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for a Dynamical Theory of a Mushy Zone**

**R. N. Hills
P. H. Roberts**

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**Department of Mathematics
University of California, Los Angeles
Los Angeles, CA. 90024-1555**

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R. N. HILLS

AND

P. H. ROBERTS

Institute of Geophysics and Planetary Physics,
University of California, Los Angeles CA 90024

Abstract.

This paper develops a thermodynamically consistent theory of the freezing of a binary alloy in a region of mixed liquid and solid phase, possibly in relative motion. Attention is focussed on the cases when the liquid has the composition of the equilibrium liquidus, but in which the diffusion of one constituent through the other in the solid phase is negligible. An isolated system can then not attain complete thermodynamic equilibrium in a finite time, only a state of quasi-equilibrium in which the composition of the solid phase is not that of the solidus and, in general, is not even uniform in space. The complete theory must admit these quasi-equilibria as the steady final states of isolated systems. This is found to be so stringent a requirement that it almost completely decides the form that the theory must take.

A simple physical situation is solved: one-dimensional freezing of a stagnant material. The Scheil–Pfann solution is recovered.

1. Introduction.

The physics of segregation is concerned with the fact that the chemical composition of, for example, a solid alloy or an aqueous solution differs, in general, even in equilibrium, from that of a co-existing melt. Segregation is of particular practical importance in device manufacturing and materials purification but it presents some hard fluid dynamical questions. The difference in composition means that, on solidification, the material that is released at the freezing solid/liquid interface, being denser or lighter than the surrounding melt, may, in the presence of gravity, drive compositional convection in the fluid.

Solidification of a material from the melt often produces a partially solidified region in which a solid microstructure is embedded in a continuous liquid phase. Typically these regions are formed just ahead of the advancing solid front and can be of two sorts, a slurry or a mush. For the former, the solid phase is in the form of fine particles in suspension and these particles, at the whim of buoyancy forces, may ascend or sediment according to their density relative to the ambient fluid. As the solid particles move they will, in response to the changing environment, slowly melt or accrete new material. The term mush or mushy zone is usually applied to the phase mixture when the solid grows as a porous network (or matrix) of crystals through which the liquid percolates as, for example, in a region of dendrites.

The cornerstone of any dynamic theory of a phase mixture of a binary substance is the *equilibrium* phase diagram. For definiteness we address our remarks to binary alloys but most of what we have to say applies equally well to aqueous solutions. In principle, binary phase diagrams could be represented in the form of coexistence surfaces in a $\bar{\xi}$ - T - p space, where $\bar{\xi}$ is the mass concentration of the light constituent of the binary alloy, T is the temperature and p the pressure. Usually the dependence on pressure is weak and, for simplicity, we fix the pressure, p_0 , and relate our discussion to the situation in Figure 1 where the phase curves, the liquidus OL and the solidus OS , have equations

$$\bar{\xi}^L = \xi^L(p_0, T), \quad \bar{\xi}^S = \xi^S(p_0, T). \quad (1.1)$$

Throughout, an unbarred light constituent concentration indicates that its value lies on a phase line OL or OS . Let us follow the changes

that occur upon progressive *equilibrium solidification* of an alloy melt of uniform composition ξ_0 . As this is chilled, the point on Figure 1 representing its state descends along AL_0 , and the alloy starts to freeze at $T = T_0$, corresponding to the point, L_0 , on the liquidus at which $\xi_0 = \xi^L(p_0, T_0)$. The solid that starts to form has the composition corresponding to S_0 . If further cooling is so slow that equilibrium is maintained, the representative points for the two phases follow the liquidus L_0L_1 and the solidus S_0S_1 until, at S_1 where $\xi_0 = \xi^S(p_0, T_1)$, the alloy is totally solidified.

This discussion is, of course, idealized. The assumption of equilibrium throughout is seldom realized in practice. The front acts as a source of both rejected material and of heat arising from the latent heat of solidification. The mechanisms for removing these sources is, in the solid, only diffusion and, in the melt, diffusion and convection. Roughly speaking, when these processes cannot adequately disperse these sources, the two phase region results.

The structure and evolution of a region of mixed phase is extremely complicated and it is hardly surprising that none of the attempts that have so far been made to describe its thermo- and fluid mechanical behaviour has been totally satisfactory. The common starting point seems unobjectionable however: mixture theory. The idea is that, although on the microscale of crystal dimensions, the mass fraction, $\phi(\mathbf{x})$, of the solid phase can only be 0 or 1, it should be possible, when the gross macroscopic behaviour of a region of mixed phase is sought, to consider only an average, smoothly varying $\phi(\mathbf{x})$ that can take any value in $[0,1]$. The price of using such a broad scale variable ϕ to characterize the phase mixture is that the theory can say nothing regarding, for example, the growth of the tips and side branches of the dendrites themselves. On that scale interfacial energy effects are known to be important but this does not mean that they are necessarily important on the broader macroscale of our theory (see Roberts and Loper, 1987, § 3). We shall assume that they make only a negligible contribution to the theory developed here.

It is clear that the mixture is 'reactive'; melting or freezing can change the amount of solid present and the theory must make explicit the nature of the associated rate processes. One simplifying assumption that has been made is what Loper and Roberts (1987) called the "fast melt-

ing approximation" (although, for the purposes of the present paper, it would have been more appropriate to call it the "fast freezing approximation"). In that approach it is supposed that phase equilibrium is established so rapidly, compared with the rate at which the mixed phase region evolves, that, with a negligible error, the liquid and solid compositions in the two phase region are determined by the liquidus and solidus. We might expect that fast melting is tenable provided the solid grains in the two phase region are so small that all diffusion processes are effectively instantaneous. Were this not true of the diffusion of heat, it would be unrealistic to assume a common mean temperature for the solid and liquid phases. But since the diffusion of chemical species in a solid is so slow compared with that of heat (indeed, it is usually assumed that material diffusion in the solid simply does not exist!), the grains of solid in the phase mixture may well not be in chemical equilibrium with the surrounding fluid even though both are at the same temperature. In such cases, the fast melting/freezing approximation will perform well only if external changes are imposed at a rate small compared with the rates of chemical and convective equilibration. Usually diffusion processes occur so slowly in the solid that the fast freezing approximation has a limited range of usefulness.

More characteristic of real systems is the approximation towards which this paper works, namely that convective and diffusive mixing in the melt is so efficient as to be effectively instantaneous, so maintaining the melt on the liquidus, but, by contrast, diffusion in the solid is so slow as to be effectively negligible. The final equilibrium state approached by an isolated system is then not the maximum entropy state of complete chemical and thermal equilibrium; it is one of 'quasi-equilibrium'¹ in which not only arbitrary gradients of ϕ exist (see above), but also arbitrary distributions of $\bar{\xi}^S$. To be sure these would, over astronomically large timescales, be evened out, but the transition from quasi-equilibrium to complete equilibrium is not one with which we are primarily concerned. In fact, although in the first instance our theory will contain small rate parameters (such as Λ below) that, over a sufficiently large timescale, will

¹ Metallurgists commonly use the term para-equilibrium for a similar, but not identical, concept. We therefore prefer to use the prefix 'quasi-'

drive an isolated system to its maximum entropy state, we shall later set these parameters to zero, and will show that as a result the final steady state of the system, although static, is nevertheless non-uniform in composition.

We aim to create the simplest possible theory that will admit the physical processes described above. To motivate our model, we consider the formation and growth of solid by likening each grain of the mixed phase to an onion, the innermost core having the composition corresponding to S_0 in Figure 1. The outer layers are successively richer in light constituent, since as T decreases, the new material laid down on the surface of the grain will have a composition corresponding to a point on Figure 1 that moves continuously to the right along S_0S_1 . Because of the small diffusivity of the interior of the grain, the various compositions of the different skins of the onion do not even out. (This process is usually termed coring (see Chalmers, 1964).) Clearly, a full description of the system will demand a detailed specification of the internal structure of a grain. And yet, since that composition and associated internal energy will be 'locked up' in the grain when we eventually neglect solid diffusion, the complications of such a detailed theory should be largely unnecessary. The internal make-up of the grain is not, however, totally irrelevant. For example, one can scarcely discuss mass conservation for the internal constituents of the mushy zone unless one keeps an integrated record of the overall composition of the grains. The simplest possible approach, it seems to us, is to make use of one variable, an average of ξ^S over the grain; we shall denote this by $\bar{\xi}^S$, and overbars on other variables will indicate that they are evaluated off the equilibrium phase curves. We shall also introduce the Gibbs free energy, $\Phi^S(p, T, \bar{\xi}^S)$, representing the solid grains as a whole. Strictly, this too is a simplification; the true energy, $\bar{\Phi}^S$, will depend upon the complex grain micro-structure and not simply on the mean $\bar{\xi}^S$. Nevertheless, $\bar{\Phi}^S$ must approach Φ^S as $\bar{\xi}^S$ tends to the solidus concentration. We shall actually use Φ^S as our $\bar{\Phi}^S$, just as though the light constituent were uniformly distributed throughout the grain. Evidently we shall be guilty, to some degree, of oversimplification, but the complications to which our simplistic model leads should convince the reader, as it has convinced us, that analysis of the detailed model is premature.

The evolution of $\bar{\xi}^S$ in a freezing system may be governed by quite simple considerations. As we have seen, the smaller values of the light constituent concentration within the grain reduce the mean $\bar{\xi}^S$ below the surface value. The point representing the mean $\bar{\xi}^S$ will therefore describe a sequence of states such as the one shown by the dashed curve to the left of the solidus in Figure 1. The complete solidification of the alloy is then postponed until the temperature $T' (< T_1)$ is reached, provided this temperature lies above the eutectic temperature corresponding to the point E . Otherwise there is a eutectic transition such as that illustrated in Figure 1. It is only because we are following the growth of a grain from the initiation of freezing that we can, in principle, monitor the average $\bar{\xi}^S$; the problem of melting grains is more complex, since it is necessary to have a knowledge of the history of the grains, that is, the composition of successive layers of the onion as they are stripped off the grain by melting. It is to avoid these complications that we restrict ourselves to solidification processes in this paper.

An earlier, somewhat elementary, approach to segregation was presented by Scheil (1947) and exploited by Pfann (1952) to discuss the important process of zone-melting of an alloy. Strictly in these papers (Scheil, 1947; Pfann, 1952) the concern was with sharp interfaces between the phases rather than a mixed phase region but recently Fowler (1985) has attempted to incorporate a Scheil-Pfann equation into the theory of mushy zones of Roberts and Loper (1983) and Hills, Loper and Roberts (1983). It is therefore important that we understand how such an equation arises. First, in the fast melting limit, the concentrations of the light constituent in the phases are determined by the liquidus and solidus and, in a particular model, these phase curves are assumed to be in constant ratio to one another. The constant of proportionality, k_0 , is termed the distribution coefficient and

$$\xi^S = k_0 \xi^L. \quad (1.2)$$

Mass diffusion in the solid is taken as negligible but, by contrast, in the liquid mixing is assumed complete, meaning that the concentration is uniform. (This set of circumstances is sometimes called simple freezing.) By considering an isolated unit volume of the mixture, we find that

the light constituent mass concentration, ξ^M , of the phase mixture is determined by

$$\xi^M = \phi \xi^S + (1 - \phi) \xi^L. \quad (1.3)$$

This equation holds quite generally even when ξ^S , ξ^L are replaced by their off-equilibrium values, so that when mixing is complete in the liquid we have

$$\xi^M = \phi \bar{\xi}^S + (1 - \phi) \xi^L. \quad (1.4)$$

When the temperature is lowered, the mass $d(\rho\phi)$ that freezes onto the solid grains will have the current composition of the solidus so that

$$d(\rho\phi \bar{\xi}^S) = \xi^S d(\rho\phi) = k_0 \xi^L d(\rho\phi). \quad (1.5)$$

We shall ignore changes in density and, since the overall contents of the unit volume have not changed, $d\xi^M = 0$. By (1.4) and (1.5) we therefore have

$$k_0 \xi^L d\phi + d[(1 - \phi) \xi^L] = 0, \quad (1.6)$$

which integrates to give

$$\xi^L = \xi_0 (1 - \phi)^{k_0 - 1}, \quad (1.7)$$

where ξ_0 is the composition of the mixed phase region when solid first appears (see above). It then follows from (1.5) that

$$\bar{\xi}^S = \xi_0 [1 - (1 - \phi)^{k_0}] / \phi. \quad (1.8)$$

One of the objectives of this paper is to show how a generalized Scheil-Pfann equation can arise from a *dynamic* theory of a two-phase mushy region that generalizes (1.2) and admits a quasi-equilibrium state.

2. Basic Equations.

We follow the general approach of Hills, Loper and Roberts (1983) and model each of the liquid and solid phases by a diffusive theory and the mush itself by a general mixture theory. The balance equations for total mass, energy and the linear momentum for the liquid phase are (see Hills, Loper and Roberts, 1983, eqs. (2.3), (2.8), (2.7))

$$\partial_t \rho + \nabla \cdot [\rho(\phi \mathbf{v}^S + (1 - \phi) \mathbf{v}^L)] = 0, \quad (2.1)$$

$$\rho r - \nabla \cdot \mathbf{q} - \rho \frac{DU}{Dt} - \mathbf{g} \cdot \mathbf{w} + \boldsymbol{\sigma}^S : \mathbf{D}^S + \boldsymbol{\sigma}^L : \mathbf{D}^L = 0, \quad (2.2)$$

$$\rho(1 - \phi) \frac{D^L v_i^L}{Dt} = \rho(1 - \phi) F_i^L + \nabla_k \sigma_{ki}^L + g_i + \frac{1}{2} m^S w_i. \quad (2.3)$$

Here ρ is the total density of the phase mixture, ϕ the mass concentration of the solid, U the internal energy per unit mass of phase mixture, r the heat supply to the mixture per unit mass per unit time, and m^S the solid phase conversion rate (see equation (2.6)). The vectors \mathbf{v}^S , \mathbf{v}^L , \mathbf{q} , \mathbf{g} , \mathbf{F}^L are respectively the barycentric velocities of the solid and the liquid, the heat flux vector, a diffusive force between the phases and an applied body force per unit mass for the liquid phase. The relative velocity, \mathbf{w} , is defined by

$$\mathbf{w} = \mathbf{v}^L - \mathbf{v}^S. \quad (2.4)$$

The total stress tensors for solid and liquid phases are σ_{ij}^S , σ_{ij}^L , and D_{ij}^S , D_{ij}^L are the rate of deformation tensors. The motional derivatives D^L/Dt and D/Dt are evaluated using the barycentric velocities \mathbf{v}^L and \mathbf{v} ($= \phi \mathbf{v}^S + (1 - \phi) \mathbf{v}^L$) respectively.

Thermostatic considerations suggest that, rather than the internal energy U , we should instead describe our theory using the Gibbs energy $\Phi = U - ST + p/\rho$ as the thermodynamic potential, where S is the entropy per unit mass. Then the entropy growth postulate is (Hills, Loper and Roberts, 1983, eq. (2.11))

$$\begin{aligned} \Re \equiv & -\rho \left(\frac{D\Phi}{Dt} + S \frac{DT}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} + \frac{p}{\rho^2} \frac{D\rho}{Dt} \right) + T \nabla \cdot \mathbf{k} \\ & - \nabla \cdot \mathbf{q} - \mathbf{g} \cdot \mathbf{w} + \boldsymbol{\sigma}^S : \mathbf{D}^S + \boldsymbol{\sigma}^L : \mathbf{D}^L \geq 0, \end{aligned} \quad (2.5)$$

where \mathbf{k} is the entropy flux vector. Formally we should also have an evolution equation for the linear momentum of the solid phase but later we shall assume (as in previous theories) that the solid is rigid and then its momentum equation has to be abandoned (see Hills, Loper and Roberts, 1983). Strictly, such an assumption is not physically realistic, for it supposes that the solid matrix is able to sustain any applied stress and is unable to respond to temperature variations by expansion or contraction. It is possible to construct a theory in which this restriction on the nature of the solid is relaxed (see Hills and Roberts, 1987a,b), but we do not choose to do so here, preferring to highlight other aspects of the general problem.

To complete the set of governing equations we need to discuss the evolution equations for the light constituent concentrations $\bar{\xi}^S$, $\bar{\xi}^L$ and the solid phase concentration ϕ . As indicated in the introduction, for the model and the range of solidification rates we have in mind, the diffusion and convection processes in the liquid phase are efficient enough for the liquid concentration $\bar{\xi}^L$ to remain on the liquidus, $\bar{\xi}^L = \xi^L(p, T)$. But, by contrast, the corresponding solid concentration departs from its equilibrium phase curve due to the vanishingly small diffusion rates in the solid. We shall denote the rate at which the solid phase is formed by m^S , and the rate at which light constituent enters the solid phase by m_1^S , so that

$$m^S = \partial_t(\rho\phi) + \nabla \cdot (\rho\phi\mathbf{v}^S), \quad (2.6)$$

$$m_1^S = \partial_t(\rho\phi\bar{\xi}^S) + \nabla \cdot (\rho\phi\bar{\xi}^S\mathbf{v}_1^S), \quad (2.7)$$

where \mathbf{v}_1^S is the velocity of the light constituent in the solid. The rates m^S and m_1^S are related, but the way in which they are related raises the spectre of a very difficult issue: history dependence. Consider a mush at rest. While we are freezing material, it is reasonable to suppose, as in (1.5), that $m_1^S = \xi^S m^S$ where ξ^S is the solidus composition for the current state in which the grain finds itself. Then $\bar{\xi}^S$, which is the single parameter needed to describe a grain (when its composition is 'frozen in' by the absence of solid diffusion), can be obtained by integration, as in (1.8). When a grain is melting we have $m_1^S = \hat{\xi}^S m^S$, where $\hat{\xi}^S$ is the current surface composition of the grain. Continued melting progressively unlocks the past history of the grains and changes $\hat{\xi}^S$ in a

way that is available only when a record of the past history has been kept, that is, for melting the single parameter $\bar{\xi}^S$ is an insufficient description of the solid. We avoid the aspects of history dependence by concentrating instead on solidification. It now becomes clear that the relative rate M , defined by

$$M \equiv m_1^S - \xi^S m^S, \quad (2.8)$$

plays a fundamental rôle. Generally, when diffusion within the grain carries constituents across its boundary, we are not entitled to assume $M = 0$. Thus, to develop a completely general theory we must take $M \neq 0$ and suppose also that the diffusion in the solid is non-negligible.

The evolution equations for $\bar{\xi}^S$ and ϕ follow from mass conservation of the light constituent. (For a general discussion see Hills and Roberts (1987c).) First we can reformulate (2.7) in terms of the barycentric velocity \mathbf{v} as

$$\rho\phi \frac{D\bar{\xi}^S}{Dt} = (\xi^S - \bar{\xi}^S)\rho \frac{D\phi}{Dt} + \rho\phi(1-\phi)\mathbf{w} \cdot \nabla \xi^S - \nabla \cdot \mathbf{h} + M, \quad (2.9)$$

where the flux vector \mathbf{h} is related to the individual velocities $\mathbf{v}_1^S, \mathbf{v}_2^S$, of the solid's constituents by

$$\mathbf{h} = \rho\phi\bar{\xi}^S(1-\bar{\xi}^S)(\mathbf{v}_1^S - \mathbf{v}_2^S) + \rho\phi(1-\phi)(\xi^S - \bar{\xi}^S)\mathbf{w}. \quad (2.10)$$

Conservation of light material for the whole phase mixture gives

$$\rho \frac{D\xi^M}{Dt} + \nabla \cdot \mathbf{i} = 0, \quad (2.11)$$

where the flux \mathbf{i} is given by

$$\mathbf{i} = \rho\phi\bar{\xi}^S(\mathbf{v}_1^S - \mathbf{v}^S) + \rho(1-\phi)\xi^L(\mathbf{v}_1^L - \mathbf{v}^L) + \rho\phi(1-\phi)(\xi^L - \bar{\xi}^S)\mathbf{w}. \quad (2.12)$$

Thus, using (1.4), we obtain

$$\rho(\xi^L - \bar{\xi}^S) \frac{D\phi}{Dt} = \rho(1-\phi) \frac{D\xi^L}{Dt} + \nabla \cdot \mathbf{i} + \rho\phi \frac{D\bar{\xi}^S}{Dt}, \quad (2.13)$$

or, equivalently,

$$\rho(\xi^L - \xi^S) \frac{D\phi}{Dt} = \rho(1-\phi) \frac{D\xi^L}{Dt} + \rho\phi(1-\phi) \mathbf{w} \cdot \nabla \xi^S + \nabla \cdot (\mathbf{i} - \mathbf{h}) + M. \quad (2.14)$$

The general theory we develop will involve only the barycentric velocities \mathbf{v}^S , \mathbf{v}^L , \mathbf{v} and the relative velocity \mathbf{w} . In particular, the fluxes \mathbf{i} and \mathbf{h} and the relative rate M will be the subject of constitutive postulates. From (2.12) the fluxes should depend on the relative velocity \mathbf{w} and this necessitates the use of the full mixture theory for the co-existing phases. Equations (2.10) and (2.12) become the means by which the detailed motion of the constituents within each phase can, if necessary, be determined.

3. Constitutive Equations.

Foremost in our considerations of a constitutive theory is the fact that, since we are dealing with a mixture of two phases of the same material, the Gibbs energy for the whole should be the proportionate sum of the separate energies for the two phases, that is, the lever rule must hold:

$$\Phi = \phi\Phi^S(p, T, \bar{\xi}^S) + (1 - \phi)\Phi^L(p, T, \bar{\xi}^L). \quad (3.1)$$

The chemical potentials for the phases are defined by

$$\bar{\mu}^\gamma = \frac{\partial\Phi^\gamma}{\partial\bar{\xi}^\gamma}, \quad (\gamma = S, L), \quad (3.2)$$

and then the equilibrium phase curves (1.1) are obtained by simultaneously solving the equations (see Hills, Loper and Roberts, 1983, eq. (4.8))

$$\bar{\mu}^S = \bar{\mu}^L, \quad \Phi^S - \bar{\mu}^S\bar{\xi}^S = \Phi^L - \bar{\mu}^L\bar{\xi}^L. \quad (3.3)$$

For the liquid phase, we incorporate the assumption that the concentration is determined by the liquidus by making the substitution $\bar{\xi}^L = \xi^L(p, T)$ in (3.1) and throughout employ the notation $\mu = \bar{\mu}^L|_{\bar{\xi}^L = \xi^L}$. Using (3.1), (2.9) and (2.14), the entropy growth postulate (2.5) becomes

$$\begin{aligned} -\chi M - a_p \frac{Dp}{Dt} - a_T \frac{DT}{Dt} + \psi \nabla \cdot \mathbf{i} + \chi \nabla \cdot \mathbf{h} \\ + T \nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{q} - \mathbf{w} \cdot \mathbf{b} + \hat{\sigma}^S : \mathbf{D}^S + \hat{\sigma}^L : \mathbf{D}^L \geq 0, \end{aligned} \quad (3.4)$$

where

$$\psi = [\xi^L - \xi^S]^{-1} [\Phi^L - \Phi^S + \bar{\mu}^S(\bar{\xi}^S - \xi^S)], \quad (3.5a)$$

$$\chi = \bar{\mu}^S - \psi = [\xi^L - \xi^S]^{-1} [\Phi^S - \Phi^L + \bar{\mu}^S(\xi^L - \bar{\xi}^S)], \quad (3.5b)$$

$$a_p = \rho \left\{ \phi \frac{\partial\Phi^S}{\partial p} + (1 - \phi) \frac{\partial\Phi^L}{\partial p} + (1 - \phi)[\mu - \psi] \frac{\partial\xi^L}{\partial p} - \frac{1}{\rho} \right\}, \quad (3.6)$$

$$a_T = \rho \left\{ \phi \frac{\partial\Phi^S}{\partial T} + (1 - \phi) \frac{\partial\Phi^L}{\partial T} + (1 - \phi)[\mu - \psi] \frac{\partial\xi^L}{\partial T} + S \right\}, \quad (3.7)$$

$$\mathbf{b} = \mathbf{g} + p\nabla\phi + \rho\phi(1-\phi)\chi\nabla\xi^S, \quad (3.8)$$

$$\hat{\sigma}_{ij}^S = \sigma_{ij}^S + p\phi\delta_{ij}, \quad \hat{\sigma}_{ij}^L = \sigma_{ij}^L + p(1-\phi)\delta_{ij}, \quad (3.9)$$

and the partial derivatives of Φ^L are obtained by assuming that $\Phi^L = \Phi^L(p, T, \bar{\xi}^L)$ and, after the differentiation, setting $\bar{\xi}^L = \xi^L(p, T)$. Assuming that neither the fluxes nor the stresses depend on Dp/Dt or DT/Dt we can use the usual argument to deduce immediately that $a_p = a_T = 0$ so that

$$\begin{aligned} \frac{1}{\rho} &= \phi \frac{\partial \Phi^S}{\partial p} + (1-\phi) \frac{\partial \Phi^L}{\partial p} + (1-\phi) [\mu - \psi] \frac{\partial \xi^L}{\partial p}, \\ S &= - \left\{ \phi \frac{\partial \Phi^S}{\partial T} + (1-\phi) \frac{\partial \Phi^L}{\partial T} + (1-\phi) [\mu - \psi] \frac{\partial \xi^L}{\partial T} \right\}. \end{aligned} \quad (3.10)$$

It is important to note that an equivalent statement to (3.3) is

$$\bar{\xi}^L = \xi^L(p, T), \quad \chi = 0, \quad (3.11a)$$

since $\chi = 0$ reduces both of (3.3) to the same condition

$$\bar{\mu}^S = \bar{\mu}^L \quad \text{or} \quad \psi = \mu, \quad (3.11b)$$

which, when $\bar{\xi}^L = \xi^L$, solves to give $\bar{\xi}^S = \xi^S$. Thus in equilibrium, (3.10) becomes the familiar lever rules for specific volume and entropy.

To make further progress, we must be more specific as to the constitutive model. It is not too serious an approximation to assume the solid phase is rigid so that $\mathbf{D}^S = \mathbf{0}$ and the solid stress tensor becomes whatever is necessary to balance the forces acting. As a result the penultimate term in the inequality (3.4) drops out of our considerations. Next we come to the choice of the independent thermodynamic variables. So far in the development we have employed $p, T, \bar{\xi}^S, \phi$, but the dissipation in (3.4) associated with the fluxes $\mathbf{i}, \mathbf{h}, \mathbf{k}$ suggests that ψ and χ will play a fundamental rôle. Also, to guide our thinking, we have the diffusive theory of Landau and Lifshitz (1959, Chapter VI) which is often used to describe a single-phase alloy melt. There, the chemical potential, rather

than the pressure, is taken as the independent variable. From (3.2)₁ and the definitions (3.5), we see that

$$\psi = \psi(p, T, \bar{\mu}^S), \quad \chi = \chi(p, T, \bar{\mu}^S), \quad (3.12)$$

and we can invert these equations and (3.2)₁ and adopt

$$\psi, \quad T, \quad \chi, \quad \phi, \quad (3.13)$$

as our independent variables. We shall postulate that the fluxes \mathbf{i} , \mathbf{h} , \mathbf{k} , \mathbf{q} (generically denoted by Θ) are linear in \mathbf{w} and the gradients of the set (3.13), *viz.*

$$\Theta = \alpha_\psi^\Theta \nabla \psi + \alpha_T^\Theta \nabla T + \alpha_\chi^\Theta \nabla \chi + \alpha_\phi^\Theta \nabla \phi + \alpha_w^\Theta \mathbf{w} \equiv \Theta_0 + \alpha_w^\Theta \mathbf{w}. \quad (3.14)$$

The liquid phase is taken to be linear viscous in terms of the barycentric velocity \mathbf{v}^L

$$\sigma_{ij}^L = -p^L \delta_{ij} + \eta_1 D_{rr}^L \delta_{ij} + 2\eta_2 D_{ij}^L, \quad (3.15)$$

where all the coefficients are assumed general functions of the set (3.13). Upon substitution of (3.14)–(3.15) in the inequality (3.4), we will obtain terms involving second gradients of the set (3.13). Making the physically realistic assumption that these can be arbitrarily specified and that M and \mathbf{g} do not involve these gradients, we deduce

$$\mathbf{q}_0 = T\mathbf{k}_0 + \psi\mathbf{i}_0 + \chi\mathbf{h}_0. \quad (3.16)$$

Without further discussion, we assume that the \mathbf{w} contributions of the fluxes are such that the subscript zero may be removed throughout (3.16). Inequality (3.4) becomes

$$-\chi M - \mathbf{k}_0 \cdot \nabla T - \mathbf{i}_0 \nabla \cdot \psi - \mathbf{h}_0 \cdot \nabla \chi + \mathbf{w} \cdot \hat{\mathbf{b}} + \hat{\boldsymbol{\sigma}}^L : \mathbf{D}^L \geq 0, \quad (3.17)$$

with

$$\hat{\mathbf{b}} = \mathbf{b} - \alpha_w^i \nabla \psi - \alpha_w^k \nabla T - \alpha_w^h \nabla \chi.$$

There remain only the constitutive equations for the relative rate M and the diffusive force \mathbf{g} . Thus far our understanding of M has arisen

from considering static situations. Realistically, we must expect that when there is relative velocity between liquid and solid phases then M will be modified. From (3.17), the dissipation associated with M is $-\chi M$ and since in equilibrium (when $\chi = 0$) M should vanish, an appropriate assumption for M is

$$M = M_0 + \mathbf{w} \cdot (\alpha_\psi^m \nabla \psi + \alpha_T^m \nabla T + \alpha_\chi^m \nabla \chi + \alpha_\phi^m \nabla \phi), \quad (3.18)$$

where $M_0 = -\Lambda \chi$ and Λ is an intrinsic relaxation time for the freezing process. The diffusive force \mathbf{g} characterizes the momentum interactions between the phases and the form we adopt is suggested by (3.17) and (3.18), *viz.*

$$\begin{aligned} \mathbf{g} = & -p \nabla \phi - \rho \phi (1 - \phi) \chi \nabla \xi^S - [\alpha_w^i + \chi \alpha_\psi^m] \nabla \psi - [\alpha_w^k + \chi \alpha_T^m] \nabla T \\ & - [\alpha_w^h + \chi \alpha_\chi^m] \nabla \chi - \chi \alpha_\phi^m \nabla \phi - \nu \mathbf{w}. \end{aligned} \quad (3.19)$$

It then follows from inequality (3.17) that

$$p^L = (1 - \phi)p, \quad \alpha_\phi^\ominus = 0. \quad (3.20)$$

The last condition shows that the fluxes do not contain a Fickian type contribution proportional to $\nabla \phi$ (see Hills and Roberts, 1987d). Were this not true, then the $\nabla \phi$ terms would prevent *any* $\phi(\mathbf{x})$ being a possible solution in the equilibrium state.

The inequality (3.17) reduces to

$$\begin{aligned} \mathfrak{R} \equiv & \Lambda \chi^2 - \alpha_\psi^i (\nabla \psi)^2 - \alpha_T^k (\nabla T)^2 - \alpha_\chi^h (\nabla \chi)^2 - (\alpha_T^i + \alpha_\psi^k) \nabla \psi \cdot \nabla T \\ & - (\alpha_\chi^i + \alpha_\psi^h) \nabla \psi \cdot \nabla \chi - (\alpha_\chi^k + \alpha_T^h) \nabla \chi \cdot \nabla T \\ & + \nu w^2 + \eta_1 (\text{tr } \mathbf{D}^L)^2 + 2\eta_2 \mathbf{D}^L : \mathbf{D}^L \geq 0. \end{aligned} \quad (3.21)$$

4. Diffusionless Solid: Full Theory.

When an isolated system comes into equilibrium it will, according to (3.5) and (3.21), be in a state

$$\mathbf{v}^L = \mathbf{w} = 0, \quad \chi = 0, \quad T = T_0, \quad \psi = \bar{\mu}^S = \bar{\mu}_0^S, \quad (4.1)$$

where $T_0, \bar{\mu}_0^S$ are constants and we have put ourselves in a frame where $\mathbf{v}^S = 0$. According to (3.12), p is a constant so that the last of (4.1), which by (3.11) is $\mu(p, T)$, is indeed a constant. An important feature of equilibrium should be that $\phi(\mathbf{x})$ can be non-uniform: the distribution of the solid and liquid phases should be able to vary from point to point in the equilibrium state. Substituting (3.19), (3.20) into (2.3) shows that we must have $\alpha_\phi^m = 0$. The density ρ and entropy S will not be spatially uniform and will vary according to (3.10). In short, within the framework of the $\bar{\xi}^L = \xi^L$ theory, the system correctly attains its maximum entropy state when $\mathfrak{R} = 0$.

But, if diffusion processes within the solid are slow, an astronomically long time may elapse before the maximum entropy state is reached. On a more practical timescale, the system will attain a ‘quasi-equilibrium’ state that is static but in which \mathfrak{R} , although non-zero, is nevertheless vanishingly small reflecting the minute contributions from M_0 and \mathbf{h}_0 . For practical considerations, we can neglect these contributions and assume

$$M_0 = 0, \quad \mathbf{h}_0 = \mathbf{0}, \quad (4.2)$$

not because, as in (4.1), $\chi = 0$, but because

$$\begin{aligned} \Lambda = 0, \quad \alpha_\beta^h = 0, \quad (\beta = \phi, T, \chi), \\ \alpha_w^h = \rho\phi(1 - \phi)(\xi^S - \bar{\xi}^S). \end{aligned} \quad (4.3)$$

From (2.10) we see that there is then no diffusion within the solid. Immediately we deduce from (3.21) that

$$\alpha_\chi^\ominus = 0, \quad (4.4)$$

and Onsager symmetry arguments suggest that

$$\alpha_T^i = \alpha_\psi^k. \quad (4.5)$$

The entropy production inequality can then be recast as

$$\mathfrak{R} \equiv -\mathbf{i}_0^2/\alpha_\psi^i + (\kappa/T) (\nabla T)^2 + \nu w^2 + \eta_1 (\text{tr } \mathbf{D}^L)^2 + 2\eta_2 \mathbf{D}^L : \mathbf{D}^L \geq 0, \quad (4.6)$$

where

$$\begin{aligned} \mathbf{i}_0 &= \alpha_\psi^i \nabla \psi + \alpha_T^i \nabla T, \quad \mathbf{k}_0 = -(\kappa/T) \nabla T + (\alpha_T^i/\alpha_\psi^i) \mathbf{i}_0, \\ \kappa/T &= \alpha_T^k - (\alpha_T^i)^2 / \alpha_\psi^i. \end{aligned} \quad (4.7)$$

From (4.6), when an isolated system comes into quasi-equilibrium and \mathfrak{R} vanishes, we have

$$\mathbf{v}^L = \mathbf{w} = \mathbf{0}, \quad T = T_0, \quad \psi = \psi_0, \quad (4.8)$$

where again T_0, ψ_0 are constants and we are in a reference frame in which $\mathbf{v}^S = \mathbf{0}$. *There is no suggestion that χ is zero or, therefore, $\bar{\xi}^S = \xi^S$.* In this quasi-equilibrium state, χ (like ϕ) may depend on the spatial variable \mathbf{x} in an arbitrary way. This does not imply, of course, that the theory will fail to determine χ . The governing equations will determine not only ϕ but also the χ of the final quasi-equilibrium state from any initial specified state. By (3.12)₁, the last of (4.8) gives a relationship between $\bar{\mu}^S$ and p , neither of which will generally be constant across the system.

It is essential to verify that the state (4.8) is a hydrostatic solution of (2.2), (2.9), (2.14), and, more importantly, (2.3) when the applied body force and heat supply are zero. We shall need some thermodynamic differential identities which follow immediately from the definitions (3.5). We find

$$(\xi^L - \xi^S) d\chi = -\sigma_p^\chi dp - \sigma_T^\chi dT - \sigma_\xi^\chi d\bar{\xi}^S, \quad (4.9)$$

where

$$\begin{aligned} \sigma_p^\chi &= \left[\Delta + (\bar{\xi}^S - \xi^L) \frac{\partial \bar{\mu}^S}{\partial p} \right], \quad \sigma_T^\chi = - \left[\frac{\mathfrak{S}}{T} - (\bar{\xi}^S - \xi^L) \frac{\partial \bar{\mu}^S}{\partial T} \right], \\ \sigma_\xi^\chi &= (\bar{\xi}^S - \xi^L) \frac{\partial \bar{\mu}^S}{\partial \bar{\xi}^S}, \end{aligned} \quad (4.10)$$

and

$$\begin{aligned}\Delta &= v^L - v^S - (\psi - \mu) \frac{\partial \xi^L}{\partial p} - \chi \frac{\partial \xi^S}{\partial p}, \\ \frac{\mathfrak{S}}{T} &= S^L - S^S + (\psi - \mu) \frac{\partial \xi^L}{\partial T} + \chi \frac{\partial \xi^S}{\partial T},\end{aligned}\quad (4.11)$$

with

$$v^S = \frac{\partial \Phi^S}{\partial p}, \quad S^S = -\frac{\partial \Phi^S}{\partial T}, \quad \text{etc.} \quad (4.12)$$

There is an expression similar to (4.9) for $-d\psi$ but with the coefficients σ_β^ψ ($\beta = p, T, \xi$) being obtained by replacing $(\bar{\xi}^S - \xi^L)$ in (4.10) by $(\bar{\xi}^S - \xi^S)$. By using these identities and the constitutive theory we may show that (2.3) becomes

$$\begin{aligned}\rho(1 - \phi) \frac{Dw_i^L}{Dt} &= \rho(1 - \phi) F_i^L - a_\psi \nabla_i \psi - a_\chi \nabla_i \chi - a_T \nabla_i T \\ &\quad - \left(\nu - \frac{1}{2} m^S \right) w_i + \left[\eta_1 D_{rr}^L \delta_{ij} + 2\eta_2 D_{ij}^L \right]_{,j},\end{aligned}\quad (4.13)$$

where

$$\begin{aligned}a_\psi &= \alpha_w^i + \chi \alpha_\psi^m + b(\xi^L - \bar{\xi}^S), \quad a_\chi = \alpha_w^h + \chi \alpha_\chi^m + b(\xi^S - \bar{\xi}^S), \\ a_T &= \alpha_w^k + \chi \alpha_T^m + b\mathfrak{S}/T + \rho\phi(1 - \phi)\chi(\partial \xi^S / \partial T), \\ b &= (1 - \phi) [1 + \rho\phi\chi(\partial \xi^S / \partial p)] / \Delta.\end{aligned}\quad (4.14)$$

For the state (4.8) to be possible we must have $a_\chi = 0$ and, using (4.3)₃, we obtain

$$\chi \alpha_\chi^m = -(\xi^S - \bar{\xi}^S) [\rho\phi(1 - \phi) + b], \quad (4.15)$$

so that by insisting on quasi-equilibrium being maintained once established, we have determined a material coefficient for the relative rate M . We note that, on approach to equilibrium when $\bar{\xi}^S \rightarrow \xi^S$, $\chi \rightarrow 0$, the identity (4.9) shows that α_χ^m remains finite in this limit, as it properly should.

It is easily verified, using (3.18), (4.7), (4.15) and (4.3), that (2.9) and (2.14) are consistent with the state (4.8) and since the energy equation (2.2) reduces to

$$\rho T \frac{DS}{Dt} + T \nabla \cdot \mathbf{k} = \rho r + \mathfrak{R}, \quad (4.16)$$

it too is consistent with the quasi-equilibrium state.

It is perhaps surprising that, in the final resting point (4.8) of an isolated system, $\bar{\xi}^S$ and p are not constant. Indeed, by (3.5) and (4.9) we have

$$\begin{aligned} (\xi^L - \xi^S) \nabla \psi = & \left[\Delta + (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial p} \right] \nabla p - \left[\frac{\mathfrak{S}}{T} - (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial T} \right] \nabla T \\ & + (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial \bar{\xi}^S} \nabla \bar{\xi}^S, \end{aligned}$$

so that, in quasi-equilibrium where (4.8) holds

$$\left[\Delta + (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial p} \right] \nabla p = (\xi^S - \bar{\xi}^S) \frac{\partial \bar{\mu}^S}{\partial \bar{\xi}^S} \nabla \bar{\xi}^S.$$

In general, neither ∇p nor $\nabla \bar{\xi}^S$ are zero. If, as seems plausible,

$$p \left[\Delta + (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial p} \right] \gg \bar{\xi}^S (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial \bar{\xi}^S},$$

large variations in $\bar{\xi}^S$ can be balanced by quite small changes in p , *i.e.* p will be almost uniform across the system, even though $\bar{\xi}^S$ is not.

The more significant aspects of this section have been decided. In the remainder we examine a secondary issue: what values to take for the remaining coefficients α_ψ^\ominus , α_ψ^m , *etc.*. From (2.12) we are led to assume

$$\alpha_w^i = \rho \phi (1 - \phi) (\xi^L - \bar{\xi}^S), \quad (4.17)$$

and it is helpful to rewrite (4.7)₁ as

$$\mathbf{i}_0 = \alpha_\psi^i \nabla \mu + \alpha_T^i \nabla T + \alpha_\psi^i \nabla (\psi - \mu). \quad (4.18)$$

If we insist that, in complete equilibrium when $\psi = \mu$, the flux i should reduce to the fast-melting form of Hills, Loper and Roberts (1983) then

$$\alpha_{\psi}^i \left. \frac{\partial \bar{\mu}^L}{\partial \bar{\xi}^L} \right|_* = -\rho(1 - \phi)D, \quad \alpha_{\psi}^i \left. \frac{\partial \bar{\mu}^L}{\partial T} \right|_* + \alpha_T^i = -\rho(1 - \phi) \frac{Dk_T}{T},$$

$$\alpha_{\psi}^i \left. \frac{\partial \bar{\mu}^L}{\partial p} \right|_* = -\rho(1 - \phi) \frac{Dk_p}{p}. \quad (4.19)$$

Here, a subscript asterisk denotes that an off-equilibrium quantity is actually evaluated on the appropriate phase line, for example $S_*^S = S^S(p, T, \xi^S(p, T))$. The coefficients D , k_T , k_p are respectively the mass transfer coefficient, the thermal diffusion ratio and the baro-diffusion ratio (see Landau and Lifshitz, 1959).

From the definition (3.5a), we obtain the differential form

$$(\xi^L - \xi^S)d(\psi - \mu) = \hat{\sigma}_p dp - \hat{\sigma}_T dT + \hat{\sigma}_{\xi} d\bar{\xi}^S, \quad (4.20)$$

where

$$\hat{\sigma}_p = \Delta - \Delta_*^L + (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial p} - (\xi^L - \xi^S) \left. \frac{\partial \bar{\mu}^L}{\partial p} \right|_*,$$

$$\hat{\sigma}_T = \frac{\mathfrak{S}}{T} - \frac{L_*^L}{T} + (\bar{\xi}^S - \xi^S) \frac{\partial \bar{\mu}^S}{\partial T} - (\xi^L - \xi^S) \left. \frac{\partial \bar{\mu}^L}{\partial T} \right|_*,$$

$$\hat{\sigma}_{\xi} = (\bar{\xi}^S - \xi^L) \frac{\partial \bar{\mu}^S}{\partial \bar{\xi}^S}, \quad (4.21)$$

and Δ_*^L , L_*^L are the volume expansion and latent heats of the fast melting theory (see Hills, Loper and Roberts, 1983)

$$\Delta_*^{\alpha} = v_*^L - v_*^S - (\xi^L - \xi^S) \left. \frac{\partial \bar{\mu}^{\alpha}}{\partial p} \right|_* = (\xi^L - \xi^S) \left. \frac{\partial \bar{\mu}^{\alpha}}{\partial \bar{\xi}^{\alpha}} \right|_* \frac{\partial \xi^{\alpha}}{\partial p},$$

$$L_*^{\alpha} = S_*^L - S_*^S + (\xi^L - \xi^S) \left. \frac{\partial \bar{\mu}^{\alpha}}{\partial T} \right|_* = (\xi^L - \xi^S) \left. \frac{\partial \bar{\mu}^{\alpha}}{\partial \bar{\xi}^{\alpha}} \right|_* \frac{\partial \xi^{\alpha}}{\partial T}. \quad (4.22)$$

Using (4.20), we find that

$$\begin{aligned} \mathbf{i} = & -\rho(1-\phi)D \left\{ \nabla \bar{\xi}^L(p, T) + \hat{k}_p \nabla p + \hat{k}_T \nabla T + \hat{k}_\xi \nabla \bar{\xi}^S \right\} \\ & + \rho\phi(1-\phi)(\xi^L - \bar{\xi}^S)\mathbf{w}, \end{aligned} \quad (4.23)$$

where

$$\begin{aligned} \hat{k}_p = & \frac{k_p}{p} + \left. \frac{\partial \bar{\mu}^L}{\partial \bar{\xi}^L} \right|_*^{-1} \frac{\hat{\sigma}_p}{(\xi^L - \xi^S)}, \quad \hat{k}_T = \frac{k_T}{T} - \left. \frac{\partial \bar{\mu}^L}{\partial \bar{\xi}^L} \right|_*^{-1} \frac{\hat{\sigma}_T}{(\xi^L - \xi^S)}, \\ \hat{k}_\xi = & \left[\frac{\bar{\xi}^S - \xi^S}{\xi^L - \xi^S} \right] \frac{\partial \bar{\mu}^S}{\partial \bar{\xi}^S} / \left. \frac{\partial \bar{\mu}^L}{\partial \bar{\xi}^L} \right|_*. \end{aligned} \quad (4.24)$$

Incorporating these considerations, the resultant energy equation is

$$\begin{aligned} & -\tilde{\alpha}_p T \frac{Dp}{Dt} + \rho \tilde{c}_p \frac{DT}{Dt} + \rho T \gamma_\xi \frac{D\bar{\xi}^S}{Dt} - \rho \left(\mathfrak{S} - \chi T \frac{\partial \xi^S}{\partial T} \right) \frac{D\phi}{Dt} \\ & + T \nabla \cdot \left[\left(\left. \frac{\partial \bar{\mu}^L}{\partial \bar{\xi}^L} \right|_* \frac{k_T}{T} - \left. \frac{\partial \bar{\mu}^L}{\partial T} \right|_* \right) \mathbf{i}_0 + \alpha_w^k \mathbf{w} \right] \\ & = \rho r + \nabla \cdot (\kappa \nabla T) + \frac{i_0^2}{\rho(1-\phi)D} \left. \frac{\partial \bar{\mu}^L}{\partial \bar{\xi}^L} \right|_* + \nu w^2 \\ & + \eta_1 (\text{tr } \mathbf{D}^L)^2 + 2\eta_2 \mathbf{D}^L : \mathbf{D}^L, \end{aligned} \quad (4.25)$$

and

$$\begin{aligned} \frac{\tilde{\alpha}_p}{\rho} = & - \left\{ \phi \frac{\partial \bar{S}^S}{\partial p} + (1-\phi) \left[\frac{\partial S^L}{\partial p} + \left. \frac{\partial S^L}{\partial \bar{\xi}^L} \right|_* \frac{\partial \xi^L}{\partial p} + \frac{\hat{\sigma}_p}{(\xi^L - \xi^S)} \frac{\partial \xi^L}{\partial T} \right. \right. \\ & \left. \left. + (\psi - \mu) \frac{\partial^2 \xi^L}{\partial T \partial p} \right] \right\}, \end{aligned} \quad (4.26)$$

$$\begin{aligned} \frac{\tilde{c}_p}{T} = & - \left\{ \phi \frac{\partial \bar{S}^S}{\partial T} + (1-\phi) \left[\frac{\partial S^L}{\partial T} + \left. \frac{\partial S^L}{\partial \bar{\xi}^L} \right|_* \frac{\partial \xi^L}{\partial T} - \frac{\hat{\sigma}_T}{(\xi^L - \xi^S)} \frac{\partial \xi^L}{\partial T} \right. \right. \\ & \left. \left. + (\psi - \mu) \frac{\partial^2 \xi^L}{\partial T^2} \right] \right\}, \end{aligned} \quad (4.27)$$

$$\gamma_\xi = \left\{ \phi \frac{\partial \bar{S}^S}{\partial \bar{\xi}^S} + \frac{(1 - \phi) \hat{\sigma}_\xi}{(\xi^L - \xi^S)} \right\}. \quad (4.28)$$

In the next section we consider a reduced theory and use it to discuss the physically simple situation of a one-dimensional advancing mushy zone.

5. Diffusionless Solid: Reduced Theory.

The set of equations (2.1), (2.9), (2.14), (4.13) and (4.25) include a number of physical effects that are of no great concern for applications. The ratios k_p and k_T are usually vanishingly small and, in the same spirit, we may neglect $\hat{\sigma}_p$, $\hat{\sigma}_T$ also. To the same approximation, we have $\mathfrak{S} = L_*^S = L_*^L = L$, say, $\Delta_*^L = \Delta = v_*^L - v_*^S$, and

$$\hat{k}_\xi = \left(\frac{\bar{\xi}^S - \xi^S}{\xi^L - \xi^S} \right) \left(\frac{\partial \xi^L / \partial T}{\partial \xi^S / \partial T} \right). \quad (5.1)$$

For reasons of simplicity, we set

$$\alpha_\psi^m = \alpha_T^m = 0, \quad \alpha_w^k = \rho\phi(1 - \phi)L/T,$$

the last choice being suggested by the theory of Hills, Loper and Roberts (1983), and we assume the liquidus is linear, *viz.*

$$T_M - T = \Gamma\xi^L, \quad (5.2)$$

where T_M is the melting temperature of pure material corresponding to $\xi^L = 0$ and Γ is a constant. In what follows, we adopt (1.2) and then the reduced set of equations becomes

$$\frac{D\rho}{Dt} + \rho\nabla \cdot (\phi\mathbf{v}^S + (1 - \phi)\mathbf{v}^L) = 0, \quad (5.3)$$

$$\begin{aligned} \rho\phi \frac{D\xi^S}{Dt} = & (\xi^S - \bar{\xi}^S)\rho \frac{D\phi}{Dt} + \rho\phi(1 - \phi)\mathbf{w} \cdot \nabla \xi^S - \nabla \cdot [\rho\phi(1 - \phi)\mathbf{w}] \\ & - [(1 - \phi)(\xi^S - \bar{\xi}^S)/\Delta\chi] \mathbf{w} \cdot \nabla \chi, \end{aligned} \quad (5.4)$$

$$\begin{aligned} \rho\xi^L(1 - k_0) \frac{D\phi}{Dt} = & \rho(1 - \phi) \frac{D\xi^L}{Dt} + \rho\phi(1 - \phi)\mathbf{w} \cdot \nabla \xi^S \\ - \nabla \cdot \left\{ \rho(1 - \phi)D \left[\nabla \xi^L + \frac{(\bar{\xi}^S - k_0\xi^L)}{k_0\xi^L(1 - k_0)} \nabla \bar{\xi}^S \right] + \rho\phi(1 - \phi)(\xi^L - \xi^S)\mathbf{w} \right\} \\ & - [(1 - \phi)(\xi^S - \bar{\xi}^S)/\Delta\chi] \mathbf{w} \cdot \nabla \chi, \end{aligned} \quad (5.5)$$

$$\begin{aligned}
(1 - \phi) \frac{D^L v_i^L}{Dt} = & \rho(1 - \phi) F_i^L - (1 - \phi) \nabla p + \rho \phi (1 - \phi) \chi k_0 \Gamma \nabla T \\
& + \frac{(1 - \phi)(\xi^S - \bar{\xi}^S)}{\Delta} \nabla \chi - (\nu - \frac{1}{2} m^S) \mathbf{w} \\
& + \{ \eta_1 D_{rr}^L \delta_{ij} + 2\eta_2 D_{ij}^L \}_{,j}, \tag{5.6}
\end{aligned}$$

$$\rho c_p^0 \frac{DT}{Dt} - \rho L \frac{D\phi}{Dt} + T \nabla \cdot \left[\frac{\rho \phi (1 - \phi) L \mathbf{w}}{T} \right] = \rho r + \nabla \cdot (\kappa \nabla T), \tag{5.7}$$

where c_p^0 is the 'lever-sum' of the specific heats of the solid and liquid phases.

In Hills, Loper and Roberts (1983), the fast-melting theory was illustrated by looking at the one-dimensional steady propagation of a solidification front with velocity V into a melt, with the distinct phases being separated by a mushy zone. We can highlight the novelty of the present theory by reconsidering this situation. It suffices to suppose that the thermodynamic parameters of the solid and liquid are equal ($c_p^S = c_p^L = c_p$, etc.) and the inverse Lewis number ($= \rho c_p D / \kappa$) is vanishingly small. We choose a coordinate system, with origin at the base of the mushy zone, which moves with a velocity V in the direction of the z -axis and define a similarity variable, $\eta = z - Vt$. If the temperature at infinity in the melt is T_∞ and the light constituent composition there is ξ_∞ , then, as in Hills, Loper and Roberts (1983), the solution in the melt is given by

$$\bar{\xi}^L = \xi_\infty, \quad T = T_\infty - (T_\infty - T_T) e^{-V(\eta - \eta_T)/D}, \tag{5.8}$$

where $D = \kappa / \rho c_p$, and η_T is the height of the mush. The temperature of the top of the mush, T_T is given by setting $\xi^L = \xi_\infty$ in the liquidus equation (5.2).

For the mush, from (5.5) and the condition that $\phi = 0$ when $\eta = \eta_T$, we obtain the Scheil-Pfann equation

$$\xi^L = \xi_\infty / (1 - \phi)^{1 - k_0}, \tag{5.9}$$

and we are assuming, as in Figure 1, that $0 < k_0 < 1$. Then, from (5.4), we obtain

$$\bar{\xi}^S = \xi_\infty [1 - (1 - \phi)^{k_0}] / \phi, \tag{5.10}$$

and it is easy to show that $\bar{\xi}^S < \xi^S$. Next, we need to determine the temperature at the base of the mushy zone. As in Hills, Loper and Roberts (1983) we assume that heat is extracted at the solid/mush interface at a rate that keeps the front advancing with a steady velocity V . Since we are dealing with an infinite geometry, mass conservation for the light constituent requires that, in the single phase solid, $\bar{\xi}^S = \xi_\infty$ and (5.10) predicts that this will happen when $\phi = 1$. Then, from (5.9) and (5.2), we have that $T = -\infty$ so that a eutectic transformation is inevitable and the temperature at the base of the mushy zone will be T_E . Consequently, there will be a jump in ϕ at this interface. The temperature distribution and layer thickness can be obtained by solving

$$\frac{d^2T}{d\eta^2} + \frac{V}{\mathcal{D}} \frac{dT}{d\eta} = \frac{L}{c_p} \frac{V}{\mathcal{D}} \frac{d\phi}{d\eta}, \quad (5.11)$$

subject to $T = T_0 - \Gamma\xi_\infty$, $dT/d\eta = (T_\infty - T_M + \Gamma\xi_\infty)V/\mathcal{D}$ on $\eta = \eta_T$, and $T = T_E$ on $\eta = 0$. The derivative of ϕ is determined from (5.2) and (5.9). For the equivalent solution in the fast-melting theory, $\phi = (T_M - T)/\Gamma\xi_\infty(1 - k_0)$ and the temperature at the base of the mushy zone is $T = T_M - \Gamma\xi_\infty/k_0$. Clearly, the layer thickness is greater for the present theory.

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FIGURE CAPTION

Figure 1. A typical phase diagram for a binary alloy showing the plot of temperature against concentration of the light constituent of the alloy for a fixed pressure p_0 . The *equilibrium* liquidus and solidus are respectively OL and OS , and the point E corresponds to the eutectic transition. The non-equilibrium (depressed) solidus is S_0S' .

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