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A continuum model for the propagation of discrete phase-change fronts in porous media in the presence of coupled heat flow, fluid flow and species transport processes

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Abstract—In this paper we derive the equations governing the transport of energy and mass in a porous medium saturated by a multiphase multi-constituent fluid mixture under conditions that yield steep continuous moving fronts and abrupt discontinuous moving phase-change interfaces. In these equations the volume fractions of each phase, the potentials, such as, the temperature, pressure and concentration, and the corresponding fluxes, are permitted to jump in value across the phase-change interfaces. As an example of application of the derived continuum model, we specialize the theory to the problem of propagation of melting/freezing interfaces in a salt–water saturated porous medium for a coupled process governed by heat flow, fluid flow and species transport.

1. INTRODUCTION

THE STUDY of phase change in fluid saturated porous media that involve coupled heat flow, fluid flow and species transport processes spans a range of disciplines in engineering and science. For example, coupled processes of this kind govern the thawing and freezing of permafrost in cold regions in response to the thermal loads imposed by man and by the seasonal temperature changes [1–3]. In bioengineering applications of cryosurgery and cryopreservation, control over the solidification patterns in the biological tissues of organs is essential for assuring the survival of the cells [4]. During the solidification of melts of many types of materials, such as semiconductor crystals, metals, and igneous rocks, there is a period of dendritic solidification during which the material can be viewed, and modelled, as a porous medium [5–7]. The uniformity of the electrical properties of silicon wafers from which microprocessors are built, depends on the distribution of the doping trace material, the convective and conductive transport processes, and the stability of the melt/solid interface [8]. In all of these problems, the phase change of interest is between the liquid and solid states. On the other hand, there is another class of problems that involve phase-change interfaces between gases and liquids, and between different liquids. These include hydrology problems such as the intrusion of sea-water into potable aquifers [9–11], environment protection problems such as the movement of toxic contaminants and radionuclide waste plumes in the subsurface [12, 13] and the fluid displacement processes, such as water, gas, steam, fire, chemical, and polymer-flooding processes, that are central to the conventional and enhanced recovery of petroleum [14–16]. Furthermore, in the chemical process industry, the patterns of heat transfer and movement of gas–liquid mixtures, and the dynamics of their phase interfaces within porous packed beds affect the efficiency of the packed beds as chemical processing units [17].

Most analyses of transport processes begin with the formulation of conservation laws and gradient-type constitutive relationships between the fluxes of the conserved quantities and the potentials that determine the state of each conserved quantity. These basic ingredients lead to governing equations that are similar in form, and in behavior. The similarities in the mathematical description of these seemingly different physical phenomena, lead to the recognition of common problems, and the development of common solutions.

The transport problems of the kind we wish to consider are often highly nonlinear, and possess coefficients of different spatial and temporal derivatives in the equation that vary rapidly in time and sharply in space at times and locations that cannot,

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NOMENCLATURE

$c^{+\alpha}$, $c^{+\alpha\mathrm{I}}$	rates of production of constituent α in all phases due to interaction with other constituents in the mixture, in the interior of the mixture, and on a discontinuity surface, respectively
$c^{+\alpha\beta}$, $c^{+\alpha\beta\mathrm{I}}$	rates of production of constituent α in phase β due to interaction with the rest of the mixture, in the interior of the mixture, and on a discontinuity surface, respectively
C	trace species concentration
$D_\mathrm{L}, D_\mathrm{T}$	longitudinal and transverse dispersion coefficients for isotropic porous medium
D_{ij}^cf, D_{ij}^cs	total trace species dispersion tensors in the fluid and solid phases
$\mathbf{j}$	generalized flux vector
$\mathbf{J}_v^\beta$, J_ε^β	diffusive momentum flux vector and diffusive energy flux
$\mathbf{k}$, $\mathbf{k}^\mathrm{f}$, $\mathbf{k}^\mathrm{s}$	thermal conductivity tensors for the mixture, and the fluid and solid phases, respectively
$\mathbf{K}$, K_{ij}	absolute permeability tensor
K_D^c	partition coefficient for distribution of trace species in solid and fluid phases
$\mathbf{m}^{+\alpha\beta}$, $\mathbf{m}^{+\alpha\beta\mathrm{I}}$	body forces per unit bulk volume on constituent α due to interaction with the rest of the mixture, in the interior of the mixture, and on the discontinuity surface, respectively
$\mathbf{m}^{+\beta}$, $\mathbf{m}^{+\beta\mathrm{I}}$	body forces per unit bulk volume on phase β due to interaction with the rest of the mixture, in the interior of the mixture, and on the discontinuity surface, respectively
$\mathbf{n}$, $\mathbf{n}^\mathrm{I}$	outward normal to the surface ∂V and to the discontinuity surface ∂V^I with respect to region V^-, respectively
P	fluid pressure variable
$\mathbf{q}$, q_i	general flux vector
$\mathbf{q}^\beta$, $\mathbf{q}^{\alpha\beta}$	energy outflux vectors for phase β per unit area of phase β and for constituent α in phase β per unit area of phase β, respectively
$Q_\mathrm{H}^{\alpha\beta}$, $Q_\mathrm{M}^{\alpha\beta}$	external sources of energy and mass for constituent α in phase β
Q_Ψ	external source rate for general property Ψ
$\mathbf{t}^\beta$, $\mathbf{t}^{\alpha\beta}$	stress tensor of phase β and of constituent α in phase β
T, T_m	temperature and phase-change temperature of material, respectively
$\mathbf{v}^\beta$, $\mathbf{v}^{\alpha\beta}$	velocities of phase β and of constituent α in phase β, respectively
$\mathbf{v}^\mathrm{I}$	velocity of the interface
$\mathbf{w}^{\alpha\beta}$	velocity of diffusion of constituent α relative to phase β.

Greek symbols

β^c	trace species adsorption coefficient
Γ	trace species equilibrium adsorption isotherm
ε^β, ε^f, ε^s	internal energies of β, fluid and solid phases, respectively
$\varepsilon^{\alpha\beta}$	internal energy of constituent α in phase β
$\varepsilon^{+\alpha\beta}$, $\varepsilon^{+\alpha\beta\mathrm{I}}$	rates of energy transfer to constituent α in phase β from all other constituents in all phases, in the interior of the mixture, and on a discontinuity surface, respectively
$\varepsilon^{+\beta}$, $\varepsilon^{+\beta\mathrm{I}}$	rates of energy transfer to phase β from other phases, in the interior, and on a discontinuity surface, respectively
$\varepsilon^{\mathrm{f}+}$, $\varepsilon^{\mathrm{f}-}$, $\varepsilon^{\mathrm{s}+}$, $\varepsilon^{\mathrm{s}-}$	internal energies of fluid and solid phases on the '+' and '−' sides of a discontinuity surface
ρ^β, ρ^f, ρ^s	densities of β, fluid and solid phases
$\rho^{\alpha\beta}$	density of constituent α in phase β; $\alpha = \mathrm{r}$, c, w and $\beta = \mathrm{f}$, s
τ^f	tortuosity of isotropic rock pore structure
ϕ	porosity of the rock
ϕ^β, ϕ^f, ϕ^s	volume fractions of β, fluid, and solid phases
Ψ	general transport property
$\tilde{\Psi}$	internal rate of production of Ψ.

Superscripts

α	property of constituent α; $\alpha = \mathrm{w}$ for water, c for trace species, r for rock
β	property of phase β; $\beta = \mathrm{f}$ for fluid phase, s for solid phase
c, r, w	properties of the trace species, rock, and water constituents, respectively
I	property of the discontinuity interface
f, s	properties of the fluid and solid phases, respectively
+, −	variables on the '+' and '−' sides of a discontinuity interface.

in general, be identified in advance. When this occurs, the governing equations can change type, or develop discontinuities in their solutions. Phase-change problems, in which phase transitions occur suddenly at a critical value of some variable result in the creation of spatially concentrated zones of change in properties with little change in the equations elsewhere.

Problems of this kind can often be made tractable by replacing the zone of spatially concentrated variable change (continuous front) with a moving surface of zero width (discontinuous or discrete moving front) [18, 19]. Jump conditions that enforce the underlying conservation laws, and provide the necessary boundary conditions for the solution of the simpler governing equations on either side of the interface, are imposed across the surface. Idealizations of this kind yield 'moving-boundary', 'free-boundary', or 'front propagation' problems in which the location of this surface must be found as part of the solution. Stefan problems, such as that due to the propagation of a freezing/melting interface, are one kind of moving-boundary problem in which the primary variable (i.e. the temperature) remains continuous while the gradient (i.e. the heat flux) becomes discontinuous at the moving boundary. Stefan problems are inherently nonlinear, even if the governing differential equations on either side of the interface are linear, because the boundary conditions are imposed on moving surfaces. Thus, for example, in reformulating a freezing/melting front problem as a moving-boundary Stefan problem, we have not eliminated the original difficulty posed by the nonlinearity in the differential equation, but have traded it for a more physical, yet difficult to solve, form by transferring the nonlinearity to the boundary conditions at the interface.

Several numerical schemes have been developed for solving the governing equations for unsteady moving-boundary problems of the Stefan type on *fixed grids* [20–26] and on *moving grids* [27–31]. A variational deforming finite element method for computing either continuous or discrete moving front problems on a *moving grid* was recently developed in ref. [32] for a system of coupled non-linear partial differential equations. The continued interest in the development of numerical solution schemes for moving-boundary problems of the Stefan type is an indication of the wide-ranging applicability and broadness of scope of this type of problem. The equations presented in this paper provided the basis for the development and implementation of such a numerical method.

2. OBJECTIVES AND SCOPE OF WORK

In this paper we derive generic governing equations for porous media problems that involve coupled heat flow, fluid flow and species transport processes with sharply defined phase-change interfaces. We describe the physical properties of the materials in terms of continuum properties and develop the conservation equations that govern the transport of mass, momentum and energy from classical *mixture theory* principles [33–35] for a *mixture* of *multiple-constituent species* segregated into *multiple physical phases* within a fluid-saturated porous medium. We also derive, by two general methods, the jump conditions that must be satisfied for these quantities to be conserved across discontinuity surfaces in the flow field.

The derived equations can be employed to formulate several types of porous media problems, such as, melting/freezing Stefan problems, the growth of semiconductor crystals, transport processes in porous packed beds, free-surface and toxic contaminant transport problems in groundwater hydrology, and fluid displacement problems in conventional and enhanced petroleum recovery processes. As an example of application of the derived equations, we specialize the general results to a water, salt, and rock system, subject to melting and solidification, and impose the *constitutive dependencies* between different interfacial variables by, for example, recognizing the dependence of the phase-change temperature on the trace species concentration and fluid pressure in coupled phase-change propagation problems. The continuum model presented in this paper complements that derived by Bennon and Incropera [36, 37] for the conservation of mass, momentum, energy and species in a binary solid–liquid phase-change system in which there are no discrete phase-change interfaces.

3. THE MATHEMATICAL MODEL

In this section we develop the equations that govern the coupled heat flow and fluid flow in a non-deformable fluid saturated porous medium under conditions that permit freezing or melting of the pore fluid. In addition, we consider the motion of a single trace species, principally salt, that is dissolved in the bulk fluid and which diffuses relative to the bulk fluid flow while being transported by it. The trace species can be adsorbed and desorbed by the porous rock and its presence significantly alters the freezing/melting phase behavior of the pore fluid. In deriving these equations we will provide for the existence in the flow domain of moving freezing or melting phase-change fronts that are modelled as sharp discontinuities in the values of certain field variables or their gradients.

In deriving the equations that govern the transport of mass and energy we will adopt an Eulerian viewpoint and express the field variables as functions of time t at locations $\mathbf{x}$ that are fixed in space. We will describe the physical properties of the materials in terms of continuum properties defined over an averaging length scale l_c that is simultaneously much larger than the largest characteristic pore size dimension d_p and much smaller than the smallest macroscopic characteristic length L of the flow field. This implies that, to be modelled as discontinuities, the dimension of the phase-change interfaces normal to the interfaces must be smaller than the length scale l_c while the dimensions of the interfaces in the tangential directions must be much larger than l_c (Fig. 1). Furthermore, the continuum properties are also temporal averages over a time scale τ_c which must be simultaneously much larger than the largest characteristic time τ_p of microscopic events occurring on the pore scale and much smaller than the smallest characteristic time T of macroscopic events of interest that occur within the flow domain.

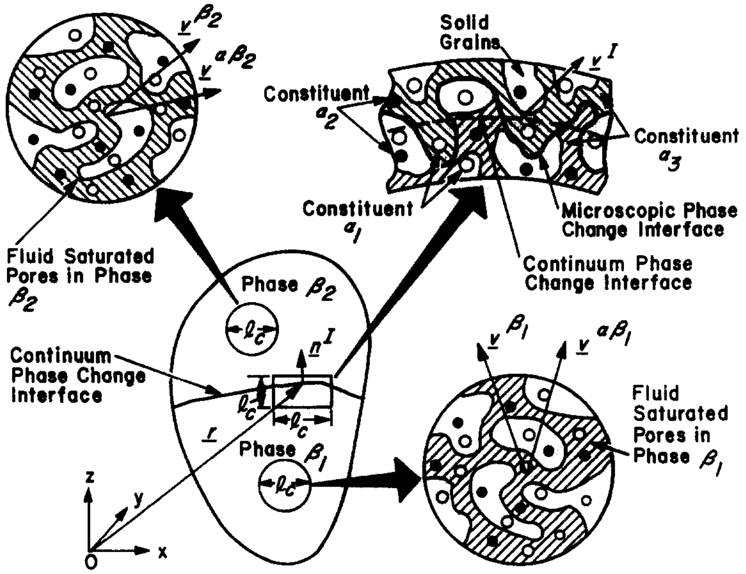

Fig. 1. A continuum view of a multiphase, multiconstituent mixture.

We view the porous medium to be composed of three different constituents α; they are: a porous rock material, $\alpha = \mathrm{r}$, water, $\alpha = \mathrm{w}$, and salt, $\alpha = \mathrm{c}$ that is present in trace amounts. Each of these constituents may undergo phase changes between two phases β, namely, the solid phase $\beta = \mathrm{s}$ and the fluid phase $\beta = \mathrm{f}$, but the constituents will be assumed not to chemically combine with one another. The identification of separate fluid and solid phases is motivated by the need to assign volume fractions for modelling the flow of the fluid phase while the transport of each constituent within each phase is modelled via mass concentrations. Volume fractions are used in recognition of the existence of 'immiscible' interfaces between the solid and fluid phases while the mass concentrations are more suitable for describing the 'miscible' distribution of the constituents within each of these two phases. Thus, salt in solution in water will be considered to be in the fluid phase whereas the salt adsorbed on to the rock or precipitated out of solution will be considered to belong to the solid phase. Changes in the rock porosity due to salt adsorption or precipitation will be initially allowed in the general formulation but, because the salt is assumed to exist only in trace amounts, changes in rock porosity due to this reason will later be assumed to be negligible. The principal impact of changes in salt concentration, therefore, will be on the density and the freezing/melting temperature of the pore fluid.

Similarly, the liquid salt–water mixture in the pores will be considered to be in the fluid phase while frozen pore fluid (i.e. ice) will belong to the solid phase. Although the general formulation allows the volume occupied by the pore fluid to change gradually over a freezing/melting zone we will later specialize the formulation by restricting the freezing/melting of pore fluid to occur only across sharp phase-change interfaces while permitting the salt in trace amounts to undergo phase changes everywhere within the flow field. Thus, on one side of a phase-change interface the pores will be filled by fluid while on the other side the pores will contain only ice so that the volume fraction of the fluid phase will suffer a jump across this sharp phase-change interface. Also, although this formulation allows the rock to dissolve and pass into solution and precipitate out of solution, for simplicity we will exclude phase changes of the rock material. Furthermore, we will not consider the movement of the solid phase (rock, solid-phase salt and ice) due either to thermal expansion or to the deformation of the solid phase under mechanical loads.

3.1. *General Formulation of the Governing Equations*

Consider the fixed region of space V, shown in Fig. 2, that is occupied by a non-deformable fluid saturated porous material and is bounded by the closed surface ∂V that is permeable to the pore fluid. Let ∂V^{I} be a sharp phase-change interface which divides the domain V into the time-dependent subdomains $V^-(t)$ and $V^+(t)$ and across which certain variables, to be identified later, suffer jump discontinuities. Let V_0^-

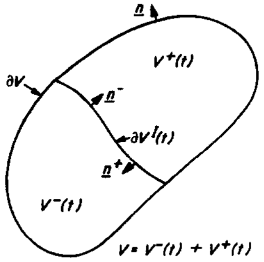

Fig. 2. Schematic diagram of the solution domain: V, fixed domain; $V^-(t)$ and $V^+(t)$, deforming subdomains; $\partial V^{\mathrm{I}}(t)$, deforming moving-discontinuity interface.

and V_0^+ be fixed subdomains which instantaneously coincide with the time varying boundaries of $V^-(t)$ and $V^+(t)$.

3.1.1. *Conservation of constituent mass*

The conservation of mass for constituent α in phase β within any fixed control volume V_0 can be expressed as a balance between the rate of increase of the mass of constituent α in phase β within the control volume, the net efflux of constituent α in phase β across its surface and the rate of production of α in phase β within the control volume. Then

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_0}\phi^\beta\rho^{\alpha\beta}\,\mathrm{d}V = -\int_{\partial V_0}\phi^\beta\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\cdot\mathbf{n}\,\mathrm{d}S + \int_{V_0}(c^{+\alpha\beta}+\phi^\beta Q_{\mathrm{M}}^{\alpha\beta})\,\mathrm{d}V. \qquad (1)$$

In this equation, ϕ^β and $\rho^{\alpha\beta}$ are the volume fraction of phase β and the mass concentration of constituent α in phase β, respectively, $\mathbf{v}^{\alpha\beta}$ is the flow rate of constituent α per unit area occupied by phase β, $c^{+\alpha\beta}$ is the rate of production of constituent α in phase β per unit bulk volume due to interaction with all other constituents in all the phases, and $Q_{\mathrm{M}}^{\alpha\beta}$ is the external mass source of constituent α in phase β. By employing the divergence theorem to convert the surface integral in equation (1) to a volume integral and appealing to the arbitrariness of the control volume V_0, we can write the conservation of mass for constituent α in phase β at every continuum point $(\mathbf{x}, t)$ in differential form as

$$\frac{\partial}{\partial t}(\phi^\beta\rho^{\alpha\beta})+\nabla\cdot(\phi^\beta\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}) = c^{+\alpha\beta}+\phi^\beta Q_{\mathrm{M}}^{\alpha\beta} \qquad (2a)$$

$$\sum_\beta \phi^\beta = 1. \qquad (2b)$$

The conservation of mass of constituent α over all phases β is obtained by summing equation (2) over all phases β

$$\frac{\partial}{\partial t}\left(\sum_\beta \phi^\beta\rho^{\alpha\beta}\right) + \nabla\cdot\left(\sum_\beta \phi^\beta\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\right) = c^{+\alpha} \qquad (3)$$

$$c^{+\alpha} \equiv \sum_\beta c^{+\alpha\beta}, \quad \sum_\alpha c^{+\alpha} = 0, \quad c^{+\alpha} = 0 \qquad (4a\text{–}c)$$

where the sum of the rates of production of all constituents in all phases must vanish as in equation (4b) for the total mass to be conserved. If no chemical reactions occur among constituents α which, however, are allowed to undergo changes in phase, then equation (4c) holds for each constituent α.

Diffusion of constituents relative to the bulk phase motion. When certain constituents exist only in trace amounts, it is more convenient to express the transport of the trace species in a particular phase relative to the bulk flow of that phase. To that end, we define the phase average mass densities ρ^β, the mass average phase flow velocities $\mathbf{v}^\beta$, and the diffusive constituent velocities $\mathbf{w}^{\alpha\beta}$ in each phase relative to the mass average phase velocities $\mathbf{v}^\beta$ by

$$\rho^\beta \equiv \sum_\alpha \rho^{\alpha\beta} \qquad (5)$$

$$\mathbf{v}^\beta \equiv \frac{1}{\rho^\beta}\sum_\alpha \rho^{\alpha\beta}\mathbf{v}^{\alpha\beta} \qquad (6)$$

$$\mathbf{w}^{\alpha\beta} \equiv \mathbf{v}^{\alpha\beta}-\mathbf{v}^\beta. \qquad (7)$$

Consequently, equation (2) can be recast in the more convenient forms of equation (8a) for constituent α in phase β and equation (8b) for constituent α in all phases

$$\frac{\partial}{\partial t}(\phi^\beta\rho^{\alpha\beta})+\nabla\cdot(\phi^\beta\rho^{\alpha\beta}\mathbf{v}^\beta) = c^{+\alpha\beta}+\phi^\beta Q_{\mathrm{M}}^{\alpha\beta} - \nabla\cdot(\phi^\beta\rho^{\alpha\beta}\mathbf{w}^{\alpha\beta}) \qquad (8a)$$

$$\frac{\partial}{\partial t}(\phi^\beta\rho^\beta)+\nabla\cdot(\phi^\beta\rho^\beta\mathbf{v}^\beta) = \sum_\alpha (c^{+\alpha\beta}+\phi^\beta Q_{\mathrm{M}}^{\alpha\beta}). \qquad (8b)$$

The last term on the right-hand side of equation (8a) represents the diffusive transport of constituent α relative to the mass average movement of all constituents in phase β. This term is usually approximated in porous media applications [9, 16] by a constitutive law of the form

$$\phi^\beta\rho^{\alpha\beta}\mathbf{w}^{\alpha\beta} = -\phi^\beta\rho^\beta \boldsymbol{D}^{\alpha\beta}\cdot\nabla\left(\frac{\rho^{\alpha\beta}}{\rho^\beta}\right) \qquad (9)$$

where $\boldsymbol{D}^{\alpha\beta}$ is a mass diffusivity tensor that is a directional function of the pore structure of the rock, the magnitude and character of the flow field, and the molecular diffusivity of the constituent.

3.1.2. *Conservation of constituent linear momentum*

The conservation of linear momentum for constituent α in phase β within the fixed control volume V_0 can be expressed as a balance between the rate of change of linear momentum within the control volume and the net efflux of momentum across its surface, the stress exerted at the surface, the external body forces and the rate of production of linear momentum of constituent α in phase β due to interaction with all other constituents in all phases. Then

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_0}\phi^\beta\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\,\mathrm{d}V = -\int_{\partial V_0}\phi^\beta\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta}\cdot\mathbf{n}\,\mathrm{d}S + \int_{\partial V_0}\phi^\beta\boldsymbol{t}^{\alpha\beta}\cdot\mathbf{n}\,\mathrm{d}S + \int_{V_0}(\mathbf{m}^{+\alpha\beta}+\phi^\beta\rho^{\alpha\beta}\mathbf{g}^{\alpha\beta} + \phi^\beta Q_{\mathrm{M}}^{\alpha\beta}\mathbf{v}_Q^{\alpha\beta})\,\mathrm{d}V. \qquad (10)$$

In equation (10), $\boldsymbol{t}^{\alpha\beta}$ is the stress tensor acting on constituent α of phase β per unit area of phase β, $\mathbf{g}^{\alpha\beta}$ is the body force per unit mass of constituent α and $\mathbf{m}^{+\alpha\beta}$ is the body force per unit bulk volume on constituent α in phase β due to the action of all other constituents. The velocity $\mathbf{v}_Q^{\alpha\beta}$ is the velocity of the external mass-source material. This can be different from the bulk velocity $\mathbf{v}^{\alpha\beta}$ of constituent α in phase β. The differential form of this integral balance relation can be obtained as in the case of mass conservation

$$\frac{\partial}{\partial t}(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta})+\nabla\cdot(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta}) = \nabla\cdot(\phi^{\beta}\boldsymbol{t}^{\alpha\beta}) + \mathbf{m}^{+\alpha\beta}+\phi^{\beta}\rho^{\alpha\beta}\mathbf{g}^{\alpha\beta}+\phi^{\beta}Q_{\mathrm{M}}^{\alpha\beta}\mathbf{v}^{\alpha\beta}. \tag{11}$$

For the linear momentum of all constituents α in all phases β to be conserved it is necessary that

$$\sum_{\alpha}\sum_{\beta}\mathbf{m}^{+\alpha\beta} = 0. \tag{12}$$

Equations of motion for the average motion of each phase. In the case of conservation of mass, it was useful to write down equation (3) for the conservation of mass of constituent α in all phases β because chemical reactions are not permitted between the constituents in the specialized model to be developed subsequently. In the case of conservation of momentum, however, it is more appropriate to develop the equations governing the average motion of each phase β for two reasons. First, we assume that the constituents exist within each phase under miscible conditions without physically identifiable interfaces between the constituents, while such interfaces do exist between different phases. Therefore, the dynamics of constituent motion is primarily influenced by bulk phase kinematics and not the motion of different constituents relative to one another within each phase. Second, because certain constituents are assumed to exist only in trace quantities and constitutive rate laws of the form of equation (9) are adopted to specify their transport relative to the average motion of each phase, the phase average equations of motion, as opposed to, say, the constituent average equations of motion, are the natural choice for directly specifying the average motion of each phase. Accordingly, we sum equation (11) over all constituents α in a particular phase β and use the decomposition of constituent velocities into the phase average and relative velocity components to obtain

$$\frac{\partial}{\partial t}(\phi^{\beta}\rho^{\beta}\mathbf{v}^{\beta})+\nabla\cdot(\phi^{\beta}\rho^{\beta}\mathbf{v}^{\beta}\mathbf{v}^{\beta}) = \nabla\cdot(\phi^{\beta}\boldsymbol{t}^{\beta}) + \mathbf{m}^{+\beta}+\mathbf{J}_{v}^{\beta}+\sum_{\alpha}(\phi^{\beta}\rho^{\alpha\beta}\mathbf{g}^{\alpha\beta}+\phi^{\beta}Q_{\mathrm{M}}^{\alpha\beta}\mathbf{v}^{\alpha\beta}) \tag{13a}$$

where $\mathbf{J}_{v}^{\beta}$ is a diffusive momentum flux defined by

$$\mathbf{J}_{v}^{\beta} \equiv \nabla\cdot\{\phi^{\beta}\sum_{\alpha}(\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{w}^{\alpha\beta}+\rho^{\alpha\beta}\mathbf{w}^{\alpha\beta}\mathbf{v}^{\beta}+\rho^{\alpha\beta}\mathbf{w}^{\alpha\beta}\mathbf{w}^{\alpha\beta})\}. \tag{13b}$$

The stress tensor $\boldsymbol{t}^{\beta}$ and the interaction body force $\mathbf{m}^{+\beta}$ for phase β are defined by

$$\boldsymbol{t}^{\beta} \equiv \sum_{\alpha}\boldsymbol{t}^{\alpha\beta} \tag{14}$$

$$\mathbf{m}^{+\beta} \equiv \sum_{\alpha}\mathbf{m}^{+\alpha\beta}. \tag{15}$$

3.1.3. *Conservation of constituent angular momentum*

We write the balance of moment of momentum for constituent α in phase β by considering the moment about the origin of coordinates of each of the infinitesimal contribution to the linear momentum balance. In doing so, we will assume that each constituent is composed of a non-polar material incapable of supporting body force couples or surface force couples that act on the constituents of the mixture arising either from external sources or from the interactions between the mixture constituents. We recognize that this simplifying assumption would not be appropriate in situations such as those involving non-polar granular materials. For example, in bubbling fluidized beds or in the pneumatic transport of particulate solids the solid particles not only translate but also spin under the action of drag forces. Subject to these simplifying assumptions, which we believe to be sufficiently general for the present application, the balance of the moment of momentum is given by

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_0}\mathbf{x}\otimes(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta})\,\mathrm{d}V = &-\int_{\partial V_0}\mathbf{x}\otimes(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta})\cdot\mathbf{n}\,\mathrm{d}\hat{S}\\ &+\int_{\partial V_0}\mathbf{x}\otimes(\phi^{\beta}\boldsymbol{t}^{\alpha\beta})\cdot\mathbf{n}\,\mathrm{d}\hat{S}\\ &+\int_{V_0}\mathbf{x}\otimes(\mathbf{m}^{+\alpha\beta}+\phi^{\beta}\rho^{\alpha\beta}\mathbf{g}^{\alpha\beta})\,\mathrm{d}V\end{aligned} \tag{16}$$

where '⊗' denotes the vector cross product operation.

The differential form (equation (17)) of the moment of momentum balance relation given by equation (16) is obtained in the standard way from the above integral statement of the balance of moment of momentum

$$\frac{\partial}{\partial t}\{\mathbf{x}\otimes(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta})\}+\nabla\cdot\{\mathbf{x}\otimes(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta})\} = \nabla\cdot\{\mathbf{x}\otimes(\phi^{\beta}\boldsymbol{t}^{\alpha\beta})\}+\mathbf{x}\otimes(\mathbf{m}^{+\alpha\beta}+\phi^{\beta}\rho^{\alpha\beta}\mathbf{g}^{\alpha\beta}). \tag{17}$$

This equation can be rewritten in the form of equation (18a) which simplifies to equation (18b) when we recognize the term within brackets on the right-hand side to be the moment of the balance of linear momentum given by equation (11), that is

$$\begin{aligned}(\nabla\mathbf{x})\otimes(\phi^{\beta}\boldsymbol{t}^{\alpha\beta}-\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta}) = &-\mathbf{x}\otimes\left\{\frac{\partial}{\partial t}(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta})+\nabla\cdot(\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta})\right.\\ &\left.-\nabla\cdot(\phi^{\beta}\boldsymbol{t}^{\alpha\beta})-\mathbf{m}^{+\alpha\beta}-\phi^{\beta}\rho^{\alpha\beta}\mathbf{g}^{\alpha\beta}\right\}\end{aligned} \tag{18a}$$

$$= 0. \tag{18b}$$

Now, because the product of an antisymmetric tensor and a symmetric tensor is zero, and $(\nabla\mathbf{x})\otimes$ is an antisymmetric tensor, equation (18b) can be seen to be a statement that the quantity $\boldsymbol{t}^{\alpha\beta}-\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta}$ is symmetric. Because the velocity product term is already symmetric, this reduces to the requirement that the constituent stress tensor $\boldsymbol{t}^{\alpha\beta}$ be symmetric. This is more clearly seen from the indicial form of this equation given by equation (19a) where e_{jkl} is the alternating tensor commonly referred to as the permutation symbol. Because of the symmetry of the velocity product term, equation (19a) reduces to equation (19b); this is equivalent to the direct statement of symmetry of $\boldsymbol{t}^{\alpha\beta}$ given by equation (19c)

$$\delta_{ij}e_{jkl}\{\phi^{\beta}t^{\alpha\beta}_{kl}-\phi^{\beta}\rho^{\alpha\beta}v^{\alpha\beta}_{k}v^{\alpha\beta}_{l}\}=0 \tag{19a}$$

$$e_{ikl}t^{\alpha\beta}_{kl}=0 \tag{19b}$$

$$t^{\alpha\beta}_{ij}=t^{\alpha\beta}_{ji}. \tag{19c}$$

A direct consequence of the symmetry of the constituent stress tensor $\boldsymbol{t}^{\alpha\beta}$ is that the stress tensor $\boldsymbol{t}^{\beta}$ for phase β, defined by equation (14), is also symmetric.

3.1.4. *Conservation of constituent energy*

Conservation of energy for constituent α in phase β within a fixed control volume V_0 requires that the rate of increase of the internal and kinetic energies of the constituent be equal to the sum of the rate of energy influx from external sources, the work done by external body forces, the rate of work input and energy influx at the boundaries of the domain, and the transfer of energy to constituent α from the other constituents in the mixture. Therefore

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}\left\{\int_{V_0}\phi^{\beta}\rho^{\alpha\beta}\left(\varepsilon^{\alpha\beta}+\frac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta}\right)\mathrm{d}V\right\}\\&\quad-\int_{\partial V_0}\phi^{\beta}\rho^{\alpha\beta}\left(\varepsilon^{\alpha\beta}+\frac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta}\right)\mathbf{v}^{\alpha\beta}\cdot\mathbf{n}\,\mathrm{d}S\\&\quad-\int_{\partial V_0}\phi^{\beta}(-\mathbf{q}^{\alpha\beta}+\mathbf{v}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta})\cdot\mathbf{n}\,\mathrm{d}S\\&\quad+\int_{V_0}\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\cdot\mathbf{g}^{\alpha\beta}\,\mathrm{d}V+\int_{V_0}\left\{\varepsilon^{+\alpha\beta}+\phi^{\beta}Q^{\alpha\beta}_{\mathrm{H}}\right.\\&\quad\left.+\phi^{\beta}Q^{\alpha\beta}_{\mathrm{M}}\left(\varepsilon^{\alpha\beta}_{Q}+\frac{1}{2}\mathbf{v}^{\alpha\beta}_{Q}\cdot\mathbf{v}^{\alpha\beta}_{Q}\right)\right\}\mathrm{d}V.\end{aligned} \tag{20}$$

In equation (20), $\varepsilon^{\alpha\beta}$ is the internal energy per unit mass of constituent α, $\mathbf{q}^{\alpha\beta}$ is the rate of energy efflux from constituent α per unit cross-sectional area of phase β at the boundary, $\boldsymbol{t}^{\alpha\beta}$ is the stress tensor acting at the boundary per unit cross-sectional area of phase β. The quantity $Q^{\alpha\beta}_{\mathrm{H}}$ is the external energy input to constituent α per unit volume of phase β while $\varepsilon^{+\alpha\beta}$ is the rate of energy transfer to constituent α in phase β from the rest of the mixture. The internal energy $\varepsilon^{\alpha\beta}_{Q}$ is the internal energy of the external mass-source material. This can be different from the bulk internal energy $\varepsilon^{\alpha\beta}$ of constituent α in phase β. The differential form of equation (20) is given by

$$\begin{aligned}&\frac{\partial}{\partial t}\left\{\phi^{\beta}\rho^{\alpha\beta}\left(\varepsilon^{\alpha\beta}+\frac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta}\right)\right\}\\&\quad+\nabla\cdot\left\{\phi^{\beta}\rho^{\alpha\beta}\left(\varepsilon^{\alpha\beta}+\frac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta}\right)\mathbf{v}^{\alpha\beta}\right\}\\&=\nabla\cdot\{\phi^{\beta}(-\mathbf{q}^{\alpha\beta}+\mathbf{v}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta})\}+\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\cdot\mathbf{g}^{\alpha\beta}\\&\quad+\varepsilon^{+\alpha\beta}+\phi^{\beta}Q^{\alpha\beta}_{\mathrm{H}}+\phi^{\beta}Q^{\alpha\beta}_{\mathrm{M}}\left(\varepsilon^{\alpha\beta}_{Q}+\frac{1}{2}\mathbf{v}^{\alpha\beta}_{Q}\cdot\mathbf{v}^{\alpha\beta}_{Q}\right)\end{aligned} \tag{21}$$

where for the energy of all constituents in all phases to be conserved it is necessary that

$$\sum_{\alpha}\sum_{\beta}\varepsilon^{+\alpha\beta}=0. \tag{22}$$

Equations for the transport of energy in each phase. As in the case of conservation of linear momentum, it is more appropriate to develop the equations governing the transport of energy in each phase β because the constituents exist within each phase under miscible conditions without physically identifiable interfaces so that the convective transport of energy is directly influenced by bulk phase kinematics rather than the separate motion of the individual constituents within each phase. Therefore, we sum equation (21) over all constituents α in a particular phase β and use the decomposition of constituent velocities into the phase average and relative velocity components to obtain

$$\begin{aligned}&\frac{\partial}{\partial t}\left\{\phi^{\beta}\rho^{\beta}\left(\varepsilon^{\beta}+\frac{1}{2}\mathbf{v}^{\beta}\cdot\mathbf{v}^{\beta}\right)\right\}\\&\quad+\nabla\cdot\left\{\phi^{\beta}\rho^{\beta}\left(\varepsilon^{\beta}+\frac{1}{2}\mathbf{v}^{\beta}\cdot\mathbf{v}^{\beta}\right)\mathbf{v}^{\beta}\right\}\\&=\nabla\cdot\{\phi^{\beta}(-\mathbf{q}^{\beta}+\mathbf{v}^{\beta}\cdot\boldsymbol{t}^{\beta})\}+\varepsilon^{+\beta}+J^{\beta}_{\varepsilon}\\&\quad+\sum_{\alpha}\left\{\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\cdot\mathbf{g}^{\alpha\beta}+\phi^{\beta}Q^{\alpha\beta}_{\mathrm{H}}\right.\\&\quad\left.+\phi^{\beta}Q^{\alpha\beta}_{\mathrm{M}}\left(\varepsilon^{\alpha\beta}_{Q}+\frac{1}{2}\mathbf{v}^{\alpha\beta}_{Q}\cdot\mathbf{v}^{\alpha\beta}_{Q}\right)\right\}\end{aligned} \tag{23a}$$

$$\begin{aligned}J^{\beta}_{\varepsilon}\equiv\sum_{\alpha}&\left\{-\frac{\partial}{\partial t}\left\{\phi^{\beta}\rho^{\alpha\beta}\frac{1}{2}(\mathbf{v}^{\beta}+\mathbf{w}^{\alpha\beta})\cdot\mathbf{w}^{\alpha\beta}\right\}\right.\\&+\nabla\cdot\{\phi^{\beta}\mathbf{w}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta}\}+\nabla\cdot\left\{\phi^{\beta}\rho^{\alpha\beta}\varepsilon^{\alpha\beta}\mathbf{w}^{\alpha\beta}\right.\\&\left.\left.+\phi^{\beta}\rho^{\alpha\beta}(\mathbf{v}^{\alpha\beta}+\mathbf{w}^{\alpha\beta})\left(\mathbf{v}^{\beta}\cdot\mathbf{w}^{\alpha\beta}+\frac{1}{2}\mathbf{w}^{\alpha\beta}\cdot\mathbf{w}^{\alpha\beta}\right)\right\}\right\}\end{aligned} \tag{23b}$$

where J^{β}_{ε} is a diffusive energy flux. The phase internal energy ε^{β}, the phase energy efflux vector $\mathbf{q}^{\beta}$ and $\varepsilon^{+\beta}$, the energy transfer to phase β from the rest of the mixture are defined by

$$\varepsilon^{\beta} \equiv \frac{1}{\rho^{\beta}} \sum_{\alpha} \rho^{\alpha\beta} \varepsilon^{\alpha\beta} \tag{24}$$

$$\mathbf{q}^{\beta} \equiv \sum_{\alpha} \mathbf{q}^{\alpha\beta} \tag{25}$$

$$\varepsilon^{+\beta} \equiv \sum_{\alpha} \varepsilon^{+\alpha\beta}. \tag{26}$$

3.2. *Jump Conditions at Phase-change Interfaces*

In Section 3.2.1 we will first consider the kinematics of a moving interface. Next, we derive the jump conditions that dictate the change of mass, momentum, and energy across a moving discontinuity interface in a very general form in two different ways. In the first method, given in Section 3.2.2, we derive the jump conditions by considering the limiting form of the integral expressions written for the conservation of a generalized transported property on the two sides of the discontinuity interface. In the second method, given in Section 3.2.3, we employ the properties of the Heaviside and Delta generalized operators to represent the transported quantity by generalized distributions with jump discontinuities on the interfaces and formally derive the jump conditions from the differential expressions that apply to continuous distributions of the transported property. Finally, in Section 3.2.3, these general relationships for the jump conditions are specialized to the present problem.

3.2.1. *Kinematics of a moving surface*

Let ∂V^{I} be an interface that divides a domain $V(t)$ into two subdomains $V^{+}(t)$ and $V^{-}(t)$ and let the equation that describes the interfacial surface be

$$S(\mathbf{x}^{\mathrm{I}}, t) = 0, \quad \mathbf{x}^{\mathrm{I}} \in \partial V^{\mathrm{I}}. \tag{27}$$

The normal vector $\mathbf{n}^{\mathrm{I}}$ to this surface is, therefore, given by

$$\mathbf{n}^{\mathrm{I}} = \frac{\nabla S}{|\nabla S|}. \tag{28a}$$

By taking the inner product of equation (28a) with $\mathbf{n}^{\mathrm{I}}$ we obtain the additional results

$$\mathbf{n}^{\mathrm{I}} \cdot \nabla S = |\nabla S|, \quad \nabla S = \mathbf{n}^{\mathrm{I}} |\nabla S|. \tag{28b,c}$$

Also, to uniquely fix the direction of the normal, we adopt the convention that the normal to the surface $\mathbf{n}^{\mathrm{I}}$ is the outnormal with respect to region $V^{-}(t)$, so that $\mathbf{n}^{\mathrm{I}} = \mathbf{n}^{-} = -\mathbf{n}^{+}$.

The velocity of any point $\mathbf{x}^{\mathrm{I}}$ on the interface is given by

$$\mathbf{v}^{\mathrm{I}} = \frac{\mathrm{d}\mathbf{x}^{\mathrm{I}}}{\mathrm{d}t}. \tag{29}$$

The velocity of a point on the interface can be obtained from the equation that defines the interface by differentiating equation (27) with respect to time. Thus, we have

$$\frac{\partial S}{\partial t} + \mathbf{v}^{\mathrm{I}} \cdot \nabla S = 0. \tag{30}$$

Combining equations (28a) and (28b) with equation (30) we obtain

$$\frac{\partial S}{\partial t} + v_n^{\mathrm{I}} \mathbf{n}^{\mathrm{I}} \cdot \nabla S = 0. \tag{31}$$

Equation (31) shows how the time derivative $\partial S/\partial t$ of a deforming surface $S(\mathbf{x}^{\mathrm{I}}, t)$ can be expressed in terms of its normal velocity $v_n^{\mathrm{I}} = \mathbf{v}^{\mathrm{I}} \cdot \mathbf{n}^{\mathrm{I}}$. It also shows that the normal velocity component v_n^{I} is the only component required to determine the evolution of the interface $S(\mathbf{x}^{\mathrm{I}}, t)$. This equation will be employed in the following sections in the derivation of the jump conditions across a moving interface.

3.2.2. *Derivation of the jump conditions across a moving interface from integral conservation laws*

The conservation of a general scalar or vector transport property Ψ in a time varying domain $V(t)$ is expressed by the integral balance relation

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{V(t)} \Psi \,\mathrm{d}V = - \int_{\partial V(t)} \{\mathbf{j} + \Psi(\mathbf{v} - \mathbf{v}^{\mathrm{S}})\} \cdot \mathbf{n}^{\mathrm{S}} \,\mathrm{d}S + \int_{V(t)} (\tilde{\Psi} + Q_{\Psi}) \,\mathrm{d}V. \tag{32}$$

In the above equation, $\mathbf{v}$ is the velocity of the material possessing the transport property Ψ, $\mathbf{j}$ is a generalized flux independent of boundary surface motion, $\tilde{\Psi}$ is the internal rate of production of Ψ, and Q_{Ψ} represents the growth of Ψ due to external sources. For example, for conservation of mass, linear momentum, and energy, Ψ is equal to ρ, $\rho\mathbf{v}$ and $\rho(\varepsilon + \frac{1}{2}\mathbf{v} \cdot \mathbf{v})$, respectively. In the energy equation $\mathbf{j}$ will be the heat flux and the work done by stresses at the surface. The second term in equation (32) includes the outflux of the property Ψ across a surface moving at a velocity $\mathbf{v}^{\mathrm{S}}$.

The jump conditions across a phase-change interface $\partial V^{\mathrm{I}}(t)$ within a fixed domain V_0 can be derived by dividing V_0 into two subdomains $V^{-}(t)$ and $V^{+}(t)$ and first writing equation (32) for each of the subdomains $V^{-}(t)$ and $V^{+}(t)$ on the two sides of the interface. The surface velocity $\mathbf{v}^{\mathrm{S}}$ is equal to zero at fixed boundaries and is equal to the interfacial velocity $\mathbf{v}^{\mathrm{I}}$ on the moving phase-change interfaces. When the two equations that result are added together, we obtain

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t} \left\{ \int_{V^{+}(t)} \Psi^{+} \,\mathrm{d}V + \int_{V^{-}(t)} \Psi^{-} \,\mathrm{d}V \right\} \\
&= \int_{V^{+}(t)} \{\tilde{\Psi}^{+} + Q_{\Psi}\} \,\mathrm{d}V + \int_{V^{-}(t)} \{\tilde{\Psi}^{-} + Q_{\Psi}\} \,\mathrm{d}V \\
&\quad - \int_{\partial V^{+}(t) \in \partial V_0} \{\mathbf{j} + \Psi\mathbf{v}\} \cdot \mathbf{n}^{\mathrm{S}} \,\mathrm{d}S \\
&\quad - \int_{\partial V^{-}(t) \in \partial V_0} \{\mathbf{j} + \Psi\mathbf{v}\} \cdot \mathbf{n}^{\mathrm{S}} \,\mathrm{d}S \\
&\quad - \int_{\partial V^{\mathrm{I}}(t)} \{(\mathbf{j} \cdot \mathbf{n} + \Psi(\mathbf{v} - \mathbf{v}^{\mathrm{I}}) \cdot \mathbf{n})^{-} \\
&\quad + (\mathbf{j} \cdot \mathbf{n} + \Psi(\mathbf{v} - \mathbf{v}^{\mathrm{I}}) \cdot \mathbf{n})^{+} - \tilde{\Psi}^{\mathrm{I}}\} \,\mathrm{d}S.
\end{aligned} \tag{33}$$

In equation (33), we have excluded the possibility of accumulation of the property Ψ on the interface by not allowing for a time-dependent surface storage term and have assumed that the external source terms Q_{Ψ} are continuous across the interface. However, we have allowed for a concentrated source term $\tilde{\Psi}^{\mathrm{I}}$ in the rate of production $\tilde{\Psi}$ at the interface by setting

$$\lim_{\mathbf{x}\to\mathbf{x}^{\mathrm{I}}}\int_{V}\tilde{\Psi}\,\mathrm{d}V=\int_{V}\tilde{\Psi}^{\mathrm{I}}\delta(S)|\nabla S|\,\mathrm{d}V=\int_{\partial V^{\mathrm{I}}(t)}\tilde{\Psi}^{\mathrm{I}}\,\mathrm{d}S \quad (34)$$

where $\delta(S)=\delta(S(\mathbf{x},t))$ is the Dirac delta function operator located at the interface $S(\mathbf{x},t)=0$. The physical interpretation of the novel source term $\tilde{\Psi}^{\mathrm{I}}$ and the need for it will be addressed later when these equations are specialized to the problems considered in this paper.

Now, if the domains $V^{+}(t)$ and $V^{-}(t)$ are considered together equation (32) must be satisfied for the total domain irrespective of the jumps across ∂V^{I}. Therefore, the sum of all terms except the interfacial term in equation (33) is separately equal to zero. As a result we obtain

$$\int_{\partial V^{\mathrm{I}}(t)}\{(\mathbf{j}\cdot\mathbf{n}+\tilde{\Psi}(\mathbf{v}-\mathbf{v}^{\mathrm{I}})\cdot\mathbf{n})^{-} \\ +(\mathbf{j}\cdot\mathbf{n}+\Psi(\mathbf{v}-\mathbf{v}^{\mathrm{I}})\cdot\mathbf{n})^{+}-\tilde{\Psi}^{\mathrm{I}}\}\,\mathrm{d}S=0. \quad (35)$$

Because the interfacial surface is arbitrary, the integrand of equation (35) must vanish at every point on the interface. Thus

$$\{(\mathbf{j}\cdot\mathbf{n}+\Psi(\mathbf{v}-\mathbf{v}^{\mathrm{I}})\cdot\mathbf{n})^{-}+(\mathbf{j}\cdot\mathbf{n}+\Psi(\mathbf{v}-\mathbf{v}^{\mathrm{I}})\cdot\mathbf{n})^{+}\}=\tilde{\Psi}^{\mathrm{I}}. \quad (36)$$

If we choose a unique normal to the interface by $\mathbf{n}^{\mathrm{I}}=\mathbf{n}^{-}=-\mathbf{n}^{+}$, then equation (36) can be recast as equation (37) or in the more compact forms given by equations (38a) and (38b)

$$\{(\mathbf{j}+\Psi(\mathbf{v}-\mathbf{v}^{\mathrm{I}}))^{-}-(\mathbf{j}+\Psi(\mathbf{v}-\mathbf{v}^{\mathrm{I}}))^{+}\}\cdot\mathbf{n}^{\mathrm{I}}=\tilde{\Psi}^{\mathrm{I}} \quad (37)$$

$$[\![\mathbf{j}+\Psi(\mathbf{v}-\mathbf{v}^{\mathrm{I}})]\!]\cdot\mathbf{n}^{\mathrm{I}}=\tilde{\Psi}^{\mathrm{I}} \quad (38a)$$

$$[\![\mathbf{J}]\!]\cdot\mathbf{n}^{\mathrm{I}}-[\![\Psi]\!]v_{n}^{\mathrm{I}}=\tilde{\Psi}^{\mathrm{I}} \quad (38b)$$

where

$$\mathbf{J}\equiv\mathbf{j}+\Psi\mathbf{v} \quad (39)$$

and $[\![\ ]\!]$ represents the jump in the enclosed physical quantity across the interface. Equation (38b) can be solved for the normal component v_{n}^{I} of the interface velocity to yield

$$v_{n}^{\mathrm{I}}=\frac{J_{n}^{+}-J_{n}^{-}-\tilde{\Psi}^{\mathrm{I}}}{\Psi^{+}-\Psi^{-}} \quad (40)$$

which we immediately recognize to be a generalized form of the familiar Rankine–Hugoniot jump conditions with an extra interfacial production term given by $\tilde{\Psi}^{\mathrm{I}}$.

3.2.3. *Derivation of the jump conditions across a moving interface from the governing differential equations applied to generalized distributions*

The differential point form of the integral balance law given by equation (32) is

$$\frac{\partial\Psi}{\partial t}+\nabla\cdot\mathbf{J}=\tilde{\Psi}+Q_{\Psi} \quad (41)$$

where it is usually assumed that all quantities appearing in this equation are sufficiently differentiable with respect to $(\mathbf{x},t)$ in $\mathbf{x}\in V$, $0\leqslant t\leqslant\infty$ for equation (41) to be meaningful. Let us now extend the definition of each of these quantities to apply to a domain containing a discontinuity interface by viewing them as generalized functions that are related to the corresponding differentiable functions defined in the separate domains $V^{+}(t)$ and $V^{-}(t)$ as follows:

$$\Psi(\mathbf{x},t)=(1-H(S))\Psi^{-}(\mathbf{x},t)+H(S)\Psi^{+}(\mathbf{x},t) \quad (42)$$

$$\mathbf{J}(\mathbf{x},t)=(1-H(S))\mathbf{J}^{-}(\mathbf{x},t)+H(S)\mathbf{J}^{+}(\mathbf{x},t) \quad (43)$$

$$\tilde{\Psi}(\mathbf{x},t)=(1-H(S))\tilde{\Psi}^{-}(\mathbf{x},t)+H(S)\tilde{\Psi}^{+}(\mathbf{x},t) \\ +\delta(S)|\nabla S|\tilde{\Psi}^{\mathrm{I}}(\mathbf{x},t). \quad (44)$$

In the above equations, $S=S(\mathbf{x},t)=0$ is the equation defining the discontinuity interface, and $H(z)$ and $\delta(z)$ the Heaviside and Dirac delta operators, respectively. These two quantities are generalized distributions defined by equations (45a) and (45b) in terms of their operational action on an analytic function $f(z)$ and are formally related by equation (46)

$$\int_{-\infty}^{\infty}H(z)f(z)\,\mathrm{d}z=\int_{0}^{\infty}f(z)\,\mathrm{d}z \quad (45a)$$

$$\int_{-\infty}^{\infty}\delta(z)f(z)\,\mathrm{d}z=f(0) \quad (45b)$$

$$\delta(z)=\frac{\mathrm{d}H(z)}{\mathrm{d}z}. \quad (46)$$

In equations (42) and (43) the Heaviside operator is used to represent the discontinuities in Ψ and $\mathbf{J}$ across the interface. In equation (44), there is an additional Delta function contribution that represents a concentrated production term located on the interface. Each set of signed quantities satisfy equation (41) in the corresponding domain on the two sides of the surface of discontinuity and the external source term is assumed to be continuous across the interface. When the above expressions for the generalized distributions Ψ, $\mathbf{J}$, and $\tilde{\Psi}$ are substituted in equation (41), we obtain

$$(1-H(S))\left\{\frac{\partial\Psi^{-}}{\partial t}+\nabla\cdot\mathbf{J}-\tilde{\Psi}^{-}-Q_{\Psi}\right\} \\ +H(S)\left\{\frac{\partial\Psi^{+}}{\partial t}+\nabla\cdot\mathbf{J}^{+}-\tilde{\Psi}^{+}-Q_{\Psi}\right\}+(\Psi^{+}-\Psi^{-})\frac{\partial H}{\partial t} \\ +(\mathbf{J}^{+}-\mathbf{J}^{-})\cdot\nabla H-\delta(S)|\nabla S|\tilde{\Psi}^{\mathrm{I}}=0. \quad (47)$$

Because the functions $\Psi^{\pm}$, $\mathbf{J}^{\pm}$ and $\tilde{\Psi}^{\pm}$ are continuous and satisfy equation (41), the first two terms of equation (47) vanish. The last term can be simplified by using the chain rule to evaluate the derivatives of $H(S(\mathbf{x}, t))$

$$\frac{\partial H(S)}{\partial t} = \frac{\partial H(S)}{\partial S}\frac{\partial S}{\partial t} = \delta(S)\frac{\partial S}{\partial t} \tag{48}$$

$$\nabla H = \frac{\partial H(S)}{\partial S}\nabla S = \delta(S)\nabla S. \tag{49}$$

When these expressions are substituted for the derivatives of H in equation (47) we obtain

$$\left\{(\Psi^{+}-\Psi^{-})\frac{\partial S}{\partial t}+(\mathbf{J}^{+}-\mathbf{J}^{-})\cdot\nabla S - \tilde{\Psi}^{\mathrm{I}}|\nabla S|\right\}\delta(S) = 0. \tag{50}$$

We now restrict equation (50) to the interface (as required by the Dirac delta function factor in this equation) and obtain equation (51a) by eliminating the time derivative of S from this equation using the kinematic relationship for motion of the surface given by equation (31). Using $\nabla S = \mathbf{n}^{\mathrm{I}}(\mathbf{n}^{\mathrm{I}}\cdot\nabla S) = \mathbf{n}^{\mathrm{I}}|\nabla S|$ to eliminate ∇S from equation (51a) we recover equation (51b) that was previously obtained by the integral balance law approach. That is

$$(\mathbf{J}^{+}-\mathbf{J}^{-})\cdot\nabla S-(\Psi^{+}-\Psi^{-})(\mathbf{n}^{\mathrm{I}}\cdot\nabla S)v_n^{\mathrm{I}} = \tilde{\Psi}^{\mathrm{I}}|\nabla S| \tag{51a}$$

$$\llbracket\mathbf{J}\rrbracket\cdot\mathbf{n}^{\mathrm{I}}-\llbracket\Psi\rrbracket\cdot v_n^{\mathrm{I}} = \tilde{\Psi}^{\mathrm{I}}. \tag{51b}$$

3.2.4. *Mass, momentum and energy conservation on moving phase-change interfaces*

We can now specialize the general jump condition given by equation (51b) to the conservation laws for species mass, momentum, and energy by comparing equations (1), (10) and (20) against the conservation law for Ψ given by equation (32). The definitions for the variables Ψ, $\mathbf{j}$, $\mathbf{J}$, $\tilde{\Psi}$ and Q_Ψ corresponding to each conservation equation and associated jump conditions are listed below.

Jump condition for conservation of species mass on a moving surface of discontinuity. From the definitions for Ψ, $\tilde{\Psi}$, $\tilde{\Psi}^{\mathrm{I}}$, $\mathbf{j}$, $\mathbf{J}$ and Q_ψ for the conservation of species mass given by equations (52) below

$$\Psi \equiv \phi^{\beta}\rho^{\alpha\beta},\quad \tilde{\Psi} \equiv c^{+\alpha\beta},\quad \tilde{\Psi}^{\mathrm{I}} \equiv c^{+\alpha\beta\mathrm{I}} \tag{52a}$$

$$\mathbf{j} \equiv 0 \tag{52b}$$

$$\mathbf{J} \equiv \phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta} \tag{52c}$$

$$Q_\Psi \equiv \phi^{\beta}Q_{\mathrm{M}}^{\alpha\beta} \tag{52d}$$

we obtain the jump condition

$$\llbracket\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\rrbracket\cdot\mathbf{n}^{\mathrm{I}}-\llbracket\phi^{\beta}\rho^{\alpha\beta}\rrbracket v_n^{\mathrm{I}} = c^{+\alpha\beta\mathrm{I}}. \tag{53}$$

The interfacial mass balance relationships analogous to equations (3) and (4) for each constituent α over all phases β are obtained by summing equation (53) over all β. Then

$$\sum_{\beta}\llbracket\phi^{\beta}\rho^{\alpha\beta}(\mathbf{v}^{\alpha\beta}-\mathbf{v}^{\mathrm{I}})\rrbracket\cdot\mathbf{n}^{\mathrm{I}} = c^{+\alpha\mathrm{I}} \tag{54}$$

with

$$c^{+\alpha\mathrm{I}} \equiv \sum_{\beta}c^{+\alpha\beta\mathrm{I}},\quad \sum_{\alpha}c^{+\alpha\mathrm{I}} = 0,\quad c^{+\alpha\mathrm{I}} = 0 \tag{55a–c}$$

where the sum of the total rates of production of constituents given by equation (55a) must vanish as in equation (55b) for the total mass of all constituents in all phases to be conserved on the interface. On the other hand, equation (55c) holds for each constituent α on the interface if no chemical reactions involving constituent α are allowed to occur.

The jump condition for constituent mass given by equation (53) is more conveniently expressed in terms of the average phase velocities and the velocities of constituent α relative to the average motion of phase β by

$$\llbracket\phi^{\beta}\rho^{\alpha\beta}(\mathbf{v}^{\beta}-\mathbf{v}^{\mathrm{I}})\rrbracket\cdot\mathbf{n}^{\mathrm{I}} = c^{+\alpha\beta\mathrm{I}}-\llbracket\phi^{\beta}\rho^{\alpha\beta}\mathbf{w}^{\alpha\beta}\rrbracket\cdot\mathbf{n}^{\mathrm{I}}. \tag{56a}$$

The last term on the right-hand side of this equation represents the jump across the interface due to the jump in the diffusive transport of constituent α in phase β relative to the average motion of phase β. For phase-change interfaces at which *no chemical transformations occur between different constituents* we can invoke equation (55c) to obtain the following jump condition for the conservation of constituent α in all phases β:

$$\sum_{\beta}\llbracket\phi^{\beta}\rho^{\alpha\beta}(\mathbf{v}^{\beta}-\mathbf{v}^{\mathrm{I}})\rrbracket\cdot\mathbf{n}^{\mathrm{I}} = -\sum_{\beta}\llbracket\phi^{\beta}\rho^{\alpha\beta}\mathbf{w}^{\alpha\beta}\rrbracket\cdot\mathbf{n}^{\mathrm{I}}. \tag{56b}$$

We emphasize here the importance of the *interfacial phase mass production terms* $c^{+\alpha\beta}$ which are *essential* for modelling of mixtures of materials in which either *chemical reactions* or *phase transitions* occur abruptly across highly concentrated zones that can be idealized as surfaces of zero thickness. In particular, they are essential in the modelling of freezing/melting processes in which the constituents do not chemically react and no phase changes occur within the domain (i.e. $c^{+\alpha\beta} = 0$) *except* at highly localized freezing/melting fronts where $c^{+\alpha\beta\mathrm{I}} \neq 0$.

Jump condition for conservation of species momentum on a moving surface of discontinuity. From the definitions for $\boldsymbol{\Psi}$, $\tilde{\boldsymbol{\Psi}}$, $\tilde{\boldsymbol{\Psi}}^{\mathrm{I}}$, $\mathbf{j}$, $\mathbf{J}$ and $\mathbf{Q}_\Psi$ for the conservation of species momentum given by equations (57a)–(57d) below

$$\boldsymbol{\Psi} \equiv \phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta},\quad \tilde{\boldsymbol{\Psi}} \equiv \mathbf{m}^{+\alpha\beta},\quad \tilde{\boldsymbol{\Psi}}^{\mathrm{I}} \equiv \mathbf{m}^{+\alpha\beta\mathrm{I}} \tag{57a}$$

$$\mathbf{j} \equiv -\phi^{\beta}\boldsymbol{t}^{\alpha\beta} \tag{57b}$$

$$\mathbf{J} \equiv \phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta}-\phi^{\beta}\boldsymbol{t}^{\alpha\beta} \tag{57c}$$

$$\mathbf{Q}_\Psi \equiv \phi^{\beta}\rho^{\alpha\beta}\mathbf{g}^{\alpha\beta}+\phi^{\beta}Q_{\mathrm{M}}^{\alpha\beta}\mathbf{v}^{\alpha\beta} \tag{57d}$$

we obtain the jump condition

$$\llbracket \phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\mathbf{v}^{\alpha\beta}-\phi^{\beta}\boldsymbol{t}^{\alpha\beta}\rrbracket\cdot\mathbf{n}^{\mathrm{I}}-\llbracket \phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\rrbracket v_n^{\mathrm{I}}=\mathbf{m}^{+\alpha\beta\mathrm{I}}. \tag{58}$$

In the jump condition for momentum given by equation (58), $\mathbf{m}^{+\alpha\beta\mathrm{I}}$ is the jump in the momentum interaction between constituent α in phase β and all other constituents in all phases. For linear momentum of the mixture as a whole to be conserved on the interface, the interfacial momentum interaction terms must sum to zero

$$\sum_{\alpha}\sum_{\beta}\mathbf{m}^{+\alpha\beta\mathrm{I}}=0. \tag{59}$$

As in the case of conservation of linear momentum in the interior of the domain, *because the kinematics of motion are directly related to the existence of different phases*, it is more useful to derive the corresponding expressions for the average motion of each phase and the diffusion of each constituent α relative to the average motion of phase β. Thus, we have

$$\begin{aligned}\llbracket \phi^{\beta}\rho^{\beta}\mathbf{v}^{\beta}\mathbf{v}^{\beta}-\phi^{\beta}\boldsymbol{t}^{\beta}\rrbracket\cdot\mathbf{n}^{\mathrm{I}}-\llbracket \phi^{\beta}\rho^{\beta}\mathbf{v}^{\beta}\rrbracket\cdot\mathbf{v}_n^{\mathrm{I}}\\ =\mathbf{m}^{+\beta\mathrm{I}}+\left\llbracket\sum_{\alpha}\phi^{\beta}\rho^{\beta}\{\mathbf{w}^{\alpha\beta}(\mathbf{v}^{\beta}-\mathbf{v}^{\mathrm{I}})\right.\\ \left.+(\mathbf{v}^{\beta}+\mathbf{w}^{\alpha\beta})\mathbf{w}^{\alpha\beta}\}\right\rrbracket\cdot\mathbf{n}^{\mathrm{I}}\end{aligned} \tag{60}$$

with

$$\mathbf{m}^{+\beta\mathrm{I}}\equiv\sum_{\alpha}\mathbf{m}^{+\alpha\beta\mathrm{I}} \tag{61}$$

$$\sum_{\beta}\mathbf{m}^{+\beta\mathrm{I}}=0 \tag{62}$$

where the terms on the right-hand side of equation (60) that are multiplied by the diffusion velocity $\mathbf{w}^{\alpha\beta}$ represent the jump in linear momentum due to the motion of the constituents in phase β relative to the average motion of this phase. In addition to equation (60) that must be satisfied by each phase, for the linear momentum of the mixture as a whole to be conserved, equation (62) must also be satisfied on the interface.

Jump condition for conservation of angular momentum on a moving surface of discontinuity. It can be shown that the jump condition obtained from considering the balance of moment of momentum on a moving discontinuity interface is satisfied if the jump condition for linear momentum given by equation (58) is satisfied. Therefore, no new results are obtained from considering the balance of moment of momentum on a moving surface of discontinuity.

Jump condition for conservation of species energy on a moving surface of discontinuity. From the definitions for Ψ, $\tilde{\Psi}$, $\tilde{\Psi}^{\mathrm{I}}$, $\mathbf{j}$, $\mathbf{J}$ and Q_{Ψ} for the conservation of species energy given by equations (63a)–(63d) below

$$\Psi\equiv\phi^{\beta}\rho^{\beta}(\varepsilon^{\alpha\beta}+\tfrac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta}),\quad \tilde{\Psi}\equiv\varepsilon^{+\alpha\beta},\quad \tilde{\Psi}^{\mathrm{I}}\equiv\varepsilon^{+\alpha\beta\mathrm{I}} \tag{63a}$$

$$\mathbf{j}\equiv-\phi^{\beta}\mathbf{v}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta}+\phi^{\beta}\mathbf{q}^{\alpha\beta} \tag{63b}$$

$$\mathbf{J}\equiv\phi^{\beta}\rho^{\beta}(\varepsilon^{\alpha\beta}+\tfrac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta})\mathbf{v}^{\alpha\beta}-\phi^{\beta}\mathbf{v}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta}+\phi^{\beta}\mathbf{q}^{\alpha\beta} \tag{63c}$$

$$\begin{aligned}Q_{\Psi}\equiv\phi^{\beta}Q_{\mathrm{H}}^{\alpha\beta}+\phi^{\beta}\rho^{\alpha\beta}\mathbf{v}^{\alpha\beta}\cdot\mathbf{g}^{\alpha\beta}\\ +\phi^{\beta}(\varepsilon_{Q}^{\alpha\beta}+\tfrac{1}{2}\mathbf{v}_{Q}^{\alpha\beta}\cdot\mathbf{v}_{Q}^{\alpha\beta})Q_{\mathrm{M}}^{\alpha\beta}\end{aligned} \tag{63d}$$

we obtain the jump condition

$$\begin{aligned}\llbracket \phi^{\beta}\rho^{\beta}(\varepsilon^{\alpha\beta}+\tfrac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta})\mathbf{v}^{\alpha\beta}-\phi^{\beta}\mathbf{v}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta}+\phi^{\beta}\mathbf{q}^{\alpha\beta}\rrbracket\cdot\mathbf{n}^{\mathrm{I}}\\ -\llbracket \phi^{\beta}\rho^{\beta}(\varepsilon^{\alpha\beta}+\tfrac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta})\rrbracket v_n^{\mathrm{I}}=\varepsilon^{+\alpha\beta\mathrm{I}}.\end{aligned} \tag{64}$$

In equation (64), $\varepsilon^{+\alpha\beta\mathrm{I}}$ is the jump in the energy interaction between constituent α in phase β and all other constituents in all phases. For the energy of the mixture as a whole to be conserved on the interface, the interfacial energy interaction terms must sum to zero

$$\sum_{\alpha}\sum_{\beta}\varepsilon^{+\alpha\beta\mathrm{I}}=0. \tag{65}$$

Because we are primarily interested in *characterizing the jump conditions at phase-change interfaces where the energetics of the phase transitions play a significant role*, it would be more useful to develop the corresponding expressions directly for each phase by summing equation (64) over all constituents α in a given phase β. Thus, we have

$$\begin{aligned}\left\llbracket\phi^{\beta}\rho^{\beta}\left(\varepsilon^{\beta}+\frac{1}{2}\mathbf{v}^{\beta}\cdot\mathbf{v}^{\beta}\right)\mathbf{v}^{\beta}-\phi^{\beta}\mathbf{v}^{\beta}\cdot\boldsymbol{t}^{\beta}+\phi^{\beta}\mathbf{q}^{\beta}\right\rrbracket\cdot\mathbf{n}^{\mathrm{I}}\\ -\left\llbracket\phi^{\beta}\rho^{\beta}\left(\varepsilon^{\beta}+\frac{1}{2}\mathbf{v}^{\beta}\cdot\mathbf{v}^{\beta}\right)\right\rrbracket v_n^{\mathrm{I}}\\ =\varepsilon^{+\beta\mathrm{I}}-\sum_{\alpha}\left\llbracket\phi^{\beta}\rho^{\alpha\beta}\left(\varepsilon^{\alpha\beta}+\frac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta}\right)\mathbf{w}^{\alpha\beta}\right.\\ \left.-\phi^{\beta}\rho^{\alpha\beta}\frac{1}{2}\mathbf{w}^{\alpha\beta}\cdot\mathbf{w}^{\alpha\beta}(\mathbf{v}^{\beta}-\mathbf{v}^{\mathrm{I}})-\phi^{\beta}\mathbf{w}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta}\right\rrbracket\cdot\mathbf{n}^{\mathrm{I}}\end{aligned} \tag{66}$$

with

$$\varepsilon^{+\beta\mathrm{I}}\equiv\sum_{\alpha}\varepsilon^{+\alpha\beta\mathrm{I}} \tag{67}$$

$$\sum_{\beta}\varepsilon^{+\beta\mathrm{I}}=0 \tag{68}$$

where the terms on the right-hand side of equation (66) that are multiplied by the diffusion velocity $\mathbf{w}^{\alpha\beta}$ represent the jump in energy due to the motion of the constituents in phase β relative to the average motion of this phase. The phase average quantities used in this equation were defined previously. Now, in a porous medium all constituents at a given location are in intimate contact with one another with a large surface area of contact between the constituents. Under the relatively slow flow conditions that we consider the thermal boundary layers extend well into the fluid filled pores so that it is reasonable to assume that all constituents coexist at a single common temperature at each continuum average location. When this assumption is made, it is not necessary to consider the energy balance for each constituent in each phase or to model the terms $\varepsilon^{+\alpha\beta}$ that represent energy transfer between constituents. The separate energy balances for the individual constituents are therefore consolidated into a single energy equation that represents the conservation of energy over all constituents in all phases. Hence

$$\begin{aligned}&\sum_{\beta}\left\llbracket \phi^{\beta}\rho^{\beta}\left(\varepsilon^{\beta}+\frac{1}{2}\mathbf{v}^{\beta}\cdot\mathbf{v}^{\beta}\right)\mathbf{v}^{\beta}-\phi^{\beta}\mathbf{v}^{\beta}\cdot\boldsymbol{t}^{\beta}+\phi^{\beta}\mathbf{q}^{\beta}\right\rrbracket\cdot\mathbf{n}^{\mathrm{I}}\\&\quad-\sum_{\beta}\left\llbracket \phi^{\beta}\rho^{\beta}\left(\varepsilon^{\beta}+\frac{1}{2}\mathbf{v}^{\beta}\cdot\mathbf{v}^{\beta}\right)\right\rrbracket\cdot v_n^{\mathrm{I}}\\&=-\sum_{\beta}\sum_{\alpha}\left\llbracket \phi^{\beta}\rho^{\alpha\beta}\left(\varepsilon^{\alpha\beta}+\frac{1}{2}\mathbf{v}^{\alpha\beta}\cdot\mathbf{v}^{\alpha\beta}\right)\mathbf{w}^{\alpha\beta}\right.\\&\quad\left.-\frac{1}{2}\phi^{\beta}\rho^{\alpha\beta}\mathbf{w}^{\alpha\beta}\cdot\mathbf{w}^{\alpha\beta}(\mathbf{v}^{\beta}-\mathbf{v}^{\mathrm{I}})-\phi^{\beta}\mathbf{w}^{\alpha\beta}\cdot\boldsymbol{t}^{\alpha\beta}\right\rrbracket\cdot\mathbf{n}^{\mathrm{I}}.\end{aligned}\tag{69}$$

3.3. *Specialization of the Governing Equations*

In this section we will specialize the equations that govern the conservation of constituent mass, linear momentum, and energy to the problem of freezing or melting of a salt–water saturated porous medium.

3.3.1. *Conservation of constituent mass*

We begin by specializing the conservation laws and jump conditions for constituent mass by summing on all phases β in equation (8). We then set $\sum_{\beta} c^{+\alpha\beta}=0$ for water, salt and rock constituents (i.e. $\alpha=\mathrm{w,c,r}$) which are assumed not to chemically combine with one another. The resulting governing equations are listed below.

Conservation of mass of water

$$\begin{aligned}&\frac{\partial}{\partial t}\{\phi\rho^{\mathrm{wf}}+(1-\phi)\rho^{\mathrm{ws}}\}+\nabla\cdot\{\phi\rho^{\mathrm{wf}}\mathbf{v}^{\mathrm{f}}\\&\quad+(1-\phi)\rho^{\mathrm{ws}}\mathbf{v}^{\mathrm{s}}\}=\{\phi Q_{\mathrm{M}}^{\mathrm{wf}}+(1-\phi)Q_{\mathrm{M}}^{\mathrm{ws}}\}\\&\quad-\nabla\cdot\{\phi\rho^{\mathrm{wf}}\mathbf{w}^{\mathrm{wf}}+(1-\phi)\rho^{\mathrm{ws}}\mathbf{w}^{\mathrm{ws}}\}.\end{aligned}\tag{70}$$

Conservation of mass of salt

$$\begin{aligned}&\frac{\partial}{\partial t}\{\phi\rho^{\mathrm{cf}}+(1-\phi)\rho^{\mathrm{cs}}\}+\nabla\cdot\{\phi\rho^{\mathrm{cf}}\mathbf{v}^{\mathrm{f}}\\&\quad+(1-\phi)\rho^{\mathrm{cs}}\mathbf{v}^{\mathrm{s}}\}=\{\phi Q_{\mathrm{M}}^{\mathrm{cf}}+(1-\phi)Q_{\mathrm{M}}^{\mathrm{cs}}\}\\&\quad-\nabla\cdot\{\phi\rho^{\mathrm{cf}}\mathbf{w}^{\mathrm{cf}}+(1-\phi)\rho^{\mathrm{cs}}\mathbf{w}^{\mathrm{cs}}\}.\end{aligned}\tag{71}$$

Conservation of mass of rock

$$\begin{aligned}&\frac{\partial}{\partial t}\{\phi\rho^{\mathrm{rf}}+(1-\phi)\rho^{\mathrm{rs}}\}+\nabla\cdot\{\phi\rho^{\mathrm{rf}}\mathbf{v}^{\mathrm{f}}\\&\quad+(1-\phi)\rho^{\mathrm{rs}}\mathbf{v}^{\mathrm{s}}\}=\{\phi Q_{\mathrm{M}}^{\mathrm{rf}}+(1-\phi)Q_{\mathrm{M}}^{\mathrm{rs}}\}\\&\quad-\nabla\cdot\{\phi\rho^{\mathrm{rf}}\mathbf{w}^{\mathrm{rf}}+(1-\phi)\rho^{\mathrm{rs}}\mathbf{w}^{\mathrm{rs}}\}\end{aligned}\tag{72}$$

where ϕ, the volume fraction of the fluid phase, is equal to the porosity of the rock.

We make a number of assumptions to simplify the above set of equations. First, we assume that the rock material does not dissolve in the fluid phase so that $\rho^{\mathrm{rf}}=\mathbf{w}^{\mathrm{rf}}=Q_{\mathrm{M}}^{\mathrm{rf}}=0$. Also, we assume that the rock constituent in the solid phase and the solid phase as a whole do not deform, so that $\mathbf{v}^{\mathrm{rs}}=\mathbf{w}^{\mathrm{rs}}=\mathbf{v}^{\mathrm{s}}=Q_{\mathrm{M}}^{\mathrm{rs}}=0$. Under these assumptions equation (72) reduces to the requirement that the porosity be independent of time (i.e. $\phi(\mathbf{x},t)=\phi(\mathbf{x})$). Next, we assume that the salt is present in the fluid and solid phases only in trace amounts (i.e. $\rho^{\mathrm{cf}}\ll\rho^{\mathrm{f}}$ and $\rho^{\mathrm{cs}}\ll\rho^{\mathrm{s}}$) so that from equations (5) to (7) we have

$$\rho^{\mathrm{f}}=\rho^{\mathrm{wf}},\quad \mathbf{v}^{\mathrm{f}}=\mathbf{v}^{\mathrm{wf}},\quad \mathbf{w}^{\mathrm{wf}}=0.\tag{73}$$

In addition, we agree to limit the change of phase of water between the liquid and solid states to take place only at sharp phase-change interfaces by setting $c^{+\mathrm{wf}}=c^{+\mathrm{ws}}=0$ so that the mass of water in each phase is conserved everywhere, except at the phase-change interfaces. Further, we neglect the diffusion of water relative to the solid in the solid phase (i.e. $\mathbf{w}^{\mathrm{ws}}=0$) and model the diffusion of salt in the fluid and solid phases by generalized Fick's laws of the form

$$\phi\rho^{\mathrm{cf}}\mathbf{w}^{\mathrm{cf}}=-\phi\rho^{\mathrm{f}}\mathbf{D}^{\mathrm{cf}}\cdot\nabla\left\{\frac{\rho^{\mathrm{cf}}}{\rho^{\mathrm{f}}}\right\}\tag{74a}$$

$$(1-\phi)\rho^{\mathrm{cs}}\mathbf{w}^{\mathrm{cs}}=-(1-\phi)\rho^{\mathrm{s}}\mathbf{D}^{\mathrm{cs}}\cdot\nabla\left\{\frac{\rho^{\mathrm{cs}}}{\rho^{\mathrm{s}}}\right\}.\tag{74b}$$

The salt dispersion tensor $\mathbf{D}^{\mathrm{cf}}$ has, in general, contributions from the molecular diffusivity of the salt in solution as well as a usually more dominant contribution from hydrodynamic dispersion due to the branching of the flow within the pore structure. The latter is akin to the more familiar turbulent dispersion in homogeneous fluids and is intimately related to the directional character of both the flow field and the pore structure. For an isotropic pore structure, the total dispersion tensor $\mathbf{D}^{\mathrm{cf}}$ is usually modelled by [9]

$$\phi D_{ij}^{\mathrm{cf}}=D_{\mathrm{T}}|\phi\mathbf{v}^{\mathrm{f}}|\delta_{ij}+(D_{\mathrm{L}}-D_{\mathrm{T}})\frac{\phi^{2}v_i^{\mathrm{f}}v_j^{\mathrm{f}}}{|\phi\mathbf{v}^{\mathrm{f}}|}+\phi D^{\mathrm{f}}\tau^{\mathrm{f}}\delta_{ij}\tag{75}$$

where we have adopted indicial notation for convenience. The quantities D_{L} and D_{T} are the longitudinal and transverse dispersion coefficients measured for unidirectional flow. The tortuosity factor τ^{f}, that modifies the molecular diffusivity D^{f}, is a measure of the ratio of the length of the actual path traversed between two points by a particle travelling within the pore structure to the rectilinear distance between the two points. The diffusivity of salt in the solid phase D_{ij}^{cs} is a complex function of the intrinsic diffusivity within the rock grains, the nature of the intergranular contact regions and the tortuosity of the rock fabric. It will, therefore, be assumed to be a parameter that is directly measured through experiments performed on the rock matrix.

Finally, we assume thermodynamic equilibrium between the salt adsorbed on the rock matrix and the salt in solution in the fluid phase and assume the applicability of an adsorption isotherm relating the mass concentrations of salt in the solid and fluid phases of the form

$$\frac{\rho^{\mathrm{cs}}}{\rho^{\mathrm{s}}} = \Gamma\left(\frac{\rho^{\mathrm{cf}}}{\rho^{\mathrm{f}}}, T, P\right) \tag{76a}$$

where T is the common temperature of the solid and fluid phases and P the fluid pressure in the fluid phase. The functional form of the adsorption isotherm that is usually assumed is that of the Freundlich equilibrium isotherm [17]

$$\frac{\rho^{\mathrm{cs}}}{\rho^{\mathrm{s}}} = \beta^{\mathrm{c}}(T, P)\left(\frac{\rho^{\mathrm{cf}}}{\rho^{\mathrm{f}}}\right)^{1/m} \tag{76b}$$

where the adsorption coefficient β^{c} and index m are experimentally determined quantities. In the present study the index m will be assumed to be equal to unity.

With these simplifying assumptions equations (70) and (71) reduce to the following.

Conservation of mass of water

$$\frac{\partial}{\partial t}(\phi\rho^{\mathrm{wf}}) + \nabla\cdot(\phi\rho^{\mathrm{wf}}\mathbf{v}^{\mathrm{f}}) = \phi Q_{\mathrm{M}}^{\mathrm{wf}}. \tag{77a}$$

Conservation of mass of salt

$$\frac{\partial}{\partial t}\left\{\phi\rho^{\mathrm{cf}} + (1-\phi)\rho^{\mathrm{s}}\beta^{\mathrm{c}}\left(\frac{\rho^{\mathrm{cf}}}{\rho^{\mathrm{f}}}\right)^{1/m}\right\} + \nabla\cdot\{\phi\rho^{\mathrm{cf}}\mathbf{v}^{\mathrm{f}}\}$$
$$= \phi Q_{\mathrm{M}}^{\mathrm{cf}} + (1-\phi)Q_{\mathrm{M}}^{\mathrm{cs}} + \nabla\cdot\{\mathbf{D}\cdot\nabla\rho^{\mathrm{cf}}\} \tag{77b}$$

where

$$\mathbf{D} \equiv \phi\mathbf{D}^{\mathrm{cf}} + (1-\phi)\mathbf{D}^{\mathrm{cs}}\frac{\beta^{\mathrm{c}}}{m}\frac{\rho^{\mathrm{s}}}{\rho^{\mathrm{f}}}\left(\frac{\rho^{\mathrm{cf}}}{\rho^{\mathrm{f}}}\right)^{1/m-1}. \tag{77c}$$

To arrive at equation (77c), we have assumed that salt exists only in trace amounts and have made use of the approximation $\nabla(\rho^{\mathrm{cf}}/\rho^{\mathrm{f}}) \approx (1/\rho^{\mathrm{f}})\nabla\rho^{\mathrm{cf}}$. Furthermore, we have assumed that

$$\left|\frac{1}{\beta^{\mathrm{c}}}\frac{\partial\beta^{\mathrm{c}}}{\partial T}\nabla T \middle/ \frac{1}{m(\rho^{\mathrm{cf}}/\rho^{\mathrm{f}})}\nabla(\rho^{\mathrm{cf}}/\rho^{\mathrm{f}})\right| \ll 1 \tag{77d}$$

$$\left|\frac{1}{\beta^{\mathrm{c}}}\frac{\partial\beta^{\mathrm{c}}}{\partial P}\nabla P \middle/ \frac{1}{m(\rho^{\mathrm{cf}}/\rho^{\mathrm{f}})}\nabla(\rho^{\mathrm{cf}}/\rho^{\mathrm{f}})\right| \ll 1 \tag{77e}$$

so that the variation in salt mass concentration in the solid phase due to temperature and fluid pressure changes is assumed to be negligible compared to the variation due to changes in the salt mass concentration in the fluid phase.

3.3.2. *Conservation of constituent linear momentum*

We next turn to specializing the momentum equations to the physical system of interest.

The equation for conservation of linear momentum of each phase β in the mixture is given by the previously derived equation (13). The diffusive movement of each constituent α in phase β relative to the average motion of phase β is determined by the constitutive law given by equation (9) for species diffusion under the influence of concentration gradients. The specific constitutive forms we have adopted for equation (9) were dealt with in greater detail in Section 3.3.1. The impact of the diffusion of constituents α in phase β on the equation for linear momentum of that phase appears in part in equation (13a) through the term $\mathbf{J}_v^{\beta}$ defined by equation (13b). Because we expect the constituent velocities in each phase to not differ significantly from the phase velocities, so that the motion of the phases will determine the dynamics of the fluid flow, we will simplify the conservation equation for the momentum of each phase by neglecting the term $\mathbf{J}_v^{\beta}$.

Finally, to completely define the momentum equation for each phase velocity $\mathbf{v}^{\beta}$ we have to specify the constitutive forms for the phase stress tensor $\boldsymbol{t}^{\beta}$ and the momentum interaction $\mathbf{m}^{+\beta}$ between each phase β and the rest of the mixture. We first assume that the fluid phase stress is adequately represented by an isotropic fluid pressure P, so that

$$\boldsymbol{t}^{\mathrm{f}} = -P\mathbf{I} \tag{78}$$

where $\mathbf{I}$ is the unit second-order tensor. A more general constitutive representation for the fluid stress $\mathbf{t}^{\mathrm{f}}$ that allows for a non-isotropic, fluid velocity gradient dependent, viscous contribution can be derived from the fundamental thermodynamic and frame-invariance principles of constitutive theory. But, as demonstrated by the experiments of Taylor [38] and of Beavers and Joseph [39], the effects of fluid velocity gradients decay rapidly within the length scale l_{c} of the continuum approximation of the pore structure (i.e. within several pore diameters) and can be neglected in the constitutive relation for the fluid stress tensor provided the viscous drag between the fluid phase and the solid phase is taken into account through the body force type momentum interaction force vector $\mathbf{m}^{+\mathrm{f}}$. Therefore, we adopt an isotropic fluid phase stress in the present application and identify the momentum interaction $\mathbf{m}^{+\mathrm{f}}$ as the sum of an equilibrium component equal to the fluid pressure exerted on the increase in void area in a given direction per unit bulk volume and a non-equilibrium component due to the viscous drag of the fluid on the solid matrix

$$\mathbf{m}^{+\mathrm{f}} = P\nabla\phi - \mathbf{K}^{-1}\mu\phi^2(\mathbf{v}^{\mathrm{f}} - \mathbf{v}^{\mathrm{s}}) \tag{79}$$

where μ is the pore fluid viscosity and $\mathbf{K}$ the permeability tensor. In writing equation (79) we have assumed slow viscous dominated flow within the pores and have neglected an added-mass inertia term that can arise due to the acceleration of the fluid as it moves around the solid particles in the porous matrix. Consistent with the neglect of the fluid inertia effects in the momentum interaction term specified by equation (79), we will also neglect the macroscopic unsteady and convective inertia terms that appear on the left-hand side of equation (13) and the fluid inertia due to the external sources of fluid mass that appear on the right-hand side. With these simplifications equation (13) becomes

$$\nabla\cdot(\phi \boldsymbol{t}^{\mathrm{f}})+\mathbf{m}^{+\mathrm{f}}+\sum_{\alpha}\phi\rho^{\alpha\mathrm{f}}\mathbf{g}^{\alpha\mathrm{f}}=0. \tag{80}$$

We can further simplify equation (80) by assuming that $\mathbf{g}^{\alpha\mathrm{f}}=\mathbf{g}$ and employing equations (78) and (79) to recast equation (80) in its final form as

$$\phi(\mathbf{v}^{\mathrm{f}}-\mathbf{v}^{\mathrm{s}})=-\frac{\mathbf{K}}{\mu}\{\nabla P-(\rho^{\mathrm{wf}}+\rho^{\mathrm{cf}})\mathbf{g}\}. \tag{81}$$

We immediately recognize equation (81) to be a slightly modified form of the familiar D'Arcy's law for fluid seepage through a deforming porous medium. If we assume that the solid phase is at rest and does not deform, the momentum equation for the solid phase is replaced by the trivial result $\mathbf{v}^{\mathrm{s}}=0$, and we recover D'Arcy's law from equation (81).

3.3.3. *Conservation of constituent energy*

We can specialize the conservation of energy for phase β to the physical system of interest by neglecting the energies related to diffusive motions and writing equation (23) for the fluid and solid phases.

Conservation of energy in the fluid phase

$$\frac{\partial}{\partial t}\left\{\phi\rho^{\mathrm{f}}\left(\varepsilon^{\mathrm{f}}+\frac{1}{2}\mathbf{v}^{\mathrm{f}}\cdot\mathbf{v}^{\mathrm{f}}\right)\right\}+\nabla\cdot\left\{\phi\rho^{\mathrm{f}}\left(\varepsilon^{\mathrm{f}}+\frac{1}{2}\mathbf{v}^{\mathrm{f}}\cdot\mathbf{v}^{\mathrm{f}}\right)\mathbf{v}^{\mathrm{f}}\right\}$$
$$=\nabla\cdot\{\phi(-\mathbf{q}^{\mathrm{f}}+\mathbf{v}^{\mathrm{f}}\cdot\boldsymbol{t}^{\mathrm{f}})\}$$
$$+\varepsilon^{+\mathrm{f}}+\sum_{\alpha}\phi\left\{\rho^{\mathrm{f}}\mathbf{v}^{\mathrm{f}}\cdot\mathbf{g}+Q_{\mathrm{H}}^{\alpha\mathrm{f}}+Q_{\mathrm{M}}^{\alpha\mathrm{f}}\left(\varepsilon_{Q}^{\alpha\mathrm{f}}+\frac{1}{2}\mathbf{v}_{Q}^{\mathrm{f}}\cdot\mathbf{v}_{Q}^{\mathrm{f}}\right)\right\}. \tag{82a}$$

Conservation of energy in the solid phase

$$\frac{\partial}{\partial t}\{(1-\phi)\rho^{\mathrm{s}}\varepsilon^{\mathrm{s}}\}=-\nabla\cdot\{(1-\phi)\mathbf{q}^{\mathrm{s}}\}+\varepsilon^{+\mathrm{s}}$$
$$+\sum_{\alpha}(1-\phi)\{Q_{\mathrm{H}}^{\alpha\mathrm{s}}+Q_{\mathrm{M}}^{\alpha\mathrm{s}}\varepsilon_{Q}^{\alpha\mathrm{s}}\}. \tag{82b}$$

Now, because we assume that all constituents in all phases coexist at each continuum point at a common temperature T it is only necessary to write a single energy equation for all constituents. Therefore, we add equations (82a) and (82b) and use the condition that for conservation of energy in the mixture as a whole the total growth of energy $(\varepsilon^{+\mathrm{f}}+\varepsilon^{+\mathrm{s}})$ must vanish. On substituting the constitutive laws for the fluid stress $\boldsymbol{t}^{\mathrm{f}}$ and neglecting the kinetic energy terms which are usually small in comparison to the internal energy terms and the viscous dissipation terms which are small compared to the volumetric pressure work, we obtain

$$\frac{\partial}{\partial t}\{\phi\rho^{\mathrm{f}}\varepsilon^{\mathrm{f}}+(1-\phi)\rho^{\mathrm{s}}\varepsilon^{\mathrm{s}}\}+\nabla\cdot\{\phi(\rho^{\mathrm{f}}\varepsilon^{\mathrm{f}}+P)\mathbf{v}^{\mathrm{f}}\}$$
$$=-\nabla\cdot\{\phi\mathbf{q}^{\mathrm{f}}+(1-\phi)\mathbf{q}^{\mathrm{s}}\}+\phi\rho^{\mathrm{f}}\mathbf{v}^{\mathrm{f}}\cdot\mathbf{g}+\sum_{\alpha}\{\phi Q_{\mathrm{H}}^{\alpha\mathrm{f}}$$
$$+(1-\phi)Q_{\mathrm{H}}^{\alpha\mathrm{s}}+\phi Q_{\mathrm{M}}^{\alpha\mathrm{f}}\varepsilon_{Q}^{\alpha\mathrm{f}}+(1-\phi)Q_{\mathrm{M}}^{\alpha\mathrm{s}}\varepsilon_{Q}^{\alpha\mathrm{s}}\}. \tag{83}$$

To completely specify the conservation of energy it is necessary to specify constitutive relationships for the heat flux vectors $\mathbf{q}^{\mathrm{f}},\mathbf{q}^{\mathrm{s}}$, the internal energies $\varepsilon^{\mathrm{f}},\varepsilon^{\mathrm{s}}$, and the densities $\rho^{\mathrm{f}},\rho^{\mathrm{s}}$. We model the transport of heat in the fluid phase in a manner analogous to the transport of species by recognizing the separate contributions due to molecular thermal conduction and to hydrodynamic dispersion [9]. That is

$$\mathbf{q}^{\mathrm{f}}\equiv-\mathbf{k}^{\mathrm{f}}\cdot\nabla T \tag{84a}$$

$$\phi\mathbf{k}^{\mathrm{f}}\equiv\rho^{\mathrm{f}}C_{\mathrm{v}}^{\mathrm{f}}\left\{D_{\mathrm{T}}|\phi\mathbf{v}^{\mathrm{f}}|\delta_{ij}+(D_{\mathrm{L}}-D_{\mathrm{T}})\frac{\phi^{2}v_{i}^{\mathrm{f}}v_{j}^{\mathrm{f}}}{|\phi\mathbf{v}^{\mathrm{f}}|}\right\}+\phi\lambda^{\mathrm{f}}\tau^{\mathrm{f}}\delta_{ij} \tag{84b}$$

where $C_{\mathrm{v}}^{\mathrm{f}}$ is the specific heat at constant volume of the fluid in the fluid phase, λ^{f} is the molecular thermal conductivity of the fluid, and D_{L}, D_{T}, and τ^{f} are the longitudinal and transverse dispersion coefficients and pore structure tortuosity defined previously for species transport. The transport of thermal energy in the rock matrix is modelled similarly by

$$\mathbf{q}^{\mathrm{s}}\equiv-\mathbf{k}^{\mathrm{s}}\cdot\nabla T. \tag{85}$$

The thermal conductivity k_{ij}^{s} of the rock matrix, which is a function of the intrinsic thermal conductivity of the rock grains and the degree of cementation and contact between grains, will be considered to be a parameter that is directly measured through laboratory experiments.

3.4. *Specialization of the Jump Conditions*

In this section we specialize the jump conditions previously derived in Section 3.2 to the conditions across a freezing/melting interface in a salt–water saturated porous medium.

3.4.1. *Jump condition for the conservation of mass of water*

Let us first write the jump condition given by equation (56b) in expanded form for the conservation of the mass of water across the freezing/melting interface. Then

$$\begin{aligned}&\{\phi^{f+}\rho^{wf+}(\mathbf{v}^{f+}-\mathbf{v}^{I})+\phi^{s+}\rho^{ws+}(\mathbf{v}^{s+}-\mathbf{v}^{I})\}\cdot\mathbf{n}^{I}\\&\quad-\{\phi^{f-}\rho^{wf-}(\mathbf{v}^{f-}-\mathbf{v}^{I})+\phi^{s-}\rho^{ws-}(\mathbf{v}^{s-}-\mathbf{v}^{I})\}\cdot\mathbf{n}^{I}\\&=-\{\phi^{f+}\rho^{wf+}\mathbf{w}^{wf+}+\phi^{s+}\rho^{ws+}\mathbf{w}^{ws+}\}\cdot\mathbf{n}^{I}\\&\quad+\{\phi^{f-}\rho^{wf-}\mathbf{w}^{wf-}+\phi^{s-}\rho^{ws-}\mathbf{w}^{ws-}\}\cdot\mathbf{n}^{I}.\end{aligned}\tag{86}$$

We can simplify this equation by setting $\rho^{ws-}=0$ for no bound water in the solid phase on the water side of the interface, $\mathbf{v}^{s+}=\mathbf{v}^{s-}=0$ for a rigid solid phase, $\phi^{f+}=0$, $\phi^{s+}=1$ for completely frozen pore fluid on the ice side. Because we assume that salt is present only in trace quantities, the velocity of the water component is approximately equal to the corresponding phase velocity. Consequently, we have $\mathbf{w}^{wf+}\approx 0$ and $\mathbf{w}^{wf-}\approx 0$. Therefore, equation (86) reduces to

$$\phi^{f-}v_n^{f-}=-\frac{1}{\rho^{wf-}}(\phi^{s+}\rho^{ws+}-\phi^{f-}\rho^{wf-})v_n^{I}.\tag{87a}$$

It is appropriate to digress here regarding the role played by the interfacial phase mass production terms $c^{+\alpha\beta I}$. If instead of using equation (56b) for conservation of water in all phases at the interface, we had specialized the jump condition (56a) separately for the liquid and solid phases at the interface under the same assumptions, we arrive at the following expressions for the interfacial phase mass production terms:

$$c^{+wfI}=-\phi^{f-}\rho^{wf-}(\mathbf{v}^{f-}-\mathbf{v}^{I})\cdot\mathbf{n}^{I}\tag{87b}$$

$$c^{+wsI}=-\phi^{s+}\rho^{ws+}\mathbf{v}^{I}\cdot\mathbf{n}^{I}\tag{87c}$$

$$c^{+wfI}+c^{+wsI}=0\tag{87d}$$

where equation (87d), that enforces the condition that the mass of water lost by the liquid phase must equal the mass of water gained by the solid phase, yields the same result as equation (87a). Recall, however, that everywhere else in the domain, the mass of water is conserved separately in each phase.

This illustrates the critical importance of the Dirac delta-function-like interfacial production term Ψ^{I} *in equation* (40) *that modifies the standard Rankine–Hugoniot jump condition in the present multicomponent multiphase formulation.* The analogous terms in the jump conditions for the other conserved quantities are of similar significance.

Now, the volume fraction of the fluid phase ϕ^{f-} on the water side is equal to the porosity of the rock ϕ^{-}, while on the ice side the porous volume fraction of the rock ϕ^{+} is occupied by ice. If ρ^{w-} and ρ^{w+} are the densities of water and ice, respectively, then $\rho^{wf-}=\rho^{w-}$ and $\rho^{ws+}=\phi^{+}\rho^{w+}$ so that equation (87) can be recast as

$$q_n^{P+}-q_n^{P-}=\frac{1}{\rho^{w-}}(\phi^{+}\rho^{w+}-\phi^{-}\rho^{w-})v_n^{I}\tag{88}$$

where the normal fluid fluxes on the water and ice sides are defined by

$$q_n^{P-}\equiv\phi^{f-}v_n^{f-},\quad q_n^{P+}\equiv\phi^{f+}v_n^{f+}=0.\tag{89a,b}$$

Equation (88) shows that even if the ice side is impermeable, the fluid velocity normal to the interface is not equal to zero if either the fluid density or the rock porosity changes as a result of the freezing/melting process. We will usually assume that rock porosity remains unchanged (i.e. $\phi^{+}=\phi^{-}$) so that the fluid velocity on the water side at the interface is a function of the difference in density between liquid and frozen water and the velocity of propagation of the freezing/melting front.

3.4.2. *Jump condition for the conservation of mass of salt*

$$\begin{aligned}&\{\phi^{f+}\rho^{cf+}(\mathbf{v}^{f+}-\mathbf{v}^{I})+\phi^{s+}\rho^{cs+}(\mathbf{v}^{s+}-\mathbf{v}^{I})\}\cdot\mathbf{n}^{I}\\&\quad-\{\phi^{f-}\rho^{cf-}(\mathbf{v}^{f-}-\mathbf{v}^{I})+\phi^{s-}\rho^{cs-}(\mathbf{v}^{s-}-\mathbf{v}^{I})\}\cdot\mathbf{n}^{I}\\&=-\{\phi^{f+}\rho^{cf+}\mathbf{w}^{cf+}+\phi^{s+}\rho^{cs+}\mathbf{w}^{cs+}\}\cdot\mathbf{n}^{I}\\&\quad+\{\phi^{f-}\rho^{cf-}\mathbf{w}^{cf-}+\phi^{s-}\rho^{cs-}\mathbf{w}^{cs-}\}\cdot\mathbf{n}^{I}.\end{aligned}\tag{90}$$

When the assumptions used to derive the jump condition for water flux are invoked while retaining salt diffusion velocities, equation (90) reduces to

$$q_n^{C+}-q_n^{C-}=\{\rho^{cs+}-\phi^{f-}\rho^{cf-}-\phi^{s-}\rho^{cs-}\}v_n^{I}+\rho^{cf-}q_n^{P-}\tag{91}$$

where the normal salt fluxes on the water and ice sides are defined by

$$q_n^{C-}\equiv\phi^{f-}\rho^{cf-}w_n^{cf}+\phi^{s-}\rho^{cs-}w_n^{cs-}\tag{92a}$$

$$q_n^{C+}\equiv\rho^{cs+}w_n^{cs+}.\tag{92b}$$

Now, using equation (88), we can eliminate the water side fluid flux from equation (91) to obtain

$$q_n^{C+}-q_n^{C-}=\left\{\rho^{cs+}-\phi^{+}\rho^{cf-}\frac{\rho^{w+}}{\rho^{w-}}-(1-\phi^{-})\rho^{cs-}\right\}v_n^{I}.\tag{93}$$

The salt mass in the solid phase on the ice side is contained partly in the ice and partly adsorbed on the rock while on the water side only the salt adsorbed on the rock is present. Accordingly, substituting, $\rho^{cs+}=\phi^{+}\rho^{cf+}+(1-\phi^{+})\rho^{cr+}$ and $\rho^{cs-}=\rho^{cr-}$ in equation (93), we obtain

$$\begin{aligned}q_n^{C+}-q_n^{C-}=\phi^{+}\Bigg\{&\rho^{cf+}-\rho^{cf-}\frac{\rho^{w+}}{\rho^{w-}}+(1-\phi^{+})\rho^{cr+}\\&-(1-\phi^{-})\rho^{cr-}\Bigg\}v_n^{I}.\end{aligned}\tag{94}$$

The final conditions that are needed to complete the description of salt mass transfer across the freezing/melting interface require the identification of thermodynamic constitutive relations that fix the relationship between the salt mass concentration in the ice ρ^{cf+} and in the rock ρ^{cr+} on the ice side of the interface to the corresponding salt mass concentration in the liquid water ρ^{cf-} and in the rock ρ^{cr-}, respectively, on the water side of the interface. Now, the

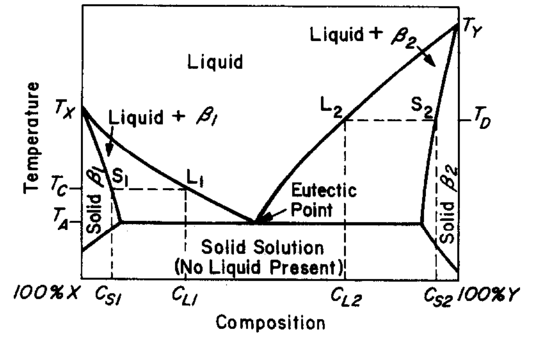

FIG. 3. Equilibrium phase diagram for a fictitious binary system X–Y at constant pressure P. S_1, L_1 and S_2, L_2 are two liquidus–solidus pairs. At T_C the binary system of Pair 1 will consist of liquid at composition C_{L1} and solid at composition C_{S1}. The partition coefficient $K_D^c(T_C, P)$ is equal to C_{S1}/C_{L1}.

compositional behavior of the phase transition from liquid water to ice in the presence of a salt is such that salt is rejected from the ice upon freezing of the salt water (Figs. 3 and 4). Theories of freezing of classical liquids, with emphasis on the anomalous behavior of certain liquids, such as water, are reviewed by Haymet [40]. The redistribution of salts in aqueous solutions upon freezing is discussed by Terwilliger and Dizio [41], Levin [42] and Korber *et al.* [43]. We assume that the movement of the interface is sufficiently slow for the salt in the liquid phase to be in equilibrium with the salt in the solid phase (this requires the temperatures, pressures, and the chemical potentials of the two phases to be equal). On the other hand, because the rock does not undergo a change in phase, and salt is captured by the rock by the unrelated phenomenon of surface adsorption, we assume that the adsorbed salt concentration on the rock remains unaltered by the freezing process. Accordingly, we model the partition of the salt between the liquid and solid phases of water and the distribution of salt attached to the rock by

$$\rho^{\mathrm{cf}+} = K_{\mathrm{D}}^{\mathrm{c}}(T,p)\rho^{\mathrm{cf}-}, \quad \rho^{\mathrm{cr}+} = \rho^{\mathrm{cr}-}. \quad (95\mathrm{a,b})$$

With these assumptions, equation (94) for the conservation of salt mass across a freezing/melting interface reduces to

$$q_n^{C+} - q_n^{C-} = \phi^+ \left\{ \rho^{\mathrm{cf}+} - \rho^{\mathrm{cf}-} \frac{\rho^{\mathrm{w}+}}{\rho^{\mathrm{w}-}} \right\} v_n^{\mathrm{I}}. \quad (96)$$

It should be recalled here that the salt diffusion fluxes are defined by equations (74a) and (74b) in terms of the salt mass concentration gradients on the two sides of the interface. Furthermore, the degree to which salt is adsorbed on the rock is modelled via adsorption coefficients β^{c} in equation (76b) which can be different in the frozen and unfrozen regions of the domain.

3.4.3. *Jump condition for the conservation of linear momentum*

To derive the specialized jump condition for the conservation of linear momentum we combine equations (60) and (62) and neglect the momentum transport terms due to species diffusion. Also, to be consistent with the restriction of a bulk phase fluid flow on the unfrozen side to the slow flow regime dominated by viscous effects and governed by D'Arcy's law, we neglect the fluid inertia terms. Combining the resulting expression with the assumptions we made previously in deriving the specialized jump conditions for the conservation of mass of water and mass of salt, we obtain

$$[\mathbf{t}^{\mathrm{s}+} - \phi^{\mathrm{f}-}\mathbf{t}^{\mathrm{f}-} - \phi^{\mathrm{s}-}\mathbf{t}^{\mathrm{s}-}]\cdot\mathbf{n}^{\mathrm{I}} \simeq 0. \quad (97)$$

In the above equation, $\mathbf{t}^{\mathrm{s}+}$ represents the stress applied on the solid phase on the ice side of the interface, $\mathbf{t}^{\mathrm{f}-}$ is the stress tensor for the stress applied on the pore fluid on the water side of the interface, and $\mathbf{t}^{\mathrm{s}-}$ represents the stress applied on the porous rock matrix on the water side of the interface.

Furthermore, recognizing that, on the water side of the interface, the volume fraction of the fluid phase, $\phi^{\mathrm{f}-}$, is equal to the porosity of the rock ϕ^-, and that the volume fraction of the solid phase, $\phi^{\mathrm{s}-}$, is equal to $(1-\phi^-)$, we obtain

$$[\mathbf{t}^{\mathrm{s}+} - \phi^-\mathbf{t}^{\mathrm{f}-} - (1-\phi^-)\mathbf{t}^{\mathrm{s}-}]\cdot\mathbf{n}^{\mathrm{I}} = 0. \quad (98)$$

Now, we can decompose the stress tensor $\mathbf{t}^{\mathrm{s}+}$ on the solid phase on the ice side of the interface into two parts according to the expression $\mathbf{t}^{\mathrm{s}+} = (1-\phi^+)\mathbf{t}^{\mathrm{sr}+} + \phi^+\mathbf{t}^{\mathrm{sp}+}$ where $\mathbf{t}^{\mathrm{sr}+}$ is the stress applied on the porous rock matrix and $\mathbf{t}^{\mathrm{sp}+}$ is the stress applied on the pore ice. Then, equation (98) becomes

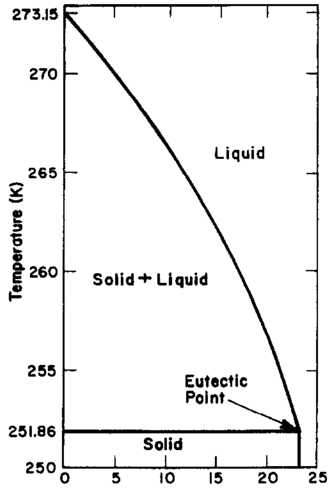

FIG. 4. Equilibrium phase diagram for NaCl–H_2O solution. Note depression of phase-change temperature with increased concentration of NaCl in solution.

$$[(1-\phi^{+})\boldsymbol{t}^{\mathrm{sr}+}+\phi^{+}\boldsymbol{t}^{\mathrm{sp}+}-\phi^{-}\boldsymbol{t}^{\mathrm{f}-}-(1-\phi^{-})\boldsymbol{t}^{\mathrm{s}-}]\cdot\mathbf{n}^{\mathrm{I}}=0. \quad (99)$$

We can proceed beyond this point only by making additional assumptions regarding the nature of stress transfer across the interface within the different constituents. If we assume that the ice at the freezing/melting front is soft compared to the rock matrix and is fluid-like and without significant rigidity, then it seems reasonable to assume that the total traction in the rock matrix is transferred unchanged across the interface. That is, we assume

$$(1-\phi^{+})\boldsymbol{t}^{\mathrm{sr}+}\cdot\mathbf{n}^{\mathrm{I}}=(1-\phi^{-})\boldsymbol{t}^{\mathrm{s}-}\cdot\mathbf{n}^{\mathrm{I}}. \quad (100)$$

Further, if the ice on the solid side of the interface is fluid-like, then we can assume the isotropic stress representations $\boldsymbol{t}^{\mathrm{f}-}=-P^{-}\boldsymbol{I}$ and $\boldsymbol{t}^{\mathrm{sp}+}=-P^{+}\boldsymbol{I}$, and invoking the arbitrariness of the unit normal to the interface, we obtain from equation (99) the result

$$\phi^{+}P^{+}-\phi^{-}P^{-}=0. \quad (101)$$

If we further assume that porosity does not change across the interface (i.e. $\phi^{+}=\phi^{-}$), then, according to equation (101), the fluid pressure on the unfrozen side will be equal to the isotropic pressure in the ice on the frozen solid side of the interface.

3.4.4. *Jump conditions for the conservation of energy*

In Section 3.2 we derived the jump conditions that must be satisfied by each phase of a multiphase continuum for energy to be conserved across a surface of discontinuity. If the phases coexist at a common temperature the energy transfer terms between different phases can be eliminated and a single jump condition can be written for the whole mixture of the different phases as in equation (69). For application to a freezing/melting interface in a porous medium with a fluid and a solid phase, we simplify this relationship by neglecting the terms on the right-hand side that represent the jump in the diffusive convective transport of internal and kinetic energies, and the work done by stresses due to this movement relative the bulk phases. This yields the following equation in expanded form:

$$\begin{aligned}&[\![\phi^{\mathrm{s}}\rho^{\mathrm{s}}(\varepsilon^{\mathrm{s}}+\tfrac{1}{2}\mathbf{v}^{\mathrm{s}}\cdot\mathbf{v}^{\mathrm{s}})\mathbf{v}^{\mathrm{s}}-\phi^{\mathrm{s}}\mathbf{v}^{\mathrm{s}}\cdot\boldsymbol{t}^{\mathrm{s}}+\phi^{\mathrm{s}}\mathbf{q}^{\mathrm{s}}\\&\quad+\phi^{\mathrm{f}}\rho^{\mathrm{f}}(\varepsilon^{\mathrm{f}}+\tfrac{1}{2}\mathbf{v}^{\mathrm{f}}\cdot\mathbf{v}^{\mathrm{f}})\mathbf{v}^{\mathrm{f}}-\phi^{\mathrm{f}}\mathbf{v}^{\mathrm{f}}\cdot\boldsymbol{t}^{\mathrm{f}}+\phi^{\mathrm{f}}\mathbf{q}^{\mathrm{f}}]\!]\cdot\mathbf{n}^{\mathrm{I}}\\&=-[\![\phi^{\mathrm{s}}\rho^{\mathrm{s}}(\varepsilon^{\mathrm{s}}+\tfrac{1}{2}\mathbf{v}^{\mathrm{s}}\cdot\mathbf{v}^{\mathrm{s}})+\phi^{\mathrm{f}}\rho^{\mathrm{f}}(\varepsilon^{\mathrm{f}}+\tfrac{1}{2}\mathbf{v}^{\mathrm{f}}\cdot\mathbf{v}^{\mathrm{f}})]\!]\cdot v_{n}^{\mathrm{I}}.\end{aligned} \quad (102)$$

We simplify this equation further by neglecting the bulk phase kinetic energies. This is consistent with the assumption of a rigid, non-deforming solid phase, and the restriction of a bulk phase fluid flow on the unfrozen side to the slow flow regime dominated by viscous effects and governed by D'Arcy's law. With this assumption, and setting $\mathbf{v}^{\mathrm{s}}=0$, $\phi^{\mathrm{s}+}=1$, $\phi^{\mathrm{f}+}=0$ and using the definition of the fluid phase stress tensor given by equation (78), we simplify equation (102) to

$$\begin{aligned}q_{n}^{\mathrm{T}+}-q_{n}^{\mathrm{T}-}&=\{\rho^{\mathrm{s}+}\varepsilon^{\mathrm{s}+}-(\phi^{\mathrm{s}-}\rho^{\mathrm{s}-}\varepsilon^{\mathrm{s}-}+\phi^{\mathrm{f}-}\rho^{\mathrm{f}-}\varepsilon^{\mathrm{f}-})\}v_{n}^{\mathrm{I}}\\&\quad+(\rho^{\mathrm{f}-}\varepsilon^{\mathrm{f}-}+P^{-})\phi^{\mathrm{f}-}v_{n}^{\mathrm{f}-}\end{aligned} \quad (103)$$

where the total energy fluxes $q_{n}^{\mathrm{T}+}$ and $q_{n}^{\mathrm{T}-}$ normal to the interface on the frozen and unfrozen sides of the interface are defined in terms of the energy fluxes for each phase by

$$q_{n}^{\mathrm{T}+}\equiv q_{n}^{\mathrm{s}+},\quad q_{n}^{\mathrm{T}-}\equiv\phi^{\mathrm{s}-}q_{n}^{\mathrm{s}-}+\phi^{\mathrm{f}-}q_{n}^{\mathrm{f}-}. \quad (104\mathrm{a,b})$$

The solid phase fluxes $\mathbf{q}^{\mathrm{s}+}$, $\mathbf{q}^{\mathrm{s}-}$ are modelled as in equation (85) by Fourier's law while the fluid phase flux $\mathbf{q}^{\mathrm{f}-}$ is modelled according to equations (84a) and (84b) that allow for the contributions from molecular conduction and hydrodynamic dispersion.

Given equation (103) we can recast the jump condition for energy in a more convenient and physically meaningful form by eliminating the fluid velocity $v_{n}^{\mathrm{f}-}$ from this equation using equations (88) and (89) and by replacing the fluid and solid phase densities and internal energies by the corresponding quantities for the rock and water constituents. The required expressions for densities were given previously when the jump conditions for mass conservation were considered. The expressions for the phase internal energies are

$$\rho^{\mathrm{s}+}\varepsilon^{\mathrm{s}+}=\phi^{+}\rho^{\mathrm{w}+}\varepsilon^{\mathrm{w}+}+(1-\phi^{+})\rho^{\mathrm{r}+}\varepsilon^{\mathrm{r}+} \quad (105\mathrm{a})$$

$$\rho^{\mathrm{f}-}\varepsilon^{\mathrm{f}-}\approx\rho^{\mathrm{w}-}\varepsilon^{\mathrm{w}-}. \quad (105\mathrm{b})$$

Substituting these expressions in equation (103), we obtain the two equivalent expressions

$$\begin{aligned}q_{n}^{\mathrm{T}+}-q_{n}^{\mathrm{T}-}&=\phi^{+}\rho^{\mathrm{w}+}(\varepsilon^{\mathrm{w}+}-\varepsilon^{\mathrm{w}-})v_{n}^{\mathrm{I}}\\&\quad-\frac{P^{-}}{\rho^{\mathrm{w}-}}(\phi^{+}\rho^{\mathrm{w}+}-\phi^{-}\rho^{\mathrm{w}-})v_{n}^{\mathrm{I}}\\&\quad+(1-\phi^{+})(\rho^{\mathrm{r}+}\varepsilon^{\mathrm{r}+}-\rho^{\mathrm{r}-}\varepsilon^{\mathrm{r}-})v_{n}^{\mathrm{I}}\end{aligned} \quad (106\mathrm{a})$$

$$\begin{aligned}q_{n}^{\mathrm{T}+}-q_{n}^{\mathrm{T}-}&=\phi^{+}\rho^{\mathrm{w}+}(h^{\mathrm{w}+}-h^{\mathrm{w}-})v_{n}^{\mathrm{I}}\\&\quad+(1-\phi^{+})(\rho^{\mathrm{r}+}\varepsilon^{\mathrm{r}+}-\rho^{\mathrm{r}-}\varepsilon^{\mathrm{r}-})v_{n}^{\mathrm{I}}.\end{aligned} \quad (106\mathrm{b})$$

From equation (106a) we see that there are three terms contributing to the jump in the energy flux across the freezing/melting interface. The first of these is derived from the change in internal energy of the water constituent upon freezing or melting. The second term arises from the work done against the fluid pressure as a result of the density change in water across the interface. In equation (106b) these two terms are recast in a more familiar form by replacing the internal energy and the pressure work by the enthalpies $h^{\mathrm{w}+}=\varepsilon^{\mathrm{w}+}+P^{+}/\rho^{\mathrm{w}+}$ and $h^{\mathrm{w}-}=\varepsilon^{\mathrm{w}-}+P^{-}/\rho^{\mathrm{w}-}$. In deriving equation (106b) we have made use of the jump condition for the conservation of linear momentum at a phase-change interface (equation (101)) and related P^{+} to P^{-} through the expression $P^{+}=\phi^{-}P^{-}/\phi^{+}$. We note that there is no corresponding term derived from the solid phase because we have assumed that the solid phase is rigid and does not deform. The third term contributing to a jump in the total energy flux is related to the jump in internal energy of the rock across the interface. Because the rock is assumed not to deform and to remain unaltered in phase, we will assume for our present application that this contribution is always identically equal to zero. With these assumptions, we obtain the final form of the jump condition for energy as

$$q_n^{\mathrm{T}+} - q_n^{\mathrm{T}-} = \phi^+ \rho^{\mathrm{w}+} (h^{\mathrm{w}+} - h^{\mathrm{w}-}) v_n^{\mathrm{I}}. \qquad (107)$$

Equation (107) is similar to the one-dimensional jump condition for energy derived by Weaver and Viskanta [44] in their study of freezing of liquid-saturated porous media.

This completes the specialization of the general jump conditions derived previously for multiphase flow in a porous medium to the specific problem of freezing and melting of a porous medium saturated by a liquid that transports a trace species. At this point we should emphasize that the derived equations presuppose the existence of a sharp phase-change interface. For certain solute species concentrations the phase-change interface thickness may not be infinitesimal and the phase transition may take place over a finite thickness (i.e. mushy zone). Under such conditions the presented formulation provides the tools for tracking the interface between the entirely solidified region and the mushy zone. In such a case, however, there may be a jump in porosity across the interface. To develop a specialized theory for a mushy zone of a distributed phase change, one can use the generic equations presented in Section 3.1.

4. CONCLUSIONS

A theoretical model for the transport of heat, water and trace amounts of salt, in a porous medium subject to solid–liquid phase change was developed from first principles. The significant results and special features of this work are identified below.

(1) The equations governing the conservation of mass, momentum, and energy of *multiple constituent species* segregated into *multiple physical phases* within a porous medium were derived from first principles in the form of a mixture theory.

(2) The jump conditions that must be satisfied for the mass, momentum, and energy to be conserved across surfaces of discontinuity in the phase properties were extracted from the conservation laws by two methods. The first method employed the traditional *limiting process applied to the integral balance relationships*. In the second method, the jump conditions were derived from the *governing differential equations by treating the discontinuous phase properties as generalized distributions with discontinuities located at moving surfaces*. The resulting jump conditions have the form of the familiar Rankine–Hugoniot relations with a modification to account for interfacial source terms. This modification is *essential* to correctly model the phase discontinuities that occur in the present multiconstituent multiphase mixture formulation.

(3) The governing equations for the propagation of freezing and melting fronts in porous media as a coupled heat flow, fluid flow, and trace species transport process were obtained by specializing the governing equations from the general mixture theory and adopting special constitutive relationships. The latter include D'Arcy's law for fluid flow, Fick's and Fourier's laws for species flux and heat flux, respectively, with dispersion coefficients that account for both molecular diffusion and convective dispersion. The adsorption of the trace species on the rock, was modelled in terms of a Freundlich adsorption isotherm.

(4) The jump conditions at the freezing and melting fronts were extracted from the jump conditions of the general mixture theory. The jump in the concentration of the species at the interface, due to its unequal distribution between the solid and liquid water phases, was modelled by a temperature and pressure dependent equilibrium partition coefficient.

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UN MODELE CONTINU POUR LA PROPAGATION DES FRONTS DE CHANGEMENT DE PHASE DANS LES MILIEUX POREUX EN PRESENCE DES MECANISMES COUPLES DE TRANSPORT DE FLUIDE, DE CHALEUR ET D'ESPECES

Résumé—On établit les équations du transport d'énergie et de masse dans un milieu poreux saturé par un mélange fluide à plusieurs phases et plusieurs constituants, dans des conditions qui réalisent des fronts raides mobiles de façon continue et des interfaces de changement de phase, abrupts et discontinus. Dans ces équations les fractions en volume de chaque phase, les potentiels tels que la température, la pression et la concentration, et les flux correspondants permettent les sauts de valeur à travers les interfaces de changement de phase. Comme exemple d'application, on spécialise la théorie au cas de la propagation des interfaces liquide/solide dans un milieu poreux saturé d'eau salée pour un mécanisme couplé de transport de chaleur, de fluide et d'espèces.

EIN KONTINUUM-MODELL FÜR DIE AUSBREITUNG VON DISKRETEN PHASENWECHSELFRONTEN IN PORÖSEN MEDIEN UNTER BERÜCKSICHTIGUNG VON WÄRME-, FLUID- UND STOFFTRANSPORTVORGÄNGEN

Zusammenfassung—Diese Abhandlung beschreibt die Herleitung von Gleichungen für den Energie- und Stofftransport in einem porösen Medium, das mit einem mehrphasigen Vielstoffgemisch gesättigt ist. Es herrschen dabei scharfe kontinuierliche Bewegungsfronten und abrupte diskontinuierlich bewegte Phasenwechselgrenzen. In diesen Gleichungen dürfen sich der Volumenanteil jeder Phase und Größen wie Temperatur, Druck und Konzentration und deren entsprechende Ströme an den Phasenwechselgrenzen sprunghaft ändern. Als Anwendungsbeispiel wurde die entwickelte Theorie auf das Problem der Ausbreitung von Fest/flüssig-Grenzschichten in mit Salzwasser gesättigten, porösen Medien für kontinuierlichen Wärme-, Fluid- und Stofftransport angewandt.

МОДЕЛЬ СПЛОШНОЙ СРЕДЫ ДЛЯ ОПИСАНИЯ РАСПРОСТРАНЕНИЯ ДИСКРЕТНЫХ ФРОНТОВ ФАЗОВЫХ ИЗМЕНЕНИЙ В ПОРИСТЫХ СРЕДАХ ПРИ НАЛИЧИИ ВЗАИМОСВЯЗАННОГО ПЕРЕНОСА ТЕПЛА, ЖИДКОСТИ И КОМПОНЕНТОВ СМЕСИ

Аннотация—Получены уравнения, описывающие перенос энергии и массы в пористой среде, насыщенной многофазной многокомпонентной смесью в условиях, когда наблюдаются крутые непрерывно перемещающиеся фронты и внезапно прерывающиеся подвижные границы раздела фаз. В уравнениях учитывается возможность скачкообразного изменения объёмной доли каждой фазы, температуры, давления, концентрации и соответствующих потоков при переходе через границу раздела. В качестве примера использования выведенной модели рассмотрена задача о распространении границ раздела между зонами плавления/затвердевания в пористой насыщенной соленой водой среде в случае взаимосвязанного процесса, определяемого передачей тепла, течением жидкости и переносом вещества.