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A CONSTITUTIVE THEORY FOR SNOW AS A CONTINUOUS MULTIPHASE MIXTURE

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Abstract—Snow on the ground is viewed in this formulation, as a saturated two-phase granular material comprised of small grains of ice with interstitial pores filled by a single vapor. The snow is considered as a continuous mixture in which the ice and vapor constituents are themselves treated as individual but interacting continua.

Mathematical modeling of the snow is accomplished using a relatively recent continuum theory for mixtures where the individual constituents are physically separate. This approach considers the volume fraction occupied by each constituent as an additional kinematic variable. Therefore, in addition to the balance equations for mass, linear momentum, angular momentum and energy, usually applied in continuum mechanics, an equation which accounts for changes in the volume fraction, called the balance of equilibrated force, is included. Balance equations for each constituent as well as for the mixture are considered. The immiscible nature of the constituents allows constitutive equations to be developed which depend only on those variables which pertain to that constituent. Exchange between the ice and vapor is accounted for by interaction terms which enter the theory through the balance equations for the constituents. Forms for these interaction terms are used which guarantee that the entropy inequality is not violated.

A one-dimensional analysis of an isothermal homogeneous snow cover suddenly subjected to a colder surface temperature reveals a thermodynamically active zone associated with a large temperature gradient, initially located near the top surface, but which moves downward with time in a wavelike fashion decreasing in intensity. Slight differences in constituent temperatures are calculated during the more active transient phase in conjunction with a decrease in snow density.

Key Words: snow, mixtures, multiphase, immiscible, porous, metamorphism, constitutive, continuum

INTRODUCTION

An improved understanding of snow as a material is of widespread interest, since a large portion of the globe is seasonally or permanently covered with it. It is also of broader scientific interest, since it exists naturally at atmospheric conditions conducive to phase change, coupled with heat flux, mass flux and deformational processes. It is an excellent model medium which may be applied to other granular or porous geologic and engineering materials where processes similar to those involved in snow metamorphism occur, but only at more extreme temperatures and pressures. The analysis presented in this paper is concerned with dry snow, which implies an absence of free water.

There are a number of general metamorphic processes occurring in a snow cover. Initially fragile atmospherically formed ice crystals will settle and deteriorate into a more stable configuration, and in the absence of a large temperature gradient will tend toward a rounded shape. Development of this rounded form is variously termed equi-temperature (LaChapelle 1969; Sommerfeld 1969) or equilibrium growth (Colbeck 1981) metamorphism.

Due to geothermal heating, temperatures at the snow/ground interface will usually remain near 0°C throughout the winter. When the snow surface temperature is at or above that of the base, melting will occur. If the situation persists free water will eventually bring the snowpack to an isothermal condition typical of a liquid saturated snowpack. Frequently, however, the surface temperature will be colder than the underlying snow establishing a temperature gradient. Such gradients in excess of approx. 10°C/m and dependent on the textural condition of the snow will induce the formation of depth hoar; striated faceted crystals which are poorly bonded together. This is termed temperature gradient (LaChapelle 1969; Sommerfeld 1969) or kinetic growth (Colbeck 1981) metamorphism.

Thermal gradients induce an upward vapor flux from the lower warmer regions toward the upper colder regions. Mass flux will proceed by a "hand to hand" mechanism (Yosida and Kojima 1950, cited in Akitaya 1974). Ice will sublime from the top of a grain (at the bottom of a pore) and the water vapor will be deposited as ice on the bottom of a slightly colder grain above (at the top of the pore).

There obviously are numerous interacting processes and conditions governing snow metamorphism, but in general snow has been studied by examining these processes independently. The snow cover is a fine grained granular or porous geologic material with an ice matrix and interstitial pores filled with water vapor and air. The development discussed here is an attempt to initiate a more unified theory for snow, using a continuum theory of multiphase mixtures. The approach of the theory, while in many ways still in a developmental stage is well-suited to this application.

To begin the discussion on mixtures, consider a continuous body which is composed of a number of materials, called constituents, which are all intermixed. Each of the constituents is itself considered to be continuous and the total collection of these constituents is termed the mixture. Early work dealing with mixture theory was primarily concerned with mixtures of gases. A basic assumption in this work is that every constituent of the mixture is considered to be simultaneously present in the same differential region of space. Mixtures satisfying this requirement are referred to as "miscible mixtures". One result of this assumption is that in order to properly retain the generality of the theory, it is expected that any state variables relevant to equations which describe the constitution of an individual material (i.e. the constitutive equations), should incorporate these same variables into all constitutive equations for all constituents of the mixture. The assumption of a mixture composed of constituents which are ideally miscible is the foundation for what is considered the Classical Theory of Mixtures.

It is readily apparent that, while the classical theory is pertinent to a number of applications, the requirement that an element of the mixture contain all of the constituents simultaneously is quite limiting to its scope of applications. Immediately, any mixture which contains immiscible constituents is necessarily excluded from a strict application of the classical theory. Examples of such mixtures are fluid and/or vapor flow in porous or granular material, particle suspensions in fluid or vapor and bubbly liquids.

Given the basis on which the theory of mixtures has developed, materials such as those just described do not even fit the classical definition of a mixture. However, adaptation to include these types of materials in the classification as a mixture have been successfully accomplished. These theories are to a large extent still in the theoretical development stage, and applications are as yet relatively few. Mixtures of this type are alternatively referred to as immiscible mixtures; mixtures with structure or microstructure, the implied structure being defined by the interfaces separating constituents; or multiphase mixtures, indicating that discrete phases are involved. In order to describe the multiphased material as a continuous mixture, but also retain the individual integrity of the constituents, regions defining a boundary-value problem must be very large relative to the size of a grain or pore space. An extremely important simplification results from treating the constituents as discrete: the constitutive relations for each constituent are considered independent of the other constituents in the mixture.

In order to address the problem of immiscible mixtures, one method is to include the volume fraction of each constituent as an additional kinematic variable. These are called the volume fraction theories. Bedford & Drumheller (1983) outline the development for a number of theories of this kind.

Goodman & Cowin (1972) developed a continuum theory for a granular or porous material assuming solid grains and vacancies in the interstitial pores. They define an additional kinematical variable called the volume distribution function, representing the portion of the material occupied by the grains. Since the volume distribution function and the motion are assumed to be kinematically independent, they must be governed by an appropriate number of balance equations. Each volume distribution function, therefore, requires an additional balance equation to those usually applied in continuum mechanics.

This concept was introduced for multiphase mixtures by Passman (1977) such that each constituent is represented by its volume fraction of the mixture, and the additional balance equation is included for each constituent as well as for the mixture. Nunziato & Walsh (1980) extended and refined the theory to include chemical reactions. The development presented here treats snow as a multiphase mixture including the mass interaction due to the phase change. This is accomplished by applying the equivalent theories of Nunziato & Walsh (1980) and Passman *et al.* (1984) to that specific problem. The approach utilized by them is outlined below.

KINEMATICS

Let $\mathbf{x}_a$ denote the current $\mathbf{X}_a$ and reference position vectors for a particle of the ath constituent and the constituent velocity is defined as

$${}^{\backprime}\mathbf{x}_a = \frac{\partial[\boldsymbol{\chi}_a(\mathbf{X}_a, t)]}{\partial t} = \mathbf{v}_a. \qquad [1]$$

The material density of each constituent, γ_a, is defined as the mass per unit volume of the material and the volume fraction of the ath constituent, ν_a represents that part per unit volume of the mixture occupied by the constituent, so $0 < \nu_a \leqslant 1$. The partial density of constituent a, ρ_a, is

$$\rho_a = \gamma_a \nu_a, \qquad [2]$$

where obviously $\rho_a < \gamma_a$ in the case of a true multiphase mixture, ρ is the bulk density for the mixture, defined by

$$\rho = \sum \rho_a; \qquad [3]$$

Σ indicates summation over all of the constituents which comprise the mixture. The mixture considered in this paper is assumed to be saturated (i.e. $\nu = 1$),

$$\sum \nu_a = \nu = 1, \qquad [4]$$

so $\dot{\nu} = 0$. The mixture velocity is defined in terms of the constituent velocities as

$$\rho \mathbf{v} = \sum \rho_a \mathbf{v}_a. \qquad [5]$$

The overdot represents a time derivative for the mixture, whereas the backward prime indicates time derivatives for the constituent. The diffusion velocity for a constituent, $\mathbf{u}_a$, measures velocity relative to that of the mixture,

$$\mathbf{u}_a = \mathbf{v}_a - \mathbf{v}. \qquad [6]$$

In addition to the balance equations for mass, linear momentum, angular momentum and energy, usually applied in continuum mechanics, this volume fraction theory for multiphase mixtures assumes an equation, called the balance of equilibrated force, to account for changes in the volume fraction. Balance equations are given for each constituent and for the mixture. The individual balance equation for each constituent is related to the other constituents through interaction terms representing an exchange between constituents. The balance equations used in this application for a saturated mixture are as follows (Passman *et al.* 1984):

$$c_a^+ = {}^{\backprime}\rho_a + \rho_a \operatorname{div} \mathbf{v}_a, \qquad \text{mass} \qquad [7]$$

$$\mathbf{m}_a^{+e} = \rho_a {}^{\backprime}\mathbf{v}_a - \operatorname{div} \mathbf{T}_a - \rho_a \mathbf{b}_a + c_a^+ \mathbf{v}_a - \pi \operatorname{grad} \nu_a, \qquad \text{linear momentum} \qquad [8]$$

$$\mathbf{M}_a^+ = \mathbf{T}_a - \mathbf{T}_a^{\mathrm{T}}, \qquad \text{angular momentum} \qquad [9]$$

$$\upsilon_a^{+e} = \rho_a {}^{\backprime}(k_a {}^{\backprime}\nu_a) - \operatorname{div} \mathbf{h}_a - \rho_a l_a + c_a^+ k_a {}^{\backprime}\nu_a + \pi, \qquad \text{equilibrated force} \qquad [10]$$

and

$$e_a^{+e} = c_a^+ \left(e_a - \frac{\mathbf{v}_a \cdot \mathbf{v}_a}{2} - \frac{k_a {}^{\backprime}\nu_a^2}{2} \right) + \mathbf{m}_a^{+e} \cdot \mathbf{v}_a + \upsilon_a^{+e} {}^{\backprime}\nu_a + \rho_a {}^{\backprime}e_a - \mathbf{T}_a \cdot \mathbf{L}_a$$

$$- \mathbf{h}_a \cdot (\boldsymbol{\nabla} {}^{\backprime}\nu_a) - \frac{\rho_a {}^{\backprime}k_a {}^{\backprime}\nu_a^2}{2} + \boldsymbol{\nabla} \cdot \mathbf{q}_a - \rho_a r_a; \qquad \text{energy} \qquad [11]$$

where c_a^+ is the mass interaction for the ath constituent, $\mathbf{m}_a^{+e}$ is the extra linear momentum interaction, $\mathbf{T}_a$ is the partial stress tensor, π is the interface pressure and $\mathbf{b}_a$ is the external body force acting on the constituent. $\mathbf{M}_a^+$ is the angular momentum interaction of the constituent. This form for the angular momentum implies that the partial stress for the constituent is not necessarily symmetric, unless $\mathbf{M}_a^+ = \mathbf{0}$.

Terminology used for the terms appearing in the balance of equilibrated force [10] reflect the similarity in form to the linear momentum balance equations [8]. Here, υ_a^{+e} represents the extra equilibrated force interaction, k_a is the equilibrated inertia, $\mathbf{h}_a$ is the equilibrated stress and l_a is the external equilibrated body force.

The energy equation [11] is also frequently referred to as the first law of thermodynamics. Here e_a^{+e} is the extra energy interaction of the ath constituent with the others, $\mathbf{q}_a$ is the constituent heat flux, r_a is the external heat supply for the constituent and e_a is the internal energy which represents all of the energy of the constituent exclusive of kinetic. $\mathbf{L}_a$ is the velocity gradient defined as $\mathbf{L}_a = \mathrm{grad}(\mathbf{v}_a)$.

Passman *et al.* (1984) use the terminology "extra" in the interaction terms for energy, momentum and equilibrated force to indicate the saturation constraint. The interactions postulated in the theory are considered to be representative of exchanges only among constituents, and in the unsaturated case will all be in balance with each other. In accordance with this, the interaction of all constituents sum to zero for the unsaturated condition, but the saturation constraint will alter the summation requirement in the case of the extra equilibrated force.

Summation of the constituent interactions:

$$\sum c_a^+ = 0, \qquad [12]$$

$$\sum \mathbf{m}_a^{+e} = \mathbf{0}, \qquad [13]$$

$$\sum \mathbf{M}_a^+ = \mathbf{0}, \qquad [14]$$

$$\sum \upsilon_a^{+e} = N\pi + \rho g \qquad [15]$$

and

$$\sum e_a^{+e} = 0, \qquad [16]$$

where N is the number of constituents and g is the equilibrated force supply.

Properties of the mixture are defined in terms of the properties of the constituents in such a way that the conservation principles for the mixture are the same as for a single continuum. Summing over all of the constituent balance equations will lead to the standard forms for the balance equations of the mixture when the following restrictions are imposed (Passman *et al.* 1984):

$$\rho \mathbf{b} = \sum \rho_a \mathbf{b}_a, \qquad [17]$$

$$\mathbf{T} - \rho \mathbf{v}\mathbf{v} = \sum (\mathbf{T}_a - \rho \mathbf{v}_a \mathbf{v}_a), \qquad [18]$$

$$\rho g = \sum \rho_a g_a, \qquad [19]$$

$$\rho l = \sum \rho_a l_a, \qquad [20]$$

$$\rho k \dot{\nu} = \sum \rho_a k_a \grave{\nu}_a, \qquad [21]$$

$$\mathbf{h} - \rho k \dot{\nu} \mathbf{v} = \sum (\mathbf{h}_a - \rho_a k_a \grave{\nu}_a \mathbf{v}_a), \qquad [22]$$

$$\rho(e + [\tfrac{1}{2}]\mathbf{v} \cdot \mathbf{v} + [\tfrac{1}{2}]k\dot{\nu}^2) = \sum \rho_a(e_a + \tfrac{1}{2}\mathbf{v}_a \cdot \mathbf{v}_a + [\tfrac{1}{2}]k_a \dot{\nu}_a^2), \qquad [23]$$

$$\mathbf{q} - \mathbf{T}^{\mathrm{T}}\mathbf{v} - \mathbf{h}\dot{\nu} - \rho(e + [\tfrac{1}{2}]\mathbf{v} \cdot \mathbf{v} + k\dot{\nu}^2)\mathbf{v} = \sum \mathbf{q}_a - \mathbf{T}_a^{\mathrm{T}}\mathbf{v}_a - \mathbf{h}_a \grave{\nu}_a - \rho_a(e_a + [\tfrac{1}{2}]\mathbf{v}_a \cdot \mathbf{v}_a + k_a \grave{\nu}_a^2)\mathbf{v}_a \qquad [24]$$

and

$$\rho(r + \mathbf{b} \cdot \mathbf{v} + l\dot{\nu}) = \rho_a(r_a + \mathbf{b}_a \cdot \mathbf{v}_a + l_a \grave{\nu}_a). \qquad [25]$$

The entropy inequality for saturated multiphase mixtures used by Passman *et al.* (1984) is

$$\sum\left[-\rho_a({}^{\backprime}\psi_a+\eta_a{}^{\backprime}\theta_a)+\mathbf{T}_a\cdot\mathbf{L}_a+\mathbf{h}_a\cdot\mathrm{grad}{}^{\backprime}\nu_a-\mathbf{q}_a{}^{\backprime}\nu.\frac{(\mathrm{grad}\,\theta_a)}{\theta_a}-\left(\upsilon_a^{+e}-\frac{\rho_a{}^{\backprime}k_a{}^{\backprime}\nu_a}{2}\right)^{\backprime}\nu_a\right.$$
$$\left.+e_a^{+e}-\mathbf{m}_a^{+e}\cdot\mathbf{v}_a-c_a^{+}\left(\psi_a-\frac{\mathbf{v}_a\cdot\mathbf{v}_a}{2}-\frac{k_a{}^{\backprime}\nu_a^2}{2}\right)\right]\Big/\theta_a\geqslant 0. \quad [26]$$

ψ_a is the Helmholtz free energy, defined as

$$\psi_a\equiv e_a-\theta_a\eta_a. \quad [27]$$

CONSTITUTIVE ASSUMPTIONS AND RESTRICTIONS

The initial constitutive assumptions chosen are those suggested by Nunziato & Walsh (1980) for multiphase mixtures with chemical reactions and diffusion:

$$(\psi_a,\eta_a,\mathbf{T}_a,\mathbf{h}_a,\mathbf{q}_a)=\mathscr{F}_a(\nu_a,\mathbf{w}_a,{}^{\backprime}\nu_a,\mathbf{u}_a,\theta_a,\mathbf{F}_a,\mathbf{g}_a,c_a), \quad [28]$$

$$(c_a^+,\upsilon_a^+,\mathbf{m}_a^+,\mathbf{M}_a^+,e_a^+)=\mathscr{G}_a(\nu\uparrow,\mathbf{w}\uparrow,{}^{\backprime}\nu\uparrow,\mathbf{u}\uparrow,\theta\uparrow,\mathbf{F}\uparrow,\mathbf{g}\uparrow,c\uparrow) \quad [29]$$

and

$$k_a=k_a(\nu_a), \quad [30]$$

where the subscript a, as usual, implies a dependence on that particular constituent, and ↑ indicates a dependence on all of the constituents. The gradients of the volume fraction and temperature are given as $\mathbf{w}_a=\mathrm{grad}\,\nu_a$ and $\mathbf{g}_a=\mathrm{grad}\,\theta_a$, $\mathbf{F}_a$ is the deformation gradient tensor, $\mathbf{F}_a=\nabla\chi_a(\mathbf{X}_a,t)$, and the quantities c_a and c are mass concentration which is used as a measure of the extent of chemical reaction.

Using the above constitutive assumptions [28], substituting into [26] and utilizing the argument established by Coleman & Noll (1963), as in Nunziato & Walsh (1980) the following restrictions are implied:

$$\eta_a=-\frac{\partial\psi_a}{\partial\theta_a}, \quad [31]$$

$$\frac{\partial\psi_a}{\partial{}^{\backprime}\nu_a}=0, \quad [32]$$

$$\frac{\partial\psi_a}{\partial\mathbf{u}_a}=0, \quad [33]$$

$$\frac{\partial\psi_a}{\partial\mathbf{g}_a}=0, \quad [34]$$

$$\mathbf{T}_a=\rho_a\mathbf{F}_a\left(\frac{\partial\psi_a}{\partial\mathbf{F}_a}\right)-\rho_a\left(\frac{\partial\psi_a}{\partial\mathbf{w}_a}\right)\mathbf{w}_a \quad [35]$$

and

$$\mathbf{h}_a=\rho_a\frac{\partial\psi_a}{\partial\mathbf{w}_a}. \quad [36]$$

These restrictions reduce the allowed dependence of the constitutive variables and provide specific forms for constitutive relations for $\mathbf{T}_a$, η_a and $\mathbf{h}_a$.

An equilibrium state is attained when constituent temperatures are equal, constant and uniform, the velocities and mass interactions are identically zero, and the mass concentrations, deformation gradients and volume fractions are constant. In addition, strong equilibrium, requires that the chemical potentials for all of the constituents be equal (Nunziato & Walsh 1980). In particular at strong equilibrium, indicated by a superscript *, it may be shown that (Nunziato & Walsh 1980)

$$\{e_a^{+e}\}^* = 0, \tag{37}$$

$$\mathbf{q}_a^* = \mathbf{0}, \tag{38}$$

$$\mathbf{m}_a^{+e*} = \mathbf{0} \tag{39}$$

and

$$(\upsilon_a^{+e})^* = \left(-\rho_a \frac{\partial \psi_a}{\partial v_a}\right)^*. \tag{40}$$

This last relation [40] may add some physical interpretation to the equilibrated force interaction. It is the negative of the form which Baer *et al.* (1985) termed the configuration pressure to represent the contact forces between grains, and Passman *et al.* (1984) state that it represents the elastic response of the particle assembly to compression.

ASSUMPTIONS FOR SNOW

This adaptation of the theory of mixtures considers snow as a porous material of two constituents, a solid constituent for the ice phase, and a single vapor constituent to describe the air and water vapor which fill the pores. The subscript notation used for the ice and vapor is i and v, respectively. Both constituents are considered isotropic. The ice is assumed incompressible in the state to be examined, indicating a constant material density for the ice, γ_i, but the vapor density, γ_v, can change.

Complete and proper interpretation of the equilibrated force equations is still developing, with much of this interpretation coming from the granular theory of Goodman & Cowin (1972), upon which the present theory for mixtures is based. In this development (Nunziato & Walsh 1980) the equilibrated stress is related to the variation of the Helmholtz free energy with the volume fraction gradient [36]. Nunziato & Cowen [17], dealing with an incompressible matrix in granular material, state that $\mathbf{h}$ can only be important if the void distribution is grossly nonuniform or if the initial void volume is large; and for fluid suspensions, Passman *et al.* (1984) assert that, $\mathbf{h}_a$ is not significant except for highly concentrated nonhomogeneous suspensions. Based on this foregoing work, the equilibrated stress term will be set to zero,

$$\mathbf{h}_a = \mathbf{0}. \tag{41}$$

Assuming very slow velocities are involved in snow metamorphism and with an incompressible matrix material the microstructural inertia effects are assumed to be insignificant and the equilibrated inertia is negligible,

$$k_a = 0. \tag{42}$$

The equilibrated force interaction is in some manner related to the pressure in the void and the material properties of the matrix (Nunziato & Walsh 1980). In the case of snow the ice is self-supporting with the vapor adding little structural support and since the curvature effects of the grains will be considered to some degree by the interface pressure, the equilibrated force supply is ignored in the formulation:

$$g_a = 0. \tag{43}$$

Assumptions [41] and [42] reduce the balance of extra equilibrated force [10] to

$$\upsilon_a^{+e} = -\rho_a l_a + \pi. \tag{44}$$

The external equilibrated body force for the mixture, l, is related to an externally controlled body force or pore pressure (Jenkins 1975). In the present development the extra equilibrated force gives the interface pressure between the constituents which is necessary for the phases to remain in contact, minus the term involving the external equilibrated body force.

Assuming the Helmholtz free energy, ψ_a, is isotropic implies that $\mathbf{T}_a$ is symmetric, so the angular momentum for the constituents are identically zero,

$$\mathbf{M}_a^+ = \mathbf{0}. \qquad [45]$$

HEAT FLUX AND INTERACTION TERMS

Written with restrictions [31]–[36], equations [12], [13] and [16], and the fact that the time rate of change of the volume fractions are negatives of each other, the inequality may be explicitly written for the two constituents in the form

$$-\frac{\mathbf{q}_i \cdot \mathbf{g}_i}{\theta_i^2} - \frac{\mathbf{q}_v \cdot \mathbf{g}_v}{\theta_v^2} - \left\{ \frac{\left(\upsilon_i^{+e} + \rho_i \dfrac{\partial \psi_i}{\partial \nu_i} \right)}{\theta_i} - \frac{\left(\upsilon_v^{+e} + \rho_v \dfrac{\partial \psi_v}{\partial \nu_v} \right)}{\theta_v} \right\}' \nu_i$$

$$+ \left[\left(\frac{1}{\theta_i} \right) - \left(\frac{1}{\theta_v} \right) \right] e_i^{+e} - \left\{ \left(\frac{\mathbf{v}_i}{\theta_i} \right) - \left(\frac{\mathbf{v}_v}{\theta_v} \right) \right\} \mathbf{m}_i^{+e}$$

$$- \left\{ \frac{\left(\mu_i - \dfrac{\mathbf{v}_i \cdot \mathbf{v}_i}{2} \right)}{\theta_i} - \frac{\left(\mu_v - \dfrac{\mathbf{v}_v \cdot \mathbf{v}_v}{2} \right)}{\theta_v} \right\} c_i^+ \geqslant 0. \qquad [46]$$

Forms for the remaining constitutive equations are arrived at by insuring that the second law [46] is satisfied. A sufficient, although not a necessary, condition that the inequality is not violated is that each of the individual terms is positive semi-definite. Assuming positive coefficients the heat fluxes become

$$\mathbf{q}_i = -q_{i_0} \mathbf{g}_i \qquad [47]$$

and

$$\mathbf{q}_v = -q_{v_0} \mathbf{g}_v, \qquad [48]$$

so that the heat flux is proportional to the temperature gradient, and the proportionality coefficient, q_{a_i}, is the thermal conductivity.

An appropriate equation describing the extra energy interaction is

$$e_i^{+e} = -e_v^{+e} = e_{i_0}^{+e}(\theta_v - \theta_i). \qquad [49]$$

This form is analogous to Newton's law of cooling, it will govern the rate and direction of the energy interaction, determined by the constituent temperatures. $e_{i_0}^{+e}$ is a positive-valued energy interaction or heat transfer coefficient.

The extra interaction of linear momentum has the following suitable form to satisfy the requirement of [46]:

$$\mathbf{m}_i^{+e} = -\mathbf{m}_v^{+e} = m_{i_0}^{+e} \left\{ \left(\frac{\mathbf{v}_v}{\theta_v} \right) - \left(\frac{\mathbf{v}_i}{\theta_i} \right) \right\}, \qquad [50]$$

where $m_{i_0}^{+e}$ is a positive-valued drag coefficient. Mass interaction as implied by the inequality [46] is

$$c_i^+ = -c_v^+ = c_{i_0}^+ \left\{ \left(\frac{\mu_v}{\theta_v} - \frac{\mu_i}{\theta_i} \right) + \left(\frac{1}{2} \right) \left(\frac{\mathbf{v}_i \cdot \mathbf{v}_i}{\theta_i} - \frac{\mathbf{v}_v \cdot \mathbf{v}_v}{\theta_v} \right) \right\}. \qquad [51]$$

This form for the mass interaction is determined by chemical potentials, kinetic energy and temperature difference effects.

In addition to satisfying the second law [46], the heat flux [47] and [48], extra energy interaction [49], extra momentum interaction [50] and mass interaction [51] all go to zero at strong equilibrium, as required. The equilibrated inertia should satisfy

$$K`\nu_i = -\left\{ \frac{\left(\upsilon_i^{+e} + \rho_i \dfrac{\partial \psi_i}{\partial \nu_i} \right)}{\theta_i} - \frac{\left(\upsilon_v^{+e} + \rho_v \dfrac{\partial \psi_v}{\partial \nu_v} \right)}{\theta_v} \right\}, \qquad [52]$$

where K is some positive value. A satisfactory form for the extra equilibrated force interaction, which is also the balance equation for the equilibrated force with assumptions [41] and [42], is for the ice,

$$\upsilon_{\mathrm{i}}^{+\mathrm{e}} = \frac{\left\{\left(\pi + \rho_{\mathrm{v}}\frac{\partial\psi_{\mathrm{v}}}{\partial\nu_{\mathrm{v}}}\right)\theta_{\mathrm{i}} - K`\nu_{\mathrm{i}}\theta_{\mathrm{i}}\theta_{\mathrm{v}} - \left(\rho_{\mathrm{i}}\frac{\partial\psi_{\mathrm{i}}}{\partial\nu_{\mathrm{i}}} + \pi\right)\theta_{\mathrm{v}}\right\}}{\{\theta_{\mathrm{v}} + \theta_{\mathrm{i}}\} + \pi}; \qquad [53]$$

and for the vapor,

$$\upsilon_{\mathrm{v}}^{+\mathrm{e}} = \frac{-\left\{\left(\pi + \rho_{\mathrm{v}}\frac{\partial\psi_{\mathrm{v}}}{\partial\nu_{\mathrm{v}}}\right)\theta_{\mathrm{i}} - K`\nu_{\mathrm{i}}\theta_{\mathrm{i}}\theta_{\mathrm{v}} - \left(\rho_{\mathrm{i}}\frac{\partial\psi_{\mathrm{i}}}{\partial\nu_{\mathrm{i}}} + \pi\right)\theta_{\mathrm{v}}\right\}}{\{\theta_{\mathrm{v}} + \theta_{\mathrm{i}}\} + \pi}. \qquad [54]$$

HELMHOLTZ FREE ENERGIES AND ASSOCIATED TERMS

In the formulation the snow is considered as a fully symmetric material. This isotropy indicates that a static density preserving alteration of the reference configuration will not alter the material response. The manner in which the assumed constitutive variables enter the formulation should satisfy the material symmetry group. Based on restrictions [32]–[34], assuming [41] and following the work of Cross (1973) dealing with mixtures of fluids and isotropic solids, suitable functions for the chosen constitutive variables are

$$(\psi_a, \eta_a, \mathbf{T}_a) = \not{f}(\nu_a, \theta_a, \mathbf{E}_a, \rho_a), \qquad [55]$$

where

$$\mathbf{E}_{\mathrm{i}} = (\tfrac{1}{2})(\mathbf{F}_{\mathrm{i}}^{\mathrm{T}}\mathbf{F}_{\mathrm{i}} - \mathbf{1}); \qquad [56]$$

$\mathbf{E}_{\mathrm{i}}$ is the Lagrangian strain tensor.

Constitutive equations may depend on these variables without violating any principles, however it does not imply that they must all be included. Dependence on variables which affect one of the constituents is not necessarily appropriate to describing all constituents. This is apparent through consideration of the principle of phase separation for multiphase mixtures, which takes into account the discrete nature of the individual constituents.

The vapor constituent is not considered to be affected by the deformation gradient and therefore the elastic strain $\mathbf{E}_{\mathrm{i}}$ of the ice constituent, so this term is not included in the constitutive assumptions for the vapor. The ice constituent is taken as incompressible, therefore including both the volume fraction and the dispersed density as variables for the ice is redundant. The constitutive variable which will be used here is the dispersed density, ρ_{i}.

The Helmholtz free energy will determine forms for the entropy [31], partial stress [35] and the equilibrated stress [36]. Consequently, proper determination of the Helmholtz function is crucial to the entire development. The form for the Helmholtz free energy for both constituents are approximated here as second-order Taylor series expansions. The Helmholtz free energy expansion for the ice is

$$\begin{aligned}\psi_{\mathrm{i}} = {} & [\psi_{\mathrm{i}_1}(\mathrm{tr}\,\mathbf{E}_{\mathrm{i}}) + \psi_{\mathrm{i}_2}(\theta_{\mathrm{i}} - \theta_{\mathrm{R}}) + \psi_{\mathrm{i}_3}(\rho_{\mathrm{i}} - \rho_{\mathrm{iR}}) + (\tfrac{1}{2})[\psi_{\mathrm{i}_4}[\mathrm{tr}(\mathbf{E}_{\mathrm{i}})]^2 + 2\psi_{\mathrm{i}_5}\,\mathrm{tr}(\mathbf{E}_{\mathrm{i}})^2 \\ & + 2\psi_{\mathrm{i}_6}(\theta_{\mathrm{i}} - \theta_{\mathrm{R}})\,\mathrm{tr}(\mathbf{E}_{\mathrm{i}}) + \psi_{\mathrm{i}_7}(\theta_{\mathrm{i}} - \theta_{\mathrm{R}})^2 + 2\psi_{\mathrm{i}_8}(\theta_{\mathrm{i}} - \theta_{\mathrm{R}})(\rho_{\mathrm{i}} - \rho_{\mathrm{iR}}) + 2\psi_{\mathrm{i}_9}(\rho_{\mathrm{i}} - \rho_{\mathrm{iR}})\,\mathrm{tr}(\mathbf{E}_{\mathrm{i}}) \\ & + \psi_{\mathrm{i}_{10}}(\rho_{\mathrm{i}} - \rho_{\mathrm{iR}})^2] + \psi_{\mathrm{iR}};\end{aligned} \qquad [57]$$

and for the vapor,

$$\begin{aligned}\psi_{\mathrm{v}} = {} & \psi_{\mathrm{v}_1}(\nu_{\mathrm{v}} - \nu_{\mathrm{vR}}) + \psi_{\mathrm{v}_2}(\theta_{\mathrm{v}} - \theta_{\mathrm{R}}) + \psi_{\mathrm{v}_3}(\rho_{\mathrm{v}} - \rho_{\mathrm{vR}}) + (\tfrac{1}{2})[\psi_{\mathrm{v}_4}(\nu_{\mathrm{v}} - \nu_{\mathrm{vR}})^2 \\ & + 2\psi_{\mathrm{v}_5}(\theta_{\mathrm{v}} - \theta_{\mathrm{R}})(\nu_{\mathrm{v}} - \nu_{\mathrm{vR}}) + \psi_{\mathrm{v}_6}(\theta_{\mathrm{v}} - \theta_{\mathrm{R}})^2 + 2\psi_{\mathrm{v}_7}(\theta_{\mathrm{v}} - \theta_{\mathrm{R}})(\rho_{\mathrm{v}} - \rho_{\mathrm{vR}}) \\ & + 2\psi_{\mathrm{v}_8}(\rho_{\mathrm{v}} - \rho_{\mathrm{vR}})(\nu_{\mathrm{v}} - \nu_{\mathrm{vR}}) + \psi_{\mathrm{v}_9}(\rho_{\mathrm{v}} - \rho_{\mathrm{vR}})^2] + \psi_{\mathrm{vR}}.\end{aligned} \qquad [58]$$

Without loss of generality the reference temperature θ_{R} will be taken as the same for both constituents.

The form for the partial stress of the ice [35] which has been developed, may be reduced through application of the chain rule and the fact that the equilibrated stress is not considered significant [41],

$$\mathbf{T}_i = \rho_i \mathbf{F}_i \left\{ \left(\frac{\partial \psi_i}{\partial \mathbf{E}_i} \right) \mathbf{F}_i^T \right\}.$$

Assuming only small strains are imposed, the deformation gradient is approximated by $\mathbf{F}_i \approx \mathbf{1}$. This small strain assumption implies that the Cauchy and the first and second Piola–Kirchhoff stresses are equivalent, so there is no difficulty posed in dealing with the Lagrangian strain tensor. The stress is then given by

$$\begin{aligned} \mathbf{T}_i &= \rho_i \left(\frac{\partial \psi_i}{\partial \mathbf{E}_i} \right) \\ &= \rho_i \{ \psi_{i_1} \mathbf{1} + \psi_{i_4} \operatorname{tr}(\mathbf{E}_i) \mathbf{1} + 2\psi_{i_5} \mathbf{E}_i + \psi_{i_6} (\theta_i - \theta_R) \mathbf{1} + \psi_{i_9} (\rho_i - \rho_{iR}) \mathbf{1} \}. \end{aligned} \qquad [59]$$

Taking the strain to be zero in the reference state leaves

$$\rho_i \psi_{i_1} \mathbf{1} = \mathbf{T}_{iR}$$

as the reference stress of the ice.

Stress of this form [59] is similar to the Duhamel–Neumann law (Sokolnikoff 1956) for a thermoelastic material, but the Duhamel–Neumann law does not include the reference stress and the term involving the partial density. This comparison offers a means to determine several of the coefficients. Letting λ and G represent the Lamé constants and α the coefficient of linear expansion, comparison of [59] with the Duhamel–Neumann law yields

$$\rho_i \psi_{i_4} = \lambda,$$

$$\rho_i \psi_{i_5} = G$$

and

$$\psi_{i_6} = -\alpha(3\lambda + 2G).$$

G is also known as the modulus of rigidity or shear modulus. These Lamé constants are related to Young's modulus, Y and Poisson's ratio Φ, as

$$\lambda = \frac{\Phi Y}{[(1+\Phi)(1-2\Phi)]}$$

and

$$G = \frac{Y}{2(1+\Phi)}.$$

The entropy of the ice, by [31] and [57], is

$$\eta_i = -[\psi_{i_2} + \psi_{i_6} \operatorname{tr}(\mathbf{E}_i) + \psi_{i_7} (\theta_i - \theta_R) + \psi_{i_8} (\rho_i - \rho_{iR})]. \qquad [60]$$

This then gives the reference entropy,

$$-\psi_{i_2} = \eta_{iR}.$$

At equilibrium, by [40] and [57], the equilibrated force interaction for the ice is given by

$$(\upsilon_i^{+e})^* = [-\rho_i \gamma_i \{ \psi_{i_3} + \psi_{i_8} (\theta_i - \theta_R) + \psi_{i_9} \operatorname{tr}(\mathbf{E}_i) + \psi_{i_{10}} (\rho_i - \rho_{iR}) \}]^*,$$

so that the reference equilibrated force interaction is

$$-\rho_{iR} \gamma_i \psi_{i_3} = \upsilon_{iR}^{+e}.$$

This will yield

$$\psi_{i_3} = \frac{-(2\pi - \gamma_v R \theta_R)}{(\rho_{iR} \gamma_i)}, \qquad [61]$$

which will be shown when the reference equilibrated force for the vapor is determined.

Using [27] the internal energy may be written as

$$\begin{aligned} e_i = {} & [\psi_{\mathrm{i}_1}(\mathrm{tr}\,\mathbf{E}_\mathrm{i}) - \psi_{\mathrm{i}_2}\theta_\mathrm{R} + \psi_{\mathrm{i}_3}(\rho_\mathrm{i} - \rho_{\mathrm{iR}})] + (\tfrac{1}{2})[\psi_{\mathrm{i}_4}[\mathrm{tr}(\mathbf{E}_\mathrm{i})]^2 + 2\psi_{\mathrm{i}_5}\,\mathrm{tr}(\mathbf{E}_\mathrm{i})^2 \\ & - 2\psi_{\mathrm{i}_6}\theta_\mathrm{R}\,\mathrm{tr}(\mathbf{E}_\mathrm{i}) - \psi_{\mathrm{i}_7}(\theta_\mathrm{i}^2 - \theta_\mathrm{R}^2) - 2\psi_{\mathrm{i}_8}\theta_\mathrm{R}(\rho_\mathrm{i} - \rho_{\mathrm{iR}}) \\ & + 2\psi_{\mathrm{i}_9}(\rho_\mathrm{i} - \rho_{\mathrm{iR}})\,\mathrm{tr}(\mathbf{E}_\mathrm{i}) + \psi_{\mathrm{i}_{10}}(\rho_\mathrm{i} - \rho_{\mathrm{iR}})^2] + \psi_{\mathrm{iR}}. \end{aligned}$$

Following the example of Passman & Batra (1984), ${}^{\backprime}e_\mathrm{i}$ is given by

$$\begin{aligned} {}^{\backprime}e_\mathrm{i} & = \mathrm{tr}\left[\left(\frac{\partial e_\mathrm{i}}{\partial \mathbf{E}_\mathrm{i}}\right){}^{\backprime}\mathbf{E}_\mathrm{i}\right] + \left(\frac{\partial e_\mathrm{i}}{\partial \theta_\mathrm{i}}\right){}^{\backprime}\theta_\mathrm{i} + \left(\frac{\partial e_\mathrm{i}}{\partial \rho_\mathrm{i}}\right){}^{\backprime}\rho_\mathrm{i} \\ & = \mathrm{tr}(\mathbf{e}_{\mathrm{i}_1}{}^{\backprime}\mathbf{E}_\mathrm{i}) + e_{\mathrm{i}_2}{}^{\backprime}\theta_\mathrm{i} + e_{i_3}{}^{\backprime}\rho_\mathrm{i}, \end{aligned} \qquad [62]$$

where, as an exception to the usual notation, the lower case boldface $\mathbf{e}$ represents a tensor.

The coefficient associated with the time derivative of the temperature, e_{i_2}, is related to the specific heat of ice at constant volume. The other coefficients in [62] represent the latent heats as a result of strain and partial density. This will allow some additional insight into the coefficients in the Helmholtz equation. The latent heat of the ice with respect to the strain is given by

$$\mathbf{e}_{\mathrm{i}_1} = [\psi_{\mathrm{i}_1} + \psi_{\mathrm{i}_4}[\mathrm{tr}(\mathbf{E}_\mathrm{i})] - \psi_{\mathrm{i}_6}\theta_\mathrm{R} + \psi_{\mathrm{i}_9}(\rho_\mathrm{i} - \rho_{\mathrm{iR}})]\mathbf{1} + 2\psi_{\mathrm{i}_5}\mathbf{E}_\mathrm{i}.$$

The specific heat of the ice is

$$e_{\mathrm{i}_2} = -\psi_{\mathrm{i}_7}\theta_\mathrm{i}.$$

The latent heat due to a change in dispersed density is

$$e_{\mathrm{i}_3} = [\psi_{\mathrm{i}_3} - \psi_{\mathrm{i}_8}\theta_\mathrm{R} + \psi_{\mathrm{i}_9}\,\mathrm{tr}(\mathbf{E}_\mathrm{i}) + \psi_{\mathrm{i}_{10}}(\rho_\mathrm{i} - \rho_{\mathrm{iR}})].$$

The chemical potential may be written in terms of the Helmholtz free energy (Nunziato & Walsh 1980) and expressed for the ice using the modified constitutive assumptions by [57] as

$$\begin{aligned} \mu_\mathrm{i} & = \frac{\partial(\rho_\mathrm{i}\psi_\mathrm{i})}{\partial\rho_\mathrm{i}} \\ & = \psi_{\mathrm{i}_1}(\mathrm{tr}\,\mathbf{E}_\mathrm{i}) + \psi_{\mathrm{i}_2}(\theta_\mathrm{i} - \theta_\mathrm{R}) + \psi_{\mathrm{i}_3}(2\rho_\mathrm{i} - \rho_{\mathrm{iR}}) + (\tfrac{1}{2})[\psi_{\mathrm{i}_4}[\mathrm{tr}(\mathbf{E}_\mathrm{i})]^2 + 2\psi_{\mathrm{i}_5}\,\mathrm{tr}(\mathbf{E}_\mathrm{i})^2 \\ & \quad + 2\psi_{\mathrm{i}_6}(\theta_\mathrm{i} - \theta_\mathrm{R})\,\mathrm{tr}(\mathbf{E}_\mathrm{i}) + \psi_{\mathrm{i}_7}(\theta_\mathrm{i} - \theta_\mathrm{R})^2 + 2\psi_{\mathrm{i}_8}(\theta_\mathrm{i} - \psi_\mathrm{R})(2\rho_\mathrm{i} - \rho_{\mathrm{iR}}) \\ & \quad + 2\psi_{\mathrm{i}_9}(2\rho_\mathrm{i} - \rho_{\mathrm{iR}})\,\mathrm{tr}(\mathbf{E}_\mathrm{i}) + \psi_{\mathrm{i}_{10}}(3\rho_\mathrm{i}^2 - 4\rho_\mathrm{i}\rho_{\mathrm{iR}} + \rho_{\mathrm{iR}}^2)] + \psi_{\mathrm{iR}}. \end{aligned} \qquad [63]$$

The reference Helmholtz free energy is determined by assuming it to yield a zero chemical potential at reference,

$$\psi_{\mathrm{i}_3}\rho_{\mathrm{iR}} = -\psi_{\mathrm{iR}}.$$

The effect of $\psi_{\mathrm{i}_1}(\mathrm{tr}\,\mathbf{E})$ and $\psi_{\mathrm{i}_9}(2\rho_\mathrm{i} - \rho_{\mathrm{iR}})\,\mathrm{tr}(\mathbf{E}_\mathrm{i})$ on the chemical potential is unknown, so for simplification it is assumed that when the partial density is equal to the reference value, these terms will cancel in the chemical potential equation, thus,

$$\psi_{\mathrm{i}_9} = -\frac{\psi_{\mathrm{i}_1}}{\rho_{\mathrm{iR}}}.$$

The Helmholtz free energy for the vapor is assumed to be an ideal gas as represented by the form, for example, in Sears & Salinger (1975),

$$\begin{aligned} \psi_\mathrm{v} & = C(\theta_\mathrm{v} - \theta_\mathrm{R}) - C\theta_\mathrm{v}\ln\left[\frac{\theta_\mathrm{v}}{\theta_\mathrm{R}}\right] - \mathbf{R}\theta_\mathrm{v}\left(\ln\left[\frac{\gamma_{\mathrm{vR}}}{\gamma_\mathrm{v}}\right]\right) - \eta_{\mathrm{vR}}(\theta_\mathrm{v} - \theta_\mathrm{R}) + \psi_{\mathrm{v}_0} \\ & = C(\theta_\mathrm{v} - \theta_\mathrm{R}) - C\theta_\mathrm{v}[\ln\theta_\mathrm{v} - \ln\theta_\mathrm{R}] - \mathbf{R}\theta_\mathrm{v}\left(\ln\gamma_{\mathrm{vR}} + \ln\left[\frac{\nu_\mathrm{v}}{\rho_\mathrm{v}}\right]\right) - \eta_{\mathrm{vR}}(\theta_\mathrm{v} - \theta_\mathrm{R}) + \psi_{\mathrm{vR}}, \end{aligned} \qquad [64]$$

where C is the specific heat capacity at constant volume and R is the ideal gas constant. The coefficients for a Taylor series expansion of [64] may be written as

$$\begin{aligned}
\psi_{v_1} &= \left.\frac{\partial \psi_v}{\partial v_v}\right|_R = -\frac{R\theta_R}{v_{vR}} & \psi_{v_2} &= \left.\frac{\partial \psi_v}{\partial \theta_v}\right|_R = -\eta_{vR} \\
\psi_{v_3} &= \left.\frac{\partial \psi_v}{\partial \rho_v}\right|_R = \frac{R\theta_R}{\rho_{vR}} & \psi_{v_4} &= \left.\frac{\partial^2 \psi_v}{\partial v_v^2}\right|_R = \frac{R\theta_R}{v_{vR}^2} \\
\psi_{v_5} &= \left.\frac{\partial^2 \psi_v}{\partial \theta_v\,\partial v_v}\right|_R = -\frac{R}{v_{vR}} & \psi_{v_6} &= \left.\frac{\partial^2 \psi_v}{\partial \theta_v^2}\right|_R = \frac{-C}{\theta_R} \\
\psi_{v_7} &= \left.\frac{\partial^2 \psi_v}{\partial \theta_v\,\partial \rho_v}\right|_R = \frac{R}{\rho_{vR}} & \psi_{v_8} &= \left.\frac{\partial^2 \psi_v}{\partial \rho_v\,\partial v_v}\right|_R = 0
\end{aligned}$$

and

$$\psi_{v_9} = \left.\frac{\partial^2 \psi_v}{\partial \rho_v^2}\right|_R = \frac{-R\theta_R}{\rho_{vR}^2}. \qquad [65]$$

Substitution of these coefficients into [58] gives

$$\begin{aligned}
\psi_v = {} & -\left(\frac{R\theta_R}{v_{vR}}\right)(v_v - v_{vR}) - \eta_{vR}(\theta_v - \theta_R) + \left(\frac{R\theta_R}{\rho_{vR}}\right)(\rho_v - \rho_{vR}) \\
& + \left(\frac{1}{2}\right)\left[\left(\frac{R\theta_R}{v_{vR}^2}\right)(v_v - v_{vR})^2 - \left(\frac{2R}{v_{vR}}\right)(\theta_v - \theta_R)(v_v - v_{vR})\right. \\
& \left. - \left(\frac{C}{\theta_R}\right)(\theta_v - \theta_R)^2 + \left(\frac{2R}{\rho_{vR}}\right)(\theta_v - \theta_R)(\rho_v - \rho_{vR}) - \left(\frac{R\theta_R}{\rho_{vR}^2}\right)(\rho_v - \rho_{vR})^2\right] + \psi_{vR}.
\end{aligned} \qquad [66]$$

The objective form for the partial stress in the vapor, by Nunziato & Walsh (1980) and [41], is

$$\begin{aligned}
\mathbf{T}_v &= -\rho_v^2\left(\frac{\partial \psi_v}{\partial \rho_v}\right)\mathbf{1} \\
&= -\rho_v^2[\psi_{v_3} + \psi_{v_7}(\theta_v - \theta_R) + \psi_{v_9}(\rho_v - \rho_{vR})]\mathbf{1}.
\end{aligned} \qquad [67]$$

In the reference state this yields a stress which is simply the negative partial pressure for an ideal gas,

$$\mathbf{T}_{vR} = -R\theta_R\rho_{vR}\mathbf{1}. \qquad [68]$$

By [40] and [58], at equilibrium the equilibrated force interaction for the vapor is

$$(\upsilon_v^{+e})^* = -\rho_v[\psi_{v_1} + \psi_{v_4}(v_v - v_{vR}) + \psi_{v_5}(\theta_v - \theta_R)]. \qquad [69]$$

Examination of this at the reference state, gives the reference extra equilibrated force interaction,

$$(\upsilon_{vR}^{+e})^* = \gamma_v R\theta_R,$$

which is the pressure for an ideal gas.

A slight retrogression at this point is helpful in ascertaining an appropriate value for the reference equilibrated force of the ice. With assumption [43], by [19], [15] reduces to

$$\sum \upsilon_a^{+e} = N\pi,$$

then

$$(\upsilon_{iR}^{+e})^* = 2\pi_R^* - \gamma_v R\theta_R \qquad \text{and} \qquad \psi_{i_3} = \frac{-(2\pi_R^* - \gamma_v R\theta_R)}{(\rho_{iR}\gamma_i)},$$

as stated previously [61]. The vapor entropy by [31] and [58] is

$$\eta_v = -[\psi_{v_2} + \psi_{v_5}(v_v - v_{vR}) + \psi_{v_6}(\theta_v - \theta_R) + \psi_{v_7}(\rho_v - \rho_{vR})].$$

So, using [27], the internal energy may be written as

$$e_v = \psi_{v_1}(\nu_v - \nu_{vR}) - \psi_{v_2}\theta_R + \psi_{v_3}(\rho_v - \rho_{vR}) + (\tfrac{1}{2})[\psi_{v_4}(\nu_v - \nu_{vR})^2 - 2\psi_{v_5}\theta_R(\nu_v - \nu_{vR}) - \psi_{v_6}(\theta_v^2 - \theta_R^2) - 2\psi_{v_7}\theta_R(\rho_v - \rho_{vR}) + \psi_{v_9}(\rho_v - \rho_{vR})^2] + \psi_{vR}. \quad [70]$$

Using a development similar to that for the ice [62], the time rate of change for the internal energy of the vapor is

$${}'e_v = e_{v_1}{}'\nu_v + e_{v_2}{}'\theta_v + e_{v_3}{}'\rho_v. \quad [71]$$

The latent heat due to a change in the volume fraction is,

$$e_{v_1} = \frac{\partial e_v}{\partial \nu_v} = \psi_{v_4}(\nu_v - \nu_{vR}).$$

The specific heat of the vapor in [71] is given by

$$e_{v_2} = \frac{\partial e_v}{\partial \theta_v} = -\psi_{v_6}\theta_v.$$

At the reference state this yields the specific heat, as it should, $e_{v_2} = C$. The latent heat with respect to the partial density of the vapor in [71] is

$$e_{v_3} = \frac{\partial e_v}{\partial \rho_v} = \psi_{v_3} - \psi_{v_7}\theta_R + \psi_{v_9}(\rho_v - \rho_{vR}).$$

The chemical potential of the vapor using the final constitutive variables is

$$\begin{aligned}\mu_v &= \frac{\partial(\rho_v\psi_v)}{\partial \rho_v}\\ &= \psi_{v_1}(\nu_v - \nu_{vR}) + \psi_{v_2}(\theta_v - \theta_R) + \psi_{v_3}(2\rho_v - \rho_{vR}) + (\tfrac{1}{2})[\psi_{v_4}(\nu_v - \nu_{vR})^2\\ &\quad + 2\psi_{v_5}(\theta_v - \theta_R)(\nu_v - \nu_{vR}) + \psi_{v_6}(\theta_v - \theta_R)^2 + 2\psi_{v_7}(\theta_v - \theta_R)(2\rho_v - \rho_{vR})\\ &\quad + 2\psi_{v_8}(2\rho_v - \rho_{vR})(\nu_v - \nu_{vR}) + \psi_{v_9}(3\rho_v^2 - 4\rho_v\rho_{vR} + \rho_{vR}^2)] + \psi_{vR}. \quad [72]\end{aligned}$$

As for the ice, the reference Helmholtz free energy is determined in this development by assuming it is valued such that it will yield a zero chemical potential at reference. This requires the reference Helmholtz free energy to be

$$\psi_{vR} = -\psi_{v_3}\rho_{vR}.$$

For equilibrium, the temperatures of the two constituents are the same, $\theta_v = \theta_i = \theta$, and the chemical potentials must be equal, so

$$\begin{aligned}&[\psi_{i_1}(\mathrm{tr}\,\mathbf{E}_i) + \psi_{i_2}(\theta - \theta_R) + \psi_{i_3}(2\rho_i - \rho_{iR})] + (\tfrac{1}{2})[\psi_{i_4}[\mathrm{tr}(\mathbf{E}_i)]^2 + 2\psi_{i_5}\,\mathrm{tr}(\mathbf{E}_i)^2\\ &\quad + 2\psi_{i_6}(\theta - \theta_R)\,\mathrm{tr}(\mathbf{E}_i) + \psi_{i_7}(\theta - \theta_R)^2 + 2\psi_{i_8}(\theta - \theta_R)(2\rho_i - \rho_{iR}) + 2\psi_{i_9}(2\rho_i - \rho_{iR})\mathrm{tr}(\mathbf{E}_i)\\ &\quad + \psi_{i_{10}}(3\rho_i^2 - 4\rho_i\rho_{iR} + \rho_{iR}^2)] + \psi_{iR}\\ &= \psi_{v_1}(\nu_v - \nu_{vR}) + \psi_{v_2}(\theta - \theta_R) + \psi_{v_3}(2\rho_v - \rho_{vR}) + (\tfrac{1}{2})[\psi_{v_4}(\nu_v - \nu_{vR})^2 + 2\psi_{v_5}(\theta - \theta_R)(\nu_v - \nu_{vR})\\ &\quad + \psi_{v_6}(\theta - \theta_R)^2 + 2\psi_{v_7}(\theta - \theta_R)(2\rho_v - \rho_{vR}) + 2\psi_{v_8}(2\rho_v - \rho_{vR})(\nu_v - \nu_{vR})\\ &\quad + \psi_{v_9}(3\rho_v^2 - 4\rho_v\rho_{vR} + \rho_{vR}^2)] + \psi_{vR}.\end{aligned}$$

At this point, ψ_{i_8} and $\psi_{i_{10}}$ are still undefined. The necessity of equivalence of the chemical potentials at equilibrium suggests a means to ascertain possible values for these terms. The terms are examined in the reference state for all variables except the temperature, since this should be the dominant term indicating the difference in chemical potential. This is an artificial means to determine the values, but, the reference conditions in the solution will be chosen as the initial values for the variables, so that, except for the temperature these values will not stray very far from the reference values for the time duration and conditions to be considered. First, $\psi_{i_{10}}$, is arbitrarily set to zero since an appropriate value for it is not known, and $\psi_{i_{10}}(3\rho_i^2 - 4\rho_i\rho_{iR} + \rho_{iR}^2)$ will not contribute appreciably as long as the partial density of the ice does not vary far from the reference. A value for ψ_{i_8} is determined by equating coefficients of similar variables. Although this forces a dependence of the ice coefficient on the vapor constituent, choosing the value at the reference state fixes it as constant, and it is assumed that the resulting value would be the appropriate one for this ice coefficient, independent of the vapor.

Examining everything in the reference state except temperature and collecting the remaining temperature related terms from the chemical potential [63] and [72] at equilibrium,

$$(\psi_{i_2} + \psi_{i_8}\rho_{iR})(\theta - \theta_R) + \psi_{i_7}(\theta - \theta_R)^2 = (\psi_{v_2} + \psi_{v_7}\rho_{vR})(\theta - \theta_R) + \psi_{v_6}(\theta - \theta_R)^2,$$

so that by equating coefficients, ψ_{i_8} can be determined in terms of known quantities,

$$\psi_{i_8} = \frac{(\psi_{v_2} - \psi_{i_2} + \psi_{v_7}\rho_{v_0})}{\rho_{iR}},$$

but another implication is that

$$\psi_{i_7} = \psi_{v_6}.$$

This last result requires that the terms related to specific heat for the ice and vapor must be equal in order to satisfy the requirement that the chemical potentials are equivalent at equilibrium, which is appropriate for ice and water vapor.

All of these specific constitutive equations which have been developed, with the exception of the extra momentum interaction, are material frame indifferent. It is argued here that the nonobjectivity of the constitutive form for the extra momentum interaction is not inappropriate, since it enters the theory through a fundamental law of dynamics, the equation of motion (balance of linear momentum equation), which itself is not material frame indifferent. However, as a side point, if the temperatures are equal, the velocity difference term which results, is objective.

ONE-DIMENSIONAL SOLUTION

The value of the interface pressure, π, the pressure necessary in a saturated mixture for the phases to remain in contact, is assumed to be approximated by the vapor pressure over a surface at equilibrium. The equilibrium vapor pressure over an ice grain will vary with temperature, θ, and the mean radius of curvature, ω (Colbeck 1980). The well-known Clausius–Clapeyron and Kelvin equations are used in a combined form to give the equilibrium vapor pressure over a grain in terms of the desired variables (Adams & Brown 1982, 1983; Gubler 1985). Assuming the fixed reference temperature is the same as the reference temperature to be used in the Clausius–Clapeyron equation, the two equations may be combined:

$$P(\theta, \omega) = P_R \exp\left[\frac{2\sigma}{(\gamma_i R\theta_R\omega)}\right] \exp\left[\left(\frac{L}{R}\right)(\theta_R^{-1} - \theta^{-1})\right],$$

where P is the equilibrium vapor pressure over the surface, L is the latent heat of sublimation and σ is the interfacial energy.

The leading coefficient involved in the mass interaction equation, $c_{i_0}^+$, is assumed to be proportional to P as well, since metamorphic processes are influenced by these same variables. Although the solution presented assumes uniform spheres, the inclusion of this type of dependence into the interaction terms indicates a means by which to incorporate microstructure. The magnitude of the proportionality, table 1, is assumed to be small since the density change in snow as a result of metamorphism in dry snow is very slight. The coefficient for the energy interaction or heat exchange is also arbitrarily assumed, table 1.

Young's modulus is approximated by fitting to a curve in Mellor's (1974) "Review of basic snow mechanics". The equation used in the calculations presented here (in pascals) to approximate the curve for a density range of approx. 150–375 kg/m³, is

$$Y = 10\exp(10\nu_i + 4).$$

Table 1. Coefficient values used in the analysis

Ice density	γ_i	917 kg/m^3
Water vapor density	γ_v	4.847×10^{-3} kg/m^3
Air density		1.3 kg/m^3
Gas constant	R	462 J/(kg · deg)
Poisson's ratio (snow)	Φ	0.2
Thermal expansion coefficient of ice	α	5×10^{-5} deg
Specific heat of ice and vapor	C	2093 J/(kg · deg)
Thermal conductivity of ice	q_{i_0}	2.2 J/(m · s · deg)
Thermal conductivity (air)	q_{v_0}	0.02 J/(m · s · deg)
Acceleration of gravity	$\mathbf{b}$	-9.81 m/s^2
Interface energy	σ	0.109 J/m^2
Latent heat of sublimation	L	2.838×10^6 J/kg
Reference temperature	θ_R	273 K
Vapor entropy (reference)	η_{vR}	9157 J/(kg · deg)
Ice entropy (reference)	η_{iR}	2303 J/(kg · deg)
Reference pressure (vapor)	P_R	610 N/m^2
Mass interaction coefficient (proportionality part)		$1 \times 10^{-12}/(s^3 \cdot deg \cdot m^4)$
Momentum interaction coefficient (constant part)	Δ	1×10^{13} kg/(m^3 · s)
Equilibrated force interaction coefficient	K	1×10^{-6} kg/(s · m · deg)
Energy interaction coefficient	$e_{i_0}^{+e}$	10 J/(m^2 · s · deg)

Application of the theory which has been developed for snow, is carried out in one dimension. This one-dimensional approach is applied in the vertical, slope normal direction, simulating a snowpack on a horizontal field. A one-dimensional model is obviously limiting to the scope of problems, as well as being inadequate to properly describe some processes. However, this is the logical first step toward implementing the theory to this physical problem.

In this application the velocity of the ice is assumed negligible, since the settlement velocity due to gravity would be very slow. Also, given the granular nature of the material, settlement involves a closer packing of grains as they move laterally and downward into voids, an effect which is not applicable in a one-dimensional model.

The vapor is considered as a single constituent in the formulation presented, but is tailored in the solution to account for only the diffusion of water vapor through the air, assuming that the air is stationary.

Passman & McTigue (1984) dealing with saturated porous media assume an equation similar to [50] (but without temperature effects) and suggest a coefficient to remain compatible with Darcy's law. This has the form $v_i^2\zeta/\kappa$, where ζ is the fluid viscosity and κ is the permeability. To remain dimensionally consistent with this but using [50], temperature must be included as well. In the context of the present application the drag on the vapor will be influenced by both drag due to air and that due to the ice matrix. To compensate for this the viscosity–permeability ratio is replaced by a larger (although at this point somewhat arbitrary) constant drag, Δ. The drag used in this two-constituent application to snow is

$$m_{i_0}^{+e} = v_i^2\theta_v\Delta.$$

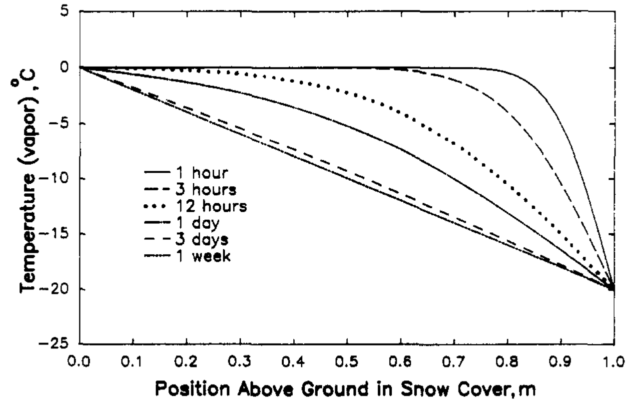

Figure 1. Temperature of the ice relative to position in the idealized snowpack.

In the numerical solution to the problem, derivatives are put in a finite difference form. The derivatives on space are in general central differenced, except at the bottom and top nodes where they are appropriately forward and backward differenced. The derivatives on time are forward differenced.

The basic approach to the explicit numerical solution used, is quite straightforward. Values for variables which do not involve time derivatives are calculated at the initial or current time for each time interval iteration or program loop. The balance equations are then used to find the rate of change of those variables which explicitly vary with time as indicated by the equations. For each iteration or loop, variables are recalculated to reflect what the value is at the end of the period which is used to step forward in time. These updated values are then assumed as the variables which are used in the balance equations for the next loop. This iterative process is progressively stepped forward in time.

Proceeding as above, the manner in which the balance equations are utilized should be noted. Considering the ice as incompressible allows the time rate of change for the volume fraction of the ice (–vapor) to be calculated directly through the equation of mass balance for the ice [11], and the time rate of change of the partial density of the vapor is determined by the mass balance for the vapor [11].

The vapor velocity is calculated using the linear momentum balance for the vapor [12]. Since the ice velocity is assumed always zero, the linear momentum balance equation for the ice [12] may be used to calculate the partial stress of the ice constituent. Then, since a form for the partial ice stress is also given through the derivative of the Helmholtz free energy [59], the strain of the ice is determined using this calculated strain in conjunction with the strain from the previous iteration, an approximation to the strain rate is found, which is used in the energy balance equation [15].

The equilibrated force interaction for the ice and vapor is given by the balance equations for the equilibrated force [53] and [54]. It is important to note that the time rate of change of the volume fraction is calculated prior, since it is necessary to solve the balance of equilibrated force equations. Time rate of change of temperature for the ice and vapor is calculated through the constituent energy balance equations [15], prior to which the mass balance equations and the momentum balance for the ice must be solved, since the time rate of change of these variables are needed.

RESULTS FROM THE ANALYSIS

As a simple example using the application, calculations are made for 1 m of ideal homogeneous snow assumed to have an ice volume fraction of 0.3, which is equivalent to snow with a density of approx. 276 kg/m^3. Initially the snow cover is assumed at 0°C, with the exception of a -20°C surface temperature (calculations are in Kelvin). Snow boundary temperatures for both the ice and the vapor are then held constant and equal.

Transient variation of temperature is seen to react quite reasonably. Figure 1 represents the variation of vapor temperature and although there is a very slight difference in constituent

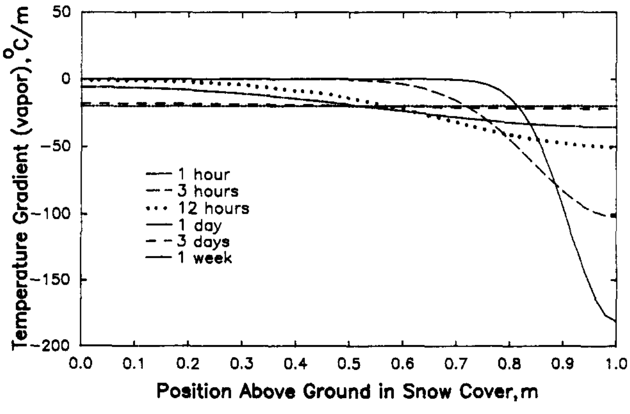

Figure 2. Temperature gradient of the ice relative to position in the snowpack.

temperatures, as discussed below, the temperature related figures shown are representative of both constituents since the curves are similar. At the end of a very short time period, most of the snow remains at the initial temperature with a very large variation in the uppermost region. Passing of time shows the temperature profile with respect to position to be migrating toward a linear function. Corresponding to temperature is the temperature gradient variation (figure 2). This negative thermal gradient in the early stages is of greater magnitude near the surface, decreasing with depth, then with the passage of time gradually moves toward a constant value throughout (figure 2).

When the surface of the snowpack is suddenly cooled as in the present situation, the underlying snowpack temperature will be lowered also. But, the mixture is composed of two distinct materials with differing thermal conductivities, these constituents should not be expected to change temperature at the same rate. Although no known physical data exist for snow in regard to differences in temperature between the ice and vapor phases, the model is predicting a very plausible trend (figure 3). Notice in the figure that it is early in the developing situation and in the upper, more active region where the most substantial difference in constituent temperatures is occurring.

Ice has a much higher thermal conductivity than does the vapor (air) and consequently will react to the imposed boundary temperature more quickly. This is the reason the vapor is at a warmer temperature than the ice, and the temperature difference between the phases is most pronounced when the temperature gradient is the largest. As a result of the boundary temperatures being held constant and equal for both constituents, it may be readily seen that, as the processes move toward a steady-state situation on the constituent temperatures tend to equilibrate. In addition to conductivity, temperatures are also affected in the formulation by other processes such as heat transfer in conjunction with the diffusion of water vapor, interaction among constituents (particularly energy) and the latent heats. The change in temperature for the vapor must account for all of the vapor in the pore, so the mass of air is used for the volumetric specific heat, $\rho_v C$, when numerically solving for the time rate of change of temperature.

The partial stress in the ice, the constituent which governs the structural integrity of the snow, is dominated by overburden thus increasing linearly with depth. The thermoelastic strain of the ice (figure 4) is shown from the isothermal section of the figure to increase slightly in magnitude with depth, as expected for a purely mechanical situation. Strain resulting from simply the overburden of the snow cover itself however, is not as large as that imposed through thermal contraction, for the temperatures, depth and snow density considered here. Strain then, in accordance with the variation in temperature for the steady-state situation, is a maximum in the coldest region at the surface.

It is during the early transitional period when the largest water vapor velocities are attained, as expected, in the very active upper region of the snowpack, with no effect being felt in the lower regions at this stage (figure 5). Subsequent transient vapor velocity profiles show a velocity becoming established, progressively deeper in the pack. Eventually, as the steady state is approached, the velocity moves toward a constant value.

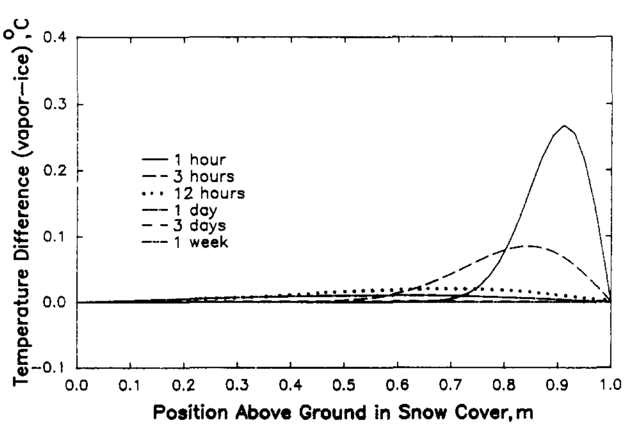

Figure 3. Difference in constituent temperature, $(\theta_v - \theta_i)$, relative to position.

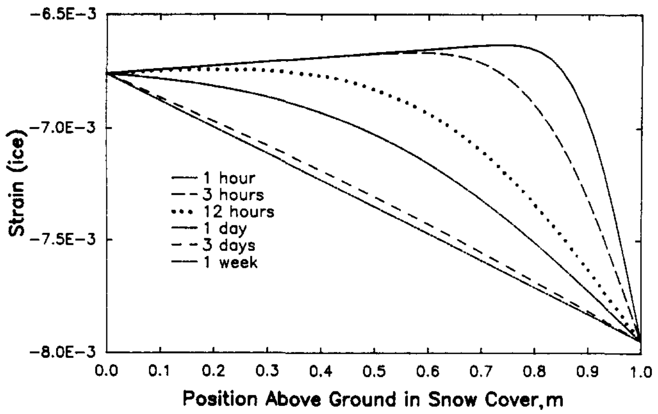

Figure 4. Strain in the ice relative to position.

The influence of the transient pattern which has been established among all of the interconnected processes, is apparent also in the values calculated here for time rate of change of the volume fraction of the ice (figure 6). For a short time after the initial conditions have been imposed, there is a relatively rapid loss of ice volume in the very thermodynamically active region located in the upper transitional zone of the snowpack. This relatively rapid volume loss is then substantially lowered with the advance of time, as the gradient terms and temperature difference between constituents are reduced. An active zone for ice volume loss, indicated by a bulge in the curve, migrates down through the snowpack with time, but at a greatly reduced magnitude. Finally, as the steady state is approached the region of maximum ice volume loss is located at the bottom of the snowpack, but is much lower than for the extreme temperature gradient so it is not readily apparent in the figure.

Kinetic growth or temperature gradient metamorphism is known to be most apparent in conjunction with large temperature gradients and warmer temperatures. Actual change in density associated with large temperature gradients are very slight and have only recently been measured (Dexter 1987).

DISCUSSION

Equations used in the application have been developed using a modern theory of multiphase mixtures, but a number of these newly established equations and coefficients are not yet well-understood. Even the most straightforward coefficients, when applied to a mixture, may be less transparent than for a single constituent. For example, the coefficient relating to heat flux, the thermal conductivity, requires closer examination. Independent thermal conductivity coefficients

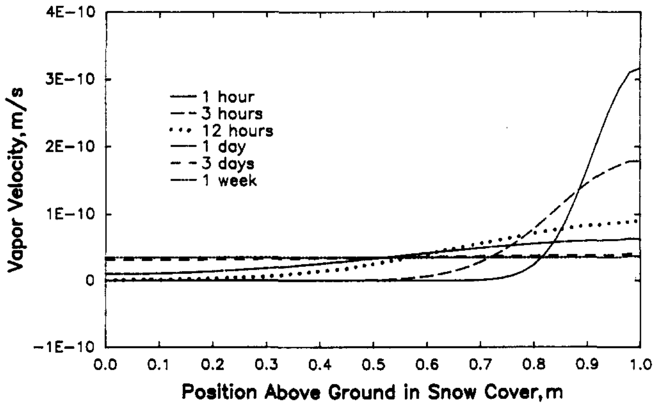

Figure 5. Water vapor velocity relative to position.

for the ice and the vapor are used in the application. This causes temperature differences to be calculated between the ice and vapor during transient temperature states. As a result of the volume fraction concept, the thermal conductivity of the snow mixture varies with the snow density, which is in keeping with the concept that density is most commonly considered to be the predominant variable affecting thermal conduction in a snowpack (Mellor 1964). Future work however, should consider the manner in which temperature, grain bonding and configuration affect the constituent thermal conductivity coefficients.

The coefficient used for the energy interaction, which effects constituent temperature differences, is based on Newton's law for cooling, and might be refined in future applications. The *K* coefficient involved in the extra equilibrated force term is not known or well-understood, and consequently it was arbitrarily chosen to be small. The mass interaction coefficient which is used in this paper is assumed to be proportional to the interface pressure, since this term varies with temperature and grain configuration. The proportionality used is assumed to be very small, in order to maintain a mass exchange between constituents which is plausible. Snow density change due to metamorphic processes alone are so small that they have only recently been physically measured (Dexter 1987). Future investigation should appropriately work toward a more complete understanding of this coefficient.

Central to the theory is the manner in which the Helmholtz free energy directly and naturally defines the stresses, entropy and equilibrated stress, based on the general theoretical requirements. The Helmholtz energies are approximated by Taylor's expansion. The ideal gas law is assumed to apply to the vapor free energy and is used to ascertain values for the coefficients of the series. A number of coefficients for the ice are arrived at by similarity to established forms. For example, similarity of the form arrived at for the stress with a thermoelastic material was utilized. Other coefficients for the free energy of the ice were calculated by equating suitable values, to arrive at a balance with the chemical potential for the vapor at equilibrium. This method of determining coefficients, i.e. by comparison with processes involved for a separate constituent, offers a method to calculate values at certain conditions. The results, seem to indicate that these values may also be appropriate at states other than those for which the coefficients were chosen to satisfy, but these would ideally be chosen by more independent methods.

Finally, the vapor, which is considered as a single constituent might be successfully subdivided into air and water vapor as two distinct constituents. (A very limited attempt at this was made in the calculation the water vapor velocity.) This obviously implies a three-constituent mixture, which is necessarily more complicated. A three-constituent model would have the advantage of distinguishing between the water vapor which is changing phase, and the essentially inert but mechanically important air constituent. As a word of caution on this; since the vapors are not physically separate it may not be suitable to apply the immiscible assumption to these two constituents.

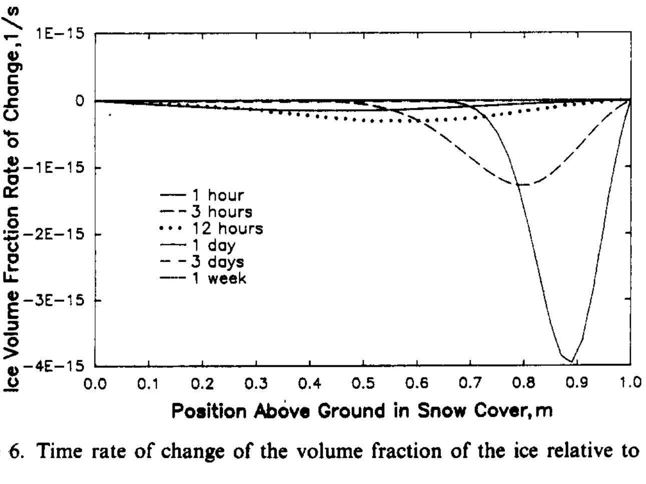

Figure 6. Time rate of change of the volume fraction of the ice relative to position.

CONCLUSIONS

Application of the multiphase mixture theory to snow is the result of a straightforward approach following guidelines set down in previous theoretical work, but which has had little application, as yet. Strict adherence to the basic principles of continuum mechanics with assurance that requisite requirements or restrictions are not violated, led to a model which is specific to snow. Although considerable manipulation and specialized formulation is required, it is carried out within the established framework of the theory. The strength of this formulation is its completeness and the fact that it does not isolate individual processes, but requires that interrelationships be accounted for.

The fact that interaction terms, which intuitively seem appropriate, are generated through the dissipation inequality within the framework of the theory is appealing, since it serves to sustain the coherent nature of the approach. Consideration of the snow as a continuous mixture, in this presentation, does not explicitly indicate the type of crystal development, except by correlation with empirically known growth conditions. It is probable, however, that interaction terms more heavily dependent on microstructure can be developed to account for crystal habit, sources and sinks on the scale of the grains, as well as other processes. A description of this type is not possible if snow is considered as a single continuum.

The description of snow, or any material, as a mixture consisting of two constituents allows for considerable simplification over a mixture requiring additional constituents. This is particularly evident in reference to the constituent interaction terms. These interaction terms are equal but of opposite sign, when only two constituents are considered. Consequently, when a form for one term is established, the other is immediately known.

Consideration of physically separated phases as autonomous but interacting materials, is important when making the transition from theory to application. Independent consideration of the individual constituents does not produce equations which are so unwieldy as to be impractical. The demonstration that this immiscible mixture concept may yield plausible results for physical situations such as the one examined in this paper, adds credence to the approach.

The theory of multiphase mixtures offers a unified, coherent, comprehensive approach to analyzing the myriad of intricately interrelated processes involved in thermodynamically active granular or porous materials. Results from the initial attempt presented here to model the snow cover by application of the theory, are quite promising and offer useful new insight into snow metamorphism as far as predicting trends, although accurate magnitudes of calculated results will only become possible as more precise coefficient values and theoretical refinement are achieved. Of course, considerable future work remains in the development of this application, but the results demonstrate that this relatively new theoretical approach may be successfully used for modeling processes as complex as the one presented. The thrust of this paper is concerned with an enhanced understanding of snow as a material, but, the most significant aspect is quite probably the demonstrated usefulness of this potentially powerful theory, which has had relatively few applications, to a broad range of problems.

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