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Dynamical Processes in Slurries and Mushes

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DYNAMICAL PROCESSES

IN SLURRIES AND MUSHES†

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Abstract

Material systems in which solid and liquid phases coexist in phase equilibrium are categorized by the mechanical configuration of the solid; in a *mush* the solid forms a rigid network with liquid occurring in the intercrystalline gaps, while a *slurry* consists of solid grains in suspension in a liquid. Due to the constraint of phase equilibrium, such systems exhibit unusual properties not found in single-phase systems. One striking example is the possibility of a reversal of the normal density-temperature relation, so that cold, rather than warm, liquid is buoyant. Furthermore, convection of heat can alter the crystalline structure of the mush, making the flow problem strongly nonlinear, and leading to novel structures such as 'chimneys' in the solid matrix. Chimneys are the cause of imperfections known as freckles in castings of alloys. These and other properties of two-phase systems are discussed and the equations governing these systems are briefly reviewed. A minimal set of Boussinesq-like equations governing a slurry are developed and the boundary conditions between a mush and the solid free region are presented.

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† The material in these notes is virtually identical to that appearing in Loper, 1991.

Introduction

The fundamental division of matter into solid, liquid or gaseous phases may not apply when the material under consideration has a micro-scale structure. Many types of 'complex' materials, such as fiber-epoxy composites, do not occur naturally, but must be are fabricated. However, there are many examples of naturally occurring composites. One long known to science is the plasma, which is a gas having three distinct elements: ions, electrons and neutral atoms. Less familiar, but of more relevance to metallurgy and material science, are the semi-solid (solid-liquid) composites known as slurries and mushes.

A slurry is defined as a liquid continuum having in suspension a large number of small solid particles which have formed by solidification from the liquid. A mush is formed when the small-scale crystals of the solid phase form a rigid framework through which the liquid may percolate. In either case, the large-scale behavior of the material is dominated by the fact that the liquid and solid phases are in intimate contact throughout a volume. Slurries may occur in molten metallic systems in rapid motion, while mushes are more common in slowly moving situations.

If the liquid is not a pure material or does not have an eutectic composition, the solid and liquid have differing compositions. This difference leads to a number of novel effects not found in single-phase systems or in semi-solid systems in which the two phases have the same composition.

In what follows the thermodynamic and fluid-dynamic equations governing slurries and mushes will be briefly reviewed, and some of their important and novel physical effects will be elucidated. For clarity of exposition, attention will be focused on semi-solid materials composed of two constituents; more complicated materials typically behave similarly. This review will not be comprehensive as the literature on these subjects is voluminous and diverse. A bibliography of the literature on this subject through 1986 may be found in Loper (1987).

Thermodynamic Equilibrium

Consider a system composed of two constituents. We will refer to the principal constituent as A and the minor or impurity constituent as B. The equilibrium thermodynamic state of the system is characterized by three variables: pressure, p, temperature T and mass fraction of B, ξ. (In many engineering situations, the variation of pressure is negligible and may be ignored.) In an equilibrium situation, these three variables may be externally prescribed. In a nonequilibrium situation, there may be as many as five independent thermodynamic variables for a two-constituent system (Loper and Roberts, 1978).

The system may be characterized as semi-solid if the state variables p, T and ξ lie below the liquidus and above the solidus or eutectic line in the phase diagram; that is, within the hatched region of Figure 1, taken from Roberts and Loper (1987). The liquidus and solidus lines in the equilibrium phase diagram are obtained by equating the chemical potentials of each of the two constituent in the two phases (Roberts and Loper, 1987), and may be expressed alternatively as $T_L(p, \xi)$ and $T_S(p, \xi)$ or as $\xi_L(p, T)$ and $\xi_S(p, T)$. The former representation conforms best to the curves in Figure 1, while the latter representation is more useful analytically.

An important variable characterizing the physical state of the system is the mass fraction of solid, ϕ. This is related to the various mass fractions of B by the relation

$$\xi = \phi\,\xi_s + (1-\phi)\,\xi_L. \tag{1}$$

This equation is often referred to as the lever rule. With ξ being directly externally prescribed and ξ_L and ξ_s being indirectly prescribed through p and T, (1) solves for ϕ. Note that the equilibrium relations $\xi_L(p, T)$ and $\xi_s(p, T)$ imply that the thermodynamic state of one phase is insensitive to the amount of the second phase that is present.

The differential form of the liquidus relation may be expressed as

$$\hat{\mu}_L \mathrm{d}\xi_L = \delta \mathrm{d}p - (L/T)\mathrm{d}T, \tag{2}$$

where $\hat{\mu}_L = (\xi_L - \xi_s)\partial\mu_L/\partial\xi$, μ_L being the relative chemical potential of the liquid phase, δ is the change of specific volume upon melting at constant composition and L is the latent heat of solidification. If $\mathrm{d}\xi_L = 0$, (2) is referred to as the Clausius-Clapeyron relation, and describes the variation of the melting point with pressure. For a dilute ideal solution, $\hat{\mu}_L$ is independent of ξ_L. Typically $\hat{\mu}_L > 0$ so that the the addition of an impurity lowers the melting point of a material.

A useful practical approximation of the solidus is to assume that

$$\xi_s = \lambda\,\xi_L, \tag{3}$$

where the coefficient λ is constant and satisfies $0 \leq \lambda < 1$. For simplicity of exposition in the following discussion, attention will be limited to the case $\lambda = 0$ or equivalently $\xi_s = 0$, so that none of constituent B is incorporated into the solid phase. This approximation removes the knotty problems of history dependence and diffusion of material in the solid phase (Hills and Roberts, 1988a).

Equations of State

The differential form of the chemical potential of a single phase material composed of two constituents is

$$\mathrm{d}\mu = (1/\rho)\mathrm{d}p - s\,\mathrm{d}T + \tilde{\mu}\mathrm{d}\xi, \tag{4}$$

where s is the specific entropy, ρ is the density and $\tilde{\mu}$ is the difference in the chemical potentials of the two constituents. This is a generalization of the Gibbs-Duhem relation for a pure substance. The equations of state of the material are the three relations $\rho(p, T, \xi)$,

$s(p, T, \xi)$, and $\tilde{\mu}(p, T, \xi)$. The equations of state for a two-phase material are superficially similar, but as we shall see the coefficients are substantially different.

Equation of State for Density

The equation of state for density of the system is

$$\frac{1}{\rho} = \frac{\phi}{\rho_S} + \frac{1-\phi}{\rho_L}, \tag{5}$$

where by the lever rule ρ_S is a function of p, T and ξ_S while ρ_L is a function of p, T and ξ_L. The differential form of the latter function is

$$d\rho_L = \rho_L(\beta dp - \alpha dT - \rho_L \delta d\xi_L), \tag{6}$$

where α is the coefficient of thermal expansion, β is the isothermal compressibility and δ is the change of specific volume with composition. These coefficients are each functions of the three independent thermodynamic variables, but are commonly assumed to be constant in practice. The coefficient β must be positive else the material is compressively unstable. For normal materials, $\alpha > 0$; "hot fluid rises". If the impurity B is less dense than A, then $\delta > 0$.

In thermodynamic equilibrium the differentials dp, dT and $d\xi_L$ appearing on the right hand side of (6) are not independent, but are related by (2). If we use (2) to eliminate $d\xi_L$ from (6) the result is

$$d\rho_L = \rho_L\left[\left(\beta - \frac{\delta\delta}{\hat{\mu}_L}\right)dp - \left(\alpha - \frac{L\delta}{T\hat{\mu}_L}\right)dT\right]. \tag{7}$$

This equation describes the variation of density of the liquid phase of a liquid-solid material when the two phases are in thermodynamic equilibrium. Note that it is possible that $\delta\delta/\hat{\mu}_L > \beta$ and/or $L\delta/T\hat{\mu}_L > \alpha$. In the former case, the usual pressure-density relation is reversed. However, since the liquid is only one part of a composite system, this does not imply compressional instability, as it would for a one-phase system. If the latter condition holds, the usual temperature-density relation is reversed; now "cold fluid rises"! If the material is a slurry having solid in suspension, this reversal of thermal expansion coefficient has no direct dynamic effect. However, for a mush having the solid rigidly connected to a boundary, this reversal has a strong dynamical effect. For example, this effect leads to the formation of chimneys and freckles in castings (Copley, et al., 1970).

With $\xi_S = 0$, the differential form of (5) may be expressed as (Loper and Roberts, 1978)

$$d\rho = \rho(\beta^* dp - \alpha^* dT - \delta^* d\xi), \tag{8}$$

where

$$\beta^* = \beta + \rho\delta^2\left(\frac{1-\phi}{\hat{\mu}_L \xi_L}\right), \qquad \alpha^* = \alpha + \frac{\rho\delta L}{T}\left(\frac{1-\phi}{\hat{\mu}_L \xi_L}\right) \tag{9), (10}$$

and

$$\delta^* = \delta + \frac{\delta}{\xi_L}. \tag{11}$$

Note that (8) bears a superficial resemblance to (6), but the starred coefficients may be significantly different from their normal (unstarred) values. In (9) - (11) the first terms on the right-hand sides are the normal coefficients and the second terms are the contributions due to the change of phase. The detailed forms of these coefficients are unimportant; the point is that the density of a mixture of two phases behaves fundamentally different than either phase in isolation, and the modified coefficients can become large if the composition of the material is nearly pure constituent A (i.e., if $\xi_L \to 0$).

Equation of State for Entropy

The differential form of the equation of state for entropy of the liquid phase is

$$\mathrm{d}s_L = -\frac{\alpha}{\rho}\mathrm{d}p + \frac{C_p}{T}\mathrm{d}T + \bar{s}\,\mathrm{d}\xi_L, \tag{12}$$

where C_p is the specific heat at constant pressure and $\bar{s}$ is the heat of reaction. If $s > 0$ heat must be added to maintain a constant temperature as ξ_L is increased (this is an endothermic process). If an isolated parcel of liquid experiences a change of pressure (due, say, to vertical motion in a hydrostatic environment) at constant composition and entropy, the temperature changes according to the dry adiabat:

$$\left.\frac{\mathrm{d}T}{\mathrm{d}p}\right)_{s,\,\xi_L} = \frac{\alpha T}{\rho C_p}. \tag{13}$$

With $\xi_s = 0$, the differential form of the equation of state for entropy of a semi-solid material is

$$\mathrm{d}s = -\frac{\alpha^*}{\rho}\mathrm{d}p + \frac{C_p^*}{T}\mathrm{d}T + \bar{s}^*\mathrm{d}\xi, \tag{14}$$

where

$$C_p^* = C_p + \frac{L^2}{T}\left(\frac{1-\phi}{\hat{\mu}_L \xi_L}\right) \qquad \text{and} \qquad \bar{s}^* = \bar{s} + \frac{L}{T\xi_L}. \tag{15), (16}$$

As with the equation of state for density, the coefficients of the equation of state for entropy of a two phase material are fundamentally different than those of a single-phase material, and they can become large as $\xi_L \to 0$.

If an isolated parcel of the two-phase material experiences a change of pressure at constant composition and entropy, the temperature changes according to the wet adiabat:

$$\left.\frac{\mathrm{d}T}{\mathrm{d}p}\right)_{s,\,\xi} = \frac{\alpha^* T}{\rho C_\mathrm{p}^*}. \tag{17}$$

This gradient is fundamentally different than the dry adiabat, no matter how small the fraction of the second phase. (This change of adiabatic gradients is familiar in atmospheric dynamics.)

Equation of State for Chemical Potential

The differential form of the chemical potential difference of a single phase material composed of two constituents is

$$\mathrm{d}\tilde{\mu} = \delta \mathrm{d}p - s\,\mathrm{d}T + \bar{\mu}\mathrm{d}\xi, \tag{18}$$

where $\bar{\mu}$ is the change of chemical-potential difference with composition. The chemical potential difference of a two-phase material is

$$\mathrm{d}\tilde{\mu} = \delta^* \mathrm{d}p - \bar{s}^*\,\mathrm{d}T + \bar{\mu}^*\,\mathrm{d}\xi, \tag{19}$$

where remarkably (Hills and Roberts, 1988b)

$$\bar{\mu}^* = 0. \tag{20}$$

This means that the chemical potential of the material, and of each phase in thermodynamic equilibrium, is a linear function of the composition. It follows that the functions $1/\rho$ and s are linear functions of ξ and $\tilde{\mu}$ is independent of ξ. Further β^*/ρ, α^*/ρ and C_p^* are linear functions of ξ, while δ^* and $\bar{s}^*$ are independent of ξ.

Conservation Equations

A powerful way to treat a material with a microstructure is to assume that it is a single continuum with macroscopic properties which parameterize the microstructure. In this section, the macroscopic governing equations of slurries and mushes are presented, and the Boussinesq approximate forms are outlined. In the Boussinesq approximation, the density is treated as a constant everywhere except in the buoyancy term. In a slurry having the solid particles in suspension, attention is focused on the barycentric velocity, defined by (22), while in a mush having the solid in the form of a rigid matrix, attention is focused on the velocity of the liquid phase.

Conservation of Total Mass

Conservation of total mass is governed by

$$\partial\rho/\partial t + \nabla\cdot(\rho \mathbf{u}) = 0, \tag{21}$$

where ρ is given by (5) and the barycentric velocity $\mathbf{u}$ is defined by

$$\rho \mathbf{u} = \phi \rho_S \mathbf{u}_S + (1 - \phi)\rho_L \mathbf{u}_L \,, \tag{22}$$

with $\mathbf{u}_S$ and $\mathbf{u}_L$ being the velocities of the material in the solid and liquid phases. A word of caution is in order at this point. It may happen that the velocity of the liquid phase has small-scale structure as it percolates through the solid phase; this structure is not modeled by (22).

In the Boussinesq approximation of a slurry, this conservation equation is reduced to

$$\nabla\cdot\mathbf{u} = 0 \,. \tag{23}$$

In the Boussinesq approximation of a mush, the solid phase is commonly constrained to move in rigid-body motion (although compaction of the solid phase is important in some geophysical settings; see McKenzie, 1984). In this case the barycentric velocity may be expressed as

$$\mathbf{u} = \mathbf{u}_S + (1 - \phi)\mathbf{w} \,, \tag{24}$$

where $\mathbf{w} = \mathbf{u}_L - \mathbf{u}_S$. Now conservation of total mass requires that

$$\nabla\cdot[(1 - \phi)\mathbf{w}] = 0 \,. \tag{25}$$

Conservation of Impurity

Conservation of mass of constituent B is governed by

$$\rho \mathrm{D}\xi/\mathrm{D}t = -\nabla\cdot\mathbf{i} \,, \tag{26}$$

where $\mathrm{D}/\mathrm{D}t = \partial/\partial t + \mathbf{u}\cdot\nabla$ is the time derivative following the barycentric motion and $\mathbf{i}$ is the flux of constituent B relative to the mass center.

In a normal single-phase material composed of two constituents, the diffusive flux is given by Fick's law (e.g., $\mathbf{i} = -k\nabla\xi$) yielding a simple diffusive equation. However for a semi-solid material, the material flux $\mathbf{i}$ is assumed to be a linear function of the gradients of the independent thermodynamic variables:

$$\mathbf{i} = k_p \nabla p - k_T \nabla T - k_\xi \nabla \xi \,. \tag{27}$$

The coefficient k_p is a measure of the flux due to relative motion of solid and liquid induced by particle sedimentation in a slurry or by fluid buoyancy in a mush, the coefficient k_T is a measure of an effective Soret effect, and the coefficient k_ξ is the usual Fick coefficient. A remarkable property of the semi-solid material is that (Hills and Roberts, 1988b)

$$k_\xi = 0 \,. \tag{28}$$

A physical explanation of this unusual property is as follows. In a single phase system, an excess of constituent B can be removed from a parcel of liquid only by diffusion down the concentration gradient. However, if solid phase having a deficit of B is present, the excess may be removed by melting some of the solid, diluting the liquid.

Commonly the pressure gradient is governed by the hydrostatic balance, $\nabla p = -\rho \mathbf{g}$, and the Soret term is small, so that (26) becomes

$$\rho \mathrm{D}\xi/\mathrm{D}t = \nabla\cdot(k_{\mathrm{p}}\rho \mathbf{g}). \tag{29}$$

Physically the term within the divergence operator on the right-hand side of eq. (29) represents the sedimentation of the solid particles. For the exact form of the coefficient k_{p}, see Reference 7. This equation applies to a slurry, while for a mush, it is more convenient to consider ξ_{L} rather than ξ since the solid phase is immobile. The equation appropriate for a Boussinesq mush (having $\xi_{\mathrm{s}} = 0$) is (Hills, et al., 1983)

$$\frac{\mathrm{D}\xi_{\mathrm{L}}}{\mathrm{D}t} = \frac{\mathrm{D}_{\mathrm{s}}(\phi\xi_{\mathrm{L}})}{\mathrm{D}t} + \mathrm{D}_0\nabla\cdot[(1-\phi)\nabla\xi_{\mathrm{L}}], \tag{30}$$

where $\mathfrak{D}$ is the material diffusivity, $\mathrm{D}_{\mathrm{s}}/\mathrm{D}t = \partial/\partial t + \mathbf{u}_{\mathrm{s}}\cdot\nabla$ is the motional derivative following the solid phase and a subscript 0 denotes a constant value. The first term on the right hand side of (30) represents the increase (or decrease) of composition of the liquid due to freezing (or melting) of the solid phase, while the second is the familiar Fickian diffusive term, complicated by the presence of the solid phase. This diffusive term does occur if conservation of impurity in the liquid phase alone is considered, but it is absent from the equation governing the conservation of impurity in the system as a whole. Commonly the material diffusion term is negligibly small.

Conservation of Momentum

The form of this equation differs for a slurry and a mush, because of the differing mechanical configurations of the solid phase.

Slurry. We shall assume the system to be in nearly hydrostatic balance, with the hydrostatic pressure, p_{H}, given by

$$p_{\mathrm{H}} = f(t) - g_0\int_{z_0}^{z} \rho(p)\,\mathrm{d}z, \tag{31}$$

where z is the upward coordinate, g_0 is the magnitude of $\mathbf{g}$ and *f(t)* is a function of integration. Normally *f(t)* is a constant (p_0, say), but if we allow for the possibility that the static slurry is in uniform motion with respect to the frame of reference, *f(t)* may be a linear function of time. We shall assume that this motion is small, and variations of density with pressure are also small, so that (31) may be simplified to

$$p_{\mathrm{H}} = p_0 - g_0\rho_0(z-z_0). \tag{32}$$

Subtracting the hydrostatic balance, the Boussinesq form of the Navier-Stokes equation is

$$\rho_0 \mathrm{D}\mathbf{u}/\mathrm{D}t = -\nabla p' + \rho' \mathbf{g} + \eta_0 \nabla^2 \mathbf{u}, \tag{33}$$

where η is the dynamic viscosity, $p' = p - p_H$ is the reduced pressure and $\rho' = \rho - \rho_0$ is the reduced density. Here a subscript 0 denotes a constant reference value.

The reduced density is given by an integrated version of (8). We may use (31) to write this as:

$$\rho' = -\rho_0\left[\alpha_0^*(T-T_0) + \delta_0^*(\xi-\xi_0)\right]. \tag{34}$$

The motion of the solid relative to the liquid is governed by normal sedimentation theory (e.g., see Ch. 9 of Happel and Brenner, 1983). However, the solid particles are subject to melting or freezing if thermodynamic equilibrium is disturbed. This makes the stability analysis of such systems different from that for a nonreactive assemblage of particles.

Mush. The solid phase is assumed to be rigidly attached to a substrate so that only the motion of the liquid phase is of concern. The percolation of the liquid phase relative to the solid is assumed to be governed by Darcy's law:

$$\frac{\eta_0 \mathbf{w}}{\gamma(1-\phi)} + \nabla p' - \rho_L' \mathbf{g} = 0, \tag{35}$$

where ρ_L' is the reduced liquid density and $\gamma(\phi)$ is the permeability. The hydrostatic relation is now given by

$$p_H = p_0 - g_0 \rho_{L0}(z-z_0). \tag{36}$$

rather than (32), but the difference is slight in the Boussinesq approximation. The reduced liquid density is given by an integrated version of (7). Using (36), this is:

$$\rho_L' = -\rho_{L0}\left(\alpha - \frac{L\delta}{T\hat{\mu}_L}\right)_0 (T-T_0). \tag{37}$$

A major problem in closure of this theory is determination of the permeability function $\gamma(\phi)$. The particular form of the function depends on the mechanical configuration of the solid phase on the microscale. This form can be strongly modified by the fluid flow, making the problem very nonlinear. A striking example of this nonlinear coupling is seen in the appearance of chimneys in the model experiment of Copley et al. (1970). This coupling in fact introduces the problem of history dependence into the formulation as the permeability depends on the history of the fluid flow. A further complication is the fact that the structure of the solid changes with time due to phase coarsening (i.e., Ostwald ripening). A common approximation to the permeability function is the Carmen-Kozeny relation:

$$\gamma = \gamma_0(1-\phi)^3/\phi^2. \tag{38}$$

In metallurgical applications, it a usually a good assumption that the solid phase of a mush forms a rigid framework. However, in geological applications, the large spatial and time scales allow for significant deformation of the solid phase, which introduces yet another complication into the theory (McKenzie, 1984).

Conservation of Energy

The temperature of a parcel of fluid can change due to the normal processes of thermal diffusion and adiabatic compression, represented by the first and second terms on the right hand side, and also by the release or absorption of latent heat of fusion as solid phase melts or freezes, represented by the last term:

$$\rho C_p \frac{DT}{Dt} = k\nabla^2 T + \alpha T \rho \mathbf{u}\cdot\mathbf{g} + \rho L \frac{D_s \phi}{Dt}. \tag{39}$$

The specific heat C_p and thermal conductivity k are volume-averaged combinations of those of the solid and liquid. For simplicity, we have assumed the two to be equal. For the case of unequal conductivities, see Worster (1986). In writing (39) we have assumed that the thermodynamic pressure is essentially the hydrostatic pressure, and have neglected all regenerative heating terms; for their form, see Hills et al. (1983).

The adiabatic compression term is negligibly small in most metallurgical applications, but it may be important in geophysical applications. The normal process of thermal diffusion is non-local in that it requires macroscopic spatial gradients of temperature. In contrast the process of change of phase is local and very rapid since in the continuum approximation the solid and liquid phases are in intimate contact on the micro-scale. Consequently, local phase change may dominate thermal diffusion. Note also that the relative motion of liquid and solid acts to transport heat in the direction of the liquid phase in a process similar to a heat pipe.

A Simple Model of a Mush

The equations developed in the previous sections will now be combined and further simplified into a minimum set of Boussinesq equations governing the dynamics of a mush. In this simplification, wherever possible the thermodynamic coefficients will be assumed constant. However, it should be pointed out that the approximation of ϕ constant should be avoided, since this variable can assume any value between 0 and 1 without disturbing the thermodynamic equilibrium.

An important equation in this development is the integral form of the liquidus relation (2). Using the hydrostatic balance (36), this is

$$\xi_L = \xi_{L0} - \left(\frac{\rho_L \delta g}{\hat{\mu}_L}\right)_0 (z - z_0) - \left(\frac{L}{T\hat{\mu}_L}\right)_0 (T - T_0). \tag{40}$$

The equation of conservation of impurity in the liquid phase (30) may be expressed as

$$(1-\phi)\left[\frac{\mathrm{D_s}\xi_\mathrm{L}}{\mathrm{D}t}+\mathbf{w}\cdot\nabla\xi_\mathrm{L}\right] = \xi_\mathrm{L}\frac{\mathrm{D_s}\phi}{\mathrm{D}t}+\mathrm{D}_0\nabla\cdot\left[(1-\phi)\nabla\xi_\mathrm{L}\right]. \tag{41}$$

Eliminating ξ_L from (41) using (40) yields

$$\begin{aligned}\frac{\mathrm{D_s}T}{\mathrm{D}t}+\mathbf{w}\cdot\nabla T &= -\left(\frac{T\hat{\mu}_\mathrm{L}\xi_\mathrm{L}}{L}\right)_0\frac{1}{(1-\phi)}\frac{\mathrm{D_s}\phi}{\mathrm{D}t}\\ -\left(\frac{Tg\rho_\mathrm{L}\delta}{L}\right)_0&(\mathbf{u}_\mathrm{s}+\mathbf{w})\cdot\hat{\mathbf{z}}+\mathrm{D}_0\left[\nabla^2T-\frac{\nabla T\cdot\nabla\phi}{(1-\phi)}\right].\end{aligned} \tag{42}$$

In writing (42) we have assumed that deviations of ξ_L from its reference value are small.

The Boussinesq version of the energy equation (39) is

$$\frac{\mathrm{D_s}T}{\mathrm{D}t}+(1-\phi)\mathbf{w}\cdot\nabla T = \kappa_0\nabla^2T-\left(\frac{\alpha Tg}{C_\mathrm{p}}\right)_0\left[\mathbf{u}_\mathrm{s}+(1-\phi)\mathbf{w}\right]\cdot\hat{\mathbf{z}}+\left(\frac{L}{C_\mathrm{p}}\right)_0\frac{\mathrm{D_s}\phi}{\mathrm{D}t}, \tag{43}$$

where $\kappa = k/\rho C_\mathrm{p}$ is the thermal diffusivity.

Solving (42) and (43) for the time derivatives of T and ϕ, we obtain

$$\begin{aligned}(1-\phi+A_0)\frac{\mathrm{D_s}T}{\mathrm{D}t} &= -(1-\phi)(1+A_0)\mathbf{w}\cdot\nabla T+\left[A_0\kappa_0-\mathrm{D}_0(1-\phi)\right]\nabla^2T\\ -\mathrm{D}_0\nabla T\cdot\nabla\phi-\left(\frac{\alpha Tg}{C_\mathrm{p}}\right)_0&\left[(A_0+B_0-\phi B_0)\mathbf{u}_\mathrm{s}\cdot\hat{\mathbf{z}}+(1-\phi)(A_0+B_0)\mathbf{w}\cdot\hat{\mathbf{z}}\right]\end{aligned} \tag{44}$$

and

$$\begin{aligned}(1-\phi+A_0)\frac{\mathrm{D_s}\phi}{\mathrm{D}t} &= -\left(\frac{C_\mathrm{p}}{L}\right)_0(1-\phi)\left[\phi\mathbf{w}\cdot\nabla T+(\kappa_0-\mathrm{D}_0)\nabla^2T\right]\\ +\left(\frac{C_\mathrm{p}}{L}\right)_0\mathrm{D}_0\nabla T\cdot\nabla\phi+&\left(\frac{\alpha Tg}{L}\right)_0(1-\phi)\left[(1-B_0)\mathbf{u}_\mathrm{s}\cdot\hat{\mathbf{z}}+(1-\phi-B_0)\mathbf{w}\cdot\hat{\mathbf{z}}\right],\end{aligned} \tag{45}$$

where

$$A = \frac{C_\mathrm{p}T\xi_\mathrm{L}\hat{\mu}_\mathrm{L}}{L^2} \qquad \text{and} \qquad B = \frac{C_\mathrm{p}\rho_\mathrm{L}\delta}{\alpha L}. \qquad (46), (47)$$

If pressure effects are small, as is the case for metallurgical applications, the terms proportional to g in (44) and (45) may be neglected. Similarely the terms involving material diffusion may normally be neglected compared with those involving thermal diffusion. If the coordinate frame is fixed to the solid phase, $\mathbf{u}_\mathrm{s} = 0$ and $\mathrm{D_s}/\mathrm{D}t = \partial/\partial t$. Equations (44) and (45) are two of the minimal set of equations of our Boussinesq theory. The first of these is a predictive equation for the temperature, complete with diffusive term, although the effective diffusivity is less than that of a single-phase material. The second is a predictive equation for the mass fraction of solid. This contains no Laplacian term for this variable. Hence discontinuities of ϕ are allowed by the theory. This is in accord with the fact that thermodynamic equilibrium is insensitive to the relative amounts of the phases present.

We may substitute (37) and (38) into the momentum equation (35) to obtain

$$\frac{\eta_0\phi^2\mathbf{w}}{(1-\phi)^4\gamma_0}+\nabla p'-\rho_{\mathrm{L}0}\left(\alpha-\frac{L\delta}{T\hat{\mu}_{\mathrm{L}}}\right)_0(T-T_0)g\hat{\mathbf{z}} = 0. \tag{48}$$

If $\phi << 1$, this Darcy equation may be supplemented with the normal viscous term:

$$\frac{\eta_0\phi^2\mathbf{w}}{(1-\phi)^4\gamma_0}-\eta_0\nabla^2[(1-\phi)\mathbf{w}]+\nabla p'-\rho_{\mathrm{L}0}\left(\alpha-\frac{L\delta}{T\hat{\mu}_{\mathrm{L}}}\right)_0(T-T_0)g\hat{\mathbf{z}} = 0. \tag*{(48)$'$}$$

Equations (25), (44), (45) and (48) or (48)′ form a set of four equations for the four unknowns p', T, $\mathbf{w}$ and ϕ. This set involves a Laplacian of the thermodynamic variable T, a Laplacian of the dynamic variable $\mathbf{w}$ [two of $\mathbf{w}$ if (48)′ is used], and a gradient of ϕ.

Boundary Conditions

Commonly the mushy zone is bounded by one of three regions (a) a solid-free fluid composed of the melt, (b) a solid composed of the equivalent sub-eutectic solid phase, or (c) a rigid boundary composed of a different material. We shall consider the appropriate equations for each of these boundaries.

An adjacent solid-free region

The Boussinesq equations governing the solid-free region adjacent to the mush are

$$\nabla\cdot\mathbf{u} = 0, \tag{49}$$

$$\frac{\mathrm{D}\mathbf{u}}{\mathrm{D}t} = -\frac{\nabla p'}{\rho_{\mathrm{L}0}}+g_0\left[\alpha_0(T-T_0)+\rho_{\mathrm{L}0}\delta_0(\xi_{\mathrm{L}}-\xi_{\mathrm{L}0})\right]\hat{\mathbf{z}}+\frac{\eta_0}{\rho_{\mathrm{L}0}}\nabla^2\mathbf{u}, \tag{50}$$

$$\frac{\mathrm{D}\xi_{\mathrm{L}}}{\mathrm{D}t} = \mathrm{D}_0\nabla^2\xi_{\mathrm{L}}, \tag{51}$$

$$\frac{\mathrm{D}T}{\mathrm{D}t} = \kappa_0\nabla^2 T-\frac{g_0\alpha_0}{C_{\mathrm{p}0}}\mathbf{u}\cdot\hat{\mathbf{z}}. \tag{52}$$

Note that these equations involve the variables p', T, $\mathbf{u}$ and ξ_{L}, which are different than the principal unknowns in the mush, and effectively contain one Laplacian each of T and ξ_{L} and two of $\mathbf{u}$.

Since the full set of equations in the mush has one Laplacian of T and two of $\mathbf{w}$ plus a gradient of ϕ while that in the solid-free region has one Laplacian of each of T and ξ_L and two of $\mathbf{u}$, we need to specify two vector conditions and five scalar conditions at the interface dividing the mush and solid-free region; one for each Laplacian, one for the gradient of ϕ and one extra for the unknown position of the interface. These conditions are continuity of velocity, stress, temperature, heat flux, fluid composition, and compositional flux, plus an additional condition on. Since the governing equations lack spatial derivative of the mass fraction of solid, ϕ, no condition can be directly placed on this variable. In fact, we must allow for a jump in the value of ϕ at the interface, making the flux conditions non-continuous. Worster (1986) argued for an extra condition that the normal gradient of the liquidus condition in the solid-free region is zero, but that requirement was an artifact of his similarity solution; it is not a general requirement. Fowler (1985) in considering this problem chose to use liquid composition rather than temperature as the primary thermodynamic variable in the mush. This formulation yields derivatives of ϕ, which appear to require an additional boundary condition. Fowler (1985) chose the condition that $\phi \rightarrow 0$ as the mush liquid interface is approached. This additional condition is not required in the present formulation.

Neglecting changes of volume upon change of phase, continuity of velocity is simply

$$\langle (1-\phi)\mathbf{w} \rangle = \mathbf{0}, \tag{53}$$

where the symbol $\langle x \rangle$ denotes the jump in quantity x across the interface; this is one of the vector conditions. At the low speeds typical of porous flow, the normal stress condition reduces to continuity of pressure:

$$\langle p' \rangle = 0. \tag{54}$$

This is one component of the second vector condition; the additional condition of continuity of tangential stress is not displayed explicitly here, see p. 150 of Batchelor (1970).

Continuity of temperature requires that

$$\langle T \rangle = 0\ , \tag{55}$$

while continuity of heat flux must account for the possibility of freezing at the interface:

$$\left\langle k\frac{\partial T}{\partial n} \right\rangle = \rho_s v_n L \langle \phi \rangle . \tag{56}$$

where v_n is the normal component of the velocity of advance of the interface with respect to the solid due to freezing or melting:

$$v_n = (\mathbf{v} - \mathbf{u}_s)\cdot\hat{\mathbf{n}}. \tag{57}$$

Here $\hat{\mathbf{n}}$ is a unit vector, locally normal to the interface, and v is the velocity of the interface.

The liquid composition must be continuous across the interface. This, combined with the continuity of T and the fact that the fluid within the mush is at the liquidus, yields the equivalent condition that the liquidus condition is satisfied on the solid-free side of the interface:

$$\left[\xi_{\mathrm{L}} - \xi_{\mathrm{L0}} + \left(\frac{\rho_{\mathrm{L}}\delta g}{\hat{\mu}_{\mathrm{L}}}\right)_0 (z - z_0) + \left(\frac{L}{T\hat{\mu}_{\mathrm{L}}}\right)_0 (T - T_0)\right]_{\mathrm{f}} = 0, \tag{58}$$

where a subscript f denotes evaluation on the solid-free side of the interface. Continuity of flux of impurity at the interface is satisfied if:

$$\mathrm{D}\left\langle (1-\phi)\frac{\partial \xi_{\mathrm{L}}}{\partial n}\right\rangle = \xi_{\mathrm{L}} v_{\mathrm{n}} \langle \phi \rangle. \tag{59}$$

Note that the diffusivity within the liquid phase is constant across the interface. Using (40) and the Boussinesq approximation, this condition may be expressed as

$$\left[\frac{\partial \xi_{\mathrm{L}}}{\partial n} + \left(\frac{\rho_{\mathrm{L}}\delta g}{\hat{\mu}_{\mathrm{L}}}\right)_0 \frac{\partial z}{\partial n} + \left(\frac{L}{T\hat{\mu}_{\mathrm{L}}}\right)_0 \frac{\partial T}{\partial n}\right]_{\mathrm{f}} =$$

$$\phi_{\mathrm{m}}\left[\left(\frac{\rho_L \delta g}{\hat{\mu}_{\mathrm{L}}}\right)_0 \frac{\partial z}{\partial n} + \left(\frac{L}{T\hat{\mu}_{\mathrm{L}}}\right)_0 \frac{\partial T}{\partial n} - \xi_{\mathrm{L0}} v_{\mathrm{n}}\left(\frac{1}{\mathrm{D}_0} + \frac{1}{A_0 \kappa_0}\right)\right]_{\mathrm{m}}, \tag{60}$$

where a subscript m denotes evaluation on the mush side of the interface. Note that Worster's supplementary condition is that the left hand side of (60) is zero.

The full set of boundary conditions between the mush and the liquid region consists of the six conditions (53) – (56), (58) and (60), plus continuity of tangential stress.

An adjacent sub-eutectic region

Assuming the solid to be incompressible, the energy equation within it is simply

$$\frac{\mathrm{D_s}T}{\mathrm{D}t} = \kappa_0 \nabla^2 T. \tag{61}$$

Apart from the dynamic conditions, we need to specify three scalar conditions at the interface: one for each Laplacian of temperature in (44) and (61) and one to determine the location of the interface. These three conditions are all thermal: the temperature within the solid is the eutectic value,

$$[T]_{\mathrm{S}} = T_{\mathrm{E}}(p), \tag{62}$$

where $[\ ]_{\mathrm{S}}$ denotes conditions on the solid side of the interface and a subscript E denotes an eutectic value, the temperature is continuous,

$$\langle T \rangle = 0\,, \tag{63}$$

and the heat flux balances the solidification at the interface,

$$\left[k\frac{\partial T}{\partial n}\right]_{\mathrm{m}} - \left[k\frac{\partial T}{\partial n}\right]_{\mathrm{s}} = -\rho_{\mathrm{s}}(1-\phi)Lv_{\mathrm{n}}\,. \tag{64}$$

Condition (62) is valid for all ξ provided $\xi_{\mathrm{S}} = 0$. If this is not the case alternative conditions apply; see Hills et al. (1983).

The only dynamic condition that is usually applied is that the normal component of the velocity be continuous across the interface:

$$[\mathbf{w}]_{\mathrm{m}}\cdot\hat{\mathbf{n}} = 0\,. \tag{65}$$

Since there is no Laplacian of velocity in the Darcy equation, no condition may be prescribed on the tangential velocity. Also, since the solid is rigid, we can specify no condition on the stress at the interface.

The freezing of the liquid remaining in the mush to form the solid involves solidification of both pure solvent and pure solute, in that proportion which ensures continuity of flux of solute at the boundary. Consequently, this condition serves only to determine the average composition of the solid phase.

$$\xi_{\mathrm{s}} = \xi_{\mathrm{E}} + \frac{D_0}{v_{\mathrm{n}}}[1-\phi]_{\mathrm{m}}\left[\frac{\partial \xi_{\mathrm{L}}}{\partial n}\right]_{\mathrm{m}}\,. \tag{66}$$

In writing (66) we have used the fact that $\xi_{\mathrm{L}} = \xi_{\mathrm{E}}$ in the mush adjacent to the solid.

In summary, at a sub-eutectic boundary we have 4 conditions: (62) - (65).

An adjacent rigid boundary

In experiments and in metallurgical applications, it is common for the mush to be bounded at least in part by a rigid boundary of known position. The rigid crystalline matrix is invariably attached to this boundary, which necessarily must move with velocity $\mathbf{u}_{\mathrm{S}}$.

The most general thermal condition specified at the rigid interface is continuity of temperature and heat flux

$$\langle T \rangle = 0 \qquad \text{and} \qquad \left\langle k\frac{\partial T}{\partial n}\right\rangle = 0\,. \qquad (67),\ (68)$$

These conditions require solution of the heat equation within the rigid boundary.
Commonly (67) and (68) are replaced by

$$a_1 T + a_2 \partial T/\partial n = a_3\,, \tag{69}$$

where a_{i} are specified functions, obviating the need to solve for the temperature within the solid. Continuity of flux of impurity requires that

$$\left[\frac{\partial \xi_L}{\partial n}\right]_m = 0. \tag{70}$$

The condition of no normal flow, (65), again applies.

Final Remarks

The preceding sections have presented the equations governing a semi-solid material, under the assumptions that thermodynamic equilibrium prevails locally and that the microscale properties of the material may be parameterized within a continuum theory, and have discussed some of their novel properties. The study of this subject is still very much in its infancy, with the governing equations not yet well established and the novel physical effects not yet well understood.

The lack of progress in this area is not due to a lack of potential applications. In addition to the solidification of metallic alloys, the study of semi-solid systems has potential applications in several areas of geophysics including the solidification of the core, dynamics of magma chambers and dynamics of temperate glaciers (Huppert, 1986; Fowler, 1987).

The lack of progress is due in large part to the physical complexity of these semi-solid systems, which is reflected in the intricacy of the mathematical models and the relatively large number of physical parameters. One serious impediment to progress in this area is a lack of experiments to quantify the coefficients of the theories and to verify and illustrate the physical phenomena. Although there are several groups currently performing experiments (Kerr et al., 1990; Tait and Jaupart, 1989; Chen and Chen, 1991; Tait, et al., 1992), much still remains to be done.

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