase mixture is incompressible. In the present theory, the incompressibility of a phase does not imply that $tr \mathbf{D}_1 = 0$ since $\bar{\rho}_1 \neq 0$ (cit. [2.12]₁).

required, needs to be ascertained from very careful experiments. The form [5.12] is already sufficiently simple, and it should be possible to experimentally find the dependence of λ_{11} , λ_{22} , μ_{11} , and μ_{22} on θ , $\bar{\rho}_1$, and $\bar{\rho}_2$. It should also be noted that time averaging of [5.11] will give rise to turbulent contributions in the stress tensors which are more complicated than in a single phase situation. (In single phase flow, the stress tensor cannot depend on the spin rate \mathbf{W} —at least as long as we accept the principle of the material frame indifference.) Time averaging of the conservation laws of section 2 produces a set of averaged equations which are significantly more complicated than the single phase conservation laws, and the study of turbulence in multiphase mixtures is also significantly more difficult than in the single phase situation.

It is very common in the 2-phase flow literature to formulate theories in terms of the volumetric fractions. Except for the case when both phases are incompressible, I do not see that such a formulation yields any simplicity, and in the present article, I have found no need for formulating the theory in such a manner. All the results of the present theory, however, do reduce in terms of the volumetric fractions $\mathcal{V}_\alpha/\mathcal{V}$ by noting the functional relationship $\bar{G}_\alpha = \bar{G}_\alpha \mathcal{V}_\alpha/\mathcal{V}$. \bar{G}_α is the “partial” and \bar{G}_α is the “true” volume-averaged variable, and they are defined in section 2. A further discussion of linearized constitutive equations for a special case of two-phase flow is presented by Dobran (1982b).

The constitutive equations derived in this article also apply to the porous media when the elastic properties of the porous matrix are neglected. To illustrate the consistency of the theory with Darcy’s law it is sufficient to consider the flow of an incompressible fluid of phase α through a rigid porous matrix. The porosity of this matrix is $\phi_\alpha \equiv \mathcal{V}_\alpha/\mathcal{V}$, and the true density of the fluid is $\bar{\rho}_\alpha$. Since the phase α is considered to be incompressible, we have from the conservation of mass equation [2.12]₁

$$\nabla \cdot \tilde{\mathbf{v}}_\alpha = 0, \quad [5.14]$$

and since $\text{tr}(\nabla \tilde{\mathbf{v}}_\alpha) = \nabla \cdot \tilde{\mathbf{v}}_\alpha = 0$, then also $\text{tr} \mathbf{D}_\alpha = 0$, and the stress tensor from [4.10] is reduced to the following form:

$$\mathbf{T}_\alpha = -\phi_\alpha \bar{\pi}_\alpha \mathbf{I} + 2\mu_{\alpha\alpha} \mathbf{D}_\alpha + \mathbf{O}(\epsilon^2). \quad [5.15]$$

The momentum supply for phase α is obtained from [4.5] by neglecting virtual mass and Soret effects, and by assuming that the porous matrix is stationary ($\tilde{\mathbf{v}}_\gamma = \mathbf{0}$), i.e.

$$\hat{\mathbf{p}}_\alpha = -\xi_{\alpha\alpha} \tilde{\mathbf{v}}_\alpha + \mathbf{0}(\epsilon^2). \quad [5.16]$$

Substituting $\bar{\pi}_\alpha = \bar{\pi}_\alpha (\mathcal{V}_\alpha/\mathcal{V})$ and $\bar{\rho}_\alpha = \bar{\rho}_\alpha (\mathcal{V}_\alpha/\mathcal{V})$, [5.15] and [5.16] into the momentum equation [2.14]₁ results in the following expression:

$$\bar{\rho}_\alpha \tilde{\dot{\mathbf{v}}}_\alpha = -\nabla \bar{\pi}_\alpha + \frac{\mu_{\alpha\alpha}}{\phi_\alpha} \nabla^2 \tilde{\mathbf{v}}_\alpha + \bar{\rho}_\alpha \tilde{\mathbf{b}}_\alpha - \frac{\xi_{\alpha\alpha}}{\phi_\alpha} \tilde{\mathbf{v}}_\alpha. \quad [5.17]$$

Equation [5.17] is the desired result. Its similarity with the classical form of Darcy’s law (Scheidegger 1974) is evident when it is assumed that $\tilde{\mathbf{v}}_\alpha = \mathbf{0}$, $\nabla^2 \tilde{\mathbf{v}}_\alpha = \mathbf{0}$, and when the coefficient $\xi_{\alpha\alpha}/\phi_\alpha$ is identified with μ_α/k_α , where μ_α is the viscosity of phase α and k_α is its permeability. The inclusion of the term $\nabla^2 \tilde{\mathbf{v}}_\alpha$ into the classical expression of Darcy’s law is discussed by Neale & Nader (1974) in order to account for the boundary layer effect which physically occurs near a solid boundary and near the interface of a porous medium and a fluid. The coefficient $\mu_{\alpha\alpha}/\phi_\alpha$ in [5.17] appears to be satisfactorily related to the viscosity of phase α , μ_α (*cit.* Neale & Nader 1974).

To account for the compressibility of the porous medium an account must be taken in the constitutive assumption [3.27] of the elastic properties of the matrix.

6. CONCLUDING REMARKS

In this article, a linearized theory of the constitutive equations for multiphase mixtures of fluids was presented. This theory is based on the conservation and balance equations of multiphase mixtures proposed by Dobran (1982a). The constitutive assumption included the temperature gradient, velocity gradients, density gradients, and accelerations. No allowance is made in the theory for multiple temperatures, phase change, memory effects and non-local effects. Inclusion of multiple temperatures into the theory is necessary for mixtures where phases exhibit significant thermal nonequilibrium, and the inclusion of non-local effects should be important for mixtures where the interfacial areas are large or for mixtures with significant microstructural characteristics (non-dispersed mixtures). Many of these effects can be accounted for within the analysis without conceptually changing the basic methodology of this article.

The constitutive equations were obtained for an arbitrary number of phases, and these equations reduced to some special results from previous investigations. The coefficients in the linearized constitutive equations are found to be consistent with the results from models based on the experimental data. The experimental data are lacking, however, to establish the values of the viscosity coefficients $\lambda_{\alpha\beta}$ and $\mu_{\alpha\beta}$, and, consequently, the analytic modeling of multiphase flows is precluded by a set of parabolic differential equations. Since the parabolic system of equations requires more boundary conditions than the now widely used first order system of hyperbolic equations, the solution of the former system of equations should yield more meaningful results than the solution of the latter system of conservation and balance equations.

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APPENDIX A

The coefficients in the constitutive equations [4.4]–[4.9] are restricted by the second law of thermodynamics [3.31], and it is this restriction which is studied in this appendix for a 2-phase mixture of fluids. For a mixture of 3 or more phases, analogous procedure can be carried out.

Substituting the constitutive equations [4.4]–[4.9] into the second law of thermodynamics [3.31], and utilizing [2.7], [2.8], [3.32], [3.33] and [3.34], the following equation

is obtained:

$$\begin{aligned}
 & \left[\sum_{\beta=1}^2 \omega_{0,\beta}^{\alpha} (tr \mathbf{D}_{\beta}) \right] + \left[\sum_{\beta,\sigma=1}^2 \left\{ \frac{1}{3} \hat{\omega}_{1,\beta\sigma}^{\alpha} + \hat{\omega}_{2,\beta\sigma}^{\alpha} + \delta_{\alpha\sigma} \left[\lambda_{\alpha\beta} + \frac{2}{3} \mu_{\alpha\beta} \right] \right\} (tr \mathbf{D}_{\beta})(tr \mathbf{D}_{\sigma}) \right] \\
 & + \left[\sum_{\beta,\sigma=1}^2 \left\{ \hat{\omega}_{1,\beta\sigma}^{\alpha} + 2\mu_{\alpha\beta} \delta_{\alpha\sigma} \right\} tr \left\{ \left[\mathbf{D}_{\beta} - \frac{3+\sqrt{6}}{3} (tr \mathbf{D}_{\beta}) \mathbf{I} \right] \left[\mathbf{D}_{\sigma} - \frac{3+\sqrt{6}}{3} (tr \mathbf{D}_{\sigma}) \mathbf{I} \right] \right\} \right] \\
 & + \left[\sum_{\beta,\sigma=1}^2 \left\{ 2\varphi_{\alpha\beta} \delta_{\alpha\sigma} - 2\hat{\varphi}_{\beta\sigma}^{\alpha} - \hat{\omega}_{3,\beta\sigma}^{\alpha} \right\} tr \{ \mathbf{W}_{\sigma}^T \mathbf{W}_{\beta} \} \right] \\
 & + \left[\left(\frac{\kappa_{\alpha}}{\theta} + \omega_0^{\alpha} \right) \nabla \theta \cdot \nabla \theta + \sum_{\beta=1}^2 \left\{ \frac{\zeta_{\alpha\beta}}{\theta} + \left(\frac{\partial \Psi_{\alpha}(\theta, \bar{\rho}_{\alpha})}{\partial \theta} - \gamma_{\alpha} \right) \left(\frac{\bar{\rho}_{\beta}}{\rho} - \delta_{\alpha\beta} \right) + \hat{\omega}_{5,\beta}^{\alpha} \right\} \nabla \theta \cdot \tilde{\mathbf{v}}_{\beta} \right. \\
 & + \sum_{\beta=1}^2 \left\{ \frac{\nu_{\alpha\beta}}{\theta} + \hat{\omega}_{6,\beta}^{\alpha} \right\} \nabla \theta \cdot \tilde{\mathbf{v}}_{\beta} + \sum_{\beta=1}^2 \left\{ \omega_{4,\beta}^{\alpha} \right\} \nabla \theta \cdot \nabla \bar{\rho}_{\beta} \\
 & + \sum_{\beta,\sigma=1}^2 \left\{ \left[\zeta_{\alpha\beta} \left(\delta_{\alpha\sigma} - \frac{\bar{\rho}_{\sigma}}{\rho} \right) + \hat{\omega}_{10,\beta\sigma}^{\alpha} \right] \tilde{\mathbf{v}}_{\beta} \cdot \tilde{\mathbf{v}}_{\sigma} + \left[-\hat{\eta}_{\beta\sigma}^{\alpha} + \Delta_{\alpha\sigma} \left(\delta_{\alpha\beta} - \frac{\bar{\rho}_{\beta}}{\rho} \right) \right. \right. \\
 & \left. \left. + \hat{\omega}_{11,\beta\sigma}^{\alpha} \right] \tilde{\mathbf{v}}_{\beta} \cdot \tilde{\mathbf{v}}_{\sigma} + [\hat{\omega}_{7,\beta\sigma}^{\alpha}] \nabla \bar{\rho}_{\beta} \cdot \nabla \bar{\rho}_{\sigma} + [\hat{\omega}_{8,\beta\sigma}^{\alpha}] \nabla \bar{\rho}_{\beta} \cdot \tilde{\mathbf{v}}_{\sigma} \right. \\
 & \left. + [\hat{\omega}_{9,\beta\sigma}^{\alpha}] \nabla \bar{\rho}_{\beta} \cdot \tilde{\mathbf{v}}_{\sigma} + [\hat{\omega}_{12,\beta\sigma}^{\alpha}] \tilde{\mathbf{v}}_{\beta} \cdot \tilde{\mathbf{v}}_{\sigma} \right\} \Big] + 0(\epsilon^3) = \phi_{\alpha} \geq 0, \tag{A1}
 \end{aligned}$$

where the Kronecker delta $\delta_{\alpha\sigma}$ is defined as follows:

$$\delta_{\alpha\sigma} = \begin{cases} 1, & \alpha = \sigma \\ 0, & \alpha \neq \sigma \end{cases},$$

and the new coefficients are given as

$$\begin{aligned}
 \zeta_{\alpha 2} &= -\zeta_{\alpha 1}, & \nu_{\alpha 2} &= -\nu_{\alpha 1}, \\
 \varphi_{\alpha 2} &= -\varphi_{\alpha 1}, & \xi_{\alpha 2} &= -\xi_{\alpha 1}, \\
 \Delta_{\alpha 2} &= -\Delta_{\alpha 1}, & \eta_{11}^{\alpha} &= \eta_{22}^{\alpha} = -\eta_{12}^{\alpha} = -\eta_{21}^{\alpha}, \\
 \hat{\eta}_{11}^{\alpha} &= \hat{\eta}_{22}^{\alpha} = -\hat{\eta}_{12}^{\alpha} = -\hat{\eta}_{21}^{\alpha} = 2\eta_{11}^{\alpha}, \\
 \hat{\varphi}_{11}^{\alpha} &= 0, & \hat{\varphi}_{12}^{\alpha} &= \varphi_{\alpha 1}, & \hat{\varphi}_{21}^{\alpha} &= 0, & \hat{\varphi}_{22}^{\alpha} &= \varphi_{\alpha 2}, \\
 \hat{\omega}_{1,11}^{\alpha} &= \omega_{1,11}^{\alpha}, & \hat{\omega}_{1,12}^{\alpha} &= \frac{1}{2} \omega_{1,12}^{\alpha}, & \hat{\omega}_{1,21}^{\alpha} &= \frac{1}{2} \omega_{1,12}^{\alpha}, & \hat{\omega}_{1,22}^{\alpha} &= \omega_{1,22}^{\alpha}, \\
 \hat{\omega}_{2,11}^{\alpha} &= \omega_{2,11}^{\alpha}, & \hat{\omega}_{2,12}^{\alpha} &= \frac{1}{2} \omega_{2,12}^{\alpha}, & \hat{\omega}_{2,21}^{\alpha} &= \frac{1}{2} \omega_{2,12}^{\alpha}, & \hat{\omega}_{2,22}^{\alpha} &= \omega_{2,22}^{\alpha}, \\
 \hat{\omega}_{3,11}^{\alpha} &= \hat{\omega}_{3,22}^{\alpha} = -\hat{\omega}_{3,12}^{\alpha} = -\hat{\omega}_{3,21}^{\alpha} = \omega_{3,11}^{\alpha}, \\
 \hat{\omega}_{5,1}^{\alpha} &= -\hat{\omega}_{5,2}^{\alpha} = \omega_{5,1}^{\alpha}, & \hat{\omega}_{6,1}^{\alpha} &= -\hat{\omega}_{6,2}^{\alpha} = \omega_{6,1}^{\alpha}, \\
 \hat{\omega}_{7,11}^{\alpha} &= \omega_{7,11}^{\alpha}, & \hat{\omega}_{7,22}^{\alpha} &= \omega_{7,22}^{\alpha}, & \hat{\omega}_{7,12}^{\alpha} &= \frac{1}{2} \omega_{7,12}^{\alpha}, & \hat{\omega}_{7,21}^{\alpha} &= \frac{1}{2} \omega_{7,12}^{\alpha}, \\
 \hat{\omega}_{8,11}^{\alpha} &= -\hat{\omega}_{8,12}^{\alpha} = \omega_{8,11}^{\alpha}, & \hat{\omega}_{8,21}^{\alpha} &= -\hat{\omega}_{8,22}^{\alpha} = \omega_{8,21}^{\alpha},
 \end{aligned}$$

is obtained:

$$\begin{aligned}
 & \left[\sum_{\beta=1}^2 \omega_{0,\beta}^\alpha (tr \mathbf{D}_\beta) \right] + \left[\sum_{\beta,\sigma=1}^2 \left\{ \frac{1}{3} \hat{\omega}_{1,\beta\sigma}^\alpha + \hat{\omega}_{2,\beta\sigma}^\alpha + \delta_{\alpha\sigma} \left[\lambda_{\alpha\beta} + \frac{2}{3} \mu_{\alpha\beta} \right] \right\} (tr \mathbf{D}_\beta)(tr \mathbf{D}_\sigma) \right] \\
 & + \left[\sum_{\beta,\sigma=1}^2 \left\{ \hat{\omega}_{1,\beta\sigma}^\alpha + 2\mu_{\alpha\beta} \delta_{\alpha\sigma} \right\} tr \left\{ \left[\mathbf{D}_\beta - \frac{3+\sqrt{6}}{3} (tr \mathbf{D}_\beta) \mathbf{I} \right] \left[\mathbf{D}_\sigma - \frac{3+\sqrt{6}}{3} (tr \mathbf{D}_\sigma) \mathbf{I} \right] \right\} \right] \\
 & + \left[\sum_{\beta,\sigma=1}^2 \left\{ 2\varphi_{\alpha\beta} \delta_{\alpha\sigma} - 2\hat{\varphi}_{\beta\sigma}^\alpha - \hat{\omega}_{3,\beta\sigma}^\alpha \right\} tr \left\{ \mathbf{W}_\sigma^T \mathbf{W}_\beta \right\} \right] \\
 & + \left[\left(\frac{\kappa_\alpha}{\theta} + \omega_0^\alpha \right) \nabla \theta \cdot \nabla \theta + \sum_{\beta=1}^2 \left\{ \frac{\zeta_{\alpha\beta}}{\theta} + \left(\frac{\partial \Psi_\alpha(\theta, \bar{\rho}_\alpha)}{\partial \theta} - \gamma_\alpha \right) \left(\frac{\bar{\rho}_\beta}{\rho} - \delta_{\alpha\beta} \right) + \hat{\omega}_{5,\beta}^\alpha \right\} \nabla \theta \cdot \tilde{\mathbf{v}}_\beta \right. \\
 & + \sum_{\beta=1}^2 \left\{ \frac{\nu_{\alpha\beta}}{\theta} + \hat{\omega}_{6,\beta}^\alpha \right\} \nabla \theta \cdot \tilde{\mathbf{v}}_\beta + \sum_{\beta=1}^2 \left\{ \omega_{4,\beta}^\alpha \right\} \nabla \theta \cdot \nabla \bar{\rho}_\beta \\
 & + \sum_{\beta,\sigma=1}^2 \left\{ \left[\zeta_{\alpha\beta} \left(\delta_{\alpha\sigma} - \frac{\bar{\rho}_\sigma}{\rho} \right) + \hat{\omega}_{10,\beta\sigma}^\alpha \right] \tilde{\mathbf{v}}_\beta \cdot \tilde{\mathbf{v}}_\sigma + \left[-\hat{\eta}_{\beta\sigma}^\alpha + \Delta_{\alpha\sigma} \left(\delta_{\alpha\beta} - \frac{\bar{\rho}_\beta}{\rho} \right) \right. \right. \\
 & + \hat{\omega}_{11,\beta\sigma}^\alpha \left. \right] \tilde{\mathbf{v}}_\beta \cdot \tilde{\mathbf{v}}_\sigma + [\hat{\omega}_{7,\beta\sigma}^\alpha] \nabla \bar{\rho}_\beta \cdot \nabla \bar{\rho}_\sigma + [\hat{\omega}_{8,\beta\sigma}^\alpha] \nabla \bar{\rho}_\beta \cdot \tilde{\mathbf{v}}_\sigma \\
 & \left. + [\hat{\omega}_{9,\beta\sigma}^\alpha] \nabla \bar{\rho}_\beta \cdot \tilde{\mathbf{v}}_\sigma + [\hat{\omega}_{12,\beta\sigma}^\alpha] \tilde{\mathbf{v}}_\beta \cdot \tilde{\mathbf{v}}_\sigma \right\} \right] + 0(\epsilon^3) = \phi_\alpha \geq 0, \tag{A1}
 \end{aligned}$$

where the Kronecker delta $\delta_{\alpha\sigma}$ is defined as follows:

$$\delta_{\alpha\sigma} = \begin{cases} 1, & \alpha = \sigma \\ 0, & \alpha \neq \sigma \end{cases},$$

and the new coefficients are given as

$$\begin{aligned}
 & \zeta_{\alpha 2} = -\zeta_{\alpha 1}, \quad \nu_{\alpha 2} = -\nu_{\alpha 1}, \\
 & \varphi_{\alpha 2} = -\varphi_{\alpha 1}, \quad \xi_{\alpha 2} = -\xi_{\alpha 1}, \\
 & \Delta_{\alpha 2} = -\Delta_{\alpha 1}, \quad \eta_{11}^\alpha = \eta_{22}^\alpha = -\eta_{12}^\alpha = -\eta_{21}^\alpha, \\
 & \hat{\eta}_{11}^\alpha = \hat{\eta}_{22}^\alpha = -\hat{\eta}_{12}^\alpha = -\hat{\eta}_{21}^\alpha = 2\eta_{11}^\alpha, \\
 & \hat{\varphi}_{11}^\alpha = 0, \quad \hat{\varphi}_{12}^\alpha = \varphi_{\alpha 1}, \quad \hat{\varphi}_{21}^\alpha = 0, \quad \hat{\varphi}_{22}^\alpha = \varphi_{\alpha 2}, \\
 & \hat{\omega}_{1,11}^\alpha = \omega_{1,11}^\alpha, \quad \hat{\omega}_{1,12}^\alpha = \frac{1}{2} \omega_{1,12}^\alpha, \quad \hat{\omega}_{1,21}^\alpha = \frac{1}{2} \omega_{1,12}^\alpha, \quad \hat{\omega}_{1,22}^\alpha = \omega_{1,22}^\alpha, \\
 & \hat{\omega}_{2,11}^\alpha = \omega_{2,11}^\alpha, \quad \hat{\omega}_{2,12}^\alpha = \frac{1}{2} \omega_{2,12}^\alpha, \quad \hat{\omega}_{2,21}^\alpha = \frac{1}{2} \omega_{2,12}^\alpha, \quad \hat{\omega}_{2,22}^\alpha = \omega_{2,22}^\alpha, \\
 & \hat{\omega}_{3,11}^\alpha = \hat{\omega}_{3,22}^\alpha = -\hat{\omega}_{3,12}^\alpha = -\hat{\omega}_{3,21}^\alpha = \omega_{3,11}^\alpha, \\
 & \hat{\omega}_{3,1}^\alpha = -\hat{\omega}_{3,2}^\alpha = \omega_{3,1}^\alpha, \quad \hat{\omega}_{6,1}^\alpha = -\hat{\omega}_{6,2}^\alpha = \omega_{6,1}^\alpha, \\
 & \hat{\omega}_{7,11}^\alpha = \omega_{7,11}^\alpha, \quad \hat{\omega}_{7,22}^\alpha = \omega_{7,22}^\alpha, \quad \hat{\omega}_{7,12}^\alpha = \frac{1}{2} \omega_{7,12}^\alpha, \quad \hat{\omega}_{7,21}^\alpha = \frac{1}{2} \omega_{7,12}^\alpha, \\
 & \hat{\omega}_{8,11}^\alpha = -\hat{\omega}_{8,12}^\alpha = \omega_{8,11}^\alpha, \quad \hat{\omega}_{8,21}^\alpha = -\hat{\omega}_{8,22}^\alpha = \omega_{8,21}^\alpha,
 \end{aligned}$$

and using [A2] it is necessary and sufficient that

$$\begin{aligned} C_{11}^\alpha &= \omega_{1,11}^\alpha + 2\mu_{\alpha 1} \delta_{\alpha 1} \geq 0 \\ C_{22}^\alpha &= \omega_{1,22}^\alpha + 2\mu_{\alpha 2} \delta_{\alpha 2} \geq 0 \end{aligned} \tag{A8}$$

$$\begin{aligned} C_{11}^\alpha C_{22}^\alpha &= (\omega_{1,11}^\alpha + 2\mu_{\alpha 1} \delta_{\alpha 1})(\omega_{1,22}^\alpha + 2\mu_{\alpha 2} \delta_{\alpha 2}) \geq \frac{1}{4}(C_{12}^\alpha + C_{21}^\alpha)^2 \\ &= \frac{1}{4}(\omega_{1,12}^\alpha + 2\mu_{\alpha 1} \delta_{\alpha 2} + 2\mu_{\alpha 2} \delta_{\alpha 1})^2 \end{aligned}$$

for $\alpha = 1, 2$.

Also for $\alpha = 1, 2$,

$$\sum_{\beta, \sigma=1}^2 \{2\varphi_{\alpha\beta} \delta_{\alpha\sigma} - 2\hat{\varphi}_{\beta\sigma}^\alpha - \hat{\omega}_{3, \beta\sigma}^\alpha\} \text{tr} \{\mathbf{W}_\sigma^T \mathbf{W}_\beta\} \equiv \sum_{\beta, \sigma=1}^2 D_{\beta\sigma}^\alpha \text{tr} \{\mathbf{W}_\sigma^T \mathbf{W}_\beta\} \geq 0, \tag{A9}$$

which implies that

$$\begin{aligned} D_{11}^\alpha &= 2\varphi_{\alpha 1} \delta_{\alpha 1} - \omega_{3,11}^\alpha \geq 0 \\ D_{22}^\alpha &= -2\varphi_{\alpha 2} \delta_{\alpha 1} - \omega_{3,11}^\alpha \geq 0 \end{aligned} \tag{A10}$$

$$\begin{aligned} D_{11}^\alpha D_{22}^\alpha &= (2\varphi_{\alpha 1} \delta_{\alpha 1} - \omega_{3,11}^\alpha)(2\varphi_{\alpha 2} \delta_{\alpha 2} - 2\varphi_{\alpha 2} - \omega_{3,11}^\alpha) \geq \frac{1}{4}(D_{12}^\alpha + D_{21}^\alpha)^2 \\ &= [\varphi_{\alpha 1}(\delta_{\alpha 2} - 1) + \varphi_{\alpha 2} \delta_{\alpha 1} + \omega_{3,11}^\alpha]^2. \end{aligned}$$

Before considering the remaining quadratic form in [A1], it is of some interest to examine the quadratic forms in the second law of thermodynamics for the multiphase mixture which are analogous to the forms [A3], [A5], [A7] and [A9]. Summing up α in [A1] these forms yield:

$$\begin{aligned} \sum_{\alpha=1}^2 \omega_{0,\beta}^\alpha &= 0; \quad \beta = 1, 2 \\ \sum_{\alpha=1}^2 B_{11}^\alpha &= \frac{1}{3} \left(\sum_{\alpha=1}^2 \omega_{1,11}^\alpha \right) + \left(\sum_{\alpha=1}^2 \omega_{2,11}^\alpha \right) + \lambda_{11} + \frac{2}{3} \mu_{11} \geq 0 \\ \sum_{\alpha=1}^2 B_{22}^\alpha &= \frac{1}{3} \left(\sum_{\alpha=1}^2 \omega_{1,22}^\alpha \right) + \left(\sum_{\alpha=1}^2 \omega_{2,22}^\alpha \right) + \lambda_{22} + \frac{2}{3} \mu_{22} \geq 0 \\ \left(\sum_{\alpha=1}^2 B_{11}^\alpha \right) \left(\sum_{\alpha=1}^2 B_{22}^\alpha \right) &\geq \frac{1}{4} \left[\sum_{\alpha=1}^2 (B_{12}^\alpha + B_{21}^\alpha) \right]^2 \\ &= \frac{1}{4} \left[\frac{1}{3} \left(\sum_{\alpha=1}^2 \omega_{1,12}^\alpha \right) + \left(\sum_{\alpha=1}^2 \omega_{2,12}^\alpha \right) + \lambda_{21} + \frac{2}{3} \mu_{21} + \lambda_{12} + \frac{2}{3} \mu_{12} \right]^2 \\ \sum_{\alpha=1}^2 C_{11}^\alpha &= \sum_{\alpha=1}^2 \omega_{1,11}^\alpha + 2\mu_{11} \geq 0 \\ \sum_{\alpha=1}^2 C_{22}^\alpha &= \sum_{\alpha=1}^2 \omega_{1,22}^\alpha + 2\mu_{22} \geq 0 \end{aligned} \tag{A11}$$

$$\begin{aligned} \left(\sum_{\alpha=1}^2 C_{11}^{\alpha}\right)\left(\sum_{\alpha=1}^2 C_{22}^{\alpha}\right) &\geq \frac{1}{4}\left[\sum_{\alpha=1}^2 (C_{12}^{\alpha} + C_{21}^{\alpha})\right]^2 = \frac{1}{4}\left[\sum_{\alpha=1}^2 \omega_{1,12}^{\alpha} + 2\mu_{12} + 2\mu_{21}\right]^2 \\ \sum_{\alpha=1}^2 D_{11}^{\alpha} &= 2\varphi_{11} - \sum_{\alpha=1}^2 \omega_{3,11}^{\alpha} \geq 0 \\ \sum_{\alpha=1}^2 D_{22}^{\alpha} &= -2\varphi_{12} - \sum_{\alpha=1}^2 \omega_{3,11}^{\alpha} \geq 0 \\ \left(\sum_{\alpha=1}^2 D_{11}^{\alpha}\right)\left(\sum_{\alpha=1}^2 D_{22}^{\alpha}\right) &\geq \frac{1}{4}\left[\sum_{\alpha=1}^2 (D_{12}^{\alpha} + D_{21}^{\alpha})\right]^2 = \left[\varphi_{11} - \varphi_{12} - \sum_{\alpha=1}^2 \omega_{3,11}^{\alpha}\right]^2. \end{aligned}$$

When use is made of [4.19] for a highly dispersed mixture, [A11] is reduced to

$$\begin{aligned} \lambda_{11} + \frac{2}{3}\mu_{11} &\geq 0, & \lambda_{22} + \frac{2}{3}\mu_{22} &\geq 0 \\ \left(\lambda_{11} + \frac{2}{3}\mu_{11}\right)\left(\lambda_{22} + \frac{2}{3}\mu_{22}\right) &\geq \frac{1}{4}\left(\lambda_{12} + \frac{2}{3}\mu_{12} + \lambda_{21} + \frac{2}{3}\mu_{21}\right)^2 \\ \mu_{11} &\geq 0, & \mu_{22} &\geq 0, & \mu_{11}\mu_{22} &\geq \frac{1}{4}(\mu_{12} + \mu_{21})^2 \\ \varphi_{11} &\geq 0, & \varphi_{12} &\leq 0, & -\varphi_{11}\varphi_{12} &\geq \frac{1}{4}(\varphi_{11} - \varphi_{12})^2. \end{aligned} \tag{A12}$$

These results are consistent with the theory of mixtures with a negligible interfacial area (Bowen 1973).

The remaining quadratic form in [A1] can be written as follows:

$$\mathbf{V}A^{\alpha}\mathbf{V}^T, \tag{A13}$$

where \mathbf{V} is the vector which consists of components $(\nabla\theta, \tilde{\mathbf{v}}_1, \tilde{\mathbf{v}}_2, \hat{\tilde{\mathbf{v}}}_1, \hat{\tilde{\mathbf{v}}}_2, \nabla\bar{\rho}_1, \nabla\bar{\rho}_2)$, and A^{α} is the symmetric matrix with the components:

$$\begin{aligned} a_{11}^{\alpha} &= \frac{\kappa_{\alpha}}{\theta} + \omega_0^{\alpha} \\ a_{12}^{\alpha} = a_{21}^{\alpha} &= -a_{13}^{\alpha} = -a_{31}^{\alpha} = \frac{1}{2}\left[\frac{\zeta_{\alpha 1}}{\theta} + \left(\frac{\partial\Psi_{\alpha}(\theta, \bar{\rho}_{\alpha})}{\partial\theta} - \gamma_{\alpha}\right)\left(\frac{\bar{\rho}_1}{\rho} - \delta_{\alpha 1}\right) + \omega_{5,1}^{\alpha}\right] \\ a_{14}^{\alpha} = a_{41}^{\alpha} &= -a_{15}^{\alpha} = -a_{51}^{\alpha} = \frac{1}{2}\left[\frac{\nu_{\alpha 1}}{\theta} + \omega_{6,1}^{\alpha}\right] \\ a_{16}^{\alpha} = a_{61}^{\alpha} &= \frac{1}{2}\omega_{4,1}^{\alpha} \\ a_{17}^{\alpha} = a_{71}^{\alpha} &= \frac{1}{2}\omega_{4,2}^{\alpha} \\ a_{22}^{\alpha} = -a_{23}^{\alpha} &= -a_{32}^{\alpha} = a_{33}^{\alpha} = \zeta_{\alpha 1}\left(\delta_{\alpha 1} - \frac{\bar{\rho}_1}{\rho}\right) + \omega_{10,1}^{\alpha} \end{aligned}$$

$$\begin{aligned}
 a_{24}^{\alpha} &= a_{42}^{\alpha} = -a_{25}^{\alpha} = -a_{52}^{\alpha} = -a_{43}^{\alpha} = -a_{34}^{\alpha} = a_{35}^{\alpha} = a_{53}^{\alpha} = \frac{1}{2} \left[-2\eta_{11}^{\alpha} + \Delta_{\alpha 1} \left(\delta_{\alpha 1} - \frac{\bar{\rho}_1}{\rho} \right) + \omega_{11,11}^{\alpha} \right] \\
 a_{26}^{\alpha} &= a_{62}^{\alpha} = -a_{36}^{\alpha} = -a_{63}^{\alpha} = \frac{1}{2} \omega_{8,11}^{\alpha} \\
 a_{27}^{\alpha} &= a_{72}^{\alpha} = -a_{37}^{\alpha} = -a_{73}^{\alpha} = \frac{1}{2} \omega_{8,21}^{\alpha} \\
 a_{44}^{\alpha} &= -a_{45}^{\alpha} = -a_{54}^{\alpha} = a_{55}^{\alpha} = \omega_{12,11}^{\alpha} \\
 a_{46}^{\alpha} &= a_{64}^{\alpha} = -a_{56}^{\alpha} = -a_{65}^{\alpha} = \frac{1}{2} \omega_{9,11}^{\alpha} \\
 a_{47}^{\alpha} &= a_{74}^{\alpha} = -a_{57}^{\alpha} = -a_{75}^{\alpha} = \frac{1}{2} \omega_{9,21}^{\alpha} \\
 a_{66}^{\alpha} &= \omega_{7,11}^{\alpha}, \quad a_{67}^{\alpha} = a_{76}^{\alpha} = \frac{1}{2} \omega_{7,12}^{\alpha}, \quad a_{77}^{\alpha} = \omega_{7,22}^{\alpha}
 \end{aligned} \tag{A14}$$

The necessary and sufficient conditions for the quadratic form [A13] to be positive semi-definite are that all principal minors of the matrix A_{ij}^{α} be positive semi-definite, i.e.

$$\begin{aligned}
 a_{11}^{\alpha} &= \frac{\kappa_{\alpha}}{\theta} + \omega_0^{\alpha} \geq 0, \quad a_{22}^{\alpha} = \zeta_{\alpha 1} \left(\delta_{\alpha 1} - \frac{\bar{\rho}_1}{\rho} \right) + \omega_{10,11}^{\alpha} \geq 0 \\
 a_{44}^{\alpha} &= \omega_{12,11}^{\alpha} \geq 0, \quad a_{66}^{\alpha} = \omega_{7,11}^{\alpha} \geq 0, \quad a_{77}^{\alpha} = \omega_{7,22}^{\alpha} \geq 0 \\
 a_{11}^{\alpha} a_{22}^{\alpha} - a_{12}^{\alpha} a_{21}^{\alpha} &= \left(\frac{\kappa_{\alpha}}{\theta} + \omega_0^{\alpha} \right) \left[\zeta_{\alpha 1} \left(\delta_{\alpha 1} - \frac{\bar{\rho}_1}{\rho} \right) + \omega_{10,11}^{\alpha} \right] \\
 &\quad - \frac{1}{4} \left[\frac{\zeta_{\alpha 1}}{\theta} + \left(\frac{\partial \Psi_{\alpha}(\theta, \bar{\rho}_{\alpha})}{\partial \theta} - \gamma_{\alpha} \right) \left(\frac{\bar{\rho}_1}{\rho} - \delta_{\alpha 1} \right) + \omega_{5,1}^{\alpha} \right]^2 \geq 0 \\
 a_{22}^{\alpha} a_{44}^{\alpha} - a_{24}^{\alpha} a_{42}^{\alpha} &\geq 0, \quad a_{44}^{\alpha} a_{66}^{\alpha} - a_{46}^{\alpha} a_{64}^{\alpha} \geq 0, \quad a_{66}^{\alpha} a_{77}^{\alpha} - a_{67}^{\alpha} a_{76}^{\alpha} \geq 0 \tag{A15} \\
 \det \begin{pmatrix} a_{44}^{\alpha} & -a_{46}^{\alpha} & -a_{47}^{\alpha} \\ -a_{46}^{\alpha} & a_{66}^{\alpha} & a_{67}^{\alpha} \\ -a_{47}^{\alpha} & a_{67}^{\alpha} & a_{77}^{\alpha} \end{pmatrix} &\geq 0
 \end{aligned}$$

It is sufficient in [A15]₁₀, but not necessary, that

$$a_{46}^{\alpha} a_{47}^{\alpha} a_{67}^{\alpha} \geq \frac{1}{2} a_{66}^{\alpha} (a_{47}^{\alpha} a_{47}^{\alpha} + a_{44}^{\alpha} a_{77}^{\alpha}).$$