On the Thermodynamics of Chemically Reacting Fluid Mixtures

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Introduction

After a long history of special theories of diffusion and chemical reactions, TRUESDELL [1957] established the basic thermomechanical balance laws for mixtures,[1] and BOWEN,[2] MÜLLER [1968], and TRUESDELL [1968] proposed workable forms for the second law. Using this framework together with the COLEMAN-NOLL [1963] interpretation of the second law, MÜLLER [1968][3] developed a theory of non-reacting fluid mixtures,[4] and BOWEN [1969] established a general theory for mixtures of chemically reacting elastic materials.[5]

In this paper I discuss chemically reacting, but inviscid, fluid mixtures. Among the new results I establish are the following:

(i) The stress-diffusion matrix is symmetric. The stress diffusion matrix is that matrix whose (α, β) entry is the derivative of the stress vector of constituent α with respect to the velocity of constituent β.

(ii) When the diffusion velocity $\boldsymbol{u}_\alpha$ of constituent α is small, the diffusive energy flux is approximated by its classical counterpart $\sum \mu_\alpha \rho_\alpha \boldsymbol{u}_\alpha$, where μ_α is the chemical potential and ρ_α the density of α.

(iii) The elasticity matrix corresponding to a strong equilibrium state is symmetric. This matrix plays a crucial role in the linearized theory and in wave propagation studies.

(iv) When the diffusion velocities and the gradients of density and temperature are small, and when the underlying state is one of strong equilibrium, to within second order terms the heat flux depends only on the temperature gradient and the diffusion velocities, and the mass supply (due to chemical reactions) depends only on the chemical potentials.

For convenience, I omit smoothness hypotheses; it will be clear from the context what these ought to be.

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[1] See also NACHBAR, WILLIAMS, & PENNER [1959], KELLY [1964], and GREEN & NAGHDI [1969].

[2] See TRUESDELL [1969] (Footnote on p. 88).

[3] Thermodynamic theories were put forth before 1968 by ERINGEN & INGRAM [1965], GREEN & NAGHDI [1965, 1967], CROCHET & NAGHDI [1966, 1967], GREEN & STEEL [1966], Mills [1966, 1967], BOWEN [1967], INGRAM & ERINGEN [1967], and ATKIN [1967]. As MÜLLER [1968] and TRUESDELL [1969] have pointed out, all of the above theories suffer from serious defects.

[4] See also DUNWOODY & MÜLLER [1968], GREEN & NAGHDI [1968], DORIA [1969], CRAINE, GREEN & NAGHDI [1970], and DUNWOODY [1970].

[5] See also BOWEN & WIESE [1969], GREEN & NAGHDI [1969], BOWEN & GARCIA [1970].

1. Preliminary Definitions. Terminology

Throughout this paper $\mathbb{R}$, $\mathbb{R}^+$, and $\mathscr{V}$ denote, respectively, the reals, the strictly positive reals, and the vector space associated with three-dimensional Euclidean space. Given a (second-order) tensor $\boldsymbol{S}$, $\boldsymbol{S}^T$ designates its transpose and $\operatorname{sym} \boldsymbol{S} = \frac{1}{2}(\boldsymbol{S} + \boldsymbol{S}^T)$ its symmetric part. We denote the tensor product of two vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ by $\boldsymbol{u} \otimes \boldsymbol{v}$.

The mixtures we study will have N constituents; for convenience, we identify the set of constituents with the set $\{1, \ldots, N\}$. Further, the letters α and β will always denote constituents, and we write $\sum f_\alpha$ and $\sum_\alpha f_\alpha$ for $\sum_{\alpha=1}^{N} f_\alpha$. We use the following notation:

ρ_α is the *mass density* of constituent α,

$\boldsymbol{v}_\alpha$ is the *velocity* of α.

In addition, we write

$$\begin{aligned} \rho &= \sum \rho_\alpha, & c_\alpha &= \frac{\rho_\alpha}{\rho}, \\ \boldsymbol{v} &= \sum c_\alpha \boldsymbol{v}_\alpha, & \boldsymbol{u}_\alpha &= \boldsymbol{v}_\alpha - \boldsymbol{v}; \end{aligned} \tag{1.1}$$

ρ is the *total mass density*, c_α the *concentration* of α, $\boldsymbol{v}$ the *velocity of the mixture*, and $\boldsymbol{u}_\alpha$ the *diffusion velocity* of α. Clearly,

$$\sum c_\alpha = 1, \qquad \sum c_\alpha \boldsymbol{u}_\alpha = \boldsymbol{0}. \tag{1.2}$$

Since we are dealing with a fluid mixture, it is more convenient to work with the spatial description of any given motion. Thus a motion is specified by prescribing $\boldsymbol{v}_\alpha(\boldsymbol{x}, t)$ and $\rho_\alpha(\boldsymbol{x}, t)$ as functions of spatial position $\boldsymbol{x} \in \mathscr{R}$ and time t; here $\mathscr{R}$ denotes a fixed region of space occupied by the mixture during some time interval.

We write grad and div for the spatial gradient and spatial divergence, *i.e.*, the gradient and divergence with respect to $\boldsymbol{x}$ holding t fixed. Given a scalar field $f(\boldsymbol{x}, t)$ and a vector field $\boldsymbol{f}(\boldsymbol{x}, t)$, we define the material time derivatives $\dot{f}(\boldsymbol{x}, t)$ and $\dot{\boldsymbol{f}}(\boldsymbol{x}, t)$ through

$$\dot{f} = \frac{\partial f}{\partial t} + (\operatorname{grad} f) \cdot \boldsymbol{v}, \qquad \dot{\boldsymbol{f}} = \frac{\partial \boldsymbol{f}}{\partial t} + (\operatorname{grad} \boldsymbol{f}) \boldsymbol{v}; \tag{1.3}$$

we then have the identity

$$\operatorname{grad} \dot{f} = \dot{\overline{\operatorname{grad} f}} + (\operatorname{grad} \boldsymbol{v})^T \operatorname{grad} f. \tag{1.4}$$

2. Basic Laws

For the basic laws of our theory we postulate the following:

balance of mass for each constituent

$$\dot{\rho}_\alpha + \rho_\alpha \operatorname{div} \boldsymbol{v}_\alpha + \boldsymbol{u}_\alpha \cdot \operatorname{grad} \rho_\alpha = \rho c_\alpha^+, \tag{2.1}$$

balance of momentum for each constituent

$$\rho_\alpha \dot{\boldsymbol{v}}_\alpha + \rho_\alpha (\operatorname{grad} \boldsymbol{v}_\alpha) \boldsymbol{u}_\alpha = \operatorname{div} \boldsymbol{T}_\alpha + \rho_\alpha \boldsymbol{b}_\alpha + \rho_\alpha \boldsymbol{l}_\alpha^+ \tag{2.2}$$

balance of energy for the mixture[1]

$$\rho\dot{e} = -\operatorname{div}(\boldsymbol{q}+\boldsymbol{j}) + \sum(\boldsymbol{T}_\alpha - \rho_\alpha \boldsymbol{u}_\alpha \otimes \boldsymbol{u}_\alpha)\cdot \operatorname{grad}\boldsymbol{v} + \sum \rho_\alpha \boldsymbol{b}_\alpha \cdot \boldsymbol{u}_\alpha + \rho r, \tag{2.3}$$

growth of entropy for the mixture

$$\rho\dot{s} \geqq -\operatorname{div}\left(\frac{\boldsymbol{q}}{\theta}\right) + \frac{\rho r}{\theta}. \tag{2.4}$$

Here

$\boldsymbol{T}_\alpha$ is the *stress tensor* for α,

$\boldsymbol{b}_\alpha$ is the *body force* for α,

$\boldsymbol{l}_\alpha^+$ is the *momentum supply* for α,

c_α^+ is the *mass supply* for α,

e is the *internal energy*,

$\boldsymbol{q}$ is the *heat flux*,

$\boldsymbol{j}$ is the *diffusive energy flux*,

r is the *heat supply*,

s is the *entropy*,

θ is the *temperature*.

We also postulate that

$$\sum c_\alpha^+ = 0, \qquad \sum(c_\alpha \boldsymbol{l}_\alpha^+ + c_\alpha^+ \boldsymbol{u}_\alpha) = 0; \tag{2.5}$$

then (1.1), (2.1), and (2.2) imply the laws of mass and momentum balance for the mixture:

$$\begin{gathered} \dot{\rho} + \rho \operatorname{div}\boldsymbol{v} = 0, \\ \rho\dot{\boldsymbol{v}} = \operatorname{div}(\boldsymbol{T} - \sum \rho_\alpha \boldsymbol{u}_\alpha \otimes \boldsymbol{u}_\alpha) + \sum \rho_\alpha \boldsymbol{b}_\alpha, \end{gathered} \tag{2.6}$$

where

$$\boldsymbol{T} = \sum \boldsymbol{T}_\alpha \tag{2.7}$$

is (the inner part of) the *total stress*.

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[1] In MÜLLER's [1968] theory the term $\boldsymbol{j}$ is not present in the energy equation and the term $\boldsymbol{q}/\theta$ in the entropy inequality is replaced by an arbitrary entropy flux $\boldsymbol{\Phi}$. To see that there is no contradiction between MÜLLER's theory and the one presented here, let $\boldsymbol{q}'$ denote the heat flux in the former. If we define a new "heat flux" $\boldsymbol{q}$ by $\boldsymbol{q} = \theta\boldsymbol{\Phi}$ and a diffusive energy flux $\boldsymbol{j}$ by $\boldsymbol{j} = \boldsymbol{q}' - \boldsymbol{q}$, then MÜLLER's equations (2.16), (3.4) reduce to my (2.3), (2,4). The difference is simply a matter of taste. Indeed, within the context of the classical theory of mixtures I would view the quantity $\sum \mu_\alpha \rho_\alpha \boldsymbol{u}_\alpha$, where μ_α is the chemical potential of α, as a flux of energy (as does ECKART [1940]), while MÜLLER would view $-(\sum \mu_\alpha \rho_\alpha \boldsymbol{u}_\alpha)/\theta$ as a flux of entropy (as do MEIXNER & REIK [1959] and DE GROOT & MAZUR [1962]). I take the point of view that the "heat flux" is that vector field which when divided by the temperature gives the entropy flux.

The theory presented here falls within BOWEN's [1969] framework provided we take $\boldsymbol{j}$ to be a certain specified linear function of the diffusion velocities.

If we use (2.2) to eliminate $\boldsymbol{b}_\alpha$ in (2.3), we find, with the aid of (1.1), (1.2), (2.1), and $(2.6)_1$,

$$\rho \dot{e}_I = -\operatorname{div}(\boldsymbol{q}+\boldsymbol{k}) + \sum \boldsymbol{T}_\alpha \cdot \operatorname{grad} \boldsymbol{v}_\alpha - \sum \boldsymbol{n}_\alpha \cdot \boldsymbol{u}_\alpha + \rho r, \tag{2.8}$$

where

$$e_I = e - \tfrac{1}{2} \sum c_\alpha \boldsymbol{u}_\alpha^2 \tag{2.9}$$

is the inner part of the internal energy and

$$\boldsymbol{k} = \boldsymbol{j} + \sum (\boldsymbol{T}_\alpha^T - \tfrac{1}{2} \rho_\alpha \boldsymbol{u}_\alpha^2 \mathbf{1}) \boldsymbol{u}_\alpha, \qquad \boldsymbol{n}_\alpha = \rho_\alpha \boldsymbol{l}_\alpha^+ + \tfrac{1}{2} \rho c_\alpha^+ \boldsymbol{u}_\alpha. \tag{2.10}$$

If we define (the inner part of) the *free energy* by

$$\psi = e_I - \theta s, \tag{2.11}$$

then (2.4) and (2.8) yield the *reduced dissipation inequality*:

$$\rho(\dot{\psi} + s\dot{\theta}) - \sum \boldsymbol{T}_\alpha \cdot \operatorname{grad} \boldsymbol{v}_\alpha + \operatorname{div} \boldsymbol{k} + \sum \boldsymbol{n}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{\theta} \boldsymbol{q} \cdot \operatorname{grad} \theta \leqq 0. \tag{2.12}$$

3. Constitutive Assumptions

We consider a mixture defined by constitutive equations in which

$$\psi,\ \boldsymbol{T}_\alpha,\ s,\ \boldsymbol{q}, \boldsymbol{j},\ \boldsymbol{l}_\alpha^+,\ c_\alpha^+ \quad \textit{are functions of} \quad (\vec{\rho}, \theta, \operatorname{grad} \vec{\rho}, \operatorname{grad} \theta, \vec{\boldsymbol{v}}), \tag{3.1}$$

where, for convenience, we have used the notation

$$\vec{\rho} = (\rho_1, \ldots, \rho_N), \qquad \operatorname{grad} \vec{\rho} = (\operatorname{grad} \rho_1, \ldots, \operatorname{grad} \rho_N), \qquad \vec{\boldsymbol{v}} = (\boldsymbol{v}_1, \ldots, \boldsymbol{v}_N). \tag{3.2}$$

We assume that the response functions are isotropic and that c_α^+ and $\boldsymbol{l}_\alpha^+$ are consistent with (2.5). Further, in order to make our theory consistent with material frame indifference, we require that

$$f(\vec{\rho}, \theta, \operatorname{grad} \vec{\rho}, \operatorname{grad} \theta, \vec{\boldsymbol{v}}) = f(\vec{\rho}, \theta, \operatorname{grad} \vec{\rho}, \operatorname{grad} \theta, \vec{\boldsymbol{v}} + \vec{\boldsymbol{a}}) \tag{3.3}$$

whenever f is one of the response functions in (3.1) and $\vec{\boldsymbol{a}} = (\boldsymbol{a}, \ldots, \boldsymbol{a})$. Clearly, (3.3) implies that

$$\sum \frac{\partial f}{\partial \boldsymbol{v}_\alpha} = \mathbf{0} \tag{3.4}$$

and that

$$f(\vec{\rho}, \theta, \operatorname{grad} \vec{\rho}, \operatorname{grad} \theta, \vec{\boldsymbol{v}}) = f(\vec{\rho}, \theta, \operatorname{grad} \vec{\rho}, \operatorname{grad} \theta, \vec{\boldsymbol{u}}), \tag{3.5}$$

where

$$\vec{\boldsymbol{u}} = (\boldsymbol{u}_1, \ldots, \boldsymbol{u}_N) \tag{3.6}$$

with $\boldsymbol{u}_\alpha$ the diffusion velocity $(1.1)_4$.

We also assume that:[1]

(A) Given a point $\boldsymbol{x}_0 \in \mathscr{R}$, a neighborhood $\mathscr{P}_0$ of $\boldsymbol{x}_0$, an initial density distribution $\vec{\rho}_0 : \mathscr{P}_0 \to (\mathbb{R}^+)^N$, a time interval $[0, t_0)$, a temperature field $\theta : \mathscr{P}_0 \times [0, t_0) \to \mathbb{R}^+$, and a velocity distribution $\vec{\boldsymbol{v}} : \mathscr{P}_0 \times [0, t_0) \to \mathscr{V}^N$; there exists a $\mathscr{P} \subset \mathscr{P}_0$ with $\boldsymbol{x}_0 \in \mathscr{P}$, a

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[1] BOWEN [1969] was the first to notice than an assumption of this type is necessary when chemical reactions are present. See also COLEMAN & GURTIN [1967], who utilize an assumption of this type in a slightly different context.

$\tau\in(\theta, t_0)$, and a solution $\vec{\rho}\colon \mathscr{P}\times[0,\tau)\to(\mathbb{R}^+)^N$ of (2.1), *i.e.* of

$$\dot{\rho}_\alpha+\rho_\alpha \operatorname{div}\boldsymbol{v}_\alpha+\boldsymbol{u}_\alpha(\vec{\rho},\vec{\boldsymbol{v}})\cdot\operatorname{grad}\rho_\alpha=\rho(\vec{\rho})\,c_\alpha^+(\vec{\rho},\theta,\operatorname{grad}\vec{\rho},\operatorname{grad}\theta,\vec{\boldsymbol{v}}) \tag{3.7}$$

on $\mathscr{P}\times(0,\tau)$, such that

$$\vec{\rho}(\boldsymbol{x},0)=\vec{\rho}_0 \quad \text{for } \boldsymbol{x}\in\mathscr{P}. \tag{3.8}$$

Of course, in (3.7) $\boldsymbol{u}_\alpha(\vec{\rho},\boldsymbol{v})$ and $\rho(\vec{\rho})$ are given by (1.1).

An array $(\vec{\rho},\theta,\vec{\boldsymbol{v}},\psi,\vec{\boldsymbol{T}},s,\boldsymbol{q},\boldsymbol{j},\vec{\boldsymbol{l}}^+,\vec{c}^+)$ of fields on $\mathscr{P}\times[0,\tau)$ (with values in appropriate spaces) will be called a *constitutive process* if it is consistent with the constitutive assumption (3.1) and balance of mass (2.1). Here $\vec{\boldsymbol{T}}=(\boldsymbol{T}_1,\dots,\boldsymbol{T}_N)$, $\vec{\boldsymbol{l}}^+=(\boldsymbol{l}_1^+,\dots,\boldsymbol{l}_N^+)$, and $\vec{c}^+=(c_1^+,\dots,c_N^+)$. Assumption (A) insures that given $\boldsymbol{x}_0$, $\vec{\rho}_0$, $\vec{\boldsymbol{v}}$, and θ there exists an associated constitutive process in some neighborhood of $\boldsymbol{x}_0$.

Note that by (1.1), $(2.10)_1$, and (3.1),

$$\boldsymbol{k}=\boldsymbol{k}(\vec{\rho},\theta,\operatorname{grad}\vec{\rho},\operatorname{grad}\theta,\vec{\boldsymbol{v}}).$$

For convenience, we introduce the following notation:

$$\begin{aligned}\operatorname{div}_0\boldsymbol{k}&=\sum\frac{\partial\boldsymbol{k}}{\partial\rho_\alpha}\cdot\operatorname{grad}\rho_\alpha+\frac{\partial\boldsymbol{k}}{\partial\theta}\cdot\operatorname{grad}\theta,\\ \operatorname{div}_1\boldsymbol{k}&=\sum\frac{\partial\boldsymbol{k}}{\partial(\operatorname{grad}\rho_\alpha)}\cdot\operatorname{grad}^2\rho_\alpha+\frac{\partial\boldsymbol{k}}{\partial(\operatorname{grad}\theta)}\cdot\operatorname{grad}^2\theta;\end{aligned} \tag{3.9}$$

thus

$$\operatorname{div}\boldsymbol{k}=\operatorname{div}_0\boldsymbol{k}+\operatorname{div}_1\boldsymbol{k}+\sum\left(\frac{\partial\boldsymbol{k}}{\partial\boldsymbol{v}_\alpha}\right)^T\cdot\operatorname{grad}\boldsymbol{v}_\alpha. \tag{3.10}$$

4. Consequences of the Second Law

Given a constitutive process[1] (2.2) and (2.3) can be used to determine the body forces $\boldsymbol{b}_\alpha$ and the heat supply r necessary to sustain the process. On the other hand, the inequality (2.4)—or equivalently (2.12)—will be satisfied in every process if and only if certain restrictions are placed on the response functions. The next theorem lists these restrictions.[2]

Theorem 4.1. *A necessary and sufficient condition that every constitutive process obey the reduced dissipation inequality* (2.12) *is that the following four statements be true:*

(i) *The total stress is a pressure:*

$$\boldsymbol{T}=-p\boldsymbol{1}. \tag{4.1}$$

(ii) *ψ, p, and s are independent of* grad $\vec{\rho}$, grad θ, *and* $\vec{\boldsymbol{v}}$*:*

$$\psi=\psi(\vec{\rho},\theta),\qquad p=p(\vec{\rho},\theta),\qquad s=s(\vec{\rho},\theta); \tag{4.2}$$

moreover,

$$p=\rho\sum\rho_\alpha\frac{\partial\psi}{\partial\rho_\alpha},\qquad s=-\frac{\partial\psi}{\partial\theta}. \tag{4.3}$$

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[1] Note that, by definition, the mass balance relations (2.1) are satisfied by every constitutive process.

[2] *Cf.* MÜLLER [1968, § 5], DORIA [1969, § 5], BOWEN & WIESE [1969, § 5], BOWEN [1969, § 6].

(iii) *The constituent stress* $\boldsymbol{T}_\alpha$ *is given by*

$$\boldsymbol{T}_\alpha = \left(\frac{\partial \boldsymbol{k}}{\partial \boldsymbol{v}_\alpha}\right)^T - \rho\,\rho_\alpha \frac{\partial \psi}{\partial \rho_\alpha}\mathbf{1}. \tag{4.4}$$

(iv) *In every constitutive process*

$$\begin{gathered}\operatorname{div}_0 \boldsymbol{k} + \rho \sum \frac{\partial \psi}{\partial \rho_\alpha}\left[\rho c_\alpha^+ - \boldsymbol{u}_\alpha \cdot \operatorname{grad}\rho_\alpha\right] + \sum \boldsymbol{n}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{\theta}\boldsymbol{q}\cdot \operatorname{grad}\theta \leqq 0,\\ \operatorname{div}_1 \boldsymbol{k} = 0.\end{gathered} \tag{4.5}$$

Proof. The proof of sufficiency follows upon direct substitution. To establish the necessity of (i)–(iv), we assume that every constitutive process obeys (2.12), or equivalently, in view of the constitutive assumption (3.1), balance of mass (2.1), and (3.10),

$$\begin{aligned}&\rho\left(\frac{\partial \psi}{\partial \theta} + s\right)\dot{\theta} - \sum\left[\rho\,\rho_\alpha \frac{\partial \psi}{\partial \rho_\alpha}\mathbf{1} + \boldsymbol{T}_\alpha - \left(\frac{\partial \boldsymbol{k}}{\partial \boldsymbol{v}_\alpha}\right)^T\right]\cdot \operatorname{grad}\boldsymbol{v}_\alpha\\ &\quad + \rho\left[\sum \frac{\partial \psi}{\partial(\operatorname{grad}\rho_\alpha)}\cdot \dot{\overline{\operatorname{grad}\rho_\alpha}} + \frac{\partial \psi}{\partial(\operatorname{grad}\theta)}\cdot \dot{\overline{\operatorname{grad}\theta}} + \sum \frac{\partial \psi}{\partial \boldsymbol{v}_\alpha}\cdot \dot{\boldsymbol{v}}_\alpha\right]\\ &\quad + \rho \sum \frac{\partial \psi}{\partial \rho_\alpha}\left[\rho c_\alpha^+ - \boldsymbol{u}_\alpha \cdot \operatorname{grad}\rho_\alpha\right]\\ &\quad + \operatorname{div}_0 \boldsymbol{k} + \operatorname{div}_1 \boldsymbol{k} + \sum \boldsymbol{n}_\alpha \cdot \boldsymbol{u}_\alpha + \frac{1}{\theta}\boldsymbol{q}\cdot \operatorname{grad}\theta \leqq 0.\end{aligned} \tag{4.6}$$

It follows from Lemma 6.1 that $\dot{\theta}$, $\dot{\overline{\operatorname{grad}\rho_\alpha}}$, $\dot{\overline{\operatorname{grad}\theta}}$, $\dot{\boldsymbol{v}}_\alpha$, and $\operatorname{grad}\boldsymbol{v}_\alpha$ can be specified arbitrarily in (4.6), and this observation yields $(4.2)_{1,3}$, $(4.3)_2$, and (4.4). Next, it follows from (2.10) and (3.1) that (3.3) (and hence (3.4)) holds with $f = \boldsymbol{k}$; thus, if we sum (4.4) from 1 to α, we are led to (4.1) and $(4.3)_1$. Next, $\operatorname{div}_1 \boldsymbol{k}$ is the only term in (4.6) involving second gradients; thus it follows from $(3.9)_2$ and Lemma 6.1 that

$$\operatorname{sym}\left(\frac{\partial \boldsymbol{k}}{\partial(\operatorname{grad}\rho_\alpha)}\right) = \operatorname{sym}\left(\frac{\partial \boldsymbol{k}}{\partial(\operatorname{grad}\theta)}\right) = \mathbf{0}, \tag{4.7}$$

which implies $(4.5)_2$. Finally, (4.1)–(4.4), $(4.5)_2$, and (4.6) yield $(4.5)_1$. □

We assume for the remainder of the paper that (i)–(iv) *of Theorem* 4.1 *hold.*

Let $\boldsymbol{n}$ be a unit vector. The quantity

$$\boldsymbol{t}_\alpha(\boldsymbol{n}) = \boldsymbol{T}_\alpha \boldsymbol{n} \tag{4.8}$$

is the stress vector for constituent α (corresponding to the unit normal $\boldsymbol{n}$). By (3.1) $\boldsymbol{t}_\alpha(\boldsymbol{n})$ is a function of $(\vec{\rho}, \theta, \operatorname{grad}\vec{\rho}, \operatorname{grad}\theta, \vec{\boldsymbol{v}})$. We call the matrix $\left\|\frac{\partial \boldsymbol{t}_\alpha(\boldsymbol{n})}{\partial \boldsymbol{v}_\beta}\right\|$ (with tensor entries) the *stress-diffusion matrix.*

Theorem 4.2. *The stress-diffusion matrix is symmetric*; i.e.

$$\frac{\partial \boldsymbol{t}_\alpha(\boldsymbol{n})}{\partial \boldsymbol{v}_\beta} = \left(\frac{\partial \boldsymbol{t}_\beta(\boldsymbol{n})}{\partial \boldsymbol{v}_\alpha}\right)^T \tag{4.9}$$

for every unit vector $\boldsymbol{n}$ *and all constituents* α, β.

Proof. Let $\kappa = \boldsymbol{k}\cdot\boldsymbol{n}$. Then (4.4) implies

$$\boldsymbol{t}_\alpha(\boldsymbol{n}) = \frac{\partial\kappa}{\partial\boldsymbol{v}_\alpha} - \rho\rho_\alpha\frac{\partial\psi}{\partial\rho_\alpha}\boldsymbol{n}; \tag{4.10}$$

since the second term (4.10) is independent of $\vec{\boldsymbol{v}}$, if we differentiate $\boldsymbol{t}_\alpha(\boldsymbol{n})$ with respect to $\boldsymbol{v}_\beta$, we are led at once to (4.9). □

We call the quantity

$$\mu_\alpha = \mu_\alpha(\vec{\rho}, \theta) = \rho\left[\frac{\partial\psi}{\partial\rho_\alpha} - \frac{1}{N}\sum_\beta\frac{\partial\psi}{\partial\rho_\beta}\right] \tag{4.11}$$

the *chemical potential* of α; note that

$$\sum\mu_\alpha = 0. \tag{4.12}$$

In view of $(2.5)_1$ and (4.11), we can rewrite (4.5) as follows:

$$\operatorname{div}_0\boldsymbol{k} + \sum\left(\boldsymbol{n}_\alpha - \rho\frac{\partial\psi}{\partial\rho_\alpha}\operatorname{grad}\rho_\alpha\right)\cdot\boldsymbol{u}_\alpha + \frac{1}{\theta}\boldsymbol{q}\cdot\operatorname{grad}\theta + \rho\sum\mu_\alpha c_\alpha^+ \leqq 0. \tag{4.13}$$

Further, by (1.1), $(1.2)_2$, (2.1), $(2.5)_1$, (2.9), (2.11), (4.1)–(4.3), and (4.11), the energy equation (2.3) takes the form

$$\begin{aligned}\rho\Big(\theta\dot{s} + \tfrac{1}{2}\sum\dot{\overline{c_\alpha u_\alpha^2}}\Big) = &-\operatorname{div}\Big(\boldsymbol{q} + \boldsymbol{j} - \sum\mu_\alpha\rho_\alpha\boldsymbol{u}_\alpha\Big) - \sum(\rho_\alpha\boldsymbol{u}_\alpha\otimes\boldsymbol{u}_\alpha)\cdot\operatorname{grad}\boldsymbol{v}\\ &+\sum\rho_\alpha\boldsymbol{u}_\alpha\cdot(\boldsymbol{b}_\alpha - \operatorname{grad}\mu_\alpha) - \rho\sum\mu_\alpha c_\alpha^+ + \rho r.\end{aligned} \tag{4.14}$$

In the classical theory of fluid mixtures the diffusive energy flux has the form $\boldsymbol{j} = \sum\mu_\alpha\rho_\alpha\boldsymbol{u}_\alpha$, so that the divergence term in (4.14) reduces to $-\operatorname{div}\boldsymbol{q}$. The next theorem shows that in the general theory the diffusive energy flux is approximated by its classical counterpart.

Theorem 4.3. *The diffusive energy flux* $\boldsymbol{j} = \boldsymbol{j}(\vec{\rho}, \theta, \operatorname{grad}\vec{\rho}, \operatorname{grad}\theta, \vec{\boldsymbol{v}})$ *vanishes when the diffusion velocities vanish. Moreover,*

$$\boldsymbol{j} = \sum\mu_\alpha\rho_\alpha\boldsymbol{u}_\alpha + O(|\vec{\boldsymbol{u}}|^2) \quad \text{as} \quad \vec{\boldsymbol{u}}\to\vec{\boldsymbol{0}}. \tag{4.15}$$
[1]

Proof. Let $\Omega = (\vec{\rho}, \theta, \operatorname{grad}\vec{\rho}, \operatorname{grad}\theta)$. Since the material is isotropic, it follows from $(2.10)_1$ that $\boldsymbol{k} = \boldsymbol{k}(\Omega, \vec{\boldsymbol{v}})$ is an isotropic function. Thus, by (4.7) and Lemma 6.2,

$$\boldsymbol{k}(\Omega, \vec{\boldsymbol{0}}) = \boldsymbol{0}, \tag{4.16}$$
[2]

and we conclude from $(2.10)_1$ that

$$\boldsymbol{j}(\Omega, \vec{\boldsymbol{0}}) = \boldsymbol{0}. \tag{4.17}$$

Next, by $(1.1)_{3,4}$,

$$\frac{\partial\boldsymbol{u}_\beta}{\partial\boldsymbol{v}_\alpha} = (\delta_{\alpha\beta} - c_\alpha)\boldsymbol{1}; \tag{4.18}$$

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[1] In our definition of the chemical potentials $\mu_\alpha = \dfrac{\partial\psi}{\partial\rho_\alpha} + \nu$, with ν chosen so that (4.12) holds. In view of $(1.2)_2$, the result (4.15) is independent of the particular choice of the function ν.

[2] For binary mixtures DORIA [1969, Eq. (6.35)] established the stronger result that $\boldsymbol{k} = \varphi\boldsymbol{u}$ $(\boldsymbol{u} = \boldsymbol{u}_1 = -\boldsymbol{u}_2)$ with $\varphi = \varphi(\rho_1, \rho_2, \theta, |\boldsymbol{u}|)$, which implies, by (4.4) and (4.2), that $\boldsymbol{T}_\alpha$ is independent of grad ρ and grad θ; unfortunately, these results are restricted to binary mixtures.

thus if we differentiate $(2.10)_1$ with respect to $\boldsymbol{v}_\alpha$ and use (2.7), (4.1), and (4.4), we arrive at

$$\frac{\partial j}{\partial \boldsymbol{v}_\alpha}=\left(\rho\rho_\alpha\frac{\partial\psi}{\partial\rho_\alpha}-c_\alpha p\right)\mathbf{1} \quad \text{when} \quad \vec{\boldsymbol{v}}=\vec{\mathbf{0}}. \tag{4.19}$$

Therefore

$$j(\Omega,\vec{\boldsymbol{v}})=\sum\left(\rho\rho_\alpha\frac{\partial\psi}{\partial\rho_\alpha}-c_\alpha p\right)\boldsymbol{v}_\alpha+O(|\vec{\boldsymbol{v}}|^2) \quad \text{as} \quad \vec{\boldsymbol{v}}\to\vec{\mathbf{0}}. \tag{4.20}$$

But by (3.5), $j(\Omega,\vec{\boldsymbol{v}})=j(\Omega,\vec{\boldsymbol{u}})$; thus, by $(1.2)_2$,

$$j(\Omega,\vec{\boldsymbol{u}})=\sum\rho\rho_\alpha\frac{\partial\psi}{\partial\rho_\alpha}\boldsymbol{u}_\alpha+O(|\vec{\boldsymbol{u}}|^2) \quad \text{as} \quad \vec{\boldsymbol{u}}\to\vec{\mathbf{0}}; \tag{4.21}$$

and this result, in conjunction with $(1.2)_2$ and (4.11), implies the desired result (4.15). □

5. Results near Equilibrium[1]

Let $(\vec{\rho}_0,\theta_0)$ be given, and, for convenience, let

$$\begin{gathered}\boldsymbol{f}_\alpha=\operatorname{grad}\rho_\alpha,\quad \vec{\boldsymbol{f}}=\operatorname{grad}\vec{\rho},\quad \boldsymbol{g}=\operatorname{grad}\theta,\\ \mathscr{s}=(\vec{\rho},\theta,\vec{\boldsymbol{f}},\boldsymbol{g},\vec{\boldsymbol{v}}),\quad \mathscr{s}_0=(\vec{\rho}_0,\theta_0,\vec{\mathbf{0}},\mathbf{0},\vec{\mathbf{0}}).\end{gathered} \tag{5.1}$$

We call $\mathscr{s}_0$ an *equilibrium state* provided

$$c_\alpha^+(\mathscr{s}_0)=0 \tag{5.2}$$

for every constituent α. Let h denote the left-hand side of (4.5), or equivalently, of (4.13). It then follows from $(3,9)_1$, (3.1), (2.10), and (4.11) that

$$h=h(\mathscr{s})=\sum\frac{\partial k}{\partial\rho_\alpha}\cdot\boldsymbol{f}_\alpha+\frac{\partial k}{\partial\theta}\cdot\boldsymbol{g}+\sum\left(\boldsymbol{n}_\alpha-\rho\frac{\partial\psi}{\partial\rho_\alpha}\boldsymbol{f}_\alpha\right)\cdot\boldsymbol{u}_\alpha+\frac{1}{\theta}\boldsymbol{q}\cdot\boldsymbol{g}+\rho\sum\mu_\alpha c_\alpha^+, \tag{5.3}$$

and it is clear from Theorem 4.1 and Lemma 6.1 that

$$h(\mathscr{s})\leqq 0 \tag{5.4}$$

for every $\mathscr{s}$ in the domain of the response functions. If $\mathscr{s}_0$ is an equilibrium state, then (5.2) and (5.3) imply that $h(\mathscr{s}_0)=0$, so that

$$h(\mathscr{s})\ \textit{is a maximum at}\ \mathscr{s}=\mathscr{s}_0. \tag{5.5}$$

Thus

$$\left(\frac{\partial h}{\partial\rho_\alpha}\right)_0=\left(\frac{\partial h}{\partial\theta}\right)_0=0, \tag{5.6}$$

where the subscript "0" indicates that the corresponding function is to be evaluated at $\mathscr{s}=\mathscr{s}_0$, and we have the following result:

$$\sum_\alpha\mathring{\mu}_\alpha\left(\frac{\partial c_\alpha^+}{\partial\rho_\beta}\right)_0=\sum\mathring{\mu}_\alpha\left(\frac{\partial c_\alpha^+}{\partial\theta}\right)_0=0. \tag{5.7}$$ [2]

---

[1] In the absence of chemical reactions ($c_\alpha^+\equiv 0$) *every* $\mathscr{s}_0$ of the form $(5.1)_5$ is a strong equilibrium state; thus all of the results of this section apply also to diffusion without chemical reactions.

[2] *Cf.* BOWEN [1969, Eq. (7.19)].

Here $\overset{\circ}{\mu}_\alpha = \mu_\alpha(\vec{\rho}_0, \theta_0)$. In addition, since c_α^+ is an isotropic function,

$$\left(\frac{\partial c_\alpha^+}{\partial \boldsymbol{f}_\beta}\right)_0 = \left(\frac{\partial c_\alpha^+}{\partial \boldsymbol{g}}\right)_0 = \left(\frac{\partial c_\alpha^+}{\partial \boldsymbol{v}_\beta}\right)_0 = \boldsymbol{0}. \tag{5.8}$$

It follows from (5.2), (5.7), and (5.8) that

$$\sum c_\alpha^+(\mathscr{s})\, \overset{\circ}{\mu}_\alpha = O(|\mathscr{s} - \mathscr{s}_0|^2) \quad \text{as} \quad \mathscr{s} \to \mathscr{s}_0, \tag{5.9}$$

where

$$|\mathscr{s} - \mathscr{s}_0| = |\vec{\rho} - \vec{\rho}_0| + |\theta - \theta_0| + |\vec{\boldsymbol{f}}| + |\boldsymbol{g}| + |\vec{\boldsymbol{v}}|. \tag{5.10}$$

We say that an equilibrium state $\mathscr{s}_0$ is *strong* provided

$$\sum c_\alpha^+(\mathscr{s})\, \overset{\circ}{\mu}_\alpha = O(|\mathscr{s} - \mathscr{s}_0|^3) \quad \text{as} \quad \mathscr{s} \to \mathscr{s}_0. \tag{5.11}$$

Remark. To see that this is a natural generalization of the usual notion of strong equilibrium, we assume, for the time being, that there are R independent chemical reactions:

$$c_\alpha^+ = \sum_{r=1}^{R} \nu_{\alpha r} J_r, \tag{5.12}$$

where $\nu_{\alpha r}$ is the stoichiometric coefficient of constituent α in the reaction r divided by the molecular mass of α, and $J_r = J_r(\mathscr{s})$ is the reaction rate of reaction r. The chemical affinity of reaction r is defined by

$$A_r = A_r(\vec{\rho}, \theta) = \sum_\alpha \nu_{\alpha r}\, \mu_\alpha(\vec{\rho}, \theta). \tag{5.13}$$

In this instance it is customary to call $\mathscr{s}_0$ a "strong equilibrium state" provided[1]

$$J_r(\mathscr{s}_0) = A_r(\vec{\rho}_0, \theta_0) = 0. \tag{5.14}$$

In view of (5.12), (5.14) implies (5.2). Further, by (5.12)–(5.14),

$$\sum c_\alpha^+(\mathscr{s})\, \overset{\circ}{\mu}_\alpha \equiv 0. \tag{5.15}$$

Thus our notion of a strong equilibrium state is somewhat weaker than the standard definition. For all of our results it suffices to use the definition containing (5.11).

With a view toward determining the behavior of the response functions near equilibrium, we first determine some of the more obvious consequences of isotropy. First of all there exist scalar functions $p_\alpha(\vec{\rho}, \theta)$ such that

$$\boldsymbol{T}_\alpha(\vec{\rho}, \theta, \vec{\boldsymbol{0}}, \boldsymbol{0}, \vec{\boldsymbol{0}}) = -p_\alpha(\vec{\rho}, \theta)\boldsymbol{1}. \tag{5.16}$$

Next, if $\mathscr{s}_0$ is an equilibrium state, then, clearly,

$$z(\mathscr{s}_0) = \left(\frac{\partial z}{\partial \rho_\alpha}\right)_0 = \left(\frac{\partial z}{\partial \theta}\right)_0 = \boldsymbol{0} \quad \text{for } z = \boldsymbol{q} \text{ or } \boldsymbol{l}_\beta^+. \tag{5.17}$$

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[1] TRUESDELL [1969, p. 107]. See also BOWEN [1969, p. 121].

Further, there exist scalars $\kappa, \kappa_\alpha, \gamma_{\alpha\beta}, \gamma_\alpha$, and $\lambda_{\alpha\beta}$ such that

$$\begin{gathered}\left(\frac{\partial \mathbf{q}}{\partial \mathbf{g}}\right)_0 = -\kappa \mathbf{1}, \qquad \left(\frac{\partial \mathbf{q}}{\partial \mathbf{v}_\alpha}\right)_0 = -\kappa_\alpha \mathbf{1} \\ \left(\rho_\alpha \frac{\partial \mathbf{l}_\alpha^+}{\partial \mathbf{v}_\beta}\right)_0 = -\gamma_{\alpha\beta} \mathbf{1}, \qquad \left(\rho_\alpha \frac{\partial \mathbf{l}_\alpha^+}{\partial \mathbf{g}}\right)_0 = -\gamma_\alpha \mathbf{1}, \\ \left(\frac{1}{\rho_\alpha} \frac{\partial p_\alpha}{\partial \rho_\beta}\right)_0 \mathbf{1} - \left(\frac{\partial \mathbf{l}_\alpha^+}{\partial \mathbf{f}_\beta}\right)_0 = \lambda_{\alpha\beta} \mathbf{1},\end{gathered} \tag{5.18}$$

and, in view of (2.5), (3.4), (4.18), and (5.2),

$$\sum \kappa_\alpha = \sum_\alpha \gamma_{\alpha\beta} = \sum_\beta \gamma_{\alpha\beta} = \sum \gamma_\alpha = 0. \tag{5.19}$$

We call κ the *conductivity* and $\|\gamma_{\alpha\beta}\|$ the *momentum supply matrix.* The matrix $\|\lambda_{\alpha\beta}\|$ is of importance in applications. Indeed, if we consider the *linearized* system of momentum equations appropriate for small departures from the equilibrium state $\mathfrak{s}_0$, then (after dividing by $\rho_{\alpha 0}$) the term involving grad $\rho_{\alpha 0}$ in the α-th equation has the form $\sum_\beta \lambda_{\alpha\beta} \operatorname{grad} \rho_\beta$. For this reason we call $\|\lambda_{\alpha\beta}\|$ the *elasticity matrix.*[1]

Theorem 5.1. *Let $\mathfrak{s}_0$ be a strong equilibrium state. Then*

$$\lambda_{\beta\alpha} = \left(\frac{\partial^2 (\rho\psi)}{\partial \rho_\alpha \partial \rho_\beta}\right)_0, \tag{5.20}$$

$$\left(\frac{\partial \mathbf{q}}{\partial \mathbf{f}_\alpha}\right)_0 = \mathbf{0}, \tag{5.21}$$

$$\frac{\kappa}{\theta_0} a^2 + \sum_\beta \left[\frac{\kappa_\beta}{\theta_0} + \gamma_\beta + \left(\frac{\partial p_\beta}{\partial \theta}\right)_0 + \left(\rho \rho_\beta \frac{\partial s}{\partial \rho_\beta}\right)_0\right] a w_\beta + \sum_{\alpha,\beta} \gamma_{\alpha\beta} w_\alpha w_\beta \geqq 0 \tag{5.22}$$

$$\textit{for all } a, w_1, \dots, w_N \in \mathbb{R};$$

so that, in particular, the conductivity $\kappa \geqq 0$ and the momentum supply matrix $\|\gamma_{\alpha\beta}\|$ is positive semi-definite.

Proof. By (4.11) and (5.11),

$$\left(\frac{\partial^2 (\sum \mu_\alpha c_\alpha^+)}{\partial \mathbf{a}\, \partial \mathbf{d}}\right)_0 = \mathbf{0} \quad \textit{whenever } \mathbf{a} = \mathbf{f}_\beta, \mathbf{g}, \textit{ or } \mathbf{v}_\beta \textit{ and } \mathbf{d} = \mathbf{f}_\gamma, \mathbf{g}, \textit{ or } \mathbf{v}_\gamma. \tag{5.23}$$

Next, it follows from (4.16), (5.3), and (5.23) that

$$\left(\frac{\partial^2 h}{\partial \mathbf{f}_\alpha \partial \mathbf{f}_\beta}\right)_0 = \mathbf{0}. \tag{5.24}$$

---

[1] In fact, GURTIN [1971] has shown that in the purely mechanical theory the linearized equations for the densities have the form

$$\rho_\alpha = \rho_{0\alpha} \sum_\beta \lambda_{\alpha\beta} \Delta \rho_\beta + \text{terms involving } \dot{\rho}_\beta \text{ and } \operatorname{div} \mathbf{b}_\beta.$$

Thus the elasticity matrix plays an essential role when studying the propagation of small-amplitude disturbances.

Thus, in view of (5.5),

$$\left(\frac{\partial^2 h}{\partial \boldsymbol{f}_\alpha \partial \boldsymbol{g}}\right)_0 = \left(\frac{\partial^2 h}{\partial \boldsymbol{f}_\alpha \partial \boldsymbol{v}_\beta}\right)_0 = \mathbf{0}. \tag{5.25}$$

The first of (5.25), in conjunction with (5.3), (4.16), and (5.23), yields (5.21). On the other hand, the second of (5.25), (5.3), and (5.23) imply

$$\left(\frac{\partial^2 \boldsymbol{k}}{\partial \rho_\alpha \partial \boldsymbol{v}_\beta}\right)_0^T + \sum_\gamma \left(\frac{\partial \boldsymbol{u}_\gamma}{\partial \boldsymbol{v}_\beta}\right)_0^T \left(\frac{\partial \boldsymbol{n}_\gamma}{\partial \boldsymbol{f}_\alpha}\right)_0 - \left(\rho \frac{\partial \psi}{\partial \rho_\alpha}\right)_0 \left(\frac{\partial \boldsymbol{u}_\alpha}{\partial \boldsymbol{v}_\beta}\right)_0^T = \mathbf{0}. \tag{5.26}$$

By $(2.5)_2$, $(2.10)_2$, and (5.2),

$$\left(\frac{\partial \boldsymbol{n}_\alpha}{\partial \boldsymbol{a}}\right)_0 = \left(\rho_\alpha \frac{\partial \boldsymbol{l}_\alpha^+}{\partial \boldsymbol{a}}\right)_0 \quad \textit{and} \quad \sum \left(\frac{\partial \boldsymbol{n}_\alpha}{\partial \boldsymbol{a}}\right)_0 = \mathbf{0} \quad \textit{whenever } \boldsymbol{a} = \boldsymbol{f}_\beta, \boldsymbol{g}, \textit{or } \boldsymbol{v}_\beta, \tag{5.27}$$

and (4.4), (4.18), (5.16), $(5.18)_5$, (5.26), and (5.27) yield, after some manipulation, the result (5.20).

Next, by (5.5),

$$\boldsymbol{a} \cdot \left(\frac{\partial^2 h}{\partial \boldsymbol{g}^2}\right)_0 \boldsymbol{a} + \sum_\beta \boldsymbol{a} \cdot \left(\frac{\partial^2 h}{\partial \boldsymbol{v}_\beta \partial \boldsymbol{g}}\right)_0 \boldsymbol{w}_\beta + \sum_{\alpha,\beta} \boldsymbol{w}_\alpha \cdot \left(\frac{\partial^2 h}{\partial \boldsymbol{v}_\beta \partial \boldsymbol{v}_\alpha}\right)_0 \boldsymbol{w}_\beta \leqq 0 \tag{5.28}$$

for all vectors $\boldsymbol{a}, \boldsymbol{w}_1, \dots, \boldsymbol{w}_N$. If we take $\boldsymbol{a} = a\boldsymbol{e}$ and $\boldsymbol{w}_\alpha = w_\alpha \boldsymbol{e}$ in (5.28), where $\boldsymbol{e}$ is a unit vector, and use (4.3), (4.4), (4.16), (4.18), (5.3), (5.16), (5.18), (5.23), and (5.27), we are led to (5.22). □

As a direct consequence of (5.20) we have the following important result.

Corollary 5.1. *Let $\mathscr{s}_0$ be a strong equilibrium state. Then the elasticity matrix is symmetric:*

$$\lambda_{\alpha\beta} = \lambda_{\beta\alpha}. \tag{5.29}$$

The next corollary follows from $(1.1)_4$, (5.17)–(5.19), and (5.21); it asserts that near a strong equilibrium state to within terms of $O(|\mathscr{s} - \mathscr{s}_0|^2)$ $\boldsymbol{q}$ depends linearly on grad θ and $\vec{\boldsymbol{u}}$.

Corollary 5.2. *Let $\mathscr{s}_0$ be a strong equilibrium state. Then*

$$\boldsymbol{q} = -\kappa \boldsymbol{g} - \sum \kappa_\alpha \boldsymbol{u}_\alpha + O(|\mathscr{s} - \mathscr{s}_0|^2) \quad \textit{as} \quad \mathscr{s} \to \mathscr{s}_0, \tag{5.30}$$[1]

where $\boldsymbol{q} = \boldsymbol{q}(\mathscr{s})$.

In view of (1.1), we can take $\rho, c_1, \dots, c_N$ as independent variables in place of $\rho_1, \dots, \rho_N$, *i.e.*, *e.g.*,

$$\mu_\alpha(\rho_1, \dots, \rho_N, \theta) = \mu_\alpha(c_1 \rho, \dots, c_N \rho, \theta) = \mu_\alpha(\rho, \theta, c_1, \dots, c_N). \tag{5.31}$$

By $(1.2)_1$ and (4.12), the vectors $\vec{c} = (c_1, \dots, c_N)$ and $\vec{\mu} = (\mu_1, \dots, \mu_N)$ both lie on planes in $\mathbb{R}^N$ of dimension $N-1$. We assume that the mapping

$$\vec{c} \mapsto \vec{\mu}(\rho, \theta, \vec{c}) \tag{5.32}$$

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[1] *Cf.* MÜLLER [1968, Eq. $(7.28)_1$], DORIA [1969, Eq. (7.31)], BOWEN & GARCIA [1970, Eq. (6.14)]. All of the above treat diffusion without chemical reactions.

is invertible in some neighborhood of $\mathfrak{s}_0$. Then in this neighborhood we can express the mass supply as follows:

$$c_\alpha^+ = c_\alpha^+(\rho, \theta, \vec{\mu}, \vec{f}, g, \vec{v}). \tag{5.33}$$

Let

$$\tau_{\alpha\beta} = -\left(\frac{\partial c_\alpha^+}{\partial \mu_\beta}\right)_0; \tag{5.34}$$[1]

we call $\|\tau_{\alpha\beta}\|$ the *mass supply matrix*. The next theorem shows that to within terms of $O(|\mathfrak{s}-\mathfrak{s}_0|^2)$ c_α^+ depends only on $\mu_1, \ldots, \mu_N$.

Theorem 5.2. *Let $\mathfrak{s}_0$ be a strong equilibrium state and assume that the mapping (5.32) is invertible in some neighborhood of $\mathfrak{s}_0$. Then*

$$c_\alpha^+ = -\sum_\beta \tau_{\alpha\beta}(\mu_\beta - \mathring{\mu}_\beta) + O(|\mathfrak{s}-\mathfrak{s}_0|^2), \tag{5.35}$$

where $c_\alpha^+ = c_\alpha^+(\mathfrak{s})$. Moreover, the mass supply matrix $\|\tau_{\alpha\beta}\|$ is positive semi-definite and

$$\sum_\alpha \mathring{\mu}_\alpha \tau_{\alpha\beta} = 0. \tag{5.36}$$

Proof. First, since c_α^+ is isotropic,

$$\left(\frac{\partial c_\alpha^+}{\partial f_\beta}\right)_0 = \left(\frac{\partial c_\alpha^+}{\partial g}\right)_0 = \left(\frac{\partial c_\alpha^+}{\partial v_\beta}\right)_0 = \mathbf{0}. \tag{5.37}$$

If

$$\vec{f} = \vec{0}, \quad g = 0, \quad \vec{v} = \vec{0}, \tag{5.38}$$

then, letting

$$\begin{aligned} &\mu_\alpha' = \mu_\alpha - \mathring{\mu}_\alpha, \quad \rho' = \rho - \rho_0, \quad \theta' = \theta - \theta_0, \\ &\varepsilon = \sum |\mu_\alpha'| + |\rho'| + |\theta'|, \end{aligned} \tag{5.39}$$

we conclude from (5.2), (5.3), (5.4), (5.11), (5.33), and (5.34) that

$$\begin{aligned} 0 &\geq \sum c_\alpha^+ \mu_\alpha = \sum c_\alpha^+ \mu_\alpha' + O(\varepsilon^3) \\ &= \sum_{\alpha,\beta} \left[-\tau_{\alpha\beta}\mu_\beta' + \left(\frac{\partial c_\alpha^+}{\partial \rho}\right)_0 \rho' + \left(\frac{\partial c_\alpha^+}{\partial \theta}\right)_0 \theta'\right] \mu_\alpha' + O(\varepsilon^3) \end{aligned} \tag{5.40}$$

as $\varepsilon \to 0$. Thus

$$\left(\frac{\partial c_\alpha^+}{\partial \rho}\right)_0 = \left(\frac{\partial c_\alpha^+}{\partial \theta}\right)_0 = 0 \tag{5.41}$$

and $\|\tau_{\alpha\beta}\|$ must be positive semi-definite. Finally, the Taylor expansion of (5.33) about $\mathfrak{s}_0$ reduces to (5.35) when account is taken of (5.2), (5.37), and (5.41). □

6. Two Lemmas

Lemma 6.1. *Let $\mathfrak{s}^* = (\vec{\rho}^*, \theta^*, \vec{f}^*, g^*, \vec{v}^*)$ be an arbitrary element in the domain of the response functions. Let $\mathbf{x}_0 \in \mathscr{R}$; $\omega \in \mathbb{R}$; $\mathbf{a}_\alpha$, $\mathbf{d}_\alpha$, $\mathbf{b} \in \mathscr{V}$; and suppose that $\mathbf{F}_\alpha$, $\mathbf{G}$, and $\mathbf{L}_\alpha$ are tensors with $\mathbf{F}_\alpha$ and $\mathbf{G}$ symmetric. Then there exists a constitutive process*

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[1] The derivative $\left(\frac{\partial c_\alpha^+}{\partial \mu_1}, \ldots, \frac{\partial c_\alpha^+}{\partial \mu_N}\right)$ lies in the "tangent space" $\{(\varphi_1, \ldots, \varphi_N) \in \mathbb{R}^N \mid \sum \varphi_\alpha = 0\}$.

whose domain contains $(x_0, 0)$ *such that when* $x = x_0$ *and* $t = 0$:

$$\begin{gathered}
\mathscr{s} \equiv (\vec{\rho}, \theta, \operatorname{grad}\vec{\rho}, \operatorname{grad}\theta, \vec{v}) = \mathscr{s}^*, \\
\dot{\theta} = \omega, \quad \dot{v}_\alpha = a_\alpha, \quad \overset{\bullet}{\overline{\operatorname{grad}\rho_\alpha}} = d_\alpha, \quad \overset{\bullet}{\overline{\operatorname{grad}\theta}} = b, \\
\operatorname{grad}^2 \rho_\alpha = F_\alpha, \quad \operatorname{grad}^2 \theta = G, \quad \operatorname{grad} v_\alpha = L_\alpha.
\end{gathered} \tag{6.1}$$

Proof. Let v^* denote the mixture velocity corresponding to $\vec{v}^* = (v_1^*, \ldots, v_N^*)$ and $\vec{\rho}^* = (\rho_1^*, \ldots, \rho_N^*)$ in the sense of $(1.1)_3$, let

$$r = x - x_0, \tag{6.2}$$

and let

$$\begin{aligned}
\theta(x, t) &= \theta^* + t[\omega - g^* \cdot v^*] + [g^* + t(b - G v^*)] \cdot r + \tfrac{1}{2} r \cdot G r, \\
v_\alpha(x, t) &= v_\alpha^* + t[a_\alpha - L_\alpha v^*] + L_\alpha r + \tfrac{1}{2} r^2 e_\alpha, \\
\rho_{0\alpha}(x, t) &= \rho_\alpha^* + f_\alpha \cdot r + \tfrac{1}{2} r \cdot F_\alpha r,
\end{aligned} \tag{6.3}$$

where e_α is, as yet, unspecified. Then, in view of (1.3), θ and $\vec{v}$ satisfy $(6.1)_{1,2,3,5,7,8}$. Further, since θ^* and ρ_α^* are strictly positive, there exists a neighborhood $\mathscr{P}_0$ of x_0 and a $t_0 > 0$ such that $\theta > 0$ on $\mathscr{P}_0 \times [0, t_0)$ and $\rho_{0\alpha} > 0$ on $\mathscr{P}_0$. Thus we conclude from assumption (A) and the ensuing discussion that there exists a neighborhood $\mathscr{P} \subset \mathscr{P}_0$ of x_0, a time $\tau \in (0, t_0)$, and a constitutive process on $\mathscr{P} \times [0, \tau)$ corresponding to θ, $\vec{v}$, and $\vec{\rho}_0$. Moreover, (3.8) and $(6.3)_3$ imply that the corresponding density field $\vec{\rho}$ obeys $(6.1)_{1,6}$. Thus to complete the proof we only need to establish $(6.1)_4$. By (2.1), (1.1), and (3.1), it is clear that $\operatorname{grad} \dot{\rho}_\alpha + \rho_\alpha \operatorname{grad} \operatorname{div} v_\alpha$ can be considered a function of ($\mathscr{s}$, $\operatorname{grad}^2 \vec{\rho}$, $\operatorname{grad}^2 \theta$, $\operatorname{grad} \vec{v}$); let λ denote the value of this function at $\mathscr{s} = \mathscr{s}^*$, $\operatorname{grad}^2 \rho_\alpha = F_\alpha$, $\operatorname{grad}^2 \theta = G$, $\operatorname{grad} v_\alpha = L_\alpha$ (*i.e.* the value when $x = x_0$, $t = 0$). Then, letting $L = \operatorname{grad} v(x_0, 0)$, we conclude from (1.4) and $(6.1)_1$ that

$$\overset{\bullet}{\overline{\operatorname{grad}\rho_\alpha}}(x_0, 0) = -\rho_\alpha^* \operatorname{grad} \operatorname{div} v_\alpha(x_0, 0) + \lambda - L^T f_\alpha^*. \tag{6.4}$$

But by $(6.3)_2$,

$$\operatorname{grad} \operatorname{div} v_\alpha(x_0, 0) = e_\alpha; \tag{6.5}$$

thus $(6.1)_4$ will be satisfied provided we take

$$e_\alpha = \frac{1}{\rho_\alpha^*} [\lambda - d_\alpha^* - L^T f_\alpha^*]. \quad \square \tag{6.6}$$

Let $\mathscr{O}$ denote the orthogonal group. A function $f: \mathscr{V}^M \to \mathscr{V}$ is *isotropic* provided

$$f(Q\mathbf{w}) = Q f(\mathbf{w}) \tag{6.7}$$

for every $\mathbf{w} = (w_1, \ldots, w_M) \in \mathscr{V}^M$ and every $Q \in \mathscr{O}$, where

$$Q\mathbf{w} = (Q w_1, \ldots, Q w_M). \tag{6.8}$$

Lemma 6.2.[1] *Let* $f\colon \mathscr{V}^M \to \mathscr{V}$ *be an isotropic function of class* C^3, *and assume that for every* $\mathbf{w} \in \mathscr{V}^M$ *and every* $m \in \{1, \ldots, M\}$ *the tensor* $\dfrac{\partial f(\mathbf{w})}{\partial \mathbf{w}_m}$ *is skew. Then* $f \equiv 0$.

Proof. Choose an orthonormal basis for $\mathscr{V}$, and let $f\langle i\rangle$ and $w_m\langle i\rangle$ $(i=1,2,3)$ denote the corresponding components of f and $\mathbf{w}_m$. By hypothesis,

$$\frac{\partial f\langle i\rangle}{\partial w_m\langle j\rangle} = -\frac{\partial f\langle j\rangle}{\partial w_m\langle i\rangle}, \tag{6.9}$$

so that

$$\frac{\partial f\langle i\rangle}{\partial w_m\langle i\rangle} = 0. \tag{6.10}$$

Equations (6.9) and (6.10) imply that

$$\frac{\partial^2 f\langle i\rangle}{\partial w_m\langle j\rangle\,\partial w_n\langle j\rangle} = -\frac{\partial^2 f\langle j\rangle}{\partial w_m\langle j\rangle\,\partial w_n\langle i\rangle} = 0; \tag{6.11}$$

hence

$$\frac{\partial^3 f\langle i\rangle}{\partial w_m\langle j\rangle\,\partial w_n\langle k\rangle\,\partial w_p\langle l\rangle} = 0, \tag{6.12}$$

since two of i, j, k, and l must coincide. Therefore f must have the form

$$f(\mathbf{w}) = f(\mathbf{0}) + F(\mathbf{w}) + G(\mathbf{w}, \mathbf{w}), \tag{6.13}$$

where $F\colon \mathscr{V}^M \to \mathscr{V}$ is linear and $G\colon \mathscr{V}^M \times \mathscr{V}^M \to \mathscr{V}$ is symmetric and bilinear. It follows from (6.13) and (6.7) with $\mathbf{Q} = -\mathbf{1}$ that $f(\mathbf{0}) = 0$ and $G = \mathbf{0}$; therefore

$$f(\mathbf{w}) = F(\mathbf{w}) = \sum_{m=1}^{M} \mathbf{F}_m \mathbf{w}_m, \tag{6.14}$$

where each $\mathbf{F}_m$ is a tensor. Further,

$$\mathbf{F}_m = \frac{\partial f(\mathbf{w})}{\partial \mathbf{w}_m}, \tag{6.15}$$

so that $\mathbf{F}_m$ is skew. Finally, by (6.7) and (6.14),

$$\mathbf{Q}\mathbf{F}_m = \mathbf{F}_m \mathbf{Q} \tag{6.16}$$

for every $\mathbf{Q} \in \mathscr{O}$, and the only skew tensor with this property is $\mathbf{F}_m = \mathbf{0}$. □

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[1] For $M=3$ this theorem is a corollary of a result obtained by DORIA [1969, § 6] using different methods. See also MÜLLER [1968, § 6]. When I first established this theorem I was unaware of DORIA's result.

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