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Equations for reacting viscous fluids near chemical equilibrium (**)

1 - Introduction

Reaction-diffusion equations for mixtures of viscous fluids play an important role in everyday life and in modern technology. We mention specifically acid rain effects [9], the nuclear winter phenomenon [2], warming of the stratosphere [10], [6], and enzyme recovery from reacting mixtures [1], [7]. However, the equations are usually written down in an ad hoc manner and often vary considerably. Therefore, a rational derivation of a relevant system of equations would seem appropriate.

From an operative viewpoint the general theory of mixtures (cf. $[8]_{1,2}$) is much too cumbersome because of the large number of pertinent unknown fields. A reasonable approximation seems to be that of mixtures with one velocity field as in the *classical* theory of mixtures (cf. [4]). The notion of one velocity is appealing since it yields as simple a theory as possible but still retains all the features appropriate to the study in hand.

In this paper we develop a theory for a mixture, with one velocity field, of chemically reacting viscous fluids provided the reactions stay close to equilibrium. We derive the equations for the mixture and investigate the restrictions imposed by thermodynamics on the relevant coefficients. Relative to a previous

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work on the subject by Gurtin and Vargas [4] we generalize the model by letting the fluid mixture be viscous. As to the procedure we adhere to I. Müller's approach whereby the entropy flux is an unknown in the thermodynamic analysis to be characterized along with the other constitutive functions.

In 2 we develop the constitutive theory for a viscous mixture. In 3 we study the additional information gained by linearizing about a state of chemical equilibrium. Then 4 presents a simple model for a mixture of viscous fluids allowing for a Boussinesq approximation in the body force. This model is applicable to a layer close to chemical equilibrium, acted on by a gravitational force.

Throughout the article we employ standard notation. A superposed dot denotes the material time derivative, the subscripts α, β, ν, ω take the values 1 to N and label quantities of the pertinent constituent. Summation over repeated indices (α, β, ν, ω) is understood. The other subscripts denote partial derivatives. The symbols have the following meaning: ρ density of the mixture, $\boldsymbol{v}$ velocity of the mixture, c_α concentration of constituent α, θ temperature of the mixture, $\boldsymbol{T}$ stress tensor, $\boldsymbol{b}$ body force, e internal energy (per unit mass), η entropy, ψ free energy, $\boldsymbol{q}$ heat flux, r heat supply, $\boldsymbol{h}_\alpha$ relative mass flux of constituent α, m_α mass supply due to chemical reactions, $\boldsymbol{L}$ velocity gradient, $\boldsymbol{D}$ symmetric part of $\boldsymbol{L}$, $v = 1/\rho$ specific volume, $\mu_\alpha = \partial\psi/\partial c_\alpha$ chemical potential of constituent α.

2 - Constitutive theory

Consider a mixture of $N+1$ fluids. The balance equations are

$$\dot{\rho} + \rho\nabla\cdot\boldsymbol{v} = 0 \tag{2.1}$$

$$\rho\dot{c}_\alpha = -\nabla\cdot\boldsymbol{h}_\alpha + m_\alpha \qquad (\alpha = 1, \dots, N) \tag{2.2}$$

$$\rho\dot{\boldsymbol{v}} = \nabla\cdot\boldsymbol{T} + \rho\boldsymbol{b} \tag{2.3}$$

$$\rho\dot{e} = -\nabla\cdot\boldsymbol{q} + \boldsymbol{T}\cdot\boldsymbol{D} + \rho r \tag{2.4}$$

and express the balance of mass, the balance of mass for each constituent, the balance of linear momentum, and the balance of energy. To them we add the second law of thermodynamics in the form

$$\rho\dot{\eta} \geqslant -\nabla\cdot\left(\frac{\boldsymbol{q}}{\theta} + \boldsymbol{k}\right) + \frac{\rho r}{\theta}\,. \tag{2.5}$$

In terms of $\psi = e - \theta\eta$, (2.5) is conveniently rewritten in the form

$$\rho(\dot{\psi} + \eta\dot{\theta}) - \boldsymbol{T}\cdot\boldsymbol{D} - \theta\nabla\cdot\boldsymbol{k} + \frac{1}{\theta}\boldsymbol{q}\cdot\boldsymbol{g} \leqslant 0 . \tag{2.6}$$

We now develop the consequences of these relations, in the first instance for the case of a compressible mixture and then for an appropriately defined incompressible one.

2.1 - *Compressible mixture.* Denote by Λ the ordered array

$$\Lambda = (v,\ \theta,\ C,\ \boldsymbol{w},\ \boldsymbol{g},\ \boldsymbol{\Xi},\ \boldsymbol{D})$$

for which $C = (c_1, \ldots, c_N)$, $\boldsymbol{w} = \nabla v$, $\boldsymbol{g} = \nabla\theta$, $\boldsymbol{\Xi} = (\xi_1, \ldots, \xi_N)$ where $\xi = \nabla c_\alpha$.

The constitutive assumptions to be employed are that

$$\begin{array}{cccc} \psi = \hat{\psi}(\Lambda) & \boldsymbol{T} = \hat{\boldsymbol{T}}(\Lambda) & \eta = \hat{\eta}(\Lambda) & \boldsymbol{q} = \hat{\boldsymbol{q}}(\Lambda) \\ \boldsymbol{k} = \hat{\boldsymbol{k}}(\Lambda) & \boldsymbol{h}_\alpha = \hat{\boldsymbol{h}}_\alpha(\Lambda) & m_\alpha = \hat{m}_\alpha(\Lambda) . & \end{array} \tag{2.7}$$

We now examine the compatibility of the response functions (2.7) with the entropy inequality (2.6) using the standard arguments of Coleman and Noll. Upon differentiation and use of (2.2) we can write (2.6) as

$$\begin{aligned} &-\rho(\psi_\theta + \eta)\,\dot{\theta} - \rho\psi_{\boldsymbol{g}}\cdot\dot{\boldsymbol{g}} - \rho\psi_{\xi_\alpha}\cdot\dot{\xi}_\alpha - \rho\psi_{\boldsymbol{D}}\cdot\dot{\boldsymbol{D}} \\ &+[\boldsymbol{T} - \psi_v\boldsymbol{1} - \rho(\psi_{\boldsymbol{w}}\cdot\boldsymbol{w})\,\boldsymbol{1} + \rho\boldsymbol{w}\otimes\psi_{\boldsymbol{w}}]\cdot\boldsymbol{L} \\ &-(\psi_{\boldsymbol{w}}\cdot\nabla)\,\nabla\cdot\boldsymbol{v} + \nabla\cdot\boldsymbol{J} - (\,\frac{1}{\theta}\boldsymbol{q} + \boldsymbol{k})\cdot\boldsymbol{g} - m_\alpha\mu_\alpha - \boldsymbol{h}_\alpha\cdot\nabla\mu_\alpha \geqslant 0 \end{aligned} \tag{2.8}$$

where $\boldsymbol{J} = \theta\boldsymbol{k} + \mu_\alpha\boldsymbol{h}_\alpha$. Since $\boldsymbol{J} = \hat{\boldsymbol{J}}(\Lambda)$ and $\dot{\theta}$, $\dot{\boldsymbol{g}}$, $\dot{\xi}_\alpha$, $\dot{\boldsymbol{D}}$ appear linearly in (2.8) then the inequality can hold for all motions provided only that

$$\eta = -\psi_\theta \qquad \psi_{\boldsymbol{g}} = 0 \qquad \psi_{\boldsymbol{D}} = 0 \qquad \psi_{\xi_\alpha} = 0 \qquad (\alpha = 1, \ldots, N) .$$

As a consequence $\mu_\alpha = \mu_\alpha(v,\ \theta,\ C,\ \boldsymbol{w})$. Then inequality (2.8) reduces to

$$\begin{aligned} &[\boldsymbol{T} - \psi_v\boldsymbol{1} - \rho(\psi_{\boldsymbol{w}}\cdot\boldsymbol{w})\,\boldsymbol{1} + \rho\boldsymbol{w}\otimes\psi_{\boldsymbol{w}}]\cdot\boldsymbol{L} - (\,\frac{1}{\theta}\boldsymbol{q} + \boldsymbol{k} - \boldsymbol{J}_\theta + \boldsymbol{h}_\alpha\,\frac{\partial\mu_\alpha}{\partial\theta}\,)\cdot\boldsymbol{g} \\ &+(\boldsymbol{J}_{c_\alpha} - \boldsymbol{h}_\beta\,\frac{\partial\mu_\beta}{\partial c_\alpha}\,)\cdot\xi_\alpha + (\boldsymbol{J}_v - \boldsymbol{h}_\alpha\,\frac{\partial\mu_\alpha}{\partial v}\,)\cdot\boldsymbol{w} + \boldsymbol{J}_{\boldsymbol{g}}\cdot(\nabla\nabla\theta) + \boldsymbol{J}_{\xi_\alpha}\cdot(\nabla\nabla c_\alpha) \\ &+(\boldsymbol{J}_{\boldsymbol{w}} - \boldsymbol{h}_\alpha\otimes\frac{\partial\mu_\alpha}{\partial\boldsymbol{w}}\,)\cdot(\nabla\nabla v) + (\boldsymbol{J}_{\boldsymbol{D}} - \psi_{\boldsymbol{w}}\otimes\boldsymbol{1})\cdot(\nabla\boldsymbol{D}) - m_\alpha\mu_\alpha \geqslant 0 . \end{aligned}$$

The arbitrariness of the symmetric tensors $\nabla\nabla\theta$, $\nabla\nabla c_\alpha$, $\nabla\nabla v$ and of the third-order tensor $\nabla\boldsymbol{D}$ allows us to determine further consequences of the entropy inequality. The whole result is as follows.

The free energy ψ is independent of $\boldsymbol{g}$, Ξ, $\boldsymbol{D}$, namely

$$\psi = \psi(v,\ \theta,\ C,\ \boldsymbol{w}).$$

The entropy η is related to ψ by

$$\eta = -\psi_\theta\,. \tag{2.9}$$

The energy flux $\boldsymbol{J}$ due to diffusion satisfies

$$\begin{gathered}
\operatorname{sym}\boldsymbol{J}_{\boldsymbol{g}} = 0 \qquad \operatorname{sym}\boldsymbol{J}_{\xi_\alpha} = 0 \quad (\alpha = 1, \ldots, N) \\
\operatorname{sym}(\boldsymbol{J}_{\boldsymbol{w}} - \boldsymbol{h}_\alpha \otimes \frac{\partial\mu_\alpha}{\partial\boldsymbol{w}}) = 0 \qquad \boldsymbol{J}_D - \psi_w \otimes \boldsymbol{1} = 0\,.
\end{gathered} \tag{2.10}$$

The reduced entropy inequality is

$$\begin{gathered}
(\boldsymbol{T} - \psi_v\boldsymbol{1} - \rho(\psi_w \cdot \boldsymbol{w})\boldsymbol{1} + \rho\boldsymbol{w} \otimes \psi_w)\cdot\boldsymbol{L} - (\frac{1}{\theta}\boldsymbol{q} + \boldsymbol{k} - \boldsymbol{J}_\theta + \frac{\partial\mu_\alpha}{\partial\theta}\boldsymbol{h}_\alpha)\cdot\boldsymbol{g} \\
+(\boldsymbol{J}_{c_\alpha} - \frac{\partial\mu_\beta}{\partial c_\alpha}\boldsymbol{h}_\beta)\cdot\xi_\alpha + (\boldsymbol{J}_v - \boldsymbol{h}_\alpha\frac{\partial\mu_\alpha}{\partial v})\cdot\boldsymbol{w} - m_\alpha\mu_\alpha \geqslant 0\,.
\end{gathered}$$

As an aside, in view of the conditions (2.10) we can write

$$\begin{gathered}
\boldsymbol{J} = \psi_w\nabla\cdot\boldsymbol{v} + \tilde{\boldsymbol{J}}(v,\ \theta,\ C,\ \boldsymbol{w},\ \boldsymbol{g},\ \Xi) \\
\operatorname{sym}\tilde{\boldsymbol{J}}_{\boldsymbol{g}} = 0 \qquad \operatorname{sym}\tilde{\boldsymbol{J}}_{\xi_\alpha} = 0\,.
\end{gathered}$$

2.2 - *Incompressible mixture.* The main reason here for studying an incompressible mixture is the simplification introduced into the resulting model. The difficulties encountered in analysing the stability of a convection layer of a single compressible fluid (cf. [11]) are such as to motivate a study of an appropriately defined incompressible model, whenever this is possible.

We shall understand by an incompressible mixture of $N+1$ fluids, one in which the restriction $v = \text{constant}$ always holds. Hence, owing to (2.1), it follows that

$$\nabla\cdot\boldsymbol{v} = 0\,.$$

The thermodynamic analysis for an incompressible mixture follows that for a compressible one provided the constraint is taken into account. Accordingly, we consider the array

$$A_1 = (\theta,\ C,\ \boldsymbol{g},\ \boldsymbol{\Xi},\ \boldsymbol{D})$$

as the set of independent variables and then exploit the inequality

$$\rho(\dot{\psi} + \eta\dot{\theta}) - \boldsymbol{T}\cdot\boldsymbol{D} - \theta\nabla\cdot\boldsymbol{k} + \frac{1}{\theta}\boldsymbol{q}\cdot\boldsymbol{g} \leqslant 0 .$$

Letting again $\mu_\alpha = \partial\psi/\partial c_\alpha$ and $\boldsymbol{J} = \theta\boldsymbol{k} + \mu_\alpha \boldsymbol{h}_\alpha$ we may write the entropy inequality as

$$\rho(\psi_\theta + \eta)\,\dot{\theta} + \rho\psi_{\boldsymbol{g}}\cdot\dot{\boldsymbol{g}} + \rho\psi_{\xi_\alpha}\cdot\dot{\xi}_\alpha + \rho\psi_{\boldsymbol{D}}\cdot\dot{\boldsymbol{D}} - \boldsymbol{T}\cdot\boldsymbol{D} + \left(\frac{1}{\theta}\boldsymbol{q} + \boldsymbol{k} - \boldsymbol{J}_\theta + \boldsymbol{h}_\alpha \frac{\partial\mu_\alpha}{\partial\theta}\right)\cdot\boldsymbol{g}$$

$$+\left(\boldsymbol{h}_\beta \frac{\partial\mu_\beta}{\partial c_\alpha} - \boldsymbol{J}_{c_\alpha}\right)\cdot\xi_\alpha - \boldsymbol{J}_{\boldsymbol{g}}\cdot(\nabla\nabla\theta) - \boldsymbol{J}_{\xi_\alpha}\cdot(\nabla\nabla c_\alpha) - \boldsymbol{J}_{\boldsymbol{D}}\cdot(\nabla\boldsymbol{D}) + m_\alpha\mu_\alpha \leqslant 0 .$$

Making use of the arbitrariness of $\dot{\theta},\ \dot{\boldsymbol{g}},\ \dot{\xi}_\alpha,\ \dot{\boldsymbol{D}},\ \nabla\nabla c_\alpha$, and $\nabla\boldsymbol{D}$ the following deductions may be obtained.

The free energy is independent of $\boldsymbol{g},\ \boldsymbol{\Xi},\ \boldsymbol{D}$, viz.

$$\psi = \psi(\theta,\ C) .$$

The entropy η is determined by ψ as in (2.9).

The energy flux $\boldsymbol{J}$ satisfies

$$\text{(2.11)} \qquad \operatorname{sym}\boldsymbol{J}_{\boldsymbol{g}} = 0 \qquad \boldsymbol{J}_{\boldsymbol{D}} = 0 \qquad \operatorname{sym}\boldsymbol{J}_{\xi_\alpha} = 0 \quad (\alpha = 1, \dots, \mathrm{N}) .$$

The stress $\boldsymbol{T}$, to within an arbitrary pressure tensor $-p\mathbf{1}$, satisfies the reduced entropy inequality

$$\boldsymbol{T}\cdot\boldsymbol{D} + \left(\boldsymbol{J}_\theta - \frac{1}{\theta}\boldsymbol{q} - \boldsymbol{k} - \boldsymbol{h}_\alpha \frac{\partial\mu_\alpha}{\partial\theta}\right)\cdot\boldsymbol{g} + \left(\boldsymbol{J}_{c_\alpha} - \boldsymbol{h}_\beta \frac{\partial\mu_\beta}{\partial c_\alpha}\right)\cdot\xi_\alpha - \mu_\alpha m_\alpha \geqslant 0$$

for every motion of the mixture with a divergence-free velocity.

Let $\mathcal{V}$ be the vector space associated with the three-dimensional Euclidean space. An isotropic function $f\colon \mathcal{V}^M \to \mathcal{V}$ is such that $\boldsymbol{Q}f(\boldsymbol{u}_1, \dots, \boldsymbol{u}_M) = f(\boldsymbol{Q}\boldsymbol{u}_1, \dots, \boldsymbol{Q}\boldsymbol{u}_M)$ for any element $\boldsymbol{Q}$ of the full orthogonal group. A theorem by Gurtin [3] proves that if $\operatorname{sym}\partial f/\partial\boldsymbol{u}_i = 0$ $(i = 1, \dots, M)$ then f necessarily vanishes. Accordingly, if $\boldsymbol{J}$ is supposed isotropic then by (2.11) we conclude that $\boldsymbol{J}$ vanishes. Incidentally, if $\boldsymbol{J} = 0$ then Müller's entropy extra flux $\boldsymbol{k}$ is related to the relative mass fluxes $\boldsymbol{h}_\alpha$ by

$$\boldsymbol{k} = -\frac{1}{\theta}\mu_\alpha \boldsymbol{h}_\alpha \,.$$

3 - Linearized theory near a thermochemical equilibrium state

Although 2 gives much information on the constitutive forms for the general case, the resulting equations are still formidable from an analytical point of view. Therefore we now present a simplified theory for which the constitutive functions are linear in their respective arguments.

The theory is elaborated for successively stronger states of equilibrium. The procedure is performed in **3.1-3.2** where the development is for a compressible mixture, the incompressible case being immediately obtained by formally setting $\dot{v} = 0$.

3.1 - *Equilibrium states.* A homogeneous state $\bar{\boldsymbol{\Lambda}}$ is defined to be a solution of the governing equations of the form

$$\bar{\boldsymbol{\Lambda}} = (\bar{v},\ \bar{\theta},\ \bar{C},\ 0,\ 0,\ 0,\ 0)\,;$$

i.e. a state in which $\boldsymbol{w} = 0$, $\boldsymbol{g} = 0$, $\boldsymbol{\Xi} = 0$, $\boldsymbol{D} = 0$. A routine calculation shows that there exist constants $\varkappa$, λ_α, ζ, λ'_α, $\lambda_{\alpha\beta}$, ω_α and functions μ, λ, m^0_α, m^1_α of v, θ, C such that

$$\psi = \psi(v,\ \theta,\ C) \qquad \boldsymbol{q} = -\varkappa \boldsymbol{g} - \lambda_\alpha \xi_\alpha - \zeta \boldsymbol{w} + O(\varepsilon^2)$$

$$\boldsymbol{h}_\alpha = \lambda'_\alpha \boldsymbol{g} - \lambda_{\alpha\beta}\psi_\beta - \omega_\alpha \boldsymbol{w} + O(\varepsilon^2) \qquad m_\alpha = m^0_\alpha + m^1_\alpha \operatorname{tr}\boldsymbol{D} + O(\varepsilon^2)$$

(3.1)

$$\boldsymbol{T} = (\psi_v + m^1_\alpha \mu_\alpha)\mathbf{1} + 2\mu \boldsymbol{D} + \lambda(\operatorname{tr}\boldsymbol{D})\mathbf{1} + O(\varepsilon^2) \qquad \theta \boldsymbol{k} = -\mu_\alpha \boldsymbol{h}_\alpha$$

$$\mu \geqslant 0\,, \qquad 3\lambda + 2\mu \geqslant 0 \qquad \frac{1}{\theta}\tilde{\boldsymbol{q}}\cdot \boldsymbol{g} + \boldsymbol{h}_\alpha \cdot \nabla \mu_\alpha + m^0_\alpha \mu_\alpha \leqslant 0$$

as $\varepsilon = |\boldsymbol{\Lambda} - \bar{\boldsymbol{\Lambda}}| \to 0$; here $\tilde{\boldsymbol{q}} = \boldsymbol{q} - \mu_\alpha \boldsymbol{h}_\alpha$ and

$$|\boldsymbol{\Lambda} - \bar{\boldsymbol{\Lambda}}|^2 = |v - \bar{v}|^2 + |\theta - \bar{\theta}|^2 + |\boldsymbol{w}|^2 + |\boldsymbol{g}|^2 + \sum_\alpha [(c_\alpha - \bar{c}_\alpha)^2 + |\xi_\alpha|^2] + \boldsymbol{D}\cdot\boldsymbol{D}\,.$$

A homogeneous state for which the further restriction

$$m_\alpha(\overline{\boldsymbol{\Lambda}}) = 0$$

holds is called an *equilibrium state*. Expanding $m_\alpha(\boldsymbol{\Lambda})$ near an equilibrium state yields

$$m_\alpha = -\tau_{\alpha\beta}(c_\beta - \bar{c}_\beta) - \delta_\alpha(\theta - \bar{\theta}) - \delta'_\alpha(v - \bar{v}) - \sigma_\alpha \operatorname{tr} \boldsymbol{D} + O(\varepsilon^2)$$

where $\tau_{\alpha\beta}$, δ_α, δ'_α and σ_α are constants.

On account of the constitutive equations (3.1) the balance equations (2.1), (2.2) reduce upon linearization to

$$\bar{\rho}\dot{v} = \nabla \cdot \boldsymbol{v} \tag{3.2}$$

$$\bar{\rho}\dot{c}_\alpha = \lambda_{\alpha\beta}\Delta c_\beta + \lambda'_\alpha \Delta\theta + \omega_\alpha \Delta v + m_\alpha \tag{3.3}$$

while the energy equation (2.4) simplifies to

$$a_1\dot{\theta} + a_2\dot{v} + d_\alpha \dot{c}_\alpha = \varkappa\Delta c_\beta + \lambda_\beta \Delta c_\beta + \zeta\Delta v + \bar{\rho}r$$

where

$$a_1 = \bar{\rho}\bar{\theta}\eta_\theta = \bar{\rho}e_\theta \qquad a_2 = \bar{\rho}\bar{\theta}\eta_v = \bar{\rho}\bar{\theta}p_\theta \qquad d_\alpha = \bar{\rho}\bar{\theta}\eta_{c_\alpha} = -\bar{\rho}\bar{\theta}\frac{\partial\mu_\alpha}{\partial\theta}$$

the derivatives being evaluated at $\overline{\boldsymbol{\Lambda}}$. Here $p = -\psi_v$ is the pressure.

3.2 - *Strong equilibrium states*. For inviscid mixtures, the condition $m_\alpha\bar{\mu}_\alpha = O(\varepsilon^2)$, where $\bar{\mu}_\alpha = \mu_\alpha(\overline{\boldsymbol{\Lambda}})$, holds in equilibrium states. Accordingly, the following definition introduces an additional restriction on such states.

A strong equilibrium state is an equilibrium state for which

$$m_\alpha\bar{\mu}_\alpha = O(\varepsilon^3)\,. \tag{3.4}$$

In the neighbourhood of an equilibrium state $\overline{\boldsymbol{\Lambda}}$

$$\mu_\alpha = \bar{\mu}_\alpha + a_{\alpha\beta}(c_\beta - \bar{c}_\beta) + \gamma_\alpha(v - \bar{v}) + \chi_\alpha(\theta - \bar{\theta}) + O(\varepsilon^2) \tag{3.5}$$

where the derivatives

$$a_{\alpha\beta} = \frac{\partial\mu_\alpha}{\partial c_\beta} \qquad \gamma_\alpha = \frac{\partial\mu_\alpha}{\partial v} \qquad \chi_\alpha = \frac{\partial\mu_\alpha}{\partial\theta}$$

are evaluated at $\bar{A}$. Hence it follows that

$$\nabla\mu_\alpha = a_{\alpha\beta}\,\xi_\beta + \gamma_\alpha\,\boldsymbol{w} + \chi_\alpha\,\boldsymbol{g}\,. \tag{3.6}$$

We assume the matrix $(a_{\alpha\beta})$ is invertible and it is then possible to solve (3.5) for $c_\beta - \bar{c}_\beta$ in terms of $\mu_\alpha - \bar{\mu}_\alpha$, $v - \bar{v}$, $\theta - \bar{\theta}$ and (3.6) for ξ_β in terms of $\nabla\mu_\alpha$, $\boldsymbol{w}$, $\boldsymbol{g}$. It is at this point the strong equilibrium condition is utilized. For, substitution into $(3.1)_7$ and taking account of (3.4) gives

$$\boldsymbol{q} = -k\boldsymbol{g} - l_\alpha\nabla\mu_\alpha + O(\varepsilon^2) \qquad \boldsymbol{h}_\alpha = -l'_\alpha\,\boldsymbol{g} - l_{\alpha\beta}\nabla\mu_\beta + O(\varepsilon^2) \qquad \overline{m}_\alpha = -t_{\alpha\beta}\,(\mu_\beta - \bar{\mu}_\beta) + O(\varepsilon^2)$$

together with the positive definiteness of the matrices $(t_{\alpha\beta})$ and

$$\begin{pmatrix} k/\bar{\theta} & l_1/\bar{\theta} & \cdots & l_N/\bar{\theta} \\ l'_1 & l_{11} & \cdots & l_{1N} \\ \cdot & \cdot & \cdots & \cdot \\ l'_N & l_{N1} & \cdots & l_{NN} \end{pmatrix}.$$

In view of (3.6) the coefficients are related to those in $(3.1)_{2,3}$ as follows

$$\begin{array}{lll} \varkappa = k + l_\alpha\chi_\alpha & \lambda_\alpha = l_\beta\,a_{\beta\alpha} & \zeta = l_\alpha\gamma_\alpha \\ \lambda'_\alpha = l'_\alpha + l_{\alpha\beta}\chi_\beta & \lambda_{\alpha\beta} = l_{\alpha\nu}\,a_{\nu\beta} & \omega_\alpha = l_{\alpha\beta}\gamma_\beta \\ \tau_{\alpha\beta} = t_{\alpha\nu}\,a_{\nu\beta} & \delta_\alpha = t_{\alpha\beta}\chi_\beta & \delta'_\alpha = t_{\alpha\beta}\gamma_\beta\,. \end{array}$$

We shall further assume that the matrix $(a_{\alpha\beta})$ is positive definite; this is a reasonable assumption as Truesdell and Toupin ([12], § 158) show such a conclusion is valid for an inviscid mixture.

4 - A simplified model

We return now to an incompressible mixture and suppose $\rho = \bar{\rho}$ *except in the body force term*. This is analogous to the Boussinesq approximation for a non-reacting fluid and allows application to convection problems in a layer. The stress, in (3.1), in equilibrium is a hydrostatic pressure which we denote by $-\bar{p}\mathbf{1}$. From equation (2.3) we find, for $\boldsymbol{v} = 0$,

$$\nabla\bar{p} = \bar{\rho}\boldsymbol{b}\,.$$

For a layer we may take the components of $\boldsymbol{b}$ as $(0,\ 0,\ -g)$ where g is the gravity constant. In our Bousinnesq approximation we assume the perturbation ς to

ρ in the body force depends only on θ, c_α and so

$$b(\rho + \varsigma) = b\bar{\rho}[1 - \alpha(\theta - \bar{\theta}) + \beta_\nu(c_\nu - \bar{c}_\nu)] \qquad \text{where}$$

$$\alpha = -\frac{1}{\bar{\rho}}\rho_\theta(\bar{\Lambda}) \qquad \beta_\nu = \frac{1}{\bar{\rho}}\rho_{c_\nu}(\bar{\Lambda}).$$

Then, collecting together equations (2.3), (3.2) and (3.3), the system of equations valid near chemical equilibrium is

$$\bar{\rho}\boldsymbol{v}_{,t} = -\nabla\pi + \mu\Delta\boldsymbol{v} - \bar{\rho}\boldsymbol{b}(\alpha\vartheta + \beta_\omega\phi_\omega) \tag{4.1}$$

$$\nabla\cdot\boldsymbol{v} = 0 \tag{4.2}$$

$$\bar{\rho}\phi_{\nu,t} = \lambda_{\nu\omega}\Delta\phi_\omega + \lambda'_\nu\Delta\vartheta - \tau_{\nu\omega}\phi_\omega - \delta_\nu\vartheta \tag{4.3}$$

$$a_1\vartheta_{,t} + d_\omega\phi_{\omega,t} = \tilde{\varkappa}\Delta\vartheta + \tilde{\lambda}_\omega\Delta\phi_\omega \tag{4.4}$$

where $\vartheta = \theta - \bar{\theta}$, $\phi_\omega = c_\omega - \bar{c}_\omega$, $\pi = p - \bar{p}$ and $_{,t}$ denotes the partial time derivative. Moreover $\tilde{\varkappa} = \varkappa - \bar{\mu}_\alpha\lambda'_\alpha$, $\tilde{\lambda}_\omega = \lambda_\omega + \bar{\mu}_\alpha\lambda_{\alpha\omega}$.

The term in λ'_ν in (4.3) represents the Soret effect while the λ_ω terms in (4.4) are a Dufour effect. Such effects are important in liquid metals and in gases (see, e.g., Hurle and Jakeman [5]) but a simpler model valid in many practical situations may be achieved by their neglect. To do this we may set $\lambda'_\nu = 0$ and select $\tilde{\lambda}_\nu = d_\nu\lambda_{\nu\omega}/\bar{\rho}$. The system then reduces to (4.1), (4.2) and

$$\bar{\rho}\phi_{\nu,t} = \lambda_{\nu\omega}\Delta\phi_\omega - \tau_{\nu\omega}\phi_\omega - \delta_\nu\vartheta \qquad a_1\vartheta_{,t} = \varkappa\Delta\vartheta + \frac{d_\nu\tau_{\nu\omega}}{\bar{\rho}}\phi_\omega + \frac{d_\nu\delta_\nu}{\bar{\rho}}\vartheta.$$

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Abstract

The paper derives equations for a mixture of chemically reacting viscous fluids near chemical equilibrium. The theory is developed using continuum thermodynamics of diffusive mixtures allowing for one velocity field only.

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