

A continuum model for momentum, heat and species transport in binary solid–liquid phase change systems—I. Model formulation

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Abstract—Semi-empirical laws and microscopic descriptions of transport behavior have been integrated with principles of classical mixture theory to obtain a set of continuum conservation equations for binary, solid–liquid phase change systems. For a restricted, yet frequently encountered, class of phase change systems, the continuum equations have been cast into forms amenable to clear physical interpretation and solution by conventional numerical procedures.

1. INTRODUCTION

PROCESSES related to melting and solidification encompass a range of engineering and scientific disciplines and occur in many applications such as casting, welding, glass forming and energy storage. Problems which impede the successful implementation of phase change processes are often related to the improper ‘control’ of specific transport mechanisms. Examples include cracking due to excessive thermal stresses, pore or void formation due to improper feeding of castings, and constituent inhomogeneities resulting from uncontrolled species transport.

Due to the absorption or release of latent energy, phase change problems are nonlinear, and exact solutions are limited to a small class of problems involving pure substances in one-dimensional infinite or semi-infinite domains [1, 2]. The inability of these solutions to address multidimensional effects, non-discrete phase change and advection has focused attention on the development of suitable numerical procedures, which can be conveniently divided into two groups. The first group utilizes independent conservation equations for each phase and couples them with appropriate boundary conditions at the phase interface. Such methods are often referred to as multiple region or multiple domain solutions. The second group consists of single region (continuum) formulations which eliminate the need for separate phase conservation equations.

Multiple region solutions require the existence of discrete interfaces between regions or phases in the domain and are generally limited to pure substances [3–7]. The primary difficulty associated with their implementation centers on tracking the phase interface, which is generally an unknown function of space and time. The need for moving numerical grids and/or coordinate mapping procedures complicates the

application of this technique, and generally, simplifying assumptions regarding the geometric regularity of the phase interface are made.

Unlike pure substances, multiconstituent systems do not exhibit a sharp interface between solid and liquid phases. In fact, due to impurities (intentional or otherwise), discrete phase change rarely occurs in practice. The phase change behavior of such systems depends on many factors including the phase change environment, composition, and thermodynamic descriptions of specific phase transformations. Moreover, solidification occurs over extended temperature ranges and solid formation often occurs as a permeable crystalline-like matrix which coexists with the liquid phase.

Since they need not track phase interfaces, single region formulations are well suited for treating the continuous transition between solid and liquid phases, as well as the evolution of latent energy over a finite temperature range. Such formulations are generally developed from volume averaging techniques based on classical mixture theory. Detailed developments of the theory are available in the open literature [8–13], as are applications to inert systems such as dispersed oil droplets in water and fluid saturated granular materials [14–16]. The theories have been extended to phase change processes [17–19], although treatments have been restricted to one-dimensional, conduction dominated conditions.

While continuum formulations have been shown to provide realistic predictions of transport behavior for conduction phase change problems, inclusion of advective components of momentum, energy and species transfer does not appear to have been considered. Such an extension necessitates consideration of multiphase region morphology, as well as relative phase velocities. While classical theories clearly acknowledge the significance of these factors, the

NOMENCLATURE

A	area	\mathbf{V}	velocity vector
B	body force	\bar{V}	volume
c	specific heat	x, y, z	Cartesian coordinates.
D	mass diffusion coefficient		
\dot{E}	energy production rate	Greek symbols	
f	mass fraction	μ	viscosity
F	phase interaction force per unit volume	ρ	density
g	volume fraction or gravitational acceleration	$\bar{\rho}$	partial density
\dot{G}	momentum production rate	σ	vector component of material stress tensor
h	enthalpy	τ	stress vector
\mathbf{J}	general surface flux vector	ϕ	general scalar quantity.
k	thermal conductivity		
k_p	equilibrium partition ratio	Subscripts	
K	permeability	k	phase k
\dot{M}	mass production rate	l	liquid
\mathbf{n}	outward unit normal	liq	liquidus
p	pressure (isotropic stress component)	r	relative
\mathbf{r}	position vector	s	solid
S	source term	x	x -component.
t	time		
T	temperature	Superscripts	
u, v, w	velocity components	α	constituent α .

desire to maintain universal generality prohibits description beyond that of symbolic representations. Accordingly, the primary objective of the present work is to develop a consistent set of continuum equations for the conservation of mass, momentum, energy, and species in a binary, solid-liquid phase change system. Emphasis is placed on casting the equations into forms which are amenable to clear physical interpretation, as well as to solution by conventional finite-difference or finite-element methods. Although achieving this objective must come at the expense of a loss of generality, related assumptions and constraints will be clearly identified and justified on the basis of physical considerations. In a companion paper [20], the capabilities of the model are demonstrated through application to solidification of a binary mixture in a rectangular cavity.

2. MODEL FORMULATION

The development of conservation equations from classical mixture theory is based on the following principles [9, 13]: (i) mixture components may be viewed as isolated subsystems, if interactions with other mixture components are properly treated; (ii) all properties of the mixture are mathematical consequences of the component properties; (iii) the mean collective mixture behavior is governed by equations similar to those governing the individual components. Since these principles presume an inert mixture, application to multiphase, multiconstituent mixtures requires spe-

cial care. While the phases can generally be considered as isolated, their constituents are often inseparable due to intimate bonding on an atomic level. Furthermore, since the properties of a non-inert mixture are not direct mathematical consequences of the component properties, application of mixture theory to non-inert systems requires additional information concerning the behavior of mixture constituents on an atomic scale. For many applications this information can be extracted from constitutional (phase) diagrams or from empirical relationships.

In the present formulation a constituent represents a basic chemical element or compound, and a phase represents a quantity of matter which is homogeneous in physical structure and comprised of one or more constituents. Phases are assumed to be distinct and separable components of the continuum, although they need not be homogeneous in chemical composition. In addition, the term 'phase element' is used to represent a macroscopic phase agglomerate, such as a liquid inclusion or solid grain. A system of α constituents and k distinct separable phases is viewed as a continuum in which any location \mathbf{r} can be simultaneously occupied by all constituents and all phases (Fig. 1). The mean velocity of the constituents comprising phase k , relative to a fixed reference frame, is designated as \mathbf{V}_k and is termed the phase velocity. The absolute velocity of each constituent α in phase k , relative to a fixed reference frame, is designated as \mathbf{V}_k^α , and the diffusion velocity of constituent α in phase k is $\mathbf{V}_k^\alpha - \mathbf{V}_k$.

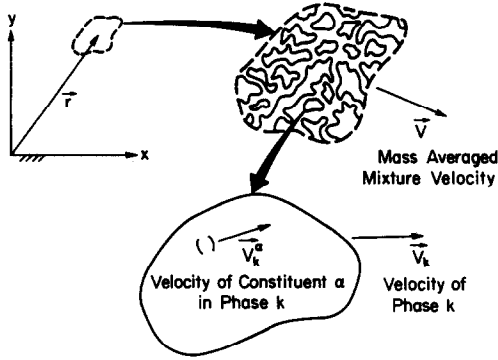


FIG. 1. Graphical representation of a multiphase, multi-constituent continuum.

The development of continuum conservation equations requires relationships between densities and volume fractions. If ρ_k^α and g_k^α are defined as the actual density and volume fraction of constituent α in phase k , respectively, the partial density of constituent α in phase k can be expressed as

$$\bar{\rho}_k^\alpha = g_k^\alpha \rho_k^\alpha. \quad (1)$$

Similarly, if ρ_k and g_k are defined as the actual density and volume fraction of phase k , respectively, the partial density of phase k is

$$\bar{\rho}_k = g_k \rho_k. \quad (2)$$

The mass fraction of constituent α in phase k is then

$$f_k^\alpha = \frac{\bar{\rho}_k^\alpha}{\bar{\rho}_k} \quad (3)$$

and the mass fraction of phase k is

$$f_k = \frac{\bar{\rho}_k}{\sum_k \bar{\rho}_k}. \quad (4)$$

If the constituents can be viewed as separable phase components, as for inert systems, simple summation rules can be used to relate phase and constituent densities. For non-inert systems, however, atomic bonding between phase constituents prohibits relating phase and constituent densities in such a simple fashion. Since explicit atomic scale calculations are impractical, recourse must be made to empirically derived representations of phase densities. Nevertheless, for the purpose of model development, it is convenient to consider fictitious volume fractions associated with non-inert constituents. Ultimately, phase diagrams, or similar atomic level descriptions, will circumvent the need for explicit consideration of these volume fractions.

An explicit statement must also be made regarding the relationship between phase volume fractions. In the present formulation the requirement that all phases do not vanish simultaneously is enforced, in which case

$$\sum_k g_k = 1. \quad (5)$$

Note that, although treatment of the phase volume fractions as continuous functions of space is implicit in the continuum formulation, application of the formulation to discrete phase change systems is not precluded. In fact, for conduction phase change problems, it has been shown that continuum formulations are equivalent to conventional conservation equations at discrete phase interfaces [21].

2.1. Conservation of a general scalar quantity

Consider the transport of a general scalar specific quantity ϕ_k associated with phase k in a multiphase mixture. For an arbitrary fixed control volume \bar{V} of surface area A , which is larger than a phase element but smaller than the characteristic domain dimension, conservation of ϕ_k can be expressed as a balance of accumulation, net outflow by advection and diffusion, and volumetric production

$$\frac{\partial}{\partial t} \int_{\bar{V}} [\rho_k \phi_k] d\bar{V}_k + \int_A [\rho_k \mathbf{V}_k \phi_k] \cdot \mathbf{n} dA_k = \int_A -\mathbf{J}_k \cdot \mathbf{n} dA_k + \int_{\bar{V}} S_k d\bar{V}_k \quad (6)$$

where \mathbf{n} is the outward unit normal to the surface, \mathbf{J}_k is a surface flux vector and S_k is a volumetric source term which includes production or annihilation of ϕ_k . In the present formulation the differential surface area dA_k is assumed to equal $g_k dA$. Since g_k is assumed to be continuous, the integrands of equation (6) are continuous and differentiable functions, and the integral theorems of Leibnitz and Gauss can be applied. Furthermore, since the control volume is arbitrary, equation (6) can be expressed in differential form as

$$\frac{\partial}{\partial t} (\bar{\rho}_k \phi_k) + \nabla \cdot (\bar{\rho}_k \mathbf{V}_k \phi_k) = -\nabla \cdot (g_k \mathbf{J}_k) + g_k S_k. \quad (7)$$

2.2. Conservation of mass

The statement of mass conservation for phase k can be obtained from equation (7) with $\phi_k = 1$, $\mathbf{J}_k = 0$, and $S_k = \dot{M}_k$, yielding

$$\frac{\partial}{\partial t} (\bar{\rho}_k) + \nabla \cdot (\bar{\rho}_k \mathbf{V}_k) = g_k \dot{M}_k. \quad (8)$$

The continuum equation for mass conservation is obtained by summing the phase conservation equations and recognizing that the production of phase k , \dot{M}_k , must come at the expense of other mixture phases ($\sum_k g_k \dot{M}_k = 0$). Hence

$$\frac{\partial}{\partial t} (\rho) + \nabla \cdot (\rho \mathbf{V}) = 0 \quad (9)$$

where the mixture density and mass averaged velocity are

$$\rho = \sum_k \bar{\rho}_k \quad (10)$$

$$\mathbf{V} = \frac{1}{\rho} \sum_k \bar{\rho}_k \mathbf{V}_k = \sum_k f_k \mathbf{V}_k. \quad (11)$$

2.3. Conservation of linear momentum

For convenience, Cartesian coordinates will be assumed and the velocity of phase k expressed as

$$\mathbf{V}_k = u_k \hat{i} + v_k \hat{j} + w_k \hat{k}. \quad (12)$$

The statement of conservation of x -momentum for phase k can be obtained from equation (7) with $\phi_k = u_k$, $\mathbf{J}_k = -\sigma_{kx}$ and $S_k = \rho_k B_{kx} + \dot{G}_{kx}$, yielding

$$\frac{\partial}{\partial t} (\bar{\rho}_k u_k) + \nabla \cdot (\bar{\rho}_k \mathbf{V}_k u_k) = \nabla \cdot (g_k \sigma_{kx}) + \bar{\rho}_k B_{kx} + g_k \dot{G}_{kx}. \quad (13)$$

The flux vector σ_{kx} represents the component of the general material stress tensor which influences x -direction momentum, while B_{kx} represents the x -component body force on phase k and \dot{G}_{kx} accounts for momentum production due to phase interactions such as drag and lift. The continuum equation governing the conservation of x -momentum can be obtained by summing equation (13) over each phase, yielding

$$\frac{\partial}{\partial t} \left(\sum_k \bar{\rho}_k u_k \right) + \nabla \cdot \left(\sum_k \bar{\rho}_k \mathbf{V}_k u_k \right) = \nabla \cdot \left(\sum_k g_k \tau_{kx} \right) - \frac{\partial}{\partial x} \left(\sum_k g_k p_k \right) + \sum_k (\bar{\rho}_k B_{kx}) + F_x \quad (14)$$

where the flux vector has been decomposed into isotropic and deviatoric components, $\sigma_{kx} = -p_k \hat{i} + \tau_{kx}$ and the net x -component force due to phase interactions is $F_x = \sum_k g_k \dot{G}_{kx}$. If the advective momentum flux is decomposed into components representing contributions from the mean mixture motion and relative phase motion

$$\sum_k \bar{\rho}_k \mathbf{V}_k u_k = \rho \mathbf{V} u + \sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(u_k - u) \quad (15)$$

where the mass averaged x -component of the mixture velocity is

$$u = \frac{1}{\rho} \sum_k \bar{\rho}_k u_k = \sum_k f_k u_k \quad (16)$$

and the x -component mixture body force is defined as

$$B_x = \frac{1}{\rho} \sum_k \bar{\rho}_k B_{kx} = \sum_k f_k B_{kx} \quad (17)$$

equation (14) can be expressed as

$$\begin{aligned} \frac{\partial}{\partial t} (\rho u) + \nabla \cdot (\rho \mathbf{V} u) &= \nabla \cdot \left(\sum_k g_k \tau_{kx} \right) \\ &- \nabla \cdot \left(\sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(u_k - u) \right) \\ &- \frac{\partial}{\partial x} \left(\sum_k g_k p_k \right) + \rho B_x + F_x. \end{aligned} \quad (18)$$

At this stage in the formulation, specific consideration must be given to the nature of the phase stress vector τ_{kx} . It is important to recognize that τ_{kx}

includes only stresses resulting from interaction of a phase with itself. The effect of interactions between phases is accommodated by the quantity F_x . Specification of τ_{kx} requires an *a priori* assessment of the continuity of each mixture phase. A phase will be considered continuous if any two points within the phase can be joined by a continuous curve which lies solely within the phase. For example, if consideration is given to the flow of a liquid through a permeable solid matrix, both solid and liquid phases would be considered continuous. On the other hand, for a dilute suspension of solid particles in a liquid, the solid phase would be discontinuous.

If each mixture phase is considered continuous, constitutive relationships are available to describe τ_{kx} . In the present formulation the behavior of each continuous phase is assumed to be Newtonian, implying that rigid phases, such as solids, are treated as highly viscous fluids. Due to the spatial variations in phase volume fractions which occur in phase change problems, appropriate averaging of classical Newtonian constitutive equations is necessary. This requirement becomes apparent if consideration is given to the rate of expansion (dilation rate) of phase k . In order to maintain consistency with the phase continuity requirement, equation (8), the dilation rate of phase k must be expressed as $\nabla \cdot (g_k \mathbf{V}_k) / g_k$. Hence only when the phase volume fraction is spatially invariant can the dilation rate be expressed as $\nabla \cdot (\mathbf{V}_k)$. It follows that, for each continuous phase, the average stress vector is expressed as

$$g_k \tau_{kx} = \mu_k \nabla (g_k u_k) - \frac{2}{3} \mu_k \nabla \cdot (g_k \mathbf{V}_k) \hat{i} + \tau_{kx}^0 \quad (19)$$

where τ_{kx}^0 represents the viscous stresses not included in $\mu_k \nabla (g_k u_k)$. In Cartesian coordinates this term is expressed as

$$\tau_{kx}^0 = \mu_k \left[\frac{\partial}{\partial x} (g_k u_k) \hat{i} + \frac{\partial}{\partial x} (g_k v_k) \hat{j} + \frac{\partial}{\partial x} (g_k w_k) \hat{k} \right]. \quad (20)$$

If phase viscosities are assumed constant, it can be shown that

$$\begin{aligned} \nabla \cdot \left(\sum_k [\tau_{kx}^0 - \frac{2}{3} \mu_k \nabla \cdot (g_k \mathbf{V}_k) \hat{i}] \right) \\ = \sum_k \frac{\partial}{\partial x} \left[\frac{1}{3} \mu_k \nabla \cdot (g_k \mathbf{V}_k) \right]. \end{aligned} \quad (21)$$

Substituting equations (19) and (21) into equation (18), it follows that

$$\begin{aligned} \frac{\partial}{\partial t} (\rho u) + \nabla \cdot (\rho \mathbf{V} u) &= \nabla \cdot \left(\sum_k \mu_k \nabla (g_k u_k) \right) \\ &- \nabla \cdot \left(\sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(u_k - u) \right) - \frac{\partial p}{\partial x} + \rho B_x + F_x \end{aligned} \quad (22)$$

where

$$p = \sum_k [g_k p_k - \frac{1}{3} \mu_k \nabla \cdot (g_k \mathbf{V}_k)]. \quad (23)$$

Prescription of the phase interaction force F_x requires careful consideration of the multiphase region morphology. For a wide range of multi-constituent solid-liquid phase change systems, the multiphase region is characterized by a fine permeable solid matrix which can often be considered stationary (static solidification) or constrained to free body translation (continuous solidification). For such systems, analogies can be drawn to flows through porous media. Specifically, Darcy's law suggests that phase interaction forces are proportional to the superficial (or discharge) liquid velocity relative to the velocity of the porous solid. That is

$$F_x = \frac{\mu_1}{K_x} (g_1 u_r) \quad (24)$$

where K_x represents the component of anisotropic permeability which influences x -direction momentum transport and $u_r = u_l - u_s$ represents the x -component relative phase velocity. If it is further assumed that phase densities are constant, the solid matrix is free of internal stress ($\nabla(g_s u_s) = \mathbf{0}$) and translates at a prescribed velocity \mathbf{V}_s , and that viscous stresses resulting from local density gradients are negligible ($\nabla(\rho/\rho_l) = \mathbf{0}$), equation (24) can be substituted into equation (22). Invoking the identities $g_l = (\rho/\rho_l) f_l$ and $f_l u_r = u - u_s$, it follows that

$$\begin{aligned} \frac{\partial}{\partial t} (\rho u) + \nabla \cdot (\rho \mathbf{V} u) &= \nabla \cdot \left(\mu_1 \frac{\rho}{\rho_l} \nabla u \right) \\ &- \frac{\mu_1}{K_x} \frac{\rho}{\rho_l} (u - u_s) - \nabla \cdot (\rho f_s f_l \mathbf{V}_r u_r) - \frac{\partial p}{\partial x} + \rho B_x. \end{aligned} \quad (25)$$

The third term on the right-hand side of equation (25) represents inertial forces established as a consequence of variations in relative phase velocities. This inertial contribution appears only in the multiphase region, where permeabilities are extremely small and the contribution is negligible compared to the Darcian damping force. Hence, the final continuum expression for momentum conservation can be written as

$$\begin{aligned} \frac{\partial}{\partial t} (\rho u) + \nabla \cdot (\rho \mathbf{V} u) &= \nabla \cdot \left(\mu_1 \frac{\rho}{\rho_l} \nabla u \right) \\ &- \frac{\mu_1}{K_x} \frac{\rho}{\rho_l} (u - u_s) - \frac{\partial p}{\partial x} + \rho B_x. \end{aligned} \quad (26)$$

Equation (26) reduces, as it must, to the appropriate single phase limits as $K_x \rightarrow 0$ (pure solid) and $K_x \rightarrow \infty$ (pure liquid). The solid velocity is set to zero for static phase change systems, or to a constant value, as prescribed by external boundary conditions, for continuous phase change systems.

For solid-liquid phase change systems in which the solid phase is discontinuous or subject to unconstrained motion, explicit consideration must be given

to phase interactions and descriptions of relative phase motion. One procedure, known as the two fluid model [16], solves conservation equations for each separable phase, such as equation (13), and couples them through expressions describing internal interactions. The prescription of such interactions relies on the ability to accurately characterize influences such as drag and lift on the solid phase, which would be difficult to assess either analytically or empirically. Furthermore, if the solid phase is discontinuous, constitutive relationships for the solid phase stress vector $\tau_{s,x}$ would require explicit consideration of complex phenomena such as collisions and mechanical interference between solid particles. In view of these difficulties, no general recommendations can be given for dealing with momentum transport in these systems.

For phase change systems the transition regions of which are not characterized by discrete separable phases, such as glassy substances and waxes, the concepts of relative phase motion and phase interactions clearly have no significance. For such systems, momentum transport might best be described by introducing an effective viscosity μ . Hence the momentum equation can be written as

$$\frac{\partial}{\partial t} (\rho u) + \nabla \cdot (\rho \mathbf{V} u) = \nabla \cdot (\mu \nabla u) - \frac{\partial p}{\partial x} + \rho B_x \quad (27)$$

where μ exhibits appropriate limits in the pure solid ($\mu \rightarrow \infty$) and pure liquid ($\mu \rightarrow \mu_l$). One representation which satisfies these limits is a harmonic mean of the phase viscosities which, for $\mu_s = \infty$, reduces to

$$\mu = \frac{\mu_l}{g_l}. \quad (28)$$

Since the phases are physically nonseparable, phase volume fractions must be considered fictitious in much the same manner as constituent volume fractions associated with phases comprised of non-separable constituents, equation (1). Ultimately, the prescription of these volume fractions relies on empirical representations. For example, density measurements could be performed on partially solidified systems, correlated with temperature, and related to a fictitious liquid volume fraction derived from equations (2), (5) and (10)

$$g_l = \frac{\rho - \rho_s}{\rho_l - \rho_s} \quad (29)$$

where ρ is the density of the partially solidified system and ρ_s and ρ_l represent the densities of the system just prior to the onset of melting and solidification, respectively.

2.4. Conservation of energy

The statement of energy conservation for phase k can be obtained from equation (7) with $\phi_k = h_k$, $\mathbf{J}_k = -k_k \nabla T$, and $S_k = \dot{E}_k$. Hence

$$\frac{\partial}{\partial t}(\bar{\rho}_k h_k) + \nabla \cdot (\bar{\rho}_k \mathbf{V}_k h_k) = \nabla \cdot (g_k k_k \nabla T) + g_k \dot{E}_k \quad (30)$$

where local thermodynamic equilibrium has been assumed ($T_k = T$) and the source term \dot{E}_k represents energy production associated with phase k . The continuum equation of energy conservation is obtained by summing the conservation equations for each phase and recognizing that $\sum_k g_k \dot{E}_k = 0$. It follows that

$$\frac{\partial}{\partial t} \left(\sum_k \bar{\rho}_k h_k \right) + \nabla \cdot \left(\sum_k \bar{\rho}_k \mathbf{V}_k h_k \right) = \nabla \cdot (k \nabla T) \quad (31)$$

where the mixture conductivity is

$$k = \sum_k g_k k_k. \quad (32)$$

The advective term may be decomposed into contributions due to the mean mixture motion and the relative phase motion

$$\sum_k \bar{\rho}_k \mathbf{V}_k h_k = \rho \mathbf{V} h + \sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(h_k - h) \quad (33)$$

where the mixture enthalpy is

$$h = \frac{1}{\rho} \sum_k \bar{\rho}_k h_k = \sum_k f_k h_k. \quad (34)$$

Substituting into equation (31), it follows that

$$\begin{aligned} \frac{\partial}{\partial t}(\rho h) + \nabla \cdot (\rho \mathbf{V} h) &= \nabla \cdot (k \nabla T) \\ - \nabla \cdot \left(\sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(h_k - h) \right) & \end{aligned} \quad (35)$$

In the present formulation the enthalpy of phase k is defined as

$$h_k = \int_0^T c_k dT + h_k^0 \quad (36)$$

where c_k represents an effective specific heat of phase k . For phases consisting of non-separable constituents, prescription of the phase specific heats and thermal conductivities must rely on empirical results. Substituting the identity

$$\nabla T = \frac{1}{c_k} \nabla h + \frac{1}{c_k} \nabla (h_k - h) \quad (37)$$

into equation (35), it follows that

$$\begin{aligned} \frac{\partial}{\partial t}(\rho h) + \nabla \cdot (\rho \mathbf{V} h) &= \nabla \cdot \left(\frac{k}{c_k} \nabla h \right) + \nabla \cdot \left(\frac{k}{c_k} \nabla (h_k - h) \right) \\ - \nabla \cdot \left(\sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(h_k - h) \right) & \end{aligned} \quad (38)$$

or, for the special case of a two-phase, solid-liquid system

$$\begin{aligned} \frac{\partial}{\partial t}(\rho h) + \nabla \cdot (\rho \mathbf{V} h) &= \nabla \cdot \left(\frac{k}{c_s} \nabla h \right) + \nabla \cdot \left(\frac{k}{c_s} \nabla (h_s - h) \right) \\ - \nabla \cdot [\rho f_s (h_1 - h_s) (\mathbf{V} - \mathbf{V}_s)] & \end{aligned} \quad (39)$$

The first two terms on the right-hand side of equation (39) represent the net Fourier diffusion flux. By expressing the flux in this manner, temperature is eliminated as an explicit dependent variable. While temperatures do not appear explicitly in the energy equation, they are implicit in the definitions of phase enthalpies prescribed by equation (36). The last term appearing in equation (39) represents the energy flux associated with relative phase motion. Transport due to relative phase motion is identically zero for situations where all phases move at the mass average velocity ($\mathbf{V}_k = \mathbf{V}$) or for conditions where the phase enthalpies are equal to the mixture enthalpy ($h_k = h$). For systems where relative phase motion has no physical significance, such as glassy substances and waxes, terms accounting for transport due to relative phase motion are omitted.

2.5. Conservation of species

The conservation requirement for species α can be obtained from equation (7) with $\phi_k = f_k^\alpha$, $\mathbf{J}_k = -\rho_k D_k^\alpha \nabla f_k^\alpha$, and $S_k = \dot{M}_k^\alpha$. That is

$$\frac{\partial}{\partial t}(\bar{\rho}_k f_k^\alpha) + \nabla \cdot (\bar{\rho}_k \mathbf{V}_k f_k^\alpha) + \nabla \cdot (\rho f_k D_k^\alpha \nabla f_k^\alpha) + g_k \dot{M}_k^\alpha \quad (40)$$

where \dot{M}_k^α represents the production or annihilation of species α in phase k . The continuum species conservation equation is obtained by summing the conservation equations for each phase and recognizing that the production of species α in phase k must be accompanied by a destruction of species α in other phases ($\sum_k g_k \dot{M}_k^\alpha = 0$). Hence

$$\begin{aligned} \frac{\partial}{\partial t} \left(\sum_k \bar{\rho}_k f_k^\alpha \right) + \nabla \cdot \left(\sum_k \bar{\rho}_k \mathbf{V}_k f_k^\alpha \right) \\ = \nabla \cdot \left(\sum_k \rho f_k D_k^\alpha \nabla f_k^\alpha \right). \end{aligned} \quad (41)$$

The advective species flux can be decomposed into contributions from the mean mixture and relative phase motions

$$\sum_k \bar{\rho}_k \mathbf{V}_k f_k^\alpha = \rho \mathbf{V} f^\alpha + \sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(f_k^\alpha - f^\alpha) \quad (42)$$

where the mixture concentration of species α is

$$f^\alpha = \frac{1}{\rho} \sum_k \bar{\rho}_k f_k^\alpha = \sum_k f_k f_k^\alpha. \quad (43)$$

Substituting equations (42) and (43) into equation (41), it follows that

$$\frac{\partial}{\partial t}(\rho f^\alpha) + \nabla \cdot (\rho \mathbf{V} f^\alpha) = \nabla \cdot \left(\sum_k \rho f_k D_k^\alpha \nabla f_k^\alpha \right) - \nabla \cdot \left(\sum_k \bar{\rho}_k (\mathbf{V}_k - \mathbf{V})(f_k^\alpha - f^\alpha) \right). \quad (44)$$

For a two-phase, solid-liquid system, diffusion in the solid phase can be neglected relative to that in the liquid phase ($D_1^\alpha \gg D_2^\alpha$). With this assumption and the identity

$$\nabla f_1^\alpha = \nabla f^\alpha + \nabla(f_1^\alpha - f^\alpha) \quad (45)$$

equation (44) may be expressed as

$$\frac{\partial}{\partial t}(\rho f^\alpha) + \nabla \cdot (\rho \mathbf{V} f^\alpha) = \nabla \cdot (\rho D \nabla f^\alpha) + \nabla [\rho D \nabla (f_1^\alpha - f^\alpha)] - \nabla \cdot [\rho f_s (f_1^\alpha - f^\alpha) (\mathbf{V} - \mathbf{V}_s)] \quad (46)$$

where the mixture mass diffusion coefficient is

$$D = f_1 D_1^\alpha. \quad (47)$$

The first two terms on the right-hand side of equation (46) represent the net diffusive (Fickian) species flux. The last term represents the species flux due to relative phase motion. If the phase velocities are equal to the mixture velocity ($\mathbf{V}_k = \mathbf{V}$) or the phase compositions are equal to that of the mixture ($f_k^\alpha = f^\alpha$), this flux is identically zero. In addition, species transport due to relative phase motion is omitted for phase change systems where relative phase motion has no physical significance (glassy substances, waxes, etc.).

For binary systems, species conservation equations need only be considered for one constituent, since overall species conservation requires $\sum_\alpha f^\alpha = 1$.

2.6. Supplementary relationships

Closure of the system of conservation equations requires supplementary relationships for phase mass fractions f_k and compositions f_k^α . For a wide range of practical applications, solidification and melting of binary systems can be closely approximated by the assumption of local composition equilibrium at phase interfaces. The assumption of interface equilibrium does not rule out the possibility of phase composition gradients, but rather implies that the resistance to the transport of constituent atoms across the interface is negligible. Under such conditions continuum and phase compositions can be related to temperature through equilibrium phase diagrams. In reference to the binary solid-liquid phase diagram of Fig. 2, conservation of species α can be expressed as

$$f^\alpha = f_s f_s^\alpha + f_l f_l^\alpha. \quad (48)$$

For saturated conditions, $f_s + f_l = 1$, and equation (48) can be expressed as

$$f_s = \frac{f_1^\alpha - f^\alpha}{f_1^\alpha - f_s^\alpha}. \quad (49)$$

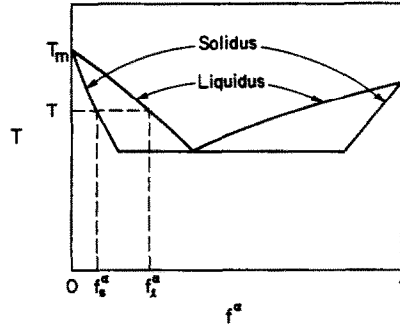


FIG. 2. Equilibrium phase diagram for a binary system.

Equation (49) is commonly termed the lever rule and is simply a statement of local conservation for species α . It should be recognized that the lever rule follows directly from the continuum expression for the mixture concentration, equation (43), without regard for the binary phase diagram. The phase diagram serves as a graphical representation of species conservation. More importantly, the phase diagram permits the description of constituent transport on an atomic scale in terms of measurable macroscopic variables such as temperature and composition.

When working with phase diagrams, it is convenient to define an equilibrium partition ratio k_p as

$$k_p = \frac{f_s^\alpha}{f_l^\alpha}. \quad (50)$$

A finite mushy region can exist for $k_p < 1$ and represents conditions for which the solute (α) has limited solubility in the solid phase. In the limit as $k_p \rightarrow 1$ (equal solute solubility in solid and liquid phases), discrete phase change behavior, without a mushy zone, will be observed. In general, the equilibrium partition ratio is temperature dependent and can be computed directly from the phase diagram. Often, however, the curvature of the solidus and liquidus lines are slight and they can be approximated as straight lines. The equilibrium partition ratio can then be interpreted as the ratio of the slopes of the liquidus and solidus lines, and equation (49) can be expressed as

$$f_s = \frac{1}{1 - k_p} \left[\frac{T - T_{\text{liq}}}{T - T_m} \right] \quad (51)$$

where T is the local temperature, T_{liq} is the liquidus temperature corresponding to f^α , and T_m is the fusion temperature of the system as $f^\alpha \rightarrow 0$. Furthermore, equations (48) and (50) can be used to relate phase and mixture compositions

$$f_s^\alpha = \left[\frac{k_p}{1 + f_s(k_p - 1)} \right] f^\alpha \quad (52)$$

$$f_l^\alpha = \left[\frac{1}{1 + f_s(k_p - 1)} \right] f^\alpha. \quad (53)$$

It is important to recognize that the assumption of

local equilibrium does not preclude the existence of non-equilibrium conditions on a larger macroscopic scale. Macroscopic redistribution of species by both advective and diffusive transport is accommodated by equation (46). If local equilibrium is unlikely, as with rapid melting and solidification, alternative means of relating mixture and phase compositions would be required.

3. CONCLUSIONS

A continuum formulation for analyzing macroscopic phase change behavior in binary, solid-liquid systems has been developed. Microscopic descriptions of transport behavior, as well as semi-empirical laws, have been integrated with principles of classical mixture theory to obtain a consistent set of equations governing the conservation of mass, momentum, energy, and species. While multiple domain solutions are most often used for the analysis of phase change problems, continuum formulations offer several distinct advantages. In addition to permitting use of the same computational framework to address a range of multiphase, multiconstituent phase change systems, continuum formulations can be adapted to single phase problems. Continuum formulations also eliminate the need to track phase interfaces and hence, the associated use of quasi-steady approximations, numerical remeshing and coordinate mapping. More importantly, continuum formulations are well suited for accommodating continuous phenomena, such as the absorption or liberation of latent energy over a finite temperature range, which are generally associated with multiconstituent systems.

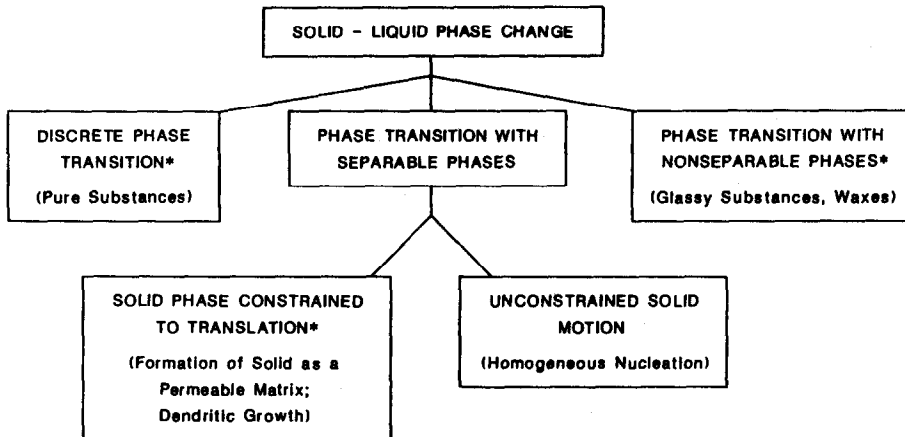
Continuum formulations are generally considered unsuitable for addressing discrete phase change and are frequently criticized for 'smearing' discrete phenomena. Such 'smearing' is inherent in the continuum formulation and is a direct consequence of approximating discontinuous functions, such as enthalpy or viscosity, with continuous functions. While the 'smearing' can be reduced by using fine computational meshes, it can never be entirely eliminated. From a practical perspective, however, the influence of 'smearing' on the prediction of macroscopic transport behavior can be reduced to acceptable (negligible) levels. Through comparisons with exact solutions, it has, for example, been verified that, for conduction dominated situations, continuum formulations yield accurate predictions, even in the limit of discrete phase change. Furthermore, due to the existence of impurities, discrete phase change rarely occurs in practice.

The complex nature of phase change processes clearly requires considerations which are unique to particular systems. In this study, a degree of generality has been sacrificed for the sake of utility, in order to develop conservation equations for several restricted, yet frequently encountered, classes of solid-liquid phase change systems. These systems are summarized

in Fig. 3, and simplifying assumptions, explicitly stated or implied at various stages in the model development, include laminar flow, Newtonian behavior of the phases, saturated mixture conditions, local thermodynamic equilibrium, and local constitutional equilibrium. Validity of these assumptions depends on the specific nature of the problem, as well as on the desired accuracy.

Consistent with the objectives of the present work, effort has focused on the development of conservation equations which are clear, concise and free of ambiguous symbolic representations. The equations have been developed in a fashion which permits and, in fact, encourages the relaxation of numerous constraints which ultimately results in the loss of generality. For example, many alternative forms of the conservation equations can be obtained. The special case of a stationary solid phase ($\mathbf{V}_s = \mathbf{0}$) can be considered, or supplementary relationships such as equations (51)–(53) (or suitable alternative expressions) can be substituted directly into the more general forms of the conservation equations. Since many binary systems exhibit a mushy region which can be characterized by a fine permeable solid matrix, the present formulation has incorporated the mushy region substructure description into the Darcian permeability. Directionality, which results from preferred growth directions or growth mechanisms, can be accommodated through the adoption of an anisotropic permeability. Furthermore, permeability components are in no way restricted to a sole dependence on scalar quantities such as temperature or composition. Permeability could, for example, be dependent on gradients of temperature and/or composition and thereby exhibit a selective directionality. Similarly, for conditions where the Darcy assumption may be inappropriate, alternative descriptions of phase interactions, such as F_i , equation (24), can be invoked or explicit supplementary relationships for relative phase velocities can be provided. Specialized processes which involve non-conservative forces or non-conservative energy production can also be incorporated through appropriate modifications of momentum source terms and relaxation of the $\sum_k g_k \dot{E}_k = 0$ constraint in the energy equation. Examples of such processes include electromagnetic casting, electromagnetic melt stirring, or processes involving radiation propagation through participating semi-transparent media.

It is also recognized that the conservation equations must be used in conjunction with one of many numerical schemes available for the solution of partial differential equations. Although this issue has not been considered explicitly, several features of the model have been introduced to achieve numerical conveniences in the solution scheme. Examples include separation of the Fourier diffusion flux, equation (39), into components which enable temperature to be eliminated as an explicit dependent variable, and decomposition of the Fickian diffusion flux, equation (46). Transformation of the governing equations into



(*) Systems which can be addressed in the context of the present formulation

FIG. 3. Classification of solid-liquid phase change systems.

forms suitable for a particular solution scheme is described in the companion paper [20].

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REFERENCES

1. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*. Oxford University Press, Oxford (1959).
2. M. N. Ozisik, *Heat Conduction*. Wiley, New York (1980).
3. W. D. Murray and F. Landis, Numerical and machine solutions of transient heat-conduction problems involving melting or freezing: Part I—method of analysis and sample solutions, *J. Heat Transfer* **81**, 106–112 (1959).
4. A. A. Lazaridis, A numerical solution of the multi-dimensional solidification (or melting) problem, *Int. J. Heat Mass Transfer* **13**, 1459–1477 (1970).
5. E. M. Sparrow, S. V. Patankar and S. Ramadhyani, Analysis of melting in the presence of natural convection in the melt region, *J. Heat Transfer* **99**, 520–526 (1977).
6. L. S. Yao, Natural convection effects in the continuous casting of a horizontal cylinder, *Int. J. Heat Mass Transfer* **27**, 697–704 (1984).
7. C. J. Ho and R. Viskanta, Heat transfer during inward melting in a horizontal tube, *Int. J. Heat Mass Transfer* **27**, 705–716 (1984).
8. R. M. Bowen, Toward a thermodynamics and mechanics of mixtures, *Archs Ration. Mech. Analysis* **24**, 370–403 (1967).
9. I. A. Muller, A thermodynamic theory of mixtures of fluids, *Archs Ration. Mech. Analysis* **28**, 1–39 (1968).
10. R. M. Bowen, Continuum theory of mixtures, Ballistic Research Laboratory Contract Report No. 45 (1971).
11. W. T. Sha and S. L. Soo, Multidomain multiphase fluid mechanics, *Int. J. Heat Mass Transfer* **21**, 1581–1595 (1978).
12. D. S. Drumheller, The theoretical treatment of a porous solid using a mixture theory, *Int. J. Solids Structures* **14**, 441–456 (1978).
13. J. W. Nunziato, A multiphase mixture theory for fluid-particle flows. In *Theory of Dispersed Multiphase Flow*, pp. 191–226. Academic Press, New York (1983).
14. S. L. Passman and J. W. Nunziato, Shearing flow of a fluid saturated granular material, *Mechanics of Structured Media, Proc. of Int. Symposium on Mechanical Behavior of Structured Media*, Amsterdam, pp. 343–353 (1981).
15. H. P. Greenspan, On centrifugal separation of a mixture, *J. Fluid Mech.* **127**, 91–101 (1983).
16. M. B. Carver, Numerical computation of phase separation in two fluid flow, *J. Fluids Engr* **106**, 147–153 (1984).
17. R. N. Hills, D. E. Loper and P. H. Roberts, A thermodynamically consistent model of a mushy zone, *Q. J. Mech. Appl. Math.* **36**, 505–539 (1983).
18. M. D. Burchardt and W. W. Bowley, Sublimation in a porous continuum developed from nonequilibrium thermodynamics, *J. Heat Transfer* **96**, 319–323 (1974).
19. V. C. Prandtl and P. R. Dawson, Application of mixture theory to continuous casting. In *Transport Phenomenon in Materials Processing* (Edited by M. M. Chen, J. Mazumder and C. L. Tucker), ASME HTD Vol. 29, pp. 47–54 (1983).
20. W. D. Bennon and F. P. Incropera, A continuum model for momentum, heat and species transport in binary solid-liquid phase change systems—II. Application to solidification in a rectangular cavity, *Int. J. Heat Mass Transfer* **30**, 2171–2187 (1987).
21. N. Shamsundar and E. M. Sparrow, Analysis of multidimensional conduction phase change via the enthalpy model, *J. Heat Transfer* **97**, 333–340 (1975).

UN MODELE CONTINU POUR LA QUANTITE DE MOUVEMENT, LA CONVECTION
DE CHALEUR ET DE MASSE DANS LES SYSTEMES A CHANGEMENT DE PHASE
SOLIDE-LIQUIDE—I. FORMULATION DU MODELE

Résumé—Des lois semi-empiriques et des descriptions microscopiques du mécanisme de transfert ont été intégrées à la théorie classique des mélanges pour obtenir un système d'équations de bilan continu pour des systèmes à changement de phase solide-liquide. Pour une classe limitée mais fréquemment rencontrée, de systèmes les équations ont été mise sous des formes permettant une interprétation physique claire et une résolution par des procédures numériques conventionnelles.

EIN MODELL FÜR IMPULS-, WÄRME- UND STOFFTRANSPORT IN BINÄREN
FEST-FLÜSSIG-PHASENWECHSELSYSTEMEN—I. MODELLANSATZ

Zusammenfassung—Halbempirische Gesetze und mikroskopische Beschreibungen des Transportverhaltens wurden mit den Prinzipien der klassischen Mischungstheorie verbunden. Es ergibt sich ein Satz von Erhaltungsgleichungen für binäre Fest-flüssig-Phasenwechsel-Systeme. Für eine bestimmte, häufig auftretende, Gruppe von Phasenwechselsystemen, wurden die Gleichungen in eine Form gebracht, die eine klare physikalische Interpretation ermöglicht und außerdem mit herkömmlichen numerischen Verfahren lösbar ist.

ФЕНОМЕНОЛОГИЧЕСКИЕ УРАВНЕНИЯ ПЕРЕНОСА КОЛИЧЕСТВА ДВИЖЕНИЯ,
ТЕПЛА И МАССЫ В БИНАРНЫХ СИСТЕМАХ ТВЕРДОЕ ТЕЛО-ЖИДКОСТЬ ПРИ
ФАЗОВЫХ ИЗМЕНЕНИЯХ—I. ФОРМУЛИРОВКА МОДЕЛИ

Аннотация—Для получения системы феноменологических уравнений переноса для бинарных систем твердое тело-жидкость при фазовых изменениях выполнено объединение полуэмпирических законов и микроскопических описаний процессов переноса с законами теории смесей. Для ограниченного, однако, часто встречающегося класса систем при фазовых переходах приводятся уравнения переноса в виде, удобном для их физической интерпретации и решения с помощью обычных численных методов.