INTERACTION MODELS FOR MIXTURES WITH APPLICATION TO PHASE TRANSITIONS

J. M. N. T. GRAY† and B. SVENDSEN
Institut für Mechanik, Technische Hochschule Darmstadt, 64289 Darmstadt, Germany

(Communicated by K. R. RAJAGOPAL)

Abstract—Continuum mixture theoryformulates balances of mass, momentum and energy for a mixture body and non-material singular surfaces. An important component of these balances are the transfers that take place between constituents. These are described by volume interactions within a mixture body and surface interactions at a singular surface. The interactions sum to zero over all the constituents in order that there is no net production of mass, momentum or energy. The principle of Euclidean frame indifference is used to formulate the functional forms of these interactions. A simple set of volume and surface interaction functions are then postulated which satisfy the summation and frame indifference requirements. These partition the mass, momentum and energy transfers into a sum of the interactions between pairs of constituents. Illustrations are presented for a classical phase change front, a phase change front in a binary mixture and two examples of phase change in a tertiary mixture which demonstrate complex reabsorption processes. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION

The theory of interacting continua, mixture theory, provides a rational mathematical framework in which to describe many problems that arise in physical, chemical and engineering contexts. The motivation for the theoretical development in this paper stems from an application to snow packs [1] which consist of complex assemblies of ice, water, water-vapour and air. Isolated regions of dry sub-freezing snow [2, 3] and wet temperate snow [4] can be described using standard mixture theory, but this is not sufficient to describe polythermal snow packs which contain a non-material singular surface at which the water is annihilated.

In standard mixture theory (e.g. [5]) it is supposed that the mixture length scale is large compared to the size of a typical mixture element and that every point in the mixture is occupied simultaneously by each constituent. Providing the physical variables, and their derivatives, are smooth, the volume integrals of the conservation laws can then be reduced to point differential form, yielding a mass, momentum and energy balance for each constituent. An important component of these balances are the mass, momentum and energy transfers that take place between the constituents. These are described by volume interactions which sum to zero over all the constituents. Morland [6] postulated simple constitutive models to partition the volume interactions into sums of binary transfers between constituents, each of which is frame indifferent (in this paper frame indifferent means Euclidean frame indifferent) under an observer transformation. The restrictions imposed by summation and frame indifference requirements in the bulk mixture are presented in detail in this paper. This leads to a minor generalisation of the volume interactions postulated by Morland [6] and allows the conditions to be contrasted with subsequent results for the interactions at singular surfaces.

Standard mixture theory is not sufficient to account for the presence of non-material singular surfaces at which there can be jumps in the physical variables, and/or their derivatives, and which may separate individual or groups of constituents from each other. Such singular surfaces occur commonly in many materials. For instance, at a classical phase change, or chemical

† To whom all correspondence should be addressed.
interaction front, or at the transition between cold and temperate regions of an ice sheet [7]. The discontinuities prevent the reduction of the volume integrals of the conservation laws to point differential form and instead determine mass, momentum and energy jump conditions (e.g. [8, 6]) across the singular surface. Surface transfers of mass, momentum and energy also take place between the constituents. These are accounted for by surface interactions which sum to zero over all constituents [9]. In this paper the summation condition and frame indifference are used to formulate the functional forms for the surface interactions, which are then constitutive. Simple constitutive models for the partitioning of the surface interactions into sums of transfers between pairs of constituents are then postulated.

2. STANDARD MIXTURE THEORY

The basic mixture theory postulate is that every point is occupied simultaneously by all constituents. This avoids having to determine which constituent occupies a given point at a given time. Each constituent \( \alpha \), therefore, occupies a volume fraction, \( \phi^\alpha \), per unit mixture volume, and by definition these volume fractions lie between zero and one and their sum over all constituents equals unity:

\[
0 \leq \phi^\alpha \leq 1, \quad \sum_\alpha \phi^\alpha = 1. \tag{2.1}
\]

Hence, at each point and time overlapping partial variables associated with a given constituent are defined. The partial density \( \rho^\alpha \) is the mass of constituent \( \alpha \) per unit mixture volume, the partial energy flux \( \mathbf{q}^\alpha \) is the energy flux per unit mixture area into constituent \( \alpha \) and the partial traction \( \mathbf{t}^\alpha \) is the force supported by constituent \( \alpha \) per unit mixture cross-section. The partial stress tensor \( \mathbf{\sigma}^\alpha \) satisfies \( \mathbf{t}^\alpha(\mathbf{n}) = \mathbf{\sigma}^\alpha \mathbf{n} \) for all unit normals \( \mathbf{n} \) and the partial pressure \( p^\alpha = -\frac{1}{3} \text{tr} \mathbf{\sigma}^\alpha \). An essential feature of mixture theory is the link between these overlapping partial variables and specific, or intrinsic, variables associated with an individual element of a single constituent. The partial density, pressure, traction, energy flux and stress are related to their intrinsic counterparts (which are indicated by a capital superscript \( \alpha \), i.e. \( \mathbb{I} \)) by a linear volume fraction scaling

\[
\rho^\alpha = \phi^\alpha \rho^\mathbb{I}, \quad p^\alpha = \phi^\alpha p^\mathbb{I}, \quad \mathbf{t}^\alpha = \phi^\alpha \mathbf{q}^\mathbb{I}, \quad \mathbf{q}^\alpha = \phi^\alpha \mathbf{q}^\mathbb{I}, \quad \mathbf{\sigma}^\alpha = \phi^\alpha \mathbf{\sigma}^\mathbb{I}. \tag{2.2}
\]

This assumes that volume fraction per unit mixture volume and the surface area fraction per unit mixture area section are equal. In addition the intrinsic velocity field \( \mathbf{v}^\mathbb{I} \) is the vector such that \( \rho^\alpha \mathbf{v}^\alpha \) is the mass flux of constituent \( \alpha \) per unit mixture volume and the intrinsic strain-rate \( \mathbf{D}^\mathbb{I} = \frac{1}{2}(\nabla \mathbf{v}^\mathbb{I} + \nabla \mathbf{v}^\mathbb{I}^T) \), where the superscript \( T \) indicates the transpose of \( \nabla \mathbf{v}^\mathbb{I} \). The total intrinsic energy per unit mass of constituent \( \alpha \) is defined as

\[
e^{\mathbb{I}} = \varepsilon^{\mathbb{I}} + \frac{1}{2} \mathbf{v}^\mathbb{I} \cdot \mathbf{v}^\mathbb{I}, \tag{2.3}
\]

where \( \varepsilon^{\mathbb{I}} \) is the intrinsic internal (stored) energy and \( \frac{1}{2} \mathbf{v}^\mathbb{I} \cdot \mathbf{v}^\mathbb{I} \) is the kinetic energy per unit mass of constituent \( \alpha \). The latent heat release \( L^{\mathbb{I}} = -L^{\mathbb{II}} \) in the phase change from constituent \( b \) to constituent \( \alpha \) is defined as the change in enthalpy \( \varepsilon^{\mathbb{I}} + p^\alpha/\rho^\alpha \) at constant temperature, that is

\[
L^{\mathbb{I}} = \varepsilon^{\mathbb{II}} - \varepsilon^{\mathbb{I}} + \frac{p^b}{\rho^b} - \frac{p^\alpha}{\rho^\alpha}. \tag{2.4}
\]

Note, that in general, the partial variables all tend to zero as the volume fraction \( \phi^\alpha \) tends to zero whilst the intrinsic variables do not.

We take advantage of the fact that the conservation laws are frame indifferent under an observer transformation to formulate the functional forms of the volume interactions. The
The original point differential form of the conservation laws [9] for constituent \( \alpha \) are

\[
\begin{align*}
\text{mass: } & \quad \frac{\partial}{\partial t} (\rho^\alpha) + \text{div}(\rho^\alpha \mathbf{v}^\alpha) = \mathcal{V}_{m}^\alpha, \\
\text{momentum: } & \quad \frac{\partial}{\partial t} (\rho^\alpha \mathbf{v}^\alpha) + \text{div}(\rho^\alpha \mathbf{v}^\alpha \otimes \mathbf{v}^\alpha) = \text{div} \mathbf{a}^\alpha + \mathbf{b}^\alpha + \mathcal{V}_{l}^\alpha, \\
\text{energy: } & \quad \frac{\partial}{\partial t} (\rho^\alpha \varepsilon^\alpha) + \text{div}(\rho^\alpha \varepsilon^\alpha \mathbf{v}^\alpha) = \text{div} \mathbf{q}^\alpha + \mathbf{r}^\alpha + \mathbf{b}^\alpha \cdot \mathbf{v}^\alpha + \mathcal{V}_{e}^\alpha,
\end{align*}
\]

where \( \mathbf{b}^\alpha \) is the external body force exerted on constituent \( \alpha \) per unit mixture volume and \( \mathbf{r}^\alpha \) is the rate of external energy supply to constituent \( \alpha \) per unit mixture volume. The volume interactions represent the transfers of mass, \( \mathcal{V}_{m}^\alpha \), linear momentum, \( \mathcal{V}_{l}^\alpha \), and energy, \( \mathcal{V}_{e}^\alpha \), (denoted by the subscripts \( \text{m}, \text{l}, \) and \( \text{e} \), respectively) to constituent \( \alpha \) from the remaining constituents. These must sum to zero

\[
\sum_{\alpha} \mathcal{V}_{m}^\alpha = 0, \quad \sum_{\alpha} \mathcal{V}_{l}^\alpha = 0, \quad \sum_{\alpha} \mathcal{V}_{e}^\alpha = 0,
\]

(2.6)

in order that there is no internal production within the bulk mixture volume. Using standard vector and tensor analysis (e.g. [10]) the general conservation laws (2.5) can be reduced to the simpler form

\[
\begin{align*}
\text{mass: } & \quad \frac{D_{\alpha} \rho^\alpha}{Dt} + \rho^\alpha \text{div} \mathbf{v}^\alpha = \mathcal{V}_{m}^\alpha, \\
\text{momentum: } & \quad \frac{\partial}{\partial t} (\rho^\alpha \mathbf{v}^\alpha) + \text{div} \mathbf{a}^\alpha + \mathbf{b}^\alpha + \mathcal{V}_{l}^\alpha, \\
\text{energy: } & \quad \frac{\partial}{\partial t} (\rho^\alpha \varepsilon^\alpha) + \text{div} \mathbf{q}^\alpha + \mathbf{r}^\alpha + \mathcal{V}_{e}^\alpha,
\end{align*}
\]

(2.7)

where

\[
\frac{D_{\alpha}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^\alpha \cdot \nabla.
\]

(2.8)

These are directly comparable to the equations derived by [6]. The internal circumstances of the body are expected to appear the same to equivalent observers and the partial density \( \rho^\alpha \), partial traction \( \mathbf{t}^\alpha \), intrinsic stored energy \( \varepsilon^\alpha \), and the normal energy flux \( q^\alpha_n = \mathbf{q}^\alpha \cdot \mathbf{n} \) are assumed frame indifferent following [11]. The stress \( \mathbf{a}^\alpha \) and the energy flux vector \( \mathbf{q}^\alpha \) are, therefore, frame indifferent and hence each of the terms \( D_{\alpha} \rho^\alpha / Dt, \rho^\alpha \text{div} \mathbf{v}^\alpha = \rho^\alpha \text{tr} \mathbf{D}^\alpha, \text{div} \mathbf{a}^\alpha, \rho^\alpha D_{\alpha} \varepsilon^\alpha / Dt \) and \( \text{div} \mathbf{q}^\alpha \) appearing in (2.7) are also frame indifferent. The mass and energy balances (2.7) are frame indifferent under the further assumptions that \( \mathcal{V}_{m}^\alpha, \mathcal{V}_{e}^\alpha \) and \( \mathbf{r}^\alpha \) are frame indifferent. The momentum balance (2.7) is frame indifferent when both the difference \( \rho^\alpha D_{\alpha} \varepsilon^\alpha / Dt - \mathbf{b}^\alpha \) and \( \mathcal{V}_{l}^\alpha \) transform as frame indifferent vectors.

It follows from these arguments that the volume interactions \( \mathcal{V}_{m}^\alpha, \mathcal{V}_{l}^\alpha, \) and \( \mathcal{V}_{e}^\alpha \) must all be frame indifferent, which is indicated by the extra subscript \( \circ \). In re-expressing the original form of the conservation laws (2.5) in the simpler form (2.7), the following relationships

\[
\begin{align*}
\mathcal{V}_{m}^{\circ} = \mathcal{V}_{m}^\alpha, \\
\mathcal{V}_{l}^{\circ} = \mathcal{V}_{l}^\alpha - \mathbf{v}^\alpha \mathcal{V}_{m}^{\circ}, \\
\mathcal{V}_{e}^{\circ} = \mathcal{V}_{e}^\alpha - \varepsilon^\alpha \mathcal{V}_{m}^{\circ} - \mathbf{v}^\alpha \cdot \mathcal{V}_{l}^{\circ}
\end{align*}
\]

(2.9)

hold. These conditions, together with the summation laws (2.6), place restrictions on the allowable functional forms for \( \mathcal{V}_{m}^\alpha, \mathcal{V}_{l}^\alpha, \) and \( \mathcal{V}_{e}^\alpha \). Note, that the process of mass transfer gives rise to non-frame indifferent contributions \( \mathbf{v}^\alpha \mathcal{V}_{m}^{\circ} \) and \( \varepsilon^\alpha \mathcal{V}_{m}^{\circ} \) to the momentum and energy balances, respectively, and the process of linear momentum transfer implies a further
non-frame indifferent contribution \( v_i^{\alpha} \cdot \mathbf{v}_\alpha^{\alpha} \) to the energy balance. This motivates the decomposition of volume interaction terms into independent transfers associated with a given process

\[
\begin{aligned}
\mathcal{V}^{\alpha}_m &= \mathcal{V}^{\alpha}_{mm}, \\
\mathcal{V}^{\alpha}_l &= \mathcal{V}^{\alpha}_{lm} + \mathcal{V}^{\alpha}_{ll}, \\
\mathcal{V}^{\alpha}_e &= \mathcal{V}^{\alpha}_{em} + \mathcal{V}^{\alpha}_{el} + \mathcal{V}^{\alpha}_{ee},
\end{aligned}
\]  

(2.10)

where \( \mathcal{V}^{\alpha}_\chi \) is the contribution to the \( \chi = m, l, e \) (mass, momentum or energy) balance due to a process associated with a mass, momentum or energy transfer \( \chi = m, l, e \). For example, \( \mathcal{V}^{\alpha}_{em} \) is an energy interaction due to mass (phase change) processes and \( \mathcal{V}^{\alpha}_{ee} \) is an energy interaction due to pure energy fluxes. Formally substituting (2.10) into (2.6) and (2.9) yields six sum conditions

\[
\begin{aligned}
\sum_{\alpha} \mathcal{V}^{\alpha}_{mm} &= 0, \\
\sum_{\alpha} \mathcal{V}^{\alpha}_{lm} &= 0, \\
\sum_{\alpha} \mathcal{V}^{\alpha}_{em} &= 0,
\end{aligned}
\]  

(2.11)

(since the processes are assumed independent) and six frame indifferent forms

\[
\begin{aligned}
\mathcal{V}^{\alpha}_{mm} &= \mathcal{V}^{\alpha}_{mm}, \\
\mathcal{V}^{\alpha}_{lm} &= \mathcal{V}^{\alpha}_{lm} - v^{\chi} \mathcal{V}^{\alpha}_{mm}, \\
\mathcal{V}^{\alpha}_{em} &= \mathcal{V}^{\alpha}_{em} - e^{\chi} \mathcal{V}^{\alpha}_{mm} - v^{\chi} \cdot (\mathbf{v}^{\alpha}_{lm} - v^{\chi} \mathcal{V}^{\alpha}_{mm}), \\
\mathcal{V}^{\alpha}_{il} &= \mathcal{V}^{\alpha}_{il}, \\
\mathcal{V}^{\alpha}_{el} &= \mathcal{V}^{\alpha}_{el} - v^{\chi} \cdot \mathcal{V}^{\alpha}_{il}, \\
\mathcal{V}^{\alpha}_{ee} &= \mathcal{V}^{\alpha}_{ee},
\end{aligned}
\]  

(2.12)

respectively, where \( \mathcal{V}^{\alpha}_{\chi \chi} \) is the frame indifferent component of the \( \chi = m, l, e \) interaction due to transfers associated with the process \( \chi = m, l, e \). Thus, the linear momentum interactions consist of a non-frame indifferent part \( \mathcal{V}^{\alpha}_{lm} \), which combines with \( v^{\chi} \mathcal{V}^{\alpha}_{mm} \) to form a frame indifferent quantity, and a frame indifferent part \( \mathcal{V}^{\alpha}_{il} \) associated with non-mass transfer linear momentum interactions. Similarly, the energy interactions consist of non-frame indifferent parts \( \mathcal{V}^{\alpha}_{em} \) and \( \mathcal{V}^{\alpha}_{el} \) which combine with \( e^{\chi} \mathcal{V}^{\alpha}_{mm} \) and \( v^{\chi} \cdot \mathcal{V}^{\alpha}_{il} \), respectively, to form frame indifferent quantities and a frame indifferent part \( \mathcal{V}^{\alpha}_{ee} \) associated with pure energy interactions. Note, that the frame indifferent sums \( \sum_{\alpha} \mathcal{V}^{\alpha}_{mm} \), \( \sum_{\alpha} \mathcal{V}^{\alpha}_{lm} \), \( \sum_{\alpha} \mathcal{V}^{\alpha}_{il} \) and \( \sum_{\alpha} \mathcal{V}^{\alpha}_{ee} \) respectively, to form frame indifferent quantities and a frame indifferent part \( \mathcal{V}^{\alpha}_{ee} \) associated with pure energy interactions. Note, that the frame indifferent sums \( \sum_{\alpha} \mathcal{V}^{\alpha}_{mm} \), \( \sum_{\alpha} \mathcal{V}^{\alpha}_{lm} \), \( \sum_{\alpha} \mathcal{V}^{\alpha}_{il} \) and \( \sum_{\alpha} \mathcal{V}^{\alpha}_{ee} \) respectively.

3. Volume Interactions

The sum relations (2.11) and the frame indifferent forms (2.12) place restrictions on the functional forms for the volume interaction terms \( \mathcal{V}^{\alpha}_{mm}, \mathcal{V}^{\alpha}_{lm}, \mathcal{V}^{\alpha}_{il}, \mathcal{V}^{\alpha}_{em}, \mathcal{V}^{\alpha}_{el} \) and \( \mathcal{V}^{\alpha}_{ee} \). We
postulate binary transfers for the volume interactions of the form

\[
\begin{align*}
\mathcal{V}^\alpha_{mm} &= \sum_b M^{ab}, \\
\mathcal{V}^\alpha_{lo} &= \sum_b \frac{1}{2} M^{ab} (v^\alpha + v^\beta), \\
\mathcal{V}^\alpha_{em} &= \sum_b \frac{1}{2} M^{ab} (\varepsilon^\alpha + \varepsilon^\beta + v^\alpha \cdot v^\beta), \\
\mathcal{V}^\alpha_{ll} &= \sum_b B^{ab}, \\
\mathcal{V}^\alpha_{\alpha} &= \sum_b \frac{1}{2} B^{ab} \cdot (v^\alpha + v^\beta), \\
\mathcal{V}^\alpha_{ee} &= \sum_b E^{\alpha b},
\end{align*}
\] (3.1)

where the rate of mass transfer $M^{ab}$, the volume interaction drag due to non-mass transfer processes $B^{ab}$ and the rate of energy supply due to non-mass and non-traction processes $E^{ab}$ to constituent $\alpha$ from constituent $b$ are defined per unit mixture volume. These satisfy the summation relations (2.11) provided that

\[
\begin{align*}
M^{ab} &= -M^{ba}, & M^{aa} &= 0, \\
B^{ab} &= -B^{ba}, & B^{aa} &= 0, \\
E^{ab} &= -E^{ba}, & E^{aa} &= 0,
\end{align*}
\] (3.2)

and satisfy the frame indifference requirements (2.12) yielding

\[
\begin{align*}
\mathcal{V}^\alpha_{mmo} &= \sum_b M^{ab}, \\
\mathcal{V}^\alpha_{lmo} &= \sum_b \frac{1}{2} M^{ab} (v^\alpha - v^\beta), \\
\mathcal{V}^\alpha_{emo} &= \sum_b \frac{1}{2} M^{ab} (\varepsilon^\alpha - \varepsilon^\beta), \\
\mathcal{V}^\alpha_{loo} &= \sum_b B^{ab}, \\
\mathcal{V}^\alpha_{\alpha} &= \sum_b \frac{1}{2} B^{ab} \cdot (v^\alpha - v^\beta), \\
\mathcal{V}^\alpha_{eco} &= \sum_b E^{\alpha b}.
\end{align*}
\] (3.3)

The first five of these equations are exactly the same as those postulated by Morland [6]. The sixth equation is a new binary interaction for pure energy processes not present in Morland’s [6] theory. This additional term makes a clear separation between the energy flux contributions from transfers with other constituents and the energy flux $q^\alpha$ within constituent $\alpha$, which were combined in Morland’s [6] definition of the heat flux.

4. NON-MATERIAL SINGULAR SURFACES

In order to solve practical problems with standard mixture theory, meaningful boundary conditions must be specified at the boundary of the mixture domain. This presents significant difficulties both in defining this boundary and in partitioning the applied conditions between the interior mixture constituents [12, 13]. The boundary of a mixture is a special case of the more general concept of a non-material singular surface, where the problems of partitioning the interactions between constituents arise on both sides of the surface.
At a non-material singular surface \( S^* \), moving with speed \( u_n \) in the direction of the normal \( n \) to \( S^* \), there are jumps in the physical variables and/or their derivatives. The point form of the mass, linear momentum and energy jump conditions for constituent \( \alpha \) \([9]\) are

\[
\begin{align*}
\text{mass: } \{m^n_\alpha\} & = \mathcal{S}^n_{m,}\, \\
\text{momentum: } \{m^n_\alpha v^n\} - \{t^n\} & = \mathcal{S}^n_{l,}\, \\
\text{energy: } \{m^n_\alpha e^n\} - \{t^n \cdot v^n\} + \{q^n_\alpha\} & = \mathcal{S}^n_{e,}\,
\end{align*}
\]  

(4.1)

where the square bracket \( \{f\} = f^+ - f^- \) is the jump across the surface of a scalar or vector quantity \( f \), and \( f^* \) is the limiting value of \( f \) in the bulk mixture as \( S^* \) is approached from the \( \pm \) side, respectively. Note, that by convention the normal \( n \) to \( S^* \) is directed towards the plus side. The normal mass flux of constituent \( \alpha \) per unit surface area is \( m^n_\alpha = \rho^n (v^n_\alpha - u_n) \) where \( v^n_\alpha \) is the normal component of the velocity field. The surface interactions \( \mathcal{S}^n_{m,}, \mathcal{S}^n_{l,}, \mathcal{S}^n_{e,} \) represent transfers of mass, linear momentum and energy, respectively, between constituent \( \alpha \) and the remaining constituents at the singular surface. The sum of each of the surface interactions over all constituents is necessarily zero,

\[
\sum_\alpha \mathcal{S}^n_{m,} = 0, \quad \sum_\alpha \mathcal{S}^n_{l,} = 0, \quad \sum_\alpha \mathcal{S}^n_{e,} = 0,
\]

(4.2)

in order that there is no surface production, only transfer between constituents, of mass, momentum and energy. The classical jump relations \([6]\) are identical to (4.1) when \( \mathcal{S}^n_{m,} = 0, \mathcal{S}^n_{l,} = 0, \mathcal{S}^n_{e,} = 0 \) for all constituents \( \alpha \).

The parallels between the theoretical development in the bulk volume and at the singular surface are very strong. For instance, note that both the original point differential (2.5) and the jump (4.1) forms of the conservation laws are written in terms of volume and surface interactions which sum to zero over all constituents, as in (2.6) and (4.2). Continuing this parallel, the original form of the jump conservation relations (4.1) is now written in a simpler form. In order to accomplish this it is useful to define the mean \([14]\) of a scalar or vector quantity \( f \) across the singular surface \( S^* \) to be \( \langle f \rangle = \frac{1}{2} (f^+ + f^-) \). For any distributive operator \( \bigcirc \) (e.g. scalar multiplication or dot products) the mean and jump of \( f \bigcirc g \) satisfy

\[
\begin{align*}
\langle f \bigcirc g \rangle & = \langle f \rangle \bigcirc \langle g \rangle + \frac{1}{4} \langle f \rangle \bigcirc \langle g \rangle, \\
\{ f \bigcirc g \} & = \{ f \} \bigcirc \langle g \rangle + \langle f \rangle \bigcirc \{ g \},
\end{align*}
\]

(4.3)

where \( f \) and \( g \) are scalar or vector functions.

Assuming that constituent \( \alpha \) exists on both sides of the singular surface \( S^* \) (i.e. the velocity \( v^n \) and total energy \( e^n \) are defined), (4.3) can be used to express the mass, momentum and energy jumps (4.1) in the form

\[
\begin{align*}
\text{mass: } \{m^n_\alpha\} & = \mathcal{S}^n_{m,0}, \\
\text{momentum: } \{m^n_\alpha v^n\} - \{t^n\} & = \mathcal{S}^n_{l,0}, \\
\text{energy: } \{m^n_\alpha e^n\} - \{t^n \cdot v^n\} + \{q^n_\alpha\} & = \mathcal{S}^n_{e,0},
\end{align*}
\]

(4.4)

The difference of two velocities is a frame indifferent vector and hence the normal mass flux \( m^n_\alpha \) and the jump in the velocity across the singular surface \( \{v^n\} \) are frame indifferent. It follows that the mass, momentum and energy jumps (4.4) are frame indifferent provided \( \mathcal{S}^n_{m,0}, \mathcal{S}^n_{l,0} \) and \( \mathcal{S}^n_{e,0} \) are frame indifferent (which is assumed and indicated by the subscript \( 0 \)). The original and frame indifferent forms of the surface interactions are related by

\[
\begin{align*}
\mathcal{S}^n_{m,0} = \mathcal{S}^n_{m,}, \\
\mathcal{S}^n_{l,0} = \mathcal{S}^n_{l,} - \{v^n\} \mathcal{S}^n_{m,0}, \\
\mathcal{S}^n_{e,0} = \mathcal{S}^n_{e,} - \{v^n\} \cdot \mathcal{S}^n_{l,0,}
\end{align*}
\]

(4.5)

which are analogous to the restrictions (2.9) in the bulk volume. In this case non-frame
indifferent contributions $\langle v^\alpha \rangle F_{\alpha \alpha}^\alpha, \langle e^\alpha \rangle F_{\alpha \alpha}^\alpha$, and $\langle v^\alpha \rangle \cdot F_{\alpha \alpha}^\alpha$ are made to the momentum and energy interactions, which suggest the decomposition into independent transfers associated with a given process

$$\begin{align*}
\mathcal{F}^\alpha_m &= F_{\alpha \alpha}^\alpha, \\
\mathcal{F}^\alpha_i &= F_{\alpha \alpha}^\alpha + F_{\alpha \alpha}^\alpha, \\
\mathcal{F}^\alpha_e &= F_{\alpha \alpha}^\alpha + F_{\alpha \alpha}^\alpha + F_{\alpha \alpha}^\alpha,
\end{align*}$$

(4.6)

by analogy with the volume interactions (2.10). The surface interaction $S_{\psi \chi}$ is defined as the component of the $\psi$ interaction due to transfers associated with process $\chi$. When (4.6) is substituted into (4.2) we obtain six sum conditions

$$\begin{align*}
\sum_{\alpha} F_{\alpha \alpha}^\alpha &= 0, \\
\sum_{\alpha} F_{\alpha \alpha}^\alpha &= 0, \\
\sum_{\alpha} F_{\alpha \alpha}^\alpha &= 0, \\
\sum_{\alpha} F_{\alpha \alpha}^\alpha &= 0, \\
\sum_{\alpha} F_{\alpha \alpha}^\alpha &= 0,
\end{align*}$$

(4.7)

as the individual surface interaction terms are independent, and making the substitution in (4.5) yields frame-indifferent forms

$$\begin{align*}
F_{\alpha \alpha}^\alpha &= F_{\alpha \alpha}^\alpha, \\
F_{\alpha \alpha}^\alpha &= F_{\alpha \alpha}^\alpha - \langle v^\alpha \rangle F_{\alpha \alpha}^\alpha, \\
F_{\alpha \alpha}^\alpha &= F_{\alpha \alpha}^\alpha - \langle e^\alpha \rangle F_{\alpha \alpha}^\alpha - \langle v^\alpha \rangle \cdot (F_{\alpha \alpha}^\alpha - \langle v^\alpha \rangle F_{\alpha \alpha}^\alpha), \\
F_{\alpha \alpha}^\alpha &= F_{\alpha \alpha}^\alpha, \\
F_{\alpha \alpha}^\alpha &= F_{\alpha \alpha}^\alpha - \langle v^\alpha \rangle \cdot F_{\alpha \alpha}^\alpha, \\
F_{\alpha \alpha}^\alpha &= F_{\alpha \alpha}^\alpha,
\end{align*}$$

(4.8)

where $F_{\alpha \alpha}^\alpha$ is the frame indifferent part of the $\psi$ interaction due to transfer associated with the process $\chi$. The surface interaction sum condition (4.7) and the frame indifferent forms (4.8) are analogous to the constraints (2.11) and (2.12) in the bulk mixture and place restrictions on the allowable functional forms for the surface interaction terms $F_{\alpha \alpha}^\alpha, F_{\alpha \alpha}^\alpha, F_{\alpha \alpha}^\alpha, F_{\alpha \alpha}^\alpha$, and $F_{\alpha \alpha}^\alpha$. Note, that the frame indifferent sums $\sum_{\alpha} F_{\alpha \alpha}^\alpha = 0, \sum_{\alpha} F_{\alpha \alpha}^\alpha = 0$ and $\sum_{\alpha} F_{\alpha \alpha}^\alpha = 0, \sum_{\alpha} F_{\alpha \alpha}^\alpha = 0$. Hence, there will a finite contribution to the total (summed) mass and energy balances (4.4) from $\sum_{\alpha} F_{\alpha \alpha}^\alpha, \sum_{\alpha} F_{\alpha \alpha}^\alpha$ and $\sum_{\alpha} F_{\alpha \alpha}^\alpha$. Equations (4.2), (4.7) and (4.8) all assume the existence of constituent $\alpha$ on both sides of the singular surface $S^\alpha$. When phase $\alpha$ is not present on the $\tau$ side its volume fraction $\phi_{\alpha \tau}$ is by definition zero and all partial variables are zero by the volume fraction scaling law (2.2). It follows that the original point jump relations (4.1) reduce to

$$\begin{align*}
m_{\alpha \tau}^\pm &= \delta_{\alpha \tau}^\pm, \\
m_{\alpha \tau}^\pm v_{\alpha \tau}^\pm &= t_{\alpha \tau}^\pm = \delta_{\alpha \tau}^\pm, \\
energy: \quad m_{\alpha \tau}^\pm e_{\alpha \tau}^\pm &= t_{\alpha \tau}^\pm \cdot v_{\alpha \tau}^\pm = q_{\alpha \tau}^\pm = \delta_{\alpha \tau}^\pm.
\end{align*}$$

(4.9)

We note that these equations do not contain any intrinsic quantities on the $\tau$ side of the singular surface $S^\alpha$, such as the internal energy $e_{\alpha \tau}^\pm$ and the total energy $e_{\alpha \tau}^\pm$ per unit mass of constituent $\alpha$ or the constituent velocity $v_{\alpha \tau}^\pm$. These intrinsic quantities therefore remain entirely arbitrary on the $\tau$ side of the singular surface where $\alpha$ does not exist. This is an important requirement of a well posed theory. The jump relation (4.9) can also be expressed
in a simpler form in which each individual term is frame indifferent

\[
\begin{align*}
\text{mass: } & \pm m_0^\alpha = \mathcal{G}_m^\alpha, \\
\text{momentum: } & \pm \mathbf{t}_0^\alpha = \mathcal{G}_t^\alpha, \\
\text{energy: } & \pm \mathcal{E}_n^\alpha = \mathcal{G}_x^\alpha.
\end{align*}
\]

(4.10)

The surface interactions, when constituent \( \alpha \) is not present on the \( \mp \) side of the singular surface, satisfy the frame indifferent forms

\[
\begin{align*}
\mathcal{G}_m^\alpha = \mathcal{G}_m^\alpha, \\
\mathcal{G}_t^\alpha = \mathcal{G}_t^\alpha - \mathbf{v}^{\mp \alpha} \cdot \mathcal{G}_m^\alpha, \\
\mathcal{G}_x^\alpha = \mathcal{G}_x^\alpha - \mathbf{e}^{\mp \alpha} \cdot \mathcal{G}_m^\alpha - \mathbf{v}^{\mp \alpha} \cdot \mathcal{G}_t^\alpha.
\end{align*}
\]

(4.11)

where in this case \( \mathbf{v}^{\mp \alpha} \cdot \mathcal{G}_m^\alpha, \mathbf{e}^{\mp \alpha} \cdot \mathcal{G}_m^\alpha \) and \( \mathbf{v}^{\mp \alpha} \cdot \mathcal{G}_t^\alpha \) are non-frame indifferent contributions to the momentum and energy interactions. Making the decomposition (4.6) the sum relations (4.7) are again satisfied and six frame indifferent forms are obtained

\[
\begin{align*}
\mathcal{G}^{\alpha}_{mm} - \mathcal{G}^{\alpha}_{mm}, \\
\mathcal{G}^{\alpha}_{tm} = \mathcal{G}^{\alpha}_{tm} - \mathbf{v}^{\mp \alpha} \cdot \mathcal{G}^{\alpha}_{mm}, \\
\mathcal{G}^{\alpha}_{em} = \mathcal{G}^{\alpha}_{em} - \mathbf{e}^{\mp \alpha} \cdot \mathcal{G}^{\alpha}_{mm} - \mathbf{v}^{\mp \alpha} \cdot (\mathcal{G}^{\alpha}_{tm} - \mathbf{v}^{\mp \alpha} \cdot \mathcal{G}^{\alpha}_{mm}), \\
\mathcal{G}^{\alpha}_{io} = \mathcal{G}^{\alpha}_{io}, \\
\mathcal{G}^{\alpha}_{eo} = \mathcal{G}^{\alpha}_{eo} - \mathbf{v}^{\mp \alpha} \cdot \mathcal{G}^{\alpha}_{io}, \\
\mathcal{G}^{\alpha}_{eo} = \mathcal{G}^{\alpha}_{eo}.
\end{align*}
\]

(4.12)

The frame indifferent jump relations and the associated constraints for constituent \( \alpha \) on the \( \pm \) side of the singular surface are formally derived from the original point jump relations (4.1) without any constraint being placed on the intrinsic variables \( \mathbf{e}^{\mp \alpha}, \mathbf{e}^{\mp \alpha} \) and \( \mathbf{v}^{\mp \alpha} \). However, it is interesting to note that if we assume that the \( \phi^{\mp \alpha} = 0 \) to make the partial variables on the \( \mp \) side of the singular surface zero and we define \( \mathbf{v}^{\mp \alpha} = \mathbf{v}^{\mp \alpha} \) and \( \mathbf{e}^{\mp \alpha} = \mathbf{e}^{\mp \alpha} \), then the jump relations (4.4) and the frame indifferent forms (4.8) for constituent \( \alpha \) present on both sides of the singular surface, reduce to the jump relations (4.10) and the frame indifferent forms (4.12), for constituent \( \alpha \) present only on the \( \pm \) side of the singular surface.

5. SURFACE INTERACTIONS

Surface interactions describe transfers of mass, momentum and energy between the constituents at a singular surface \( S^{\ast} \). These functions are dependent on the geometrical orientation of the constituents relative to the singular surface and on how the transfer takes place between the constituents. The interactions are, therefore, decomposed into independent contributions arising from interactions \( \mathcal{A}_{\phi^\chi} \) across, or between constituents on opposite sides of, the surface and interactions \( \mathcal{P}_{\phi^\chi} \) parallel to, or between constituents on the same side of, the singular surface

\[
\mathcal{G}^{\alpha}_{\phi^\chi} = \mathcal{A}^{\alpha}_{\phi^\chi} + \mathcal{P}^{\alpha}_{\phi^\chi}
\]

(5.1)

for all interactions \( \psi = m, l, e \) associated with process \( \chi = m, l, e \).

A set of surface interactions taking place across the interface is postulated by direct analogy with those in the bulk mixture (3.1). These must distinguish between transfers occurring between constituent \( \alpha \) on the plus side and constituent \( \beta \) on the minus side of the singular surface and the case where the constituent orientations are reversed. This symmetry
interaction models for mixtures

(5.2)

where the rate of mass transfer $M_{ab}$, the surface interaction drag due to non-mass transfer processes $B_{ab}$ and the rate of energy supply due to non-mass and non-traction processes $E_{ab}$ to constituent $a$ on the $±$ side of the singular surface from constituent $b$ on the $±$ side of $S^*$ are defined per unit area of $S^*$. Note, that the $±$ sign has been circled to indicate that it represents the orientation of the constituents, rather than, the limiting value of a given variable in the bulk mixture as $S^*$ is approached from the $±$ side. The $#$ symbol indicates that the variable is evaluated on the opposite side of the singular surface, e.g. $v^{a±} = v^{b±}$. Thus, the velocity and internal energy terms are paired on opposite sides of the singular surface, i.e. a velocity $v^{a±}$ is paired with a velocity $v^{b±}$ etc.

The surface interactions (5.2) satisfy the summation relations (4.7) if

\[
\begin{align*}
M_{ab} & = -M_{ba}, & M_{aa} & = 0, \\
B_{ab} & = -B_{ba}, & B_{aa} & = 0, \\
E_{ab} & = -E_{ba}, & E_{aa} & = 0,
\end{align*}
\]  

(5.3)

where we note that changing the order or the constituent indices also reverses the direction implied by the $±$ sign. Furthermore, when constituent $a$ exists on both sides of the singular surface, then (5.2) satisfy the frame indifferent forms (4.8) yielding, with the help of (4.3), the corresponding forms

\[
\begin{align*}
\mathcal{A}_{a\text{mono}} & = \sum_b 2\langle M_{ab} \rangle, \\
\mathcal{A}_{a\text{iso}} & = \sum_b -\langle M_{ab}(v^a - v^{b\#}) \rangle + \frac{1}{2}[M_{ab}\{v^a\}], \\
\mathcal{A}_{a\text{emo}} & = \sum_b -\langle M_{ab}(e^a - e^{b\#}) \rangle + \frac{1}{2}[M_{ab}\{e^a\}] - \frac{1}{4}[M_{ab}(v^a - v^{b\#})\{v^a\}], \\
\mathcal{A}_{a\text{iso}} & = \sum_b 2\langle B_{ab} \rangle, \\
\mathcal{A}_{a\text{emo}} & = \sum_b -\langle B_{ab}\cdot(v^a - v^{b\#}) \rangle + \frac{1}{2}[B_{ab}\{v^a\}], \\
\mathcal{A}_{a\text{emo}} & = \sum_b 2\langle E_{ab} \rangle.
\end{align*}
\]  

(5.4)

When either constituent $a$ does not exist on the $±$ side of $S^*$ or constituent $b$ does not exist on the $±$ side of $S^*$, then the interactions $M_{ab}$, $B_{ab}$ and $E_{ab}$ are identically zero. A particular form for these interactions that satisfy this concept identically are given by

\[
\begin{align*}
M_{ab} & = \phi^{a±}\phi^{b±} M_{ab}, \\
B_{ab} & = \phi^{a±}\phi^{b±} B_{ab}, \\
E_{ab} & = \phi^{a±}\phi^{b±} E_{ab},
\end{align*}
\]  

(5.5)
so that, if either the volume fraction \( \phi^a = 0 \) or \( \phi^b = 0 \), the appropriate interaction terms in (5.2) are also set to zero. The intrinsic interactions \( \mathcal{M}_{\alpha \beta}^{ab} \), \( \mathcal{A}_{\alpha \beta}^{ab} \) and \( \mathcal{C}_{\alpha \beta}^{ab} \) may or may not go to zero when the corresponding volume fractions do, depending on the material response.

Thus, if constituent \( \alpha \) does not exist on the \( \mp \) side of the singular surface the interactions postulated in (5.2) take on a reduced form, which satisfy the frame indifferent forms (4.12), yielding

\[
\begin{align*}
\mathcal{A}_{\alpha \beta}^{ab} & = \sum_b \mathcal{M}_{\alpha \beta}^{ab}, \\
\mathcal{A}_{\alpha \beta}^{ab} & = \sum_b \frac{1}{2} \mathcal{M}_{\alpha \beta}^{ab} (\psi^{\alpha \beta} - \psi^{\beta \alpha}), \\
\mathcal{A}_{\alpha \beta}^{ab} & = \sum_b \frac{1}{2} \mathcal{M}_{\alpha \beta}^{ab} (\epsilon^{\alpha \beta} - \epsilon^{\beta \alpha}), \\
\mathcal{A}_{\alpha \beta}^{ab} & = \sum_b \mathcal{A}_{\alpha \beta}^{ab}, \\
\mathcal{A}_{\alpha \beta}^{ab} & = \sum_b \frac{1}{2} \mathcal{A}_{\alpha \beta}^{ab} \cdot (\psi^{\alpha \beta} - \psi^{\beta \alpha}), \\
\mathcal{A}_{\alpha \beta}^{ab} & = \sum_b \mathcal{A}_{\alpha \beta}^{ab}.
\end{align*}
\]

Note again the interesting property mentioned at the end of Section 4 that when constituent \( \alpha \) is only present on the \( \pm \) side of the singular surface, the surface interactions (5.4) (valid when the constituent \( \alpha \) is present on both sides of the singular surface) reduce to (5.6) (the form when constituent \( \alpha \) is present on only one side of the singular surface) provided \( \psi^{\alpha \beta} = \psi^{\beta \alpha} \) and \( \epsilon^{\alpha \beta} = \epsilon^{\beta \alpha} \).

A set of surface interactions taking place on the same side, or parallel to, the singular surface are also possible. These must be able to distinguish whether the interaction between \( \alpha \) and \( \beta \) takes place on the plus or the minus side of the singular surface. This symmetry requirement is satisfied by summing the contributions from the two cases, as in (5.2), giving

\[
\begin{align*}
\mathcal{P}_{\alpha \beta}^{ab} & = \sum_b 2 \langle \mathcal{M}_{\alpha \beta}^{ab} \rangle, \\
\mathcal{P}_{\alpha \beta}^{ab} & = \sum_b \langle \mathcal{M}_{\alpha \beta}^{ab} (\psi^{\alpha} + \psi^{\beta}) \rangle, \\
\mathcal{P}_{\alpha \beta}^{ab} & = \sum_b \langle \mathcal{M}_{\alpha \beta}^{ab} (\epsilon^{\alpha} + \epsilon^{\beta} + \psi^{\alpha} \cdot \psi^{\beta}) \rangle, \\
\mathcal{P}_{\alpha \beta}^{ab} & = \sum_b 2 \langle \mathcal{A}_{\alpha \beta}^{ab} \rangle, \\
\mathcal{P}_{\alpha \beta}^{ab} & = \sum_b \langle \mathcal{A}_{\alpha \beta}^{ab} \cdot (\psi^{\alpha} + \psi^{\beta}) \rangle, \\
\mathcal{P}_{\alpha \beta}^{ab} & = \sum_b 2 \langle \mathcal{C}_{\alpha \beta}^{ab} \rangle,
\end{align*}
\]

where \( \mathcal{M}_{\alpha \beta}^{ab} \), \( \mathcal{A}_{\alpha \beta}^{ab} \) and \( \mathcal{C}_{\alpha \beta}^{ab} \) are the rate of mass transfer, the interaction drag due to non-mass transfer processes and the rate of energy supply due to non-mass and non-traction processes, respectively, to constituent \( \alpha \) from constituent \( \beta \), both of which are on the same \( \pm \) side of the singular surface \( S^* \). Morland and Gray [15] used a limit argument to postulate the existence of frame indifferent mass, momentum and energy interactions due to phase changes, similar to (5.7). The argument presented here, however, assumes the existence of surface interactions in the jump relations (4.1), that were neglected by Morland and Gray [15]. The physical variables do not, therefore, have to become unbounded in the vicinity of \( S^* \) to give a finite contribution to the jumps. Their theory did not encompass the further momentum and energy interactions (5.9) parallel to the surface or the interactions (5.2) which take place across the surface.
These parallel surface interactions satisfy the sum conditions (4.7) provided
\[
\begin{align*}
\mathcal{M}^{ab}_{\Xi} &= -\mathcal{M}^{ba}_{\Xi}, \quad \mathcal{M}^{an}_{\Xi} = 0, \\
\mathcal{N}^{ab}_{\Xi} &= -\mathcal{N}^{ba}_{\Xi}, \quad \mathcal{N}^{an}_{\Xi} = 0, \\
\mathcal{E}^{ab}_{\Xi} &= -\mathcal{E}^{ba}_{\Xi}, \quad \mathcal{E}^{an}_{\Xi} = 0.
\end{align*}
\] (5.8)

When constituent \(a\) exists on both sides of the singular surface then (5.7) satisfy the frame indifferent forms (4.8) yielding, with the help of (4.3),
\[
\begin{align*}
\mathcal{P}^{a\,\text{mmo}} &= \sum_b 2 \left\langle \mathcal{M}^{ab} \right\rangle, \\
\mathcal{P}^{a\,\text{imo}} &= \sum_b -\left\langle \mathcal{M}^{ab} (\mathcal{N}^{a\Xi} - \mathcal{N}^{b\Xi}) \right\rangle + \frac{1}{2} \left[ \mathcal{M}^{ab} \left[ \mathcal{N}^{a\Xi} \right] + \frac{1}{4} \left[ \mathcal{M}^{ab} (\mathcal{N}^{a\Xi} - \mathcal{N}^{b\Xi}) \right] : \left[ \mathcal{N}^{b\Xi} \right] \right], \\
\mathcal{P}^{a\,\text{emo}} &= \sum_b -\left\langle \mathcal{M}^{ab} (\mathcal{E}^{a\Xi} - \mathcal{E}^{b\Xi}) \right\rangle + \frac{1}{2} \left[ \mathcal{M}^{ab} \left[ \mathcal{E}^{a\Xi} \right] - \frac{1}{4} \left[ \mathcal{M}^{ab} (\mathcal{E}^{a\Xi} - \mathcal{E}^{b\Xi}) \right] : \left[ \mathcal{E}^{b\Xi} \right] \right], \\
\mathcal{P}^{a\,\text{ilo}} &= \sum_b 2 \left\langle \mathcal{N}^{ab} \right\rangle, \\
\mathcal{P}^{a\,\text{elo}} &= \sum_b -\left\langle \mathcal{N}^{ab} (\mathcal{N}^{a\Xi} - \mathcal{N}^{b\Xi}) \right\rangle + \frac{1}{2} \left[ \mathcal{N}^{ab} \left[ \mathcal{N}^{a\Xi} \right] \right], \\
\mathcal{P}^{a\,\text{eco}} &= \sum_b 2 \left\langle \mathcal{E}^{ab} \right\rangle,
\end{align*}
\] (5.9)

which are analogous to (5.4). When either constituent \(a\) or constituent \(b\) does not exist on the \(\pm\) side of \(S^{a}\), then the interactions \(\mathcal{M}^{ab}_{\Xi}, \mathcal{N}^{ab}_{\Xi}\) and \(\mathcal{E}^{ab}_{\Xi}\) are identically zero. This concept can be formalised by making the decomposition
\[
\begin{align*}
\mathcal{M}^{ab}_{\Xi} &= \phi^{a\pm} \phi^{b\pm} \mathcal{M}^{\Xi\Xi}_{\Xi}, \\
\mathcal{N}^{ab}_{\Xi} &= \phi^{a\pm} \phi^{b\pm} \mathcal{N}^{\Xi\Xi}_{\Xi}, \\
\mathcal{E}^{ab}_{\Xi} &= \phi^{a\pm} \phi^{b\pm} \mathcal{E}^{\Xi\Xi}_{\Xi},
\end{align*}
\] (5.10)

which is analogous to (5.5) except that the volume fractions are both evaluated on the same side of the singular surface. That is, if either the volume fraction \(\phi^{a\pm} = 0\) or \(\phi^{b\pm} = 0\) the appropriate interaction terms in (5.7) are set to zero. The frame indifferent form of these interactions when \(a\) is present only on the \(\pm\) side of the singular surface are therefore
\[
\begin{align*}
\mathcal{P}^{a\,\text{mmo}} &= \sum_b \mathcal{M}^{ab}_{\Xi}, \\
\mathcal{P}^{a\,\text{imo}} &= \sum_b -\frac{1}{2} \mathcal{M}^{ab}_{\Xi} (\mathcal{N}^{a\Xi} - \mathcal{N}^{b\Xi}), \\
\mathcal{P}^{a\,\text{emo}} &= \sum_b -\frac{1}{2} \mathcal{M}^{ab}_{\Xi} (\mathcal{E}^{a\Xi} - \mathcal{E}^{b\Xi}), \\
\mathcal{P}^{a\,\text{ilo}} &= \sum_b \mathcal{N}^{ab}_{\Xi}, \\
\mathcal{P}^{a\,\text{elo}} &= \sum_b -\frac{1}{2} \mathcal{N}^{ab}_{\Xi} (\mathcal{N}^{a\Xi} - \mathcal{N}^{b\Xi}), \\
\mathcal{P}^{a\,\text{eco}} &= \sum_b \mathcal{E}^{ab}_{\Xi}.
\end{align*}
\] (5.11)

Note, again the frame indifferent surface interactions (5.9) reduce to (5.11) when \(\phi^{a\Xi} = 0\) provided \(\mathcal{N}^{a\Xi} = \mathcal{N}^{b\Xi}\) and \(\mathcal{E}^{a\Xi} = \mathcal{E}^{b\Xi}\).

We shall show in the following sections that the across surface interactions postulated in (5.2) are sufficient to describe the jump conditions of a classical phase change front, a phase change front in a binary mixture and a phase change front between a three constituent mixture and a binary mixture. However, the parallel surface interactions (5.7) are required to describe the phase change and re-absorption at the interface between a three constituent mixture and an inert single phase.
6. CLASSICAL PHASE CHANGE FRONT

At a classical phase change front a singular surface advances into a body consisting of a single phase which is completely converted to another single phase behind the front. That is, only one phase (constituent) exists on either side of the singular surface, as illustrated in Fig. 1, and any material which crosses the surface undergoes a complete change of phase into the material on the other side. Such a front exists when there is melting/solidification from/to the solid phase to/from the liquid phase of some constituent material, e.g. as an ice sheet melts into the ocean. This motivates the constituent letters w for water and i for ice, although the results are quite general.

On the minus side of the singular surface constituent w does not exist and so the volume fraction \( \phi_w^- = 0 \). It follows that all the partial variables associated with constituent w are identically zero on the minus side of the singular surface and jump relations (4.1) for the w constituent reduce to

\[
\begin{align*}
\text{mass: } m_n^{w+} &= \mathcal{A}_m^w, \\
\text{momentum: } m_n^{w+} v_n^{w+} - t_n^{w+} &= \mathcal{A}_i^w, \\
\text{energy: } m_n^{w+} e_n^{w+} - t_n^{w+} \cdot v_n^{w+} + q_n^{w+} &= \mathcal{A}_e^w.
\end{align*}
\]

(6.1)

Note, that the interactions are all denoted as across surface quantities since the parallel surface quantities are identically zero by (5.10). Similarly, on the plus side of the interface constituent i does not exist \( \phi_i^+ = 0 \) and setting the partial variables to zero we obtain jump relations for constituent i

\[
\begin{align*}
\text{mass: } -m_n^{i-} &= \mathcal{A}_m^i, \\
\text{momentum: } -m_n^{i-} v_n^{i-} + t_n^{i-} &= \mathcal{A}_i^i, \\
\text{energy: } -m_n^{i-} e_n^{i-} + t_n^{i-} \cdot v_n^{i-} - q_n^{i-} &= \mathcal{A}_e^i.
\end{align*}
\]

(6.2)

Note, that in both sets of jump relations (6.1) and (6.2) no restrictions have been placed on any of the intrinsic quantities or the velocity field on the side of the singular surface where the constituent does not exist. In this two component system the summation relations (4.2) are

\[
\mathcal{A}_m^w + \mathcal{A}_m^i = 0, \quad \mathcal{A}_i^w + \mathcal{A}_i^i = 0, \quad \mathcal{A}_e^w + \mathcal{A}_e^i = 0,
\]

(6.3)

which provide simple connections between the surface mass, momentum and energy interaction terms (without the partitioning problems we shall encounter later). Thus, the surface
interactions can be eliminated by summing the respective mass, momentum and energy jump conditions in (6.1) and (6.2) to obtain

\[
\begin{align*}
\text{mass:} & \quad m_n^w = m_i^w = m_n, \\
\text{momentum:} & \quad (\mathbf{t}^w - \mathbf{t}^i) = m_n(\mathbf{v}^w - \mathbf{v}^i), \\
\text{energy:} & \quad m_n(e^w - e^i) - \frac{1}{2} (\mathbf{t}^w + \mathbf{t}^i) \cdot (\mathbf{v}^w - \mathbf{v}^i) + q_n^w - q_n^i = 0,
\end{align*}
\]

(6.4)

where the notation has been abbreviated since \( w \) and \( i \) are equivalent to + and −, respectively. Alternatively, using + and − instead of \( w \) and \( i \) the square bracket notation can be used to obtain the frame indifferent form of the jump relations

\[
\begin{align*}
\text{mass:} & \quad m_n = m_i = m_n, \\
\text{momentum:} & \quad [\mathbf{t}] = m_n[\mathbf{v}], \\
\text{energy:} & \quad m_n[\epsilon] - \langle \mathbf{t} \rangle \cdot [\mathbf{v}] + [q_n] = 0.
\end{align*}
\]

(6.5)

This is the single constituent form of (4.4) in which \( \langle m_n \rangle = m_n \) and all the surface interaction terms are zero. The mass and momentum balances are also equivalent to the single constituent form of the original jump relations (4.1). In addition the energy balance (6.5)_3 can be rearranged to obtain

\[
m_n[\epsilon] - [\mathbf{t} \cdot \mathbf{v}] + [q_n] = 0,
\]

(6.6)

which is the single constituent form of the original energy balance (4.1)_3.

In many situations thermal processes dominate in the energy balance and the stress-working is negligible compared to the heat conduction and the internal energy jump. It follows that the energy balances (6.5)_3 and (6.6)_3 reduce to the Stefan condition

\[
[q_n] = -m_n L^{1w},
\]

(6.7)

where we have made the common approximation that the work associated with the density change in (2.4) is negligible. When there is freezing/melting there is a net energy supply to/from the surface, \([q_n] \equiv 0\). Given that the latent heat for a phase change to \( i \) from \( w \) is positive, \( L_i^w > 0 \), the energy balance (6.7) implies \( m_n \leq 0 \) and the mass balance (6.5)_1 implies that constituents \( w \) and \( i \) will move down/up relative to the front as \( v_n^w - u_n \leq 0 \) and \( v_n^i - u_n \leq 0 \), respectively. Thus, for net freezing there will be a downward motion of constituents \( w \) and \( i \) relative to the front, as illustrated in Fig. 1, and the region associated with constituent \( i \) will expand into that of constituent \( w \).

7. PHASE CHANGE FRONT IN A BINARY MIXTURE

Consider a singular surface separating a binary mixture, consisting of constituents \( w \) and \( i \), on the plus side of \( S^* \) from a single constituent \( i \) on the minus side. Depending on the direction of propagation of the front, relative to the constituents, constituent \( w \) is annihilated or created. This configuration, for instance, describes the cold-temperate transition surface (CTS) in polythermal ice sheets [7]. The constituent letters \( w \) and \( i \) therefore can be thought of as representing water and ice, respectively, although the results are again quite general.

Constituent \( w \) exists only on the plus side of the singular surface and so the volume fraction \( \phi^w = 0 \). All the partial variables associated with constituent \( w \) on the minus side are therefore zero by the volume fraction scaling laws (2.2) and the jump conditions (4.1) reduce to

\[
\begin{align*}
\text{mass:} & \quad m_n^{w+} = \mathcal{F}_m^w, \\
\text{momentum:} & \quad m_n^{w+} \mathbf{v}_n^{w+} - \mathbf{t}^{w+} = \mathcal{F}_t^w, \\
\text{energy:} & \quad m_n^{w+} (e^{w+} - t^{w+} \cdot \mathbf{v}^{w+} + q_n^{w+} = \mathcal{F}_e^w).
\end{align*}
\]

(7.1)
In contrast to the classical phase change surface constituent $i$ exists on both sides of the interface and the jump relations are

$$
\begin{align*}
\text{mass: } [m_n^i] &= n^i, \\
\text{momentum: } [m_n^i v^i] - [t^i] &= n^i, \\
\text{energy: } [m_n^i e^i] - [t^i v^i] + [q_n^i] &= n^i.
\end{align*}
$$

(7.2)

In this simple two constituent problem the surface interactions are connected by the simple summation relations (4.2)

$$
\mathcal{F}_m^w + \mathcal{F}_m^i = 0, \quad \mathcal{F}_i^w + \mathcal{F}_i^i = 0, \quad \mathcal{F}_e^w + \mathcal{F}_e^i = 0
$$

(7.3)

and hence the two sets of jump conditions (7.1) and (7.2) can be summed to eliminate the surface interactions. The jump relations can therefore be expressed as

$$
\begin{align*}
\text{mass: } m_n^{i^=} - m_n^{w^=} &= m_n^{i^+}, \\
\text{momentum: } t_n^{i^=} - t_n^{w^=} - m_n^{w^+} (v_n^{w^+} - v_n^{v^=}) &= m_n^{i^+} [v_n^i] - t_n^{i^+}, \\
\text{energy: } m_n^{w^+} (e_n^{w^+} - e_n^{v^=}) - \frac{1}{2} (t_n^{w^+} + t_n^{v^=}) \cdot (v_n^{w^+} - v_n^{v^=}) + q_n^{w^+} - q_n^{v^=} &= -m_n^{i^+} [e_n^i] + \frac{1}{2} t_n^{i^+} \cdot [v_n^i] + \frac{1}{2} t_n^{i^+} \cdot (v_n^{i^+} - v_n^{w^+}) - q_n^{i^+},
\end{align*}
$$

(7.4)

where the terms have been rearranged so that when $\phi^{i^+} = 0$ the right-hand sides are zero and the equations reduce to those of the classical phase change surface (6.4).

![Fig. 2. A singular surface separates a binary mixture, consisting of constituents w and i, on the + side of $S^*$ from a single constituent i on the – side. For freezing there will be a downward motion of constituents w and i relative to the front and the single constituent region will expand into the binary mixture.](image)

Assuming that thermal processes dominate in the energy balance so that the stress-working is negligible and supposing that the internal energy jump of the ice $[e_n^i] = 0$, the energy balance (7.4) reduces to the Stefan condition

$$
[q_n] = -m_n^{w^+} L_{w^+}^n,
$$

(7.5)

where the work associated with the density change in (2.4) has been assumed negligible and the energy flux $q_n^{i^+} = q_n^{i^+} = q_n^{w^+}$ and $q_n^{v^=} = q_n^{i^=}$ for $\phi^{i^+} = 0$. Note the similarity of (7.5) with (6.7). When there is freezing/melting there is a net energy supply to/from the surface, $[q_n] \leq 0$. Assuming that the
latent heat for a phase change to i from w is positive, \( L^{1w} > 0 \), the energy balance (7.5) implies \( m_n^{w+} \leq 0 \) and constituent w moves down/up relative to the front. Furthermore, supposing constituent i is intrinsically incompressible, \( \rho_i = \text{const.} \), and that the velocity jump \([v_i^+] = 0 \) (i.e. \( v_i^{n+} = v_i^{n-} = v_i^{n} \)), the mass balance (7.4) implies that

\[
m_n^{w+} = -[\phi_i] \rho_i (v_i^{n} - u_n).
\]

Hence, constituent i will also move down/up relative to the front, \( v_i^{n} - u_n \leq 0 \), since \([\phi_i] < 0 \) in this configuration. Thus, for freezing there will be a downward motion of constituents w and i relative to the front, which is illustrated in Fig. 2, and the single constituent region expands into the binary mixture.

8. PHASE CHANGE FRONT IN A TERTIARY MIXTURE

Consider a three component mixture consisting of constituents i, w and a which is separated by a singular surface \( S^* \) from a binary mixture consisting of constituents i and a. Such a configuration exists, for example, in polythermal snow packs at the transition between wet temperate snow and dry sub-freezing snow [16]. The constituents i, w and a can be thought of as representing ice, water and dry air, respectively, although the results are again quite general. The fact that there are now three constituents adds a considerable degree of complexity to the problem as the interactions must be partitioned between the constituents. This is in contrast to the two earlier examples in which sum relations (6.3) and (7.3) were trivial.

In this more general situation there is a considerable benefit to be gained by writing the balance equations in their frame indifferent form. This is because the finite contributions due to the summed interactions \( \Sigma_n S_{i,n}^{w} \), \( \Sigma_n S_{w,n}^{i} \), \( \Sigma_n S_{w,n}^{w} \) and \( \Sigma_n S_{w,n}^{a} \) arise naturally from these balances. That is, the terms like the latent heat release in (7.5) appear without the need for further manipulation of the equations. The frame indifferent conservation laws for constituent w, which is not present on the minus side of \( S^* \), are

\[
\begin{align*}
\text{mass: } m_n^{w+} &= \mathcal{A}_{wo}^w + \mathcal{P}_{wo}^w, \\
\text{momentum: } -t_n^{w+} &= \mathcal{A}_{wo}^i + \mathcal{P}_{wo}^i, \\
\text{energy: } q_n^{w+} &= \mathcal{A}_{wo}^e + \mathcal{P}_{wo}^e 
\end{align*}
\]  

(8.1)

by (4.10) and by (4.4) the simplified jumps for constituent i are

\[
\begin{align*}
\text{mass: } m_i^+ &= \mathcal{A}_{i,o}^i + \mathcal{P}_{i,o}^i, \\
\text{momentum: } t^+ &= \mathcal{A}_{i,o}^i + \mathcal{P}_{i,o}^i, \\
\text{energy: } q^+ &= \mathcal{A}_{i,o}^e + \mathcal{P}_{i,o}^e 
\end{align*}
\]  

(8.2)

and for constituent a are

\[
\begin{align*}
\text{mass: } m_a^+ &= \mathcal{A}_{a,o}^a + \mathcal{P}_{a,o}^a, \\
\text{momentum: } t^+ &= \mathcal{A}_{a,o}^a + \mathcal{P}_{a,o}^a, \\
\text{energy: } q^+ &= \mathcal{A}_{a,o}^e + \mathcal{P}_{a,o}^e 
\end{align*}
\]  

(8.3)

since i and a are present on both sides of the singular surface. The appropriate forms of the surface frame indifferent interactions for constituent w are then given by (5.6) and (5.11) and for constituents i and a by (5.4) and (5.9).

There are a total of 36 independent surface interaction partitioning functions. In this configuration the volume fraction \( \phi^{w-} = 0 \) and the partitioning relations (5.5) and (5.10) imply that 12 of them are set to zero

\[
\begin{align*}
\mathcal{M}_{wi}^w &= 0, & \mathcal{M}_{wi}^w &= 0, & \mathcal{S}_{wi}^w &= 0, & \mathcal{E}_{wi}^w &= 0, & \mathcal{E}_{wi}^w &= 0, \\
\mathcal{M}_{wi}^w &= 0, & \mathcal{M}_{wi}^w &= 0, & \mathcal{S}_{wi}^w &= 0, & \mathcal{E}_{wi}^w &= 0, & \mathcal{E}_{wi}^w &= 0. 
\end{align*}
\]  

(8.4)
In addition constituent a does not react with constituents w and i in any mass transfers (phase changes) and a further six of them are zero

\[
\begin{align*}
M_{\odot}^{aw} &= 0, & M_{\odot}^{ai} &= 0, \\
R_{\odot}^{aw} &= 0, & R_{\odot}^{ai} &= 0.
\end{align*}
\]  

(8.5)

Assumptions (8.4) and (8.5) follow from the geometry of the configuration and a constitutive postulate about material behaviour of constituent a. This still leaves 18 non-zero partitioning functions, which is somewhat unwieldy. A further simplification, that there are no mutual momentum or energy interactions between the constituents that are not annihilated, is therefore made and a further eight functions are set to zero

\[
\begin{align*}
\mathcal{B}_{\odot}^{aw} &= 0, & \mathcal{B}_{\odot}^{ai} &= 0, \\
\mathcal{B}_{\odot}^{aw} &= 0, & \mathcal{B}_{\odot}^{ai} &= 0.
\end{align*}
\]  

(8.6)

Hence, the surface interactions only partition the mass momentum and energy transfers of the annihilated constituent w between the two remaining constituents, which is a reasonable assumption. Assumptions (8.4), (8.5) and (8.6) greatly simplify the frame indifferent surface interactions (5.4), (5.6), (5.9) and (5.11). The mass interactions across the surface become

\[
\begin{align*}
\mathcal{A}_{\odot}^{aw} &= M_{\odot}^{aw}, \\
\mathcal{A}_{\odot}^{iw} &= M_{\odot}^{iw}, \\
\mathcal{A}_{\odot}^{ai} &= 0.
\end{align*}
\]  

(8.7)

the mass interactions on the same side of the surface are

\[
\begin{align*}
\mathcal{P}_{\odot}^{aw} &= R_{\odot}^{aw}, \\
\mathcal{P}_{\odot}^{iw} &= R_{\odot}^{iw}, \\
\mathcal{P}_{\odot}^{ai} &= 0.
\end{align*}
\]  

(8.8)

The momentum interactions across the surface reduce to

\[
\begin{align*}
\mathcal{A}_{\odot}^{aw} &= \mathcal{B}_{\odot}^{aw} + \mathcal{B}_{\odot}^{wa} - \frac{1}{2} M_{\odot}^{aw}(v^{w+} - v^{l+}), \\
\mathcal{A}_{\odot}^{iw} &= \mathcal{B}_{\odot}^{iw} - \frac{1}{2} M_{\odot}^{iw}(v^{l-} - v^{w+}) - \frac{1}{2} M_{\odot}^{iw}[v^l], \\
\mathcal{A}_{\odot}^{ai} &= \mathcal{B}_{\odot}^{ai},
\end{align*}
\]  

(8.9)

and the momentum interactions on the same side of the surface are

\[
\begin{align*}
\mathcal{P}_{\odot}^{aw} &= \mathcal{B}_{\odot}^{aw} + \mathcal{B}_{\odot}^{wa} - \frac{1}{2} R_{\odot}^{aw}(v^{w+} - v^{l+}), \\
\mathcal{P}_{\odot}^{iw} &= \mathcal{B}_{\odot}^{iw} - \frac{1}{2} R_{\odot}^{iw}(v^{l-} - v^{w+}) - \frac{1}{2} R_{\odot}^{iw}[v^l], \\
\mathcal{P}_{\odot}^{ai} &= \mathcal{B}_{\odot}^{ai}.
\end{align*}
\]  

(8.10)
The energy interactions across the surface are

$$
\mathcal{S}_{w}^{\omega} = -\frac{1}{2} \mathcal{M}_{\omega}^{\omega}(e^{W^{+}} - e^{I^{-}}) - \frac{1}{2} \mathcal{B}_{\omega}^{\omega} \cdot (v^{W^{+}} - v^{I^{-}}) - \frac{1}{2} \mathcal{B}_{\omega}^{w} \cdot (v^{W^{+}} - v^{A^{+}}) + \mathcal{E}_{\omega}^{w} + \mathcal{E}_{\omega}^{\omega},
$$

$$
\mathcal{S}_{i}^{\omega} = -\frac{1}{2} \mathcal{B}_{i}^{\omega}(e^{-I^{-}} - e^{W^{+}}) - \frac{1}{2} \mathcal{B}_{i}^{\omega} \cdot (v^{-I^{-}} - v^{W^{+}}) + \mathcal{E}_{i}^{\omega} + \mathcal{E}_{i}^{w},
$$

$$
\mathcal{S}_{e}^{\omega} = -\frac{1}{2} \mathcal{B}_{e}^{\omega} \cdot (v^{A^{-}} - v^{W^{+}}) - \frac{1}{2} \mathcal{B}_{e}^{\omega} \cdot [v^{A}] + \mathcal{E}_{e}^{\omega},
$$

and the energy interactions on the same side of the surface become

$$
\mathcal{D}_{w}^{\omega} = \frac{1}{2} \mathcal{M}_{\omega}^{\omega}(e^{W^{+}} - e^{I^{+}}) - \frac{1}{2} \mathcal{B}_{\omega}^{w} \cdot (v^{W^{+}} - v^{I^{+}}) - \frac{1}{2} \mathcal{B}_{\omega}^{w} \cdot (v^{W^{+}} - v^{A^{+}}) + \mathcal{E}_{\omega}^{w} + \mathcal{E}_{\omega}^{\omega},
$$

$$
\mathcal{D}_{i}^{w} = -\frac{1}{2} \mathcal{M}_{i}^{w}(e^{I^{+}} - e^{W^{-}}) - \frac{1}{2} \mathcal{M}_{i}^{w} \cdot [e^{I}] + \mathcal{E}_{i}^{w} + \mathcal{E}_{i}^{\omega},
$$

$$
\mathcal{D}_{e}^{w} = -\frac{1}{2} \mathcal{B}_{e}^{w} \cdot (v^{A^{+}} - v^{W^{+}}) - \frac{1}{2} \mathcal{B}_{e}^{w} \cdot [v^{A}] + \mathcal{E}_{e}^{w}.
$$

In order to use these surface interactions in the conservation balances (8.1), (8.2) and (8.3), further constitutive assumptions must be made about the 10 independent partitioning functions which remain. Specific examples are presented here which illustrate two special cases.

In the first example the interactions across the surface are investigated further and, hence, it is supposed that the remaining interactions parallel to the surface are zero

$$
\mathcal{M}_{\omega}^{w} = 0, \quad \mathcal{B}_{\omega}^{w} = 0, \quad \mathcal{B}_{i}^{w} = 0, \quad \mathcal{E}_{\omega}^{w} = 0, \quad \mathcal{E}_{\omega}^{\omega} = 0.
$$

Using relations (5.3) the surface interaction terms can be eliminated by adding the mass balances of constituents \( w \) and \( i \) to obtain

$$
\|m_{w}^{*}\| + m_{w}^{w+} = 0
$$

(8.14)

which is analogous to (7.4). Note, that the assumption that constituent \( a \) does not undergo phase reactions with \( w \) and \( i \) uniquely partitions the transfer in the water mass balance. However, the water momentum and energy balances both contain two transfer functions \( \mathcal{B}_{\omega}^{w}, \mathcal{B}_{\omega}^{\omega} \) and \( \mathcal{E}_{\omega}^{w}, \mathcal{E}_{\omega}^{\omega} \), respectively. Two further constitutive assumptions are therefore needed to apply the individual constituent momentum and energy jump relations. However, the total energy balance is obtained by summing the constituent energy balances to eliminate the interactions, \( \mathcal{E}_{\omega}^{w} \) and \( \mathcal{E}_{\omega}^{\omega} \). Assuming that the jumps in the ice and air normal velocity and internal energy are zero (\( [v_{i}^{A}] = 0, [v_{w}^{A}] = 0, [e^{I}] = 0, [e^{A}] = 0 \)) and that the problem is thermally dominated, this yields a Stefan condition, similar to (6.7) and (7.5),

$$
[q_{w}] = -\mathcal{M}_{\omega}^{w} L_{I^{w}},
$$

(8.15)

where the total energy flux \( q_{w}^{+} = q_{w}^{I^{+}} + q_{w}^{A^{+}} + q_{w}^{w^{+}} \) on the positive side and \( q_{w}^{-} = q_{w}^{I^{-}} + q_{w}^{A^{-}} \) on the negative side. When there is freezing/melting there is a net energy supply to/from the surface, \( [q_{w}] \neq 0 \). Assuming that the latent heat for a phase change to \( i \) from \( w \) is positive, \( L_{I^{w}} > 0 \), the energy balance (8.15) implies \( m_{w}^{w+} \leq 0 \) and constituent \( w \) moves down/up relative to the front.
Supposing that constituent \( i \) is intrinsically incompressible, \( \rho^i = \text{const} \), the mass balance (8.14) reduces to
\[
m^w_{n+} = -[\phi^n_k] \rho^i (v^i_n - u_n),
\]
(8.16)

analogous to (7.6). When \([\phi^n_k] < 0\) constituent \( i \) will move down/up relative to the front, \( v^i_n - u_n \leq 0 \), however, when \([\phi^n_k] > 0\) (which is possible in this configuration) constituent \( i \) will move up/down relative to the front, \( v^i_n - u_n \leq 0 \). Thus, for net freezing two cases are possible. If \([\phi^n_k] < 0\) there will be a downward motion of constituents \( w \) and \( i \) relative to the front, which is illustrated in Fig. 3(a), and the two constituent region expands into the three constituent mixture. However, if \([\phi^n_k] < 0\) constituent \( w \) moves downward relative to the front whilst constituent \( i \) moves upward relative to the front, which is illustrated in Fig. 3(b). That is, when constituent \( w \) crosses the front it changes to phase \( i \) and is immediately reabsorbed onto the positive side of the singular surface. This is exactly what occurs in polythermal snow packs. Melt water produced in the surface layers drains through the wet temperature snow until it reaches transition with the cold dry snow. The water crosses this interface and freezes releasing its latent heat to raise the temperature of the dry snow to the melting point and is subsequently reabsorbed onto the temperate side. That is, the water sacrifices itself (in some sense) in order to allow more water to flow past it. This is an important example which demonstrates that the surface interaction terms postulated in (5.2) are sufficient to describe complex reabsorption processes.

The second example is included to demonstrate the necessity of the interactions parallel to the surface in the general theory. Consider a three component mixture consisting of constituents \( i, w \) and \( a \) which is separated by a singular surface \( S^* \) from a single inert constituent \( a \). Such a configuration exists, for example, at the free surface of a temperate snow pack with the atmosphere. This is essentially the same configuration as in the first example but with the added assumption \( \phi^i = 0 \) which implies by (5.5) that
\[
\mathcal{M}_{m} = 0, \quad \mathcal{A}_{m} = 0, \quad \mathcal{E}_{m} = 0.
\]
(8.17)

Formally the balances (8.2) and the associated partitioning functions (valid when constitutive \( i \) is present on both sides of the surface) must be replaced by similar relations valid when constituent \( i \) is present only on the positive side of \( S^* \), since \( v^i \) and \( \varepsilon^i \) are not defined. However, we use the interesting property that when \( \phi^i = 0 \) the full jump relations reduce to the single sided jump relations provided we define \( v^i = v^i^+ \) and \( \varepsilon^i = \sigma^i^+ \), which is assumed here.
Fig. 4. A single component inert phase is separated by a singular surface $S^*$ from a tertiary mixture composed of constituents $i$, $w$, and $a$. This is a special case of the configuration in Fig. 3 when $\phi^{i-} = 0$. Note that the orientation of the singular surface has been reversed in order to make the diagram look like the free surface of a snow pack. When there is melting constituent $i$ moves down relative to the front and constituent $w$ moves up relative to the front. Thus, constituent $i$ changes phase on the plus side of the front and is reabsorbed into the three component mixture.

The total energy balance is obtained by summing the constituent energy balances to eliminate the energy flux interactions. Assuming that the problem is thermally dominated the contribution from interaction drag working terms can be neglected and the total energy balance yields a Stefan condition, similar to (8.15),

$$\mathcal{E}_n = -\mathcal{M}_n \dot{T} \mathcal{E}_n,$$

where the total energy flux $q_n^+ = q_n^{i+} + q_n^{w+} + q_n^{a+}$ on the positive side and $q_n^- = q_n^{i-}$ on the negative side. When there is freezing/melting there is a net energy supply to/from the surface, $\mathcal{E}_n \geq 0$ and, assuming $\dot{T} \mathcal{E}_n > 0$, the energy balance (8.18) implies $\mathcal{M}_n \geq 0$. The mass balance (8.1), therefore implies that $m_n^{w+} \geq 0$ and constituent $w$ moves down/up relative to the front. Eliminating the surface mass interaction term $\mathcal{M}_n$ by summing the mass balances of constituents $w$ and $i$ we obtain

$$m_n^{w+} + m_n^{i+} = 0,$$

which implies that constituent $i$ will move up/down relative to the front, $v_n^i - u_n \geq 0$. Thus for melting $\mathcal{M}_n < 0$ constituent $i$ approaches the front where it changes to phase $w$ and is reabsorbed back into the three component mixture. This is illustrated in Fig. 4. Note, the sign change with respect to the orientation of the front so that the normal now points downward. This situation describes the balances at the free surface of a temperate wet snow pack, where surface warming melts the ice and the resultant water is reabsorbed (drains) back into the snow pack. Note, that in this configuration there are no mass interactions across the surface for constituents $w$ and $i$ and therefore no mechanism by which reabsorption can be achieved in the same manner as in our first example. This is a specific example which demonstrates the necessity of interactions parallel to the surface in the general theory.

9. DISCUSSION

The principle of Euclidean frame indifference has been used to formulate functional forms for the bulk mixture volume interactions (3.1) and the surface interactions (5.2) and (5.7) which occur at non-material singular surfaces. These functions partition the mass, momentum and energy interactions into a sum of transfers between pairs of constituents. A considerable advantage is achieved by applying the conservation laws in a simplified form in which the interactions are frame indifferent. The volume conservation laws (2.7) should therefore be
applied in conjunction with the volume interactions (3.3). In this form there will automatically be a finite contribution to the total (summed) mass, momentum and energy balances from $\Sigma_0 \mathcal{V}_n^{\alpha}m_0$, $\Sigma_0 \mathcal{V}_n^{\alpha}m_0$ and $\Sigma_0 \mathcal{V}_n^{\alpha}m_0$ without further manipulation.

This is also true of the surface interaction terms. When constituent $\alpha$ is present on both sides of a singular surface $\mathcal{S}^s$ then the jump relations (4.4) should be applied with the frame indifferent surface interactions (5.4) and (5.9). And, when constituent $\alpha$ is only present on one side of the singular surface the jumps (4.10) should be applied in conjunction with (5.6) and (5.11). These frame indifferent surface interactions place no restrictions on the velocity or internal energy of constituent $\alpha$ on the side where it does not exist, which is a requirement of a well posed theory. However, when $\phi^\alpha = 0$ the full frame indifferent jump relations reduce to the single sided jump relations provided we define $\mathbf{v}^{n\pm} = \mathbf{v}^{n\pm}$ and $\epsilon^{n\pm} = \epsilon^{n\pm}$. There is considerable benefit in not having to discriminate between whether full sided or single sided jumps are appropriate and we suggest that the above definitions are adopted as a convention which is a natural simplification of theory.

REFERENCES


(Received 22 October 1995; accepted 11 June 1996)