NONLINEAR DIFFUSION EQUATIONS IN FLUID MIXTURES

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ABSTRACT. The whole set of balance equations for chemically-reacting fluid mixtures is established. The diffusion flux relative to the barycentric reference is shown to satisfy a first-order, non-linear differential equation. This in turn means that the diffusion flux is given by a balance equation, not by a constitutive assumption at the outset. Next, by way of application, limiting properties of the differential equation are shown to provide Fick’s law and the Nernst-Planck equation. Moreover, known generalized forces of the literature prove to be obtained by appropriate constitutive assumptions on the stresses and the interaction forces. The entropy inequality is exploited by letting the constitutive functions of any constituent depend on temperature, mass density and their gradients thus accounting for nonlocality effects. Among the results, the generalization of the classical law of mass action is provided. The balance equation for the diffusion flux makes the system of equations for diffusion hyperbolic, provided heat conduction and viscosity are disregarded. This is ascertained by the analysis of discontinuity waves of order 2 (acceleration waves). The wave speed is derived explicitly in the case of binary mixtures.

1. Introduction. Acoustics in mixtures is deeply influenced by diffusion. Though the subject is well-known, the literature shows different models of diffusion depending on the context at hand. Also in view of the interest of diffusion phenomena in physics, chemistry, and biology, it is then worth investigating the diffusion model equations and their influences on wave propagation.

The simplest and best known model of diffusion is, of course, Fick’s law, a relation motivated by the obvious analogy between diffusion and heat conduction (see, e.g., [5]). If \( j \) is the diffusion flux and \( c \) is the concentration of the pertinent constituent then

\[
j = -D \nabla c
\]

provides \( j \) as a result of the driving force, the gradient \( \nabla c \). The (approximate) balance equation

\[
\partial_t c = -\nabla \cdot j + \zeta
\]

and the assumption that the diffusivity \( D \) be a constant provide the classical parabolic differential equation

\[
\partial_t c = D \Delta c + \zeta,
\]

which has the same form of the heat equation for the unknown temperature.

This scheme is much too simple, at least conceptually. The interaction among the constituents and the fact that diffusion describes a motion, relative to the
barycentric reference, make the pertinent equations for the concentrations (as well as for the mass fractions) of more than two constituents be a coupled system of equations rather than decoupled parabolic equations.

Despite the coarse model (1)-(2), eq. (1) is currently regarded as a reference constitutive equation for the diffusion flux $j$. It is a standard view that the pertinent diffusion flux is given by a constitutive equation where the gradient of the chemical potential is the essential term. In more general cases, for instance in more complex phenomena involving charged particles, the same view is applied by having recourse to the electrochemical potential (see e.g. [2, 13]). In phase field theories, instead, the evolution of concentrations is mainly modelled by kinetic equations in terms of an appropriate free energy function (see, e.g., [24, 8]). As a preliminary part, in this paper we re-examine the balance equations of a fluid mixture and to establish an appropriate set of equations governing the evolution of the diffusion fluxes. This in turn shows that the diffusion flux is governed by a balance equation of the rate type (evolution equation), rather than by a constitutive equation, thus eliminating the subjective character of the constitutive assumption.

The purpose of this paper is twofold. First, to prove that, despite the current orthodoxy in the literature of diffusion, the correct modelling of diffusion, in inviscid and non-conducting mixtures, provides a hyperbolic system of differential equations. For definiteness, discontinuity waves of order two are considered and the propagation speeds in two cases are derived. Hence we find how the waves speeds are affected by the constitutive properties and the concentrations of the constituents. Second, to clarify that (seemingly) conceptually different models appearing in the literature (like, e.g., the Maxwell-Stefan diffusion) can be framed within the general scheme so established. Also, the purpose is to indicate how Fick’s law (1) for the diffusion flux, or analogous equations, such as the Nernst-Planck equation, for more complex phenomena, may be obtained in particular limiting conditions.

Notation. Let $\Omega$ be a time-dependent region occupied by a mixture of $n$ constituents and denote by $x$ the position vector of a point relative to a chosen origin. The functions describing the evolution of the mixture have $\Omega \times \mathbb{R}$ as their common space-time domain. We denote by $\partial_t$ the derivative with respect to $t \in \mathbb{R}$ and by $\nabla$ the gradient operator in $\Omega$. The subscripts $\alpha, \beta = 1, 2, \ldots, n$ label the quantities pertaining to the constituents of the mixture. Hence $\rho_\alpha$ is the mass density, $v_\alpha$ the velocity, $\varepsilon_\alpha$ the internal energy density, $\theta_\alpha$ the absolute temperature, $\eta_\alpha$ the entropy density, on $\Omega \times \mathbb{R}$, of the $\alpha$th constituent. Throughout $\sum_\alpha$ and $\sum_\beta$ are shorthand for sums over (the constituents) $1, 2, \ldots, n$.

2. Balance equations for single constituents. The mass density $\rho_\alpha$ and the velocity $v_\alpha$ are required to satisfy the continuity equations

$$\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha v_\alpha) = \tau_\alpha, \quad (3)$$

where $\tau_\alpha$ is the mass produced, per unit time and unit volume, of the $\alpha$th constituent. The overall conservation of mass requires that

$$\sum_\alpha \tau_\alpha = 0. \quad (4)$$

The mass density of the mixture, $\rho$, and the barycentric velocity, $v$, are defined by

$$\rho = \sum_\alpha \rho_\alpha, \quad \rho v = \sum_\alpha \rho_\alpha v_\alpha. \quad (5)$$
Hence summation of (3) over \( \alpha \) provides
\[
\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0.
\]  
(6)

Let a superposed dot stand for the derivative along the barycentric motion, \( \dot{\psi} = \partial_t \psi + \mathbf{v} \cdot \nabla \psi \) for any function on \( \Omega \times \mathbb{R} \). Hence we can write (6) in the form
\[
\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0.
\]  
(7)

The mass fraction \( \omega_\alpha \) and the diffusion velocity \( \mathbf{u}_\alpha \) are defined by
\[
\omega_\alpha = \frac{\rho_\alpha}{\rho}, \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}.
\]

Since \( \sum_\alpha \omega_\alpha = 1 \) we may regard \( \omega_1, ..., \omega_{n-1} \) and \( \rho \) as \( n \) variables in 1-1 correspondence with \( \rho_1, \rho_2, ..., \rho_n \). Substitution of \( \rho_\alpha \) with \( \rho \omega_\alpha \) in (3) and use of (7) provides
\[
\rho \dot{\omega}_\alpha = -\nabla \cdot \mathbf{h}_\alpha + \tau_\alpha, \quad \mathbf{h}_\alpha = \rho_\alpha \mathbf{u}_\alpha.
\]  
(8)

The vector \( \mathbf{h}_\alpha \) is termed the diffusion flux. It follows that
\[
\sum_\alpha \mathbf{h}_\alpha = 0.
\]  
(9)

It is worth remarking that in continuum mechanics the mass fraction \( \rho_\alpha/\rho \) is called the concentration and denoted by \( c_\alpha \). In physics and chemistry, more often \( c_\alpha \) is the molar concentration,
\[
c_\alpha = \frac{\rho_\alpha}{M_\alpha} = \frac{\rho}{M_\alpha} \omega_\alpha,
\]  
(10)

\( M_\alpha \) being the molar mass of the \( \alpha \)th constituent. For ease of comparison with the main literature on diffusion, we adopt the notation (10) and hence hereafter \( c_\alpha \) is the molar concentration.

Still within the Eulerian description, namely in dealing with functions on \( \Omega \times \mathbb{R} \), we write the equations of motion in the form
\[
\partial_t (\rho_\alpha \mathbf{v}_\alpha) + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \nabla \cdot \mathbf{T}_\alpha + \rho_\alpha \mathbf{f}_\alpha + \mathbf{m}_\alpha,
\]  
(11)

where \( \mathbf{T}_\alpha \) is the stress tensor, \( \mathbf{f}_\alpha \) the body force, and \( \mathbf{m}_\alpha \) the growth of linear momentum, due to the action of the other constituents. Also, we write the balance of energy in the form
\[
\partial_t (\rho_\alpha (\varepsilon_\alpha + \mathbf{v}_\alpha^2/2)) + \nabla \cdot (\rho_\alpha (\varepsilon_\alpha + \mathbf{v}_\alpha^2/2) \mathbf{v}_\alpha) = \nabla \cdot (\mathbf{v}_\alpha \mathbf{T}_\alpha) + \rho_\alpha \mathbf{f}_\alpha \cdot \mathbf{v}_\alpha - \nabla \cdot \mathbf{q}_\alpha + \rho_\alpha \mathbf{r}_\alpha + c_\alpha,
\]  
(12)

where \( \mathbf{q}_\alpha \) is the heat flux, \( \mathbf{r}_\alpha \) is the external heat supply, and \( c_\alpha \) is the growth of energy. Due to the internal character, the growths \( \{\mathbf{m}_\alpha\} \) and \( \{c_\alpha\} \) are subject to
\[
\sum_\alpha \mathbf{m}_\alpha = 0, \quad \sum_\alpha c_\alpha = 0.
\]  
(13)

The balance of entropy is written in the form
\[
\partial_t (\rho_\alpha \eta_\alpha) + \nabla \cdot (\rho_\alpha \eta_\alpha \mathbf{v}_\alpha) + \nabla \cdot \phi_\alpha - \rho_\alpha s_\alpha = \sigma_\alpha,
\]  
(14)

where \( \phi_\alpha \) is the entropy flux and \( s_\alpha \) the entropy supply. Also, \( \sigma_\alpha \) is the entropy growth. The second law of thermodynamics is expressed by saying that
\[
\sum_\alpha \sigma_\alpha \geq 0,
\]  
(15)

has to hold for all admissible fields compatible with the balance equations (3), (11), (12) \([26, 3]\).
The growths \( \{m_\alpha\}, \{e_\alpha\}, \{\sigma_\alpha\} \) are non-objective in that they are related to the particular reference chosen for the Eulerian description. Objective quantities are provided in a while within the Lagrangian description.

For any function \( \phi_\alpha \) on \( \Omega \times \mathbb{R} \) we denote by \( \dot{\phi}_\alpha \) the \( \alpha \)th peculiar time derivative that is the derivative following the motion of the \( \alpha \)th constituent,

\[
\dot{\phi}_\alpha = \partial_t \phi_\alpha + \mathbf{v}_\alpha \cdot \nabla \phi_\alpha.
\]

By means of (3) we have

\[
\rho_\alpha \dot{\phi}_\alpha = \partial_t (\rho_\alpha \phi_\alpha) + \nabla \cdot (\rho_\alpha \phi_\alpha \mathbf{v}_\alpha) - \tau_\alpha \phi_\alpha.
\]

As a consequence, eqs. (3) and (11) become

\[
\rho_\alpha \dot{\mathbf{v}}_\alpha = \nabla \cdot \mathbf{T}_\alpha + \rho_\alpha \mathbf{f}_\alpha + \dot{\mathbf{p}}_\alpha,
\]

where

\[
\dot{\mathbf{p}}_\alpha := \mathbf{m}_\alpha - \tau_\alpha \mathbf{v}_\alpha.
\]

By (12) we have

\[
\partial_t (\rho_\alpha \varepsilon_\alpha) + \nabla \cdot (\rho_\alpha \varepsilon_\alpha \mathbf{v}_\alpha) + \tau_\alpha \mathbf{v}_\alpha^2/2 + \rho_\alpha (v^2/2) = \nabla \cdot (\mathbf{v}_\alpha \mathbf{T}_\alpha) + \rho_\alpha \mathbf{f}_\alpha \cdot \mathbf{v}_\alpha - \nabla \cdot \mathbf{q}_\alpha + \rho_\alpha \mathbf{r}_\alpha + e_\alpha.
\]

As a consequence of (18) it follows that

\[
\partial_t (\rho_\alpha \varepsilon_\alpha) + \nabla \cdot (\rho_\alpha \varepsilon_\alpha \mathbf{v}_\alpha) + \tau_\alpha \mathbf{v}_\alpha^2/2 = \mathbf{T}_\alpha \cdot \mathbf{L}_\alpha - \nabla \cdot \mathbf{q}_\alpha + \rho_\alpha \mathbf{r}_\alpha + e_\alpha.
\]

Hence, applying again (16) we find that

\[
\rho_\alpha \hat{\varepsilon}_\alpha = \mathbf{T}_\alpha \cdot \mathbf{L}_\alpha - \nabla \cdot \mathbf{q}_\alpha + \rho_\alpha \mathbf{r}_\alpha + \hat{\varepsilon}_\alpha,
\]

where

\[
\hat{\varepsilon}_\alpha := e_\alpha - \dot{\mathbf{p}}_\alpha \cdot \mathbf{v}_\alpha - \tau_\alpha (e_\alpha + \mathbf{v}_\alpha^2/2).
\]

By means of (4), the constraints (13) provide

\[
\sum_\alpha [\dot{\mathbf{p}}_\alpha + \tau_\alpha \mathbf{u}_\alpha] = 0,
\]

\[
\sum_\alpha [\hat{\varepsilon}_\alpha + \dot{\mathbf{p}}_\alpha \cdot \mathbf{u}_\alpha + \tau_\alpha (e_\alpha + \mathbf{u}_\alpha^2/2)] = 0.
\]

Equations (22) involve only objective vectors and scalars.

3. **Balance equations for the whole mixture.** The third principle listed by Truesdell [26] states that the motion of the mixture is governed by the same equations as is a single body. Hence, the balance of mass, linear momentum, and energy are required to take the form

\[
\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0,
\]

\[
\rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{T} + \rho \mathbf{f},
\]

\[
\rho \dot{\varepsilon} = \mathbf{T} \cdot \mathbf{D} - \nabla \cdot \mathbf{q} + \rho \mathbf{r}.
\]

In addition, the balance of moment of momentum results in the symmetry of \( \mathbf{T} \). It is known (see, e.g., [26, 3, 17]) that eqs. (23)-(25) hold with \( \rho \) and \( \mathbf{v} \) given by (5) whereas

\[
\mathbf{T} = \mathbf{T}_I - \sum_\alpha \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha,
\]

\[
\mathbf{f} = \sum_\alpha c_\alpha \mathbf{f}_\alpha,
\]

\[
\varepsilon = \varepsilon_I + \sum_\alpha c_\alpha u^2_\alpha/2,
\]

\[
\mathbf{r} = \mathbf{r}_I + \sum_\alpha c_\alpha \mathbf{f}_\alpha \cdot \mathbf{u}_\alpha
\]

\[
\mathbf{q} = \mathbf{q}_I + \mathbf{w}, \quad \mathbf{w} := \sum_\alpha [-\mathbf{u}_\alpha \mathbf{T}_\alpha + \rho_\alpha (e_\alpha + u^2_\alpha/2) \mathbf{u}_\alpha].
\]
and

$$D = \text{sym} L, \quad L = \nabla v.$$ 

The subscript $I$ denotes the inner quantities, namely the sum, or the average, of the corresponding peculiar terms,

$$T_I = \sum_\alpha T_\alpha, \quad \varepsilon_I = \sum_\alpha \omega_\alpha \varepsilon_\alpha, \quad q_I = \sum_\alpha q_\alpha, \quad r = \sum_\alpha \omega_\alpha r_\alpha.$$ 

Equation (24) can be written in the form

$$\rho \dot{\varepsilon} = \nabla \cdot T_I - \nabla \cdot \sum_\alpha \rho_\alpha u_\alpha \otimes u_\alpha + \rho f,$$  

(29)

which shows the nonlinear effect of diffusion velocities \{u_\alpha\} on the motion of the barycentric reference.

Now,

$$\dot{\varepsilon} = \dot{\varepsilon}_I + \sum_\alpha (\dot{\omega}_\alpha u_\alpha^2 / 2 + \omega_\alpha u_\alpha \cdot \dot{u}_\alpha).$$  

(30)

We can express \dot{u}_\alpha as

$$\dot{u}_\alpha = \dot{v}_\alpha - v = \dot{v}_\alpha - (u_\alpha \cdot \nabla) v_\alpha - v$$

whence, using (9), we have

$$\sum_\alpha \omega_\alpha u_\alpha \cdot \dot{u}_\alpha = \sum_\alpha [\omega_\alpha u_\alpha \cdot \dot{v}_\alpha - \omega_\alpha (u_\alpha \otimes u_\alpha) \cdot \nabla u_\alpha].$$

As a consequence, owing to (25) and (30) we obtain

$$\rho \dot{\varepsilon}_I = (T_I - \sum_\alpha \rho_\alpha u_\alpha \otimes u_\alpha) \cdot D - \nabla \cdot (q_I + w) + \rho r_I - \sum_\alpha u_\alpha \cdot (\nabla \cdot T_\alpha + \hat{p}_\alpha)$$

$$+ \sum_\alpha \rho_\alpha (u_\alpha \otimes u_\alpha) \cdot L_\alpha - \sum_\alpha (\tau_\alpha - \nabla \cdot h_\alpha) u_\alpha^2 / 2.$$

Some rearrangements provide the identities

$$\sum_\alpha (\nabla \cdot h_\alpha) u_\alpha^2 / 2 = \nabla \cdot \sum_\alpha (u_\alpha^2 / 2) h_\alpha - \sum_\alpha \rho_\alpha (u_\alpha \otimes u_\alpha) \cdot \nabla u_\alpha,$$

$$T_I \cdot D - \sum_\alpha u_\alpha \cdot (\nabla \cdot T_\alpha) = \sum_\alpha T_\alpha \cdot L_\alpha - \nabla \cdot \sum_\alpha u_\alpha T_\alpha,$$

$$\rho_\alpha (u_\alpha \otimes u_\alpha) \cdot (L_\alpha - D - \nabla u_\alpha) = 0,$$

$$w - (u_\alpha^2 / 2) h_\alpha + u_\alpha T_\alpha = \varepsilon_\alpha h_\alpha.$$

Consequently we find that

$$\rho \dot{\varepsilon}_I = \sum_\alpha T_\alpha \cdot L_\alpha - \sum_\alpha (\hat{p}_\alpha \cdot u_\alpha + \tau_\alpha u_\alpha^2 / 2) + \rho r_I - \nabla \cdot \sum_\alpha (q_\alpha + \varepsilon_\alpha h_\alpha).$$  

(31)
4. Evolution equations for the diffusion fluxes. We now determine the evolution equation for the fluxes \( \{ h_\alpha \} \) (see [17, 15]). By (17) and (18) we have

\[
(\rho_\alpha v_\alpha) = -\rho_\alpha v_\alpha \nabla \cdot v_\alpha + \nabla \cdot T_\alpha + \rho_\alpha f_\alpha + \hat{p}_\alpha + \tau_\alpha v_\alpha.
\]

By (19) we have \( \hat{p}_\alpha + \tau_\alpha v_\alpha = m_\alpha \). The peculiar derivative of \( h_\alpha = \rho_\alpha v_\alpha - \rho_\alpha v \) gives

\[
\dot{h}_\alpha = (\rho_\alpha v_\alpha) - \hat{p}_\alpha v - \rho_\alpha [\dot{v} + (u_\alpha \cdot \nabla) v]
\]
whence

\[
\dot{h}_\alpha = -(\nabla \cdot v_\alpha) h_\alpha + \nabla \cdot T_\alpha + \rho_\alpha f_\alpha + m_\alpha - \tau_\alpha v - \rho_\alpha [\dot{v} + (u_\alpha \cdot \nabla) v].
\]

Since

\[
\rho_\alpha (u_\alpha \cdot \nabla) v = L h_\alpha
\]
and

\[
(\nabla \cdot v_\alpha) h_\alpha = (\nabla \cdot v) h_\alpha + (\nabla \cdot u_\alpha) h_\alpha = (\nabla \cdot v) h_\alpha + \nabla \cdot (h_\alpha \otimes u_\alpha) - (u_\alpha \cdot \nabla) h_\alpha,
\]
substitution in (32) provides

\[
\dot{h}_\alpha + [L + (\nabla \cdot v) 1] h_\alpha = \nabla \cdot T_\alpha + \rho_\alpha f_\alpha + m_\alpha - \tau_\alpha v - \rho_\alpha \dot{v}.
\]

Substitution of \( \rho \dot{v} \) from (24) gives

\[
\dot{h}_\alpha + [L + (\nabla \cdot v) 1] h_\alpha = \nabla \cdot T_\alpha - \omega_\alpha \nabla \cdot T + \rho_\alpha f_\alpha - \rho f + m_\alpha - \tau_\alpha v.
\]

Equation (33) governs the evolution of \( h_\alpha \) relative to the barycentric reference frame. It is rather cumbersome and nonlinear. Yet it is exact, i.e., free from any approximations or constitutive assumptions. The occurrence of (33) is quite exceptional in the literature; it was derived first in [17] and re-visited in [19, 15].

It is of interest to consider some “generalized equations of motion” mainly developed as approximations to the Boltzmann equation [14, 23]. They show features that look intermediate between the equation of motion (18) and the balance equation (33).

4.1. Generalized equation of motion; Maxwell-Stefan diffusion. In the present notation, eq. (44) of [12] reads

\[
\rho_\alpha \dot{v}_\alpha = -\nabla p_\alpha + \rho_\alpha f_\alpha - \rho \sum_\beta x_\alpha x_\beta \left( D_\alpha - D_\beta \right) \nabla \ln \theta + \nabla \cdot T_\alpha + \rho \sum_\beta x_\alpha x_\beta (v_\beta - v_\alpha).
\]

The stress \( T_\alpha \) is said to represent the shearing force on \( \alpha \) and then we can identify \( -\rho_\alpha 1 + T_\alpha \) with \( T_\alpha \) of (18). It seems that chemical reactions are disregarded. Hence the remaining terms stand for the growth of linear momentum,

\[
m_\alpha = -\rho \sum_\beta x_\alpha x_\beta \left( D_\alpha - D_\beta \right) \nabla \ln \theta + \rho \sum_\beta x_\alpha x_\beta (v_\beta - v_\alpha).
\]

The restriction (13) for \( \{ m_\alpha \} \) holds provided only that

\[
D_\alpha = D_\beta = 0.
\]

The quantities \( D_\alpha \) are usually referred to as Maxwell-Stefan diffusion coefficients while \( x_\alpha \) is the \( \alpha \)th mole fraction that is related to \( \omega_\alpha \) by

\[
\omega_\alpha = \frac{M}{M} x_\alpha,
\]

\( M \) being the average molar mass. Hence \( m_\alpha \) is taken as due to the temperature gradient \( \nabla \theta \) and the velocity differences \( v_\beta - v_\alpha = u_\beta - u_\alpha \).
Other models take \( \rho_\alpha f_\alpha \) and \( m_\alpha \) so that
\[
- c_\alpha \partial_{x_\alpha} \mu_\alpha \nabla x_\alpha + c_\alpha R T \sum_\beta \frac{x_\alpha x_\beta}{D_{\alpha\beta}} (v_\beta - v_\alpha),
\]
occurs as the force on the \( \alpha \)th constituent, in addition to the term involving the temperature gradient (see (92) of [12]). Here \( c_\alpha \) is the \( \alpha \)th molar concentration, \( c_t \) the total molar concentration. The motivation for the force (36) seems to be the assumption that any deviation from equilibrium leads to a diffusion flux and that, at equilibrium, the chemical potential gradient \( \partial_{x_\alpha} \mu_\alpha \nabla x_\alpha \), regarded as driving force, is counterbalanced by molecular friction that is proportional to the velocity differences [21].

It is apparent that eq. (33) requires only that we select the growth \( m_\alpha \) whereas no subjective choice is required about the so called driving force.

5. Exploitation of the entropy inequality. Look now at the entropy inequality (15). It is convenient to express \( \phi_\alpha \) in the form
\[
\phi_\alpha = \frac{q_\alpha}{\theta_\alpha} + k_\alpha,
\]
\( k_\alpha \) being called the extra-entropy flux, while
\[
s_\alpha = \frac{r_\alpha}{\theta_\alpha}.
\]
Hence, owing to (16), inequality (15) becomes
\[
\sum_\alpha \rho_\alpha \eta_\alpha + \tau_\alpha \eta_\alpha + \nabla \cdot \left( \frac{q_\alpha}{\theta_\alpha} + k_\alpha \right) - \frac{\rho_\alpha r_\alpha}{\theta_\alpha} = \sum_\alpha \sigma_\alpha \geq 0.
\]
(37)

Upon replacing \( \nabla \cdot q_\alpha - \rho_\alpha r_\alpha \) from (20) we have
\[
\sum_\alpha \frac{1}{\theta_\alpha} \left[ \rho_\alpha (\theta_\alpha \eta_\alpha - \hat{\varepsilon}_\alpha) + \tau_\alpha \theta_\alpha \eta_\alpha + T_\alpha \cdot L_\alpha - \frac{1}{\theta_\alpha} q_\alpha \cdot \nabla \theta_\alpha + \hat{\varepsilon}_\alpha + \theta_\alpha \nabla \cdot k_\alpha \right] \geq 0.
\]
(38)

By means of the free energy
\[
\psi_\alpha = \varepsilon_\alpha - \theta_\alpha \eta_\alpha
\]
we can write the entropy inequality in the form
\[
\sum_\alpha \frac{1}{\theta_\alpha} \left[ -\rho_\alpha (\psi_\alpha + \eta_\alpha \hat{\theta}_\alpha) + \tau_\alpha \theta_\alpha \eta_\alpha + T_\alpha \cdot L_\alpha - \frac{1}{\theta_\alpha} q_\alpha \cdot \nabla \theta_\alpha + \hat{\varepsilon}_\alpha + \theta_\alpha \nabla \cdot k_\alpha \right] \geq 0.
\]
(39)

Let \( \psi_\alpha, \eta_\alpha, \tau_\alpha, T_\alpha, q_\alpha, k_\alpha \) be functions of
\[
(\theta_\alpha, \rho_\alpha, \nabla \rho_\alpha, D_\alpha, \nabla \theta_\alpha).
\]
The dependence on \( \nabla \rho_\alpha \) is motivated also by applications to the modelling of phase transitions. Moreover, we let the interaction terms \( \hat{\varepsilon}_\alpha \) and \( \hat{\theta}_\alpha \), of the \( \alpha \)th constituent, depend also on quantities pertaining to the other constituents. In addition, we assume that \( \eta_\alpha, \tau_\alpha, T_\alpha, \) and \( q_\alpha \) are continuous functions while \( \psi_\alpha \) and \( k_\alpha \) are differentiable. Hence (39) becomes
\[
\sum_\alpha \frac{1}{\theta_\alpha} \left[ -\rho_\alpha (\partial_{\theta_\alpha} \psi_\alpha + \eta_\alpha \hat{\theta}_\alpha) - \rho_\alpha \partial_{D_\alpha} \psi_\alpha \cdot \dot{D}_\alpha - \rho_\alpha \partial_{\psi_\alpha} \psi_\alpha \cdot \dot{\psi}_\alpha + ... \right] \geq 0
\]
the dots representing the remaining terms, which are independent of \(\{\hat{\theta}_a\}, \{\hat{D}_\alpha\},\) and \(\{\nabla \theta_a\}\). The arbitrariness of the peculiar time derivatives \(\{\hat{\theta}_a\}, \{\hat{D}_\alpha\},\) and \(\{\nabla \theta_a\}\) requires that
\[
\psi_a = \psi_a(\theta_a, \rho_a, \nabla \rho_a), \quad \eta_a = -\partial_{\theta_a} \psi_a.
\]
As a consequence, (39) reduces to
\[
\sum \frac{1}{\theta_a} [-\rho_a \partial_{\rho_a} \psi_a \rho_a - \rho_a \partial q_{\rho_a} \psi_a \nabla \rho_a + \tau_a \eta_a + T_\alpha \cdot L_\alpha - \frac{1}{\theta_a} q_\alpha \cdot \nabla \theta + \hat{\epsilon}_a + \theta \nabla \cdot k_\alpha] \geq 0.
\]
For any function \(g_\alpha\) on \(\Omega \times \mathbb{R}\) the identity
\[
\nabla g_\alpha = \nabla \hat{g}_\alpha - L_\alpha ^T \nabla g_\alpha.
\]
holds. Hence some rearrangements give
\[
\frac{\rho_a}{\theta_a} \partial q_{\rho_a} \psi_a \cdot \nabla \rho_a = \nabla \cdot \left( \frac{\rho_a}{\theta_a} \partial q_{\rho_a} \psi_a \rho_a \right) - \rho_a \nabla \cdot \left( \frac{\rho_a}{\theta_a} \partial q_{\rho_a} \psi_a \right) - \frac{\rho_a}{\theta_a} \nabla \rho_a \otimes \partial q_{\rho_a} \psi_a \cdot L_\alpha.
\]
Now let
\[
\delta_{\rho_a} \psi_a := \partial q_{\rho_a} \psi_a - \frac{\rho_a}{\theta_a} \nabla \cdot \left( \frac{\rho_a}{\theta_a} \partial q_{\rho_a} \psi_a \right)
\]
and replace \(\hat{\rho}_a\) with \(-\rho_a \nabla \cdot \nu_\alpha + \tau_a\). The inequality can then be written in the form
\[
\sum \frac{1}{\theta_a} \left\{ \left[ T_\alpha + \rho_a^2 \delta_{\rho_a} \psi_a \right] 1 + \rho_a \nabla \rho_a \otimes \partial q_{\rho_a} \psi_a \right\} \cdot L_\alpha - \tau_a (\rho_a \delta_{\rho_a} \psi_a - \theta_a \eta_a)
\]
\[
+ \hat{\epsilon}_a - \frac{1}{\theta_a} q_\alpha \cdot \nabla \theta_a] + \sum \nabla \cdot \left( k_\alpha - \frac{\rho_a}{\theta_a} \partial q_{\rho_a} \psi_a (\tau_a - \rho_a \nabla \cdot \nu_\alpha) \right) \geq 0.
\]
This relation suggests that we take the extra-entropy fluxes \(k_\alpha\) as
\[
k_\alpha = \frac{\rho_a}{\theta_a} \partial q_{\rho_a} \psi_a (\tau_a - \rho_a \nabla \cdot \nu_\alpha).
\]
In addition replace \(L_\alpha\) with \(D_\alpha + W_\alpha, D_\alpha \in \text{Sym}\) being the stretching and \(W_\alpha \in \text{Skw}\) the spin. The arbitrariness and linearity of \(W_\alpha\) implies that
\[
T_\alpha + \rho_a \nabla \rho_a \otimes \partial q_{\rho_a} \psi_a \in \text{Sym}, \quad \alpha = 1, 2, ..., n.
\]
Let
\[
p_\alpha = \rho_a^2 \delta_{\rho_a} \psi_a.
\]
If \(\psi_a\) is independent of \(\nabla \rho_a\) then
\[
p_\alpha = \rho_a^2 \partial q_{\rho_a} \psi_a,
\]
which is the classical form of the (partial) pressure. We can then view (43) as the general form of the pressure when the dependence on \(\nabla \rho_a\) is allowed.
Inequality (42) becomes
\[
\sum \frac{1}{\theta_a} \left\{ \left[ T_\alpha + p_\alpha 1 + \rho_a \nabla \rho_a \otimes \partial q_{\rho_a} \psi_a \right] \cdot L_\alpha - \tau_a \left( \frac{p_\alpha}{\rho_a} - \theta_a \eta_a \right) + \hat{\epsilon}_a - \frac{1}{\theta_a} q_\alpha \cdot \nabla \theta_a \right\} \geq 0.
\]
The viscous and heat-conducting constituents are modelled by letting
\[
T_\alpha + p_\alpha 1 + \rho_a \nabla \rho_a \otimes \partial q_{\rho_a} \psi_a = 2 \nu_\alpha D_\alpha + \lambda_\alpha \text{tr} D_\alpha 1,
\]
\[
q_\alpha = -\xi_\alpha \nabla \theta_a,
\]
where \(\nu_\alpha \geq 0, 2 \nu_\alpha + 3 \lambda_\alpha \geq 0, \xi_\alpha \geq 0,\) so that
\[
[T_\alpha + p_\alpha 1 + \rho_a \nabla \rho_a \otimes \partial q_{\rho_a} \psi_a] \cdot D_\alpha - \frac{1}{\theta_a} q_\alpha \cdot \nabla \theta_a \geq 0.
for any constituent $\alpha$. The compatibility of wave motion with the requirements of the entropy inequality has been investigated for a number of dissipative models as, e.g., those in [10, 16, 11]; see also [25]. Here waves are investigated in the particular case of inviscid and non-conducting constituents.

Inequality (42) reduces to
\[
\sum_\alpha \left[ \frac{1}{\theta_\alpha} (e_\alpha - p_\alpha \cdot v_\alpha - \frac{1}{2} \tau_\alpha v_\alpha^2) - \frac{\tau_\alpha}{\theta_\alpha} (e_\alpha - \theta_\alpha \eta_\alpha + \frac{p_\alpha}{\rho_\alpha}) \right] \geq 0.
\]
Again we allow for separate non-negative contributions to the inequality namely
\[
\sum_\alpha \frac{1}{\theta_\alpha} (e_\alpha - p_\alpha \cdot v_\alpha - \frac{1}{2} \tau_\alpha v_\alpha^2) \geq 0, \tag{44}
\]
\[
\sum_\alpha \frac{\tau_\alpha}{\theta_\alpha} (\psi_\alpha + \frac{p_\alpha}{\rho_\alpha}) \leq 0. \tag{45}
\]
If we regard
\[
\mu_\alpha = \psi_\alpha + \frac{p_\alpha}{\rho_\alpha}
\]
as the $\alpha$th chemical potential then inequality (45) may be viewed as the condition governing the reactions between constituents at different temperatures.

Inequality (44) is a requirement on the admissible $e_\alpha, m_\alpha, \tau_\alpha$. Often models are considered for diffusion in non-reacting mixtures with a single temperature, $\theta_\alpha = \theta$.

In such cases (44) reduces to
\[
\sum_\alpha m_\alpha \cdot u_\alpha \leq 0, \tag{46}
\]
which is the thermodynamic requirement on the momentum growths.

5.1. Remarks on the Maxwell-Stefan model. By (35), the Maxwell-Stefan model amounts to saying that the growth of linear momentum is taken in the form
\[
m_\alpha = \sum_\beta M_{\alpha \beta} (v_\beta - v_\alpha) + \sum_\beta N_{\alpha \beta} \nabla \theta
\]
where
\[
M_{\alpha \beta} = M_{\beta \alpha}, \quad N_{\alpha \beta} = -N_{\beta \alpha}.
\]
The symmetry of $M$ and the skew-symmetry of $N$ implies that $\sum_\alpha m_\alpha = 0$.

To check the compatibility with the second law we observe that, if the constituents have a single temperature and chemical reactions do not occur, then inequality (42) becomes
\[
\sum_\alpha \left\{ [T_\alpha + p_\alpha \mathbf{1} + \rho_\alpha \nabla \rho_\alpha \otimes \partial \nabla \rho_\alpha \psi_\alpha] \cdot \mathbf{D}_\alpha - m_\alpha \cdot u_\alpha - \frac{1}{\theta} q_\alpha \cdot \nabla \theta \right\} \geq 0.
\]
If, as is the case, $m_\alpha$ and $q_\alpha$ are independent of $\mathbf{D}_\alpha$ then the inequality requires that
\[
\sum_\alpha \left\{ [T_\alpha + p_\alpha \mathbf{1} + \rho_\alpha \nabla \rho_\alpha \otimes \partial \nabla \rho_\alpha \psi_\alpha] \cdot \mathbf{D}_\alpha \right\} \geq 0,
\]
\[
\sum_\alpha \{ m_\alpha \cdot u_\alpha + \frac{1}{\theta} q_\alpha \cdot \nabla \theta \} \geq 0. \tag{47}
\]
Now,
\[
\sum_{\alpha, \beta} M_{\alpha \beta} (u_\beta - u_\alpha) \cdot u_\alpha = \frac{1}{2} \sum_{\alpha, \beta} M_{\alpha \beta} (u_\beta - u_\alpha)^2.
\]
As a consequence
\[
\sum_\alpha (\mathbf{m}_\alpha \cdot \mathbf{u}_\alpha + \frac{1}{\theta} q_\alpha \cdot \nabla \theta) = \frac{1}{2} \sum_{\alpha,\beta} M_{\alpha\beta} (\mathbf{u}_\beta - \mathbf{u}_\alpha)^2 + \nabla \theta \cdot \left( \sum_{\alpha,\beta} N_{\alpha\beta} \mathbf{u}_\beta + \frac{1}{\theta} q_\alpha \right).
\]

We let
\[
M_{\alpha\beta} \geq 0, \quad \alpha, \beta = 1, 2, ..., n.
\]

Inequality (47) is then satisfied provided
\[
q_\alpha = -\xi_\alpha \nabla \theta - \theta \sum_\beta N_{\alpha\beta} \mathbf{u}_\beta, \quad \xi_\alpha \geq 0,
\]
with \(\xi_\alpha\) possibly being a tensor. It then follows that a model of the Maxwell-Stephan type for the linear momentum growths is compatible with thermodynamics provided we take the heat fluxes in the form (48).

5.2. A representation of \(m_\alpha\) in reacting mixtures. An expression for \(m_\alpha\) is now determined in the case where each constituent has the same temperature. By (44) we have
\[
\sum_\alpha (\mathbf{m}_\alpha \cdot \mathbf{u}_\alpha - \frac{1}{2} \tau_\alpha v_\alpha^2) \leq 0.
\]

To establish a thermodynamically-consistent model we let
\[
\Xi_{\alpha\beta} = \Xi_{\beta\alpha} \geq 0
\]
and take
\[
\mathbf{m}_\alpha = \sum_\beta \Xi_{\alpha\beta} (\mathbf{v}_\beta - \mathbf{v}_\alpha) + \mathbf{w}_\alpha.
\]

Hence (13) requires that
\[
\sum_\alpha \mathbf{w}_\alpha = 0.
\]

Moreover, substitution of \(\mathbf{m}_\alpha\) in the left-hand side of (49) and \(\mathbf{v}_\alpha = \mathbf{v} + \mathbf{u}_\alpha\) gives
\[
\sum_\alpha (\mathbf{m}_\alpha \cdot \mathbf{u}_\alpha - \frac{1}{2} \tau_\alpha v_\alpha^2) = -\frac{1}{2} \sum_{\alpha,\beta} \Xi_{\alpha\beta} (\mathbf{u}_\beta - \mathbf{u}_\alpha)^2 + \sum_\alpha (\mathbf{w}_\alpha \cdot \mathbf{u}_\alpha - \tau_\alpha \mathbf{v} \cdot \mathbf{u}_\alpha - \frac{1}{2} \tau_\alpha u_\alpha^2).
\]

Hence (49) holds if
\[
\sum_\alpha (\mathbf{w}_\alpha \cdot \mathbf{u}_\alpha - \tau_\alpha \mathbf{v} \cdot \mathbf{u}_\alpha - \frac{1}{2} \tau_\alpha u_\alpha^2) \leq 0.
\]

Let
\[
\mathbf{w}_\alpha = \tau_\alpha \mathbf{v} + \mathbf{c}_\alpha, \quad \sum_\alpha \mathbf{c}_\alpha = 0.
\]

As a consequence we have
\[
\mathbf{w}_\alpha \cdot \mathbf{u}_\alpha - \tau_\alpha \mathbf{v} \cdot \mathbf{u}_\alpha - \frac{1}{2} \tau_\alpha u_\alpha^2 = \mathbf{c}_\alpha \cdot \mathbf{u}_\alpha - \frac{1}{2} \tau_\alpha u_\alpha^2.
\]

The thermodynamic requirement is then
\[
\sum_\alpha (\mathbf{c}_\alpha \cdot \mathbf{u}_\alpha - \frac{1}{2} \tau_\alpha u_\alpha^2) \leq 0.
\]

A simple model arises if we restrict attention to binary mixtures. Take (50) as an equality so that
\[
\sum_\alpha \mathbf{c}_\alpha \cdot \mathbf{u}_\alpha = \frac{1}{2} \sum_\alpha \tau_\alpha u_\alpha^2.
\]
This implies that
\[ c_1 \cdot (u_1 - u_2) = \frac{1}{2} \tau_1 (u_1^2 - u_2^2), \quad c_2 \cdot (u_2 - u_1) = \frac{1}{2} \tau_2 (u_2^2 - u_1^2). \]

If \( u_2 \neq u_1 \) then we have
\[ c_\alpha = \tau_\alpha (u_1 + u_2) \]
whence
\[ m_\alpha = \sum_\beta \xi_{\alpha \beta} (v_\beta - v_\alpha) + \tau_\alpha v + \tau_\alpha (u_1 + u_2), \quad \alpha = 1, 2. \] (51)

6. Discontinuity waves. We now investigate some propagation properties of mixtures undergoing diffusion. This investigation is of interest in many respects. Here, diffusion proves to be modelled by a hyperbolic system of equations. The intrinsic nonlinearities play an essential role in the propagation modes.

The evolution of the constituents of the mixture may be described by the 2n fields \( \{ \rho_\alpha \}, \{ v_\alpha \} \) on \( \Omega \times \mathbb{R}^1 \). Diffusion may be described more conveniently by the fields \( \rho, \{ \omega_\alpha \}, v, \{ h_\alpha \} \), obviously subject to \( \sum_\alpha \omega_\alpha = 1, \sum_\alpha h_\alpha = 0 \). The pertinent differential equations are
\[ \dot{\rho} + \rho \nabla \cdot v = 0, \quad \rho \dot{\omega}_\alpha + \nabla \cdot h_\alpha = \tau_\alpha, \] (52)
\[ \rho \dot{v} = \nabla \cdot T + \rho f, \quad \dot{h}_\alpha + [L + (\nabla \cdot v)1]h_\alpha = \nabla \cdot T_\alpha - \omega_\alpha \nabla \cdot T + m_\alpha - \tau_\alpha v. \] (53)
The system is closed if we let \( \tau_\alpha \) and \( m_\alpha \) be functions of \( \rho, \{ \omega_\alpha \}, \{ h_\alpha \} \). It is natural though to let \( \tau_\alpha \) depend also on the temperature \( \theta \). In this sense we might close the system by appending eq. (31) with \( \varepsilon \) as a function also of \( \theta \). Yet, for definiteness, we regard the temperature as a parameter. This is allowed by letting
\[ T_\alpha = -p_\alpha 1, \quad p_\alpha = p_\alpha (\rho_\alpha, \eta_\alpha), \]
and making the assumption that the entropy \( \eta_\alpha \) is constant (adiabatic approximation). Of course the constancy of \( \{ \eta_\alpha \} \) is reasonable if heat conduction and viscosity are negligible. This assumption in turn is consistent with the next analysis of discontinuity waves which would be ruled out by the Navier-Stokes-Fourier model.

We now look at singular surfaces of order 2 \([27, 4]\) and let \( \rho, \{ \omega_\alpha \}, v, \{ h_\alpha \} \) be continuous everywhere whereas their time and space derivatives suffer jump discontinuities at a surface \( \sigma \). Though there are differences among the velocities of the constituents, each velocity \( v_\alpha \), and hence \( v \), is continuous in space and time.

For simplicity we restrict attention to plane discontinuity surfaces. Hence \( \sigma \subset \Omega \) is a plane moving in the direction of the unit vector \( \mathbf{n} \). Let \( \Omega^- , \Omega^+ \) be the subregions behind and ahead of \( \sigma \) so that \( \Omega = \Omega^- \cup \sigma \cup \Omega^+ \) and \( n \) is directed from \( \Omega^- \) to \( \Omega^+ \). Denote by
\[ [\phi] := \phi^- - \phi^+ \]
\( \phi^- \) and \( \phi^+ \) being the definite limits of \( \phi \) as \( \sigma \) is approached from within \( \Omega^+ \) and \( \Omega^- \).

If \([\phi] = 0 \) on \( \sigma \) then, by Maxwell’s theorem,
\[ [\nabla \phi] = [\partial_\mathbf{n} \phi] \mathbf{n}, \] (54)
\( \partial_\mathbf{n} \phi \) denoting the derivative in the direction \( \mathbf{n} \). Moreover, by the kinematical condition of compatibility, we obtain
\[ [\dot{\phi}] = -U[\partial_\mathbf{n} \phi], \] (55)
some preliminary results. Since 

\[ \tau_\alpha(\rho_\alpha, \theta) = 0 \]

and

\[ p_\alpha(\rho_\alpha, \eta_\alpha) = 0. \]

Moreover, by

\[ m_\alpha - \tau_\alpha v = \sum_\alpha \Xi_{\alpha\beta}(v_\beta - v_\alpha) + c_\alpha \]

we let \( c_\alpha \) be continuous so that

\[ [m_\alpha - \tau_\alpha v] = 0. \]

By means of (54) we obtain the following nonzero jumps,

\[ [L] = [\partial_n v] \otimes n, \]

\[ \sum_\alpha \Xi_{\alpha\beta}(v_\beta - v_\alpha) \]

In addition it follows that \([\partial_n u_\alpha]\) and \([\partial_n h_\alpha]\) are related by

\[ [\partial_n u_\alpha] = \frac{1}{\rho_\alpha} [\partial_n h_\alpha] - \frac{1}{\omega_\alpha} u_\alpha [\partial_n \omega_\alpha] - \frac{1}{\rho} u_\alpha [\partial_n \rho]. \]

Hence, by (26) we find that

\[ \nabla \cdot T = -\sum_\alpha \{ \partial_{\rho_\alpha} p_\alpha n(\omega_\alpha [\partial_n \rho] + \rho [\partial_n \omega_\alpha]) + (u_\alpha \cdot n) [\partial_n h_\alpha] \]

\[ + u_\alpha (n \cdot [\partial_n h_\alpha] - \frac{1}{\omega_\alpha} h_\alpha \cdot n [\partial_n \omega_\alpha] - \frac{1}{\rho} h_\alpha \cdot n [\partial_n \rho]) \} \]

\[ \nabla \cdot T = -\sum_\alpha \{ \partial_{\rho_\alpha} p_\alpha n(\omega_\alpha [\partial_n \rho] + \rho [\partial_n \omega_\alpha]) + (u_\alpha \cdot n) [\partial_n h_\alpha] \]

\[ + u_\alpha (n \cdot [\partial_n h_\alpha] - \frac{1}{\omega_\alpha} h_\alpha \cdot n [\partial_n \omega_\alpha] - \frac{1}{\rho} h_\alpha \cdot n [\partial_n \rho]) \} = 0, \]

\[ -U[\partial_n \rho] + \rho n \cdot [\partial_n v] = 0, \]

\[ -\rho U[\partial_n \omega_\alpha] + n \cdot [\partial_n h_\alpha] = 0, \]

\[ -\rho U[\partial_n \rho] + \sum_\beta \{ \partial_{\rho_\beta} p_\beta n(\omega_\beta [\partial_n \rho] + \rho [\partial_n \omega_\beta]) + (u_\beta \cdot n) [\partial_n h_\beta] \]

\[ + u_\beta (n \cdot [\partial_n h_\beta] - \frac{1}{\omega_\beta} h_\beta \cdot n [\partial_n \omega_\beta] - \frac{1}{\rho} h_\beta \cdot n [\partial_n \rho]) \} = 0. \]

\[ -U[\partial_n h_\alpha] + (\partial_n v) \otimes n + \partial_n v \cdot n 1 h_\alpha + \partial_{\rho_\alpha} p_\alpha n(\omega_\alpha [\partial_n \rho] + \rho [\partial_n \omega_\alpha]) \]

\[ -\omega_\alpha \sum_\beta \{ \partial_{\rho_\beta} p_\beta n(\omega_\beta [\partial_n \rho] + \rho [\partial_n \omega_\beta]) + (u_\beta \cdot n) [\partial_n h_\beta] \]

\[ + u_\beta (n \cdot [\partial_n h_\beta] - \frac{1}{\omega_\beta} h_\beta \cdot n [\partial_n \omega_\beta] - \frac{1}{\rho} h_\beta \cdot n [\partial_n \rho]) \} = 0. \]

The occurrence of \( \{u_\beta\} \) in (61) and (62) imply that the propagation modes are affected by the velocity fields ahead of the front \( \sigma \). For definiteness and simplicity we make the assumption that

\[ h_\alpha(t, x) = 0, \quad x \in \Omega^+, \]
which means that the mixture is not diffusing ahead of the wave. Equations (59) and (60) remain unchanged whereas (61) and (62) simplify to

\[- \rho U [\partial_n v] + \sum_\beta \{ \kappa \beta n(\partial_\beta \rho) + \rho [\partial_n \omega_\beta] \} = 0, \quad (63)\]

\[- U [\partial_n h_\alpha] + \kappa_\alpha n(\omega_\alpha [\partial_n \rho] + \rho [\partial_n \omega_\alpha]) - \omega_\alpha \sum_\beta \{ \kappa_\beta n(\omega_\beta [\partial_n \rho] + \rho [\partial_n \omega_\beta]) \} = 0, \quad (64)\]

where

\[\kappa_\alpha := \partial_{\rho_\alpha} p_\alpha.\]

As a consequence of (63) and (64) the jumps \[\partial_n v\] and \[\partial_n h_\alpha\] are longitudinal, say \[\partial_n v = V n, \quad \partial_n h_\alpha = H_\alpha n.\]

Moreover, in view of (9) we have

\[\sum_\alpha H_\alpha = 0. \quad (65)\]

Replacing

\[\partial_n \rho = \frac{\rho}{U} V, \quad \partial_n \omega_\alpha = \frac{1}{\rho U} H_\alpha\]

we find that (63) and (64) become

\[\rho (-U^2 + \sum_\beta \kappa_\beta \omega_\beta) V + \sum_\beta \kappa_\beta H_\beta = 0, \quad (66)\]

\[\rho \omega_\alpha (\kappa_\alpha - \sum_\beta \kappa_\beta \omega_\beta) V + (-U^2 + \kappa_\alpha) H_\alpha - \omega_\alpha \sum_\beta \kappa_\beta H_\beta = 0. \quad (67)\]

The constraints

\[\sum_\beta \omega_\beta = 1, \quad \sum_\beta H_\beta = 0\]

allow us to write (66) and (67) as

\[\rho (-U^2 + \sum_\beta (\kappa_\beta - \kappa_n) \omega_\beta + \kappa_n) V + \sum_\beta (\kappa_\beta - \kappa_n) H_\beta = 0, \quad (68)\]

\[\rho \omega_\alpha (\kappa_\alpha - \sum_\beta (\kappa_\beta - \kappa_n) \omega_\beta - \kappa_n) V + (-U^2 + \kappa_\alpha) H_\alpha - \omega_\alpha \sum_\beta (\kappa_\beta - \kappa_n) H_\beta = 0. \quad (69)\]

The admissible speeds \(U\) are those satisfying the associated determinantal equation.

We now consider two simple cases.

a) \(\kappa_\beta = \kappa, \beta = 1, \ldots, n\). Assume that \(\kappa_\beta\) takes the same value for all the constituents, say \(\kappa\). Hence we have

\[\sum_\beta \kappa_\beta \omega_\beta = \kappa \sum_\beta \omega_\beta = \kappa, \quad \sum_\beta \kappa_\beta H_\beta = \kappa \sum_\beta H_\beta = 0.\]

Equations (66) and (67) reduce to

\[(-U^2 + \kappa) V = 0, \quad (-U^2 + \kappa) H_\alpha = 0.\]

The jumps \(V\) and \(H_\alpha\) are independent and both of them propagate at the speed

\[U = \sqrt{\kappa},\]
which is the speed of acoustic waves.

b) Binary mixture. If the constituents have different values of $\kappa$ then $V$ and $H_\alpha$ are related to each other. This is easily seen if there are two constituents. The determinantal equation reduces to

$$\det \begin{bmatrix} \rho[|U|^2 + (\kappa_1 - \kappa_2)\omega_1 + \kappa_2] & \kappa_1 - \kappa_2 \\ \rho\omega_1[\kappa_1 - (\kappa_1 - \kappa_2)\omega_1 - \kappa_2] & -U^2 + \kappa_1 - \omega_1(\kappa_1 - \kappa_2) \end{bmatrix} = 0.$$  

Upon some rearrangements we obtain

$$U^4 - (\kappa_1 + \kappa_2)U^2 + \kappa_1\kappa_2 - \omega_1(\kappa_1 - \kappa_2)^2 = 0.$$  

Hence two speeds $U_+, U_-$ may occur,

$$U_+^2 = \frac{1}{2}[\kappa_1 + \kappa_2 + |\kappa_1 - \kappa_2|\sqrt{1 + 4\omega_1}],$$
$$U_-^2 = \frac{1}{2}[\kappa_1 + \kappa_2 - |\kappa_1 - \kappa_2|\sqrt{1 + 4\omega_1}].$$

As expected, if $\kappa_1 = \kappa_2 = \kappa$ then

$$U_+^2 = U_-^2 = \kappa.$$

It is worth mentioning that a similar analysis of harmonic waves, in binary mixtures, is developed in [18, 20] for non-reacting constituents subject to a non-uniform common temperature.

7. Limiting properties of the diffusion fluxes. The fluxes $\{h_\alpha\}$ are determined by the evolution equations (33) which, in view of (24), can be written in the form

$$\dot{h}_\alpha + [L + (\nabla \cdot v)1]h_\alpha = \nabla \cdot (T_\alpha - h_\alpha \otimes u_\alpha) - \omega_\alpha \nabla \cdot T + \rho_\alpha (f_\alpha - f) + m_\alpha - \tau_\alpha v. \quad (70)$$

By (26), $T$ involves all of the fluxes $\{h_\alpha\}$ in the nonlinear form $\sum_\alpha h_\alpha \otimes h_\alpha / \rho_\alpha$. Hence (70) is a system of nonlinear first-order differential equations for $\{h_\alpha\}$.

The mixture is allowed to be chemically reacting and hence $m_\alpha - \tau_\alpha v$ is given by (56). Restrict attention to binary mixtures so that (51) holds. By (10),

$$\rho_\alpha = c_\alpha M_\alpha$$

and then

$$u_\alpha = \frac{h_\alpha}{\rho_\alpha} = \frac{h_\alpha}{c_\alpha M_\alpha}.$$  

Since $v_\beta - v_\alpha = u_\beta - u_\alpha$ we then have

$$m_\alpha - \tau_\alpha v = \sum_\beta \Xi_{\alpha\beta} \left( \frac{h_\beta}{c_\beta M_\beta} - \frac{h_\alpha}{c_\alpha M_\alpha} \right) + \frac{1}{2} \tau_\alpha \left( \frac{h_\alpha}{c_\alpha M_\alpha} + \frac{h_\beta}{c_\beta M_\beta} \right), \quad \alpha = 1, 2. \quad (71)$$

Letting $\Xi = \Xi_{12}$ and

$$\zeta = \frac{\Xi}{c_1 c_2} \frac{c_1 M_1 + c_2 M_2}{c_1 c_2 M_1 M_2} + \frac{\tau_1}{2} \frac{c_1 M_1 - c_2 M_2}{c_1 c_2 M_1 M_2}$$

we obtain

$$m_\alpha - \tau_\alpha v = -\zeta h_\alpha, \quad \alpha = 1, 2.$$

In binary mixtures, the force $m_\alpha - \tau_\alpha v$ is parallel to the diffusion flux $h_\alpha$.

Additional assumptions are now made. First, diffusion occurs in stationary conditions, $h_\alpha = 0$. Second, the mixture is so dilute that we can regard the solute as diffusing in a steady solvent and then $L = 0$. Third, the nonlinear terms $h_\alpha \otimes u_\alpha$ are disregarded. Equation (70) then provides

$$\zeta h_1 = \nabla \cdot T_1 - \omega_1 \nabla \cdot (T_1 + T_2) + \rho_1 (f_1 - f). \quad (72)$$
We remark that two forms of the continuity equations occur according as we refer to the mass fraction $\omega_\alpha$ or the concentration $c_\alpha$. By (8), in the linear approximation, $\dot{\omega}_\alpha \simeq \partial_t \omega_\alpha$ we have
\begin{equation}
\rho \partial_t \omega_\alpha = -\nabla \cdot \mathbf{h}_\alpha + \tau_\alpha.
\end{equation}
By (10) and (6) we have
\begin{equation}
\dot{\omega}_\alpha = \frac{M_\alpha}{\rho} \dot{c}_\alpha - \frac{M_\alpha c_\alpha}{\rho} \nabla \cdot \mathbf{v} = \frac{M_\alpha}{\rho} [\partial_t c_\alpha + \nabla \cdot (c_\alpha \mathbf{v})].
\end{equation}
Hence (8) gives
\begin{equation}
\partial_t c_\alpha = -\nabla \cdot \left( \frac{\mathbf{h}_\alpha}{M_\alpha} + c_\alpha \mathbf{v} \right) + \frac{\tau_\alpha}{M_\alpha}.
\end{equation}
Equation (74) for $c_\alpha$ involves a convective term $c_\alpha \mathbf{v}$.

7.1. Fick’s law. Assume that the two constituents are inviscid gases and that they satisfy the ideal gas law
\begin{equation}
T_\alpha = -p_\alpha \mathbf{1}, \quad p_\alpha = \frac{R}{M_\alpha} \rho_\alpha \theta = R \theta c_\alpha,
\end{equation}
where $R$ is the gas constant. For definiteness look at the diffusion flux $\mathbf{h}_1$ of the constituent 1 (solute). Moreover assume that no body forces act upon the solution ($\mathbf{f}_1, \mathbf{f}_2 = 0$). Hence (72) gives
\begin{equation}
\zeta \mathbf{h}_1 = -R [c_1 - \omega_1 (c_1 + c_2)] \nabla \theta - R \theta [\nabla c_1 - \omega_1 \nabla (c_1 + c_2)].
\end{equation}
If, as is usually the case, we look at dilute solutions then we keep only the leading (linear) terms in $c_1$, with $c_1 = \rho \omega_1 / M_1$, to have approximately
\begin{equation}
\mathbf{h}_1 = -\frac{R (c_1 - \omega_1 c_2)}{\zeta} \nabla \theta - \frac{R \theta}{\zeta} (\nabla c_1 - \omega_1 \nabla c_2).
\end{equation}
In isothermal conditions, $\nabla \theta = 0$, (75) reduces to
\begin{equation}
\mathbf{h}_1 = -D (\nabla c_1 - \omega_1 \nabla c_2), \quad D = \frac{R \theta}{\zeta}.
\end{equation}
Now,
\begin{equation}
\nabla c_2 = \nabla \rho \omega_2 \frac{M_1}{M_2} \nabla \rho \frac{M_2}{M_2} \nabla c_1
\end{equation}
and neglect of $\omega_1 \nabla c_2$ is reasonable inasmuch as $\omega_1$ is small, i.e., in diluted mixtures. Hence Fick’s law (1) follows for diluted, isothermal mixtures.

7.2. Nernst-Planck equation. Go back to (70) and regard the solute as a (dilute) ionic current. Instead of having recourse to the electrochemical potential (see [2]), we merely apply (70) and say that
\begin{equation}
\rho_1 \mathbf{f}_1 = c_1 N_A e_1 \mathbf{E},
\end{equation}
where $N_A$ is Avogadro’s number, $e_1$ is the electric charge of the ion, $\mathbf{E}$ is the applied electric field. Hence, because $\rho \mathbf{f} = \rho_1 \mathbf{f}_1$, we have
\begin{equation}
\rho_1 \mathbf{f} = \omega_1 c_1 N_A e_1 \mathbf{E}.
\end{equation}
Again we apply the dilute solution approximation ($\omega_1 << 1$), which allows us to let
\begin{equation}
\rho_1 (\mathbf{f}_1 - \mathbf{f}) = (1 - \omega_1) c_1 N_A e_1 \mathbf{E} \simeq c_1 N_A e_1 \mathbf{E}.
In addition we assume that temperature is uniform, $\nabla \theta = 0$, and then (72) and (76) provide

$$\zeta h_1 = -R\theta (\nabla c_1 - \omega_1 \nabla c_2 - \frac{c_1 e_1}{k_B \theta} \mathbf{E})$$

whence

$$h_1 = -D (\nabla c_1 - \omega_1 \nabla c_2 - \frac{c_1 e_1}{k_B \theta} \mathbf{E}).$$

Again neglect $\omega_1 \nabla c_2$. By (74) we can then write the balance equation

$$\partial_t c_1 = \nabla \cdot \left[ D (\nabla c_1 - \frac{c_1 e_1}{k_B \theta} \mathbf{E}) - c_1 v \right] + \tau_1 M_1.$$ (77)

Equation (77) is often referred to as Nernst-Planck equation. We recognize in (77) the effect of three fluxes: the Fick-type flux $-D \nabla c_1$, the flux $(Dc_1 e_1/k_B \theta) \mathbf{E}$ driven by the electric field, the convective flux $c_1 v$.

8. Relation to other models of diffusion. The literature on diffusion phenomena exhibits various definitions of fluxes (see, e.g., [22, 6, 1]. The vectors

$$\tilde{J}_\alpha = \rho_\alpha v_\alpha, \quad J_\alpha = c_\alpha v_\alpha$$

are called observed fluxes in that $v_\alpha$ is the velocity with respect to an arbitrary observer. Diffusion fluxes account for the deviations of the velocity $v_\alpha$ from an average (or a fixed) velocity. If $G$ is any (geometric or material) point, with velocity $v_G$, we can write

$$J_\alpha = c_\alpha v_G + c_\alpha (v_\alpha - v_G)$$

and the like for $\tilde{J}_\alpha$. We say that $c_\alpha (v_\alpha - v_G$) and $\rho_\alpha (v_\alpha - v_G$) are diffusion fluxes. Among the choices of $v_G$ there is the velocity of the local center of moles,

$$v^* = \sum_\alpha x_\alpha v_\alpha, \quad x_\alpha = \frac{c_\alpha}{\sum_\beta c_\beta},$$

and the barycentric velocity $v$. The corresponding diffusion fluxes

$$j_\alpha = c_\alpha (v_\alpha - v^*), \quad h_\alpha = \rho_\alpha (v_\alpha - v)$$

have the advantage that their sum is zero. Most often [22] the symbol $\tilde{j}$ is used instead of $h$.

Another reference velocity is that of inert markers, say fixed points in a lattice. Denote such velocity by $v_M$ and let

$$j_M^\alpha = c_\alpha (v_\alpha - v_M)$$

be the diffusion flux relative to markers. Summation gives

$$c(v_M - v^*) = -\sum_\alpha j_M^\alpha,$$

where $c = \sum_\alpha c_\alpha$. Hence we have

$$j_\alpha = j_M^\alpha - \sum_\alpha \frac{c_\alpha}{c} j_M^\alpha.$$

Next the diffusive fluxes are related to thermodynamic (driving) forces through constitutive equations. For instance [22],

$$h_\alpha = -\rho D \nabla \omega_\alpha,$$

$D$ being the diffusivity. Instead, for the diffusion flux relative to markers the assumption is [22, 7]

$$j_M^\alpha = -D_\alpha^M \nabla c_\alpha.$$
As shown in the previous section, in isothermal conditions the dependence of $h_\alpha$ on $\nabla c_\alpha$ looks more motivated in connection with (70).

As a remark, by (78) we have

$$j^M_\alpha = \frac{\rho_\alpha}{M_\alpha}(v_\alpha - v_M) = \frac{\rho_\alpha}{M_\alpha}(v_\alpha - v) + \frac{\rho_\alpha}{M_\alpha}(v - v_M).$$

Multiplying by $M_\alpha$ and summing over $\alpha$ we obtain

$$\rho(v - v_M) = \sum_{\alpha} M_\alpha j^M_\alpha.$$  \hspace{1cm} (79)

Once the fluxes $j^M_\alpha$ are determined, eq. (79) provides the motion of the barycentric reference relative to the markers.

9. **Conclusions.** As a preliminary step, the whole set of balance equations for chemically-reacting fluid mixtures is established. In particular this allows us to clarify the evolution equations of the molar concentrations $\{c_\alpha\}$ and the mass fractions $\{\omega_\alpha\}$. The diffusion flux $h_\alpha = \rho_\alpha u_\alpha$, relative to the barycentric reference, is shown to satisfy the differential equation (70). This provides a crucial concept. The flux $h_\alpha$ is given by a balance equation, not by a constitutive assumption at the outset. Yet, the balance equation is operative once we specify the stresses $\{T_\alpha\}$ and the interaction forces $\{m_\alpha\}$.

By way of application, limiting properties of (70) are shown to provide Fick’s law and the Nernst-Planck equation. Moreover, known generalized forces of the literature (e.g. the Maxwell-Stefan diffusion model) prove to be obtained by appropriate constitutive assumptions on $\{T_\alpha\}$ and $\{m_\alpha\}$.

Other diffusion fluxes adopted in the literature are considered. Their balance equation follows by determining the connection with the barycentric flux $h_\alpha$.

The entropy inequality is exploited by letting the constitutive functions of the $\alpha$th constituent depend on $(\theta_\alpha, \rho_\alpha, \nabla \rho_\alpha, D_\alpha, \nabla \theta_\alpha)$, the gradients accounting for nonlocality. Among the results we mention (43) and (45) whereby the partial pressure $p_\alpha$ is given by $p_\alpha^2 \delta \rho_\alpha \psi_\alpha$ and the mass growths $\{\tau_\alpha\}$ are subject to $\sum_{\alpha} \tau_\alpha (\psi_\alpha + p_\alpha/\rho_\alpha) / \theta_\alpha \leq 0$. This in turn generalizes the classical law of mass action.

In addition to being a balance equation, eq. (70) for $h_\alpha$ makes it hyperbolic the whole system of equations (52)-(53), in the unknowns $\rho, \omega_\alpha, v, h_\alpha$. For technical simplicity, this is demonstrated by the analysis of discontinuity waves of order 2 (acceleration waves). The wave speed is derived explicitly in the case of binary mixtures.

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**REFERENCES**

[1] W. J. Boettinger, J. E. Geyer, C. E. Campbell and G. B. McFadden, Computation of the Kirkendall velocity and displacement field in a one-dimensional binary diffusion couple with a moving interface, *Proc. Royal Soc. A*, 463 (2007), 3347–3373.

[2] J. O’M. Bokris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum, New York, 1997; ch. 4.

[3] R. M. Bowen and J. C. Wiese, Diffusion in mixtures of elastic materials, *Int. J. Engng Sci.*, 7 (1969), 689–722.

[4] M. F. McCarthy, *Singular Surfaces and Waves*, in Continuum Physics II (ed. A.C. Eringen), Wiley, New York, pp. 449–521.

[5] J. Crank, *The Mathematics of Diffusion*, Oxford, at the Clarendon Press, 1956.
[6] J. A. Dantzig, W. J. Boettinger, J. A. Warren, G. B. McFadden, S. R. Coriell and R. F. Sekerka, Numerical modeling of diffusion-induced deformation, *Metall. Mat. Trans. A*, 37 (2006), 2701–2714.

[7] L. S. Darken, Diffusion, mobility and their interrelation through free energy in binary metallic systems, *Trans. AIME*, 175 (1948), 184–201.

[8] M. Fabrizio, C. Giorgi and A. Morro, A thermodynamic approach to non-isothermal phase-field evolution in continuum physics, *Physica D*, 214 (2006), 144–156.

[9] M. E. Gurtin, Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance, *Physica D*, 92 (1996), 178–192.

[10] J. B. Haddow and J. L. Wegner, Plane harmonic waves for three thermoelastic theories, *Math. Mech. Solids*, 1 (1996), 111–127.

[11] P. M. Jordan, Second-sound propagation in rigid, nonlinear conductors, *Mech. Res. Comm.*, 68 (2015), 52–59.

[12] P. J. A. M. Kerkhof and M. A. M. Geboers, Analysis and extension of the theory of multi-component fluid diffusion, *Chem. Engng Sci.*, 60 (2005), 3129–3167.

[13] B. J. Kirby, *Micro- and Nanoscale Fluid Mechanics*, Transport in microfluidic devices. Paperback reprint of the 2010 original. Cambridge University Press, Cambridge, 2013.

[14] J. C. Maxwell, On the dynamical theory of gases, *The Scientific Papers of J.C. Maxwell*, 2 (1965), 26–78.

[15] A. Morro, Governing equations in non-isothermal diffusion, *Int. J. Non-Linear Mech.*, 55 (2013), 90–97.

[16] A. Morro, Evolution equations for non-simple viscoelastic solids, *J. Elasticity*, 105 (2011), 93–105.

[17] I. Müller, Thermodynamics of mixtures of fluids, *J. Mécanique*, 14 (1975), 267–303.

[18] I. Müller, *Thermodynamics*, Pitman, London 1985, § 6.7.

[19] I. Müller, Thermodynamics of mixtures and phase field theory, *Int. J. Solids Structures*, 38 (2001), 1105–1113.

[20] I. Müller and T. Ruggeri, *Extended Thermodynamics*, Springer, New York 1993, § 2.5.

[21] S. Rehfeldt and J. Stichlmair, Measurement and calculation of multicomponent diffusion coefficients in liquids, *Fluid Phase Equilibria*, 256 (2007), 99–104.

[22] R. F. Sekerka, Similarity solutions for a binary diffusion couple with diffusivity and density dependent on composition, *Prog. Mat. Sci.*, 49 (2004), 511–536.

[23] J. Stefan, Über das Gleichgewicht und Bewegung, insbesondere die Diffusion von Gemischen, *Sitzungsbereichte der Kaiserlichen Akademie der Wissenschaften Wien*, 63 (1871), 63–124.

[24] I. Steinbach and M. Apel, Multi phase field model for solid state transformation with elastic strain, *Physica D*, 217 (2006), 153–160.

[25] B. Straughan, *Heat Waves*, Springer, New York, 2011.

[26] C. Truesdell, *Rational Thermodynamics*, Springer, New York, 1984.

[27] C. Truesdell and R. Toupin, The classical field theories, *Handbuch der Physik*, Bd. III/1, Springer, Berlin, (1960), 226–793; appendix, 794–858.

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