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Abstract.

This paper deals with the modelling of solidifying two-phase alloys and is primarily concerned with aspects of phase conversion. It briefly reviews existing theories and shows, by considering mass conservation and dissipation, how modelling proceeds when there is a clearly identifiable dominant rate process associated with the phase change.

1. Introduction.

Interest in the quantitative modelling of solidifying alloys has increased significantly during the past few years. This may be explained in part by the perennial interest of metallurgists and geologists in the solidification process, but it is also due to the increasing precision of related experiments. What these experiments have confirmed is that solidification is often a complicated but delicate balance between various rate and diffusion processes. This balance is such that, for a wide range of parameters, there frequently occurs a mixed phase region in which solid and liquid coexist over finite sized volumes. In general there are two types of such regions, the slurry and the mush. The former term is used to describe the case when the solid is in the form of fine particles in suspension, free to ascend or sediment according to their buoyancy. By contrast the solid in the mushy zone grows as a porous network of crystals or dendrites through which the liquid percolates.

Because of the intrinsic complexity and the need to get a workable theory, the various models that have been proposed for these two-phase regions have all made simplifying assumptions as to the dominant processes and, as a result, the literature contains a whole family of theories. One purpose of this paper is to review briefly the concepts that underly the formulation of these theories and so highlight the common aspects and to elucidate the inter-relationships.

Fundamental to the dynamics of solidification is the *equilibrium* phase diagram for the particular system under consideration. We shall have in mind a situation such as that shown in Figure I which, for constant pressure, p , plots the mass concentration, ξ , of the 'light' component of an alloy against temperature, T . For a point above OL , the liquidus, the material is wholly liquid, while below OS , the solidus, the material is totally solid. We may visualize a fluid alloy of uniform composition ξ_0 which is progressively but slowly chilled. The point on Figure I representing the state of the alloy descends along AL_0 and the alloy starts to freeze at $T = T_0$, corresponding to the point L_0 on the liquidus. The solid that starts to form has the composition appropriate to S_0 in Figure I. A solidification front then acts as a source of both rejected material and latent heat and for a dynamic system, when the diffusion (and convection) processes in the system cannot adequately disperse

these sources, a mixed phase region will occur.

All the existing models of the mixed phase region have a common starting point, mixture theory. The idea is that, although on the microscale of crystal dimensions, the mass fraction of solid, ϕ , is discretely 0 or 1, it should be possible, when the gross macroscopic behaviour of a region is sought, to consider only an average, smoothly varying $\phi(\mathbf{x})$ that can take any value in $[0,1]$. In contrast to many mixture theories, a region of mixed phase is 'reactive', that is melting and freezing can change the amount of each of the components of the mixture (solid and liquid) present. Clearly, underlying a binary alloy phase mixture there is a four component mixture theory with densities $\rho_1^S, \rho_2^S, \rho_1^L, \rho_2^L$ and associated velocity fields $\mathbf{v}_1^S, \mathbf{v}_2^S, \mathbf{v}_1^L, \mathbf{v}_2^L$. (We shall employ the superscript S, L for solid and liquid and the subscript 1, 2 to denote light and heavy constituent of the alloy respectively.) The associated complexity of such an approach is obvious and would almost certainly result in an intractable theory. But, for the case of a single phase melt, the simpler diffusive mixture theory of Landau and Lifshitz ([1], Chapter VI) has been successfully applied. This approach is founded on total quantities (energy, stress, etc.) and the mass centred (barycentric) velocity field, \mathbf{v}^L , where

$$\rho^L \mathbf{v}^L = \rho_1^L \mathbf{v}_1^L + \rho_2^L \mathbf{v}_2^L, \quad \rho^L = \rho_1^L + \rho_2^L. \quad (1.1)$$

In this theory, the governing equations for momentum and energy have the same form as for a single component material. In essence, the two-constituent nature of the melt is encapsulated in an additional equation for the evolution of $\bar{\xi}^L$, the mass concentration of the light constituent, and which involves a flux vector, \mathbf{i} . This equation is motivated by the conservation of the mass of the light constituent and allows us to relate \mathbf{i} to the relative velocity $\mathbf{v}_2^L - \mathbf{v}_1^L$. From the separate constitutive postulate for \mathbf{i} , with major contribution $-\rho^L D \nabla \bar{\xi}^L$, it is thereby possible to determine completely the motion of one constituent relative to the other. The diffusive theory is considerably easier to use than a general mixture theory but it can only be employed when there is no explicit constitutive dependence on relative velocities.

The central issue of the mixed phase region is the approach to equilibrium. To be tenable, the mixture theory must predict that any closed

system will equilibrate to a maximum entropy solution in which the temperature T and pressure p are constants and in which the mass fractions $\bar{\xi}^S$ and $\bar{\xi}^L$ of the light component in the solid and liquid phases are those appropriate to complete thermodynamic equilibrium, that is the solidus and liquidus composition

$$\bar{\xi}^S = \xi^S(p, T), \quad \bar{\xi}^L = \xi^L(p, T). \quad (1.2)$$

(We shall use an overbar to denote an off-equilibrium value.) It is also essential that, in this state, $\phi(\mathbf{x})$ can take any value between 0 and 1 independently for each point \mathbf{x} . This is already a potent restriction on the class of admissible theories; there is no place for a Fickian type diffusion contribution, $-\alpha \nabla \phi$, that would cause ϕ also to become uniform in equilibrium (see Hills and Roberts [2]).

A system which is not in equilibrium will generally try to regain that state by melting or freezing material. For definiteness, we shall concentrate on freezing and then we have to be concerned not only with the rate at which solid phase is formed, m^S , but also with the rate at which the light constituent enters the solid phase, m_1^S . Encapsulated in these rates are all the complexities and delicate balances of the solidification process itself and, therefore, we can only expect to make significant progress when we are able to identify dominant processes. For example, in Section 3 we consider what is sometimes called a para-equilibrium state in which the system is essentially in equilibrium with respect to one of the constituents but not with respect to the other. Then, the conversion rate associated with this former constituent proceeds, in effect, infinitely fast. Recognition of a dominant process enables us to identify certain characteristic physical rates that are usually combinations of the rates m^S and m_1^S . The next step is to specify the nature of the 'intrinsic driving force' for these characteristic rates. Recall that in equilibrium, the chemical potentials of each ingredient of the alloy are equal,

$$\tilde{\mu}_1^S = \tilde{\mu}_1^L, \quad \tilde{\mu}_2^S = \tilde{\mu}_2^L, \quad (1.3)$$

where $\tilde{\mu}_\alpha^\gamma(p, T, \bar{\xi}^\gamma)$ is the chemical potential per unit mass of constituent α ($=1, 2$) in phase γ ($=S, L$). Equations (1.2) result from (1.3) by solving for $\bar{\xi}^L$ and $\bar{\xi}^S$ as functions of p and T . Thus we might reasonably

expect that the characteristic rates are ‘driven by’ chemical potential differences but the exact specification of these differences again is intimately linked to the nature of the dominant process as we show in Section 3. While in principle, perhaps, all theories should follow as special cases of a universal theory, the complexity of such a theory which must embrace so many effects precludes the general approach and invites exploitation of the special.

The specification of the characteristic rates such as m^S and m_1^S is generally one of the more challenging aspects of any theory but in one limit, the fast-melting approximation, this difficulty is avoided. This approximation was employed by Loper and Roberts [3] and Hills, Loper and Roberts [4] who supposed that phase equilibrium is established so rapidly, compared with the rate at which the mixed phase region evolves, that with negligible error, (1.2) can be assumed to hold throughout the process. In Section 3, we show how fast melting can be recovered as the result of allowing rate coefficients to tend to infinity but with the associated dissipation vanishing.

Fast melting appears tenable provided the solid grains of the slurry or mush 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, the grains of solid may well not be in chemical equilibrium with the surrounding fluid even though both are at the same temperature, T . In such cases the fast melting approximation cannot be expected to perform well and consideration will have to be given to explicitly detailing the nature of the characteristic rate process.

As a halfway house between the fast melting approximation and a fully general theory, we might suppose that one of the two rate processes, that bring about (1.2) when the two conditions (1.3) are not satisfied, proceeds rapidly compared with the other. There are then two timescales associated with chemical equilibration, one (τ_s) short, and the other (τ_l) long. In a time of order τ_s , an initial state will evolve into a state of para-equilibrium in which, in a rough sense to be described more precisely later, one of (1.3) is satisfied and the other is not; the final evolution of an isolated system to a state (1.2) where both of (1.3) are obeyed then

proceeds very slowly, on the τ_l timescale.

In trying to model solutions of this type one must first decide which of the two phases of evolution one wishes to study in detail. If one seeks to follow the system on the τ_l timescale, one must set $\tau_s = 0$ so collapsing the transition to para-equilibrium to a single instant. Thereafter, in the same rough sense as before, one of (1.3) is continually satisfied and, after a time of order τ_l , the other is also obeyed (assuming the system is isolated). Theories of this type, which can follow a system from para-equilibrium to complete equilibrium, are studied in Section 3(d) below.

If at the other extreme one wishes to follow the system during the time it attains para-equilibrium, one sets $\tau_l = \infty$ from the outset, and abandons all hope of monitoring the approach of an isolated system to complete equilibrium. Recently Hills and Roberts [5] have developed such a theory for a solidifying phase mixture; see Section 3(b) below. To elucidate the underlying physical process, they visualized each grain in the slurry or mush as an onion whose innermost core has the composition corresponding to S_0 of Figure I. The outer layers are successively richer in light constituent since, as T decreases, the new material laid down on the surface will have a composition corresponding to a point on Figure I that continually moves to the right along S_0S_1 . It is clear that the mean $\bar{\xi}^S$ used in the mixture theory will be lower than the grain surface value because of this onion-like structure. In Section 3, we identify the important relative rate that characterizes the theory of [5].

The above discussion also serves to illuminate the differences between solidification and melting. For solidification, it is only because we follow the growth of a grain from the initiation of freezing that we can, in principle, monitor the average $\bar{\xi}^S$. The melting of grains is clearly much more complex since it is necessary to have a knowledge of the history of the grain to understand the manner in which successive layers of the onion are stripped off. Identification of the dominant rates and driving forces is obviously much more difficult when hereditary effects are involved and we do not pursue this here, instead concentrating on the more tractable problem of freezing.

2. Mass conservation and entropy production.

The solid and liquid alloys are always separately modelled by diffusive mixture theory but the treatment of the two-phase region depends upon its nature. When this is a slurry it is possible to use a diffusive mixture theory for the two-phase region also. The total momentum balance determines the evolution of the barycentric velocity \mathbf{v} and, as we shall see, the relative barycentric velocity \mathbf{w} (see eqn. (2.4)) between the phases is determined from constitutive postulates. The underlying structure of the solid phase in a mush means that the diffusive formulation is inappropriate (see Hills, Loper and Roberts [4], Appendix 1). Usually, the solid structure is assumed to be rigid and therefore all the linear momentum considerations centre on the momentum balance for the liquid phase alone. The velocity \mathbf{w} is then an *independent* variable, and the mush is modelled by a general mixture of two diffusive mixtures. The details of many of the various theories we consider have appeared elsewhere and will not, therefore, be our concern. Accordingly we shall totally ignore the concepts of momentum and energy conservation and instead concentrate on the expression of mass conservation and entropy production.

If we denote the partial densities for the light and heavy constituents for each phase by $\rho_1^S, \rho_2^S, \rho_1^L, \rho_2^L$ then the total density fields are given by

$$\rho^S = \rho_1^S + \rho_2^S, \quad \rho^L = \rho_1^L + \rho_2^L, \quad \rho = \rho^S + \rho^L, \quad (2.1)$$

and the mass concentrations by

$$\bar{\xi}^S = \rho_1^S / \rho^S, \quad \bar{\xi}^L = \rho_1^L / \rho^L, \quad \phi = \rho^S / \rho. \quad (2.2)$$

The barycentric velocities for solid, liquid and mixed phases as a whole are

$$\begin{aligned} \mathbf{v}^S &= \bar{\xi}^S \mathbf{v}_1^S + (1 - \bar{\xi}^S) \mathbf{v}_2^S, & \mathbf{v}^L &= \bar{\xi}^L \mathbf{v}_1^L + (1 - \bar{\xi}^L) \mathbf{v}_2^L, \\ \mathbf{v} &= \phi \mathbf{v}^S + (1 - \phi) \mathbf{v}^L, \end{aligned} \quad (2.3)$$

with the relative velocity, \mathbf{w} , being defined as

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

We denote the rate at which solid is created by m^S while, within the solid phase itself, the rate at which light constituent appears is m_1^S where

$$m^S = \partial_t \rho^S + \nabla \cdot (\rho^S \mathbf{v}^S), \quad m_1^S = \partial_t \rho_1^S + \nabla \cdot (\rho_1^S \mathbf{v}_1^S). \quad (2.5)$$

Here ∂_t denotes the Eulerian derivative and we employ direct vector notation wherever possible. Similar quantities are defined for the liquid phase. By considering a unit volume within the phase mixture we find that, if $\bar{\xi}^M$ denotes the mass concentration of the light constituent of the mixture as a whole, then

$$\bar{\xi}^M = \phi \bar{\xi}^S + (1 - \phi) \bar{\xi}^L. \quad (2.6)$$

The total mass of the phase mixture and the total mass of the light component are separately conserved and this leads to

$$m^S + m^L = 0, \quad m_1^S + m_1^L = 0. \quad (2.7)$$

The usual development of diffusive theories suggests that we should reformulate the definitions (2.5) and equations (2.7) in terms of the material derivative D/Dt ($= \partial_t + \mathbf{v} \cdot \nabla$) based on the barycentric velocity \mathbf{v} . From (2.5)₁ we find

$$\rho D\phi/Dt = m^S - \nabla \cdot \mathbf{j}, \quad \mathbf{j} = -\rho\phi(1 - \phi)\mathbf{w}, \quad (2.8)$$

which can be used to recast (2.5)₂ as

$$\begin{aligned} \rho\phi D\bar{\xi}^S/Dt &= m_1^S - \bar{\xi}^S m^S - \mathbf{j} \cdot \nabla \bar{\xi}^S - \nabla \cdot \mathbf{h}_0, \\ \mathbf{h}_0 &= \rho^S \bar{\xi}^S (1 - \bar{\xi}^S) (\mathbf{v}_1^S - \mathbf{v}_2^S). \end{aligned} \quad (2.9)$$

Equation (2.7)₁ becomes the usual equation for the total density ρ ,

$$D\rho/Dt + \rho \nabla \cdot \mathbf{v} = 0, \quad (2.10)$$

but, from (2.7)₂, we have

$$\rho D\bar{\xi}^M/Dt = -\nabla \cdot \mathbf{i},$$

$$\mathbf{i} = \rho\phi\bar{\xi}^S(\mathbf{v}_1^S - \mathbf{v}^S) + \rho(1-\phi)\bar{\xi}^L(\mathbf{v}_1^L - \mathbf{v}^L) + \rho\phi(1-\phi)(\bar{\xi}^L - \bar{\xi}^S)\mathbf{w}. \quad (2.11)$$

Using (2.6), we deduce

$$\rho\phi\frac{D\bar{\xi}^S}{Dt} + \rho(1-\phi)\frac{D\bar{\xi}^L}{Dt} + (\bar{\xi}^S - \bar{\xi}^L)\rho\frac{D\phi}{Dt} = -\nabla \cdot \mathbf{i}. \quad (2.12)$$

Equations (2.8)–(2.12) are tautological consequences of the definitions (2.5,6) and conservation laws (2.7). Equation (2.10) is well understood and so, henceforth, we shall ignore it and concentrate on the remaining set. The approach of diffusive theory is to change the status of some of these equations by postulating constitutive equations for some (or all) of the vectors \mathbf{i} , \mathbf{j} , \mathbf{h}_0 . For example, if a constitutive equation is given for \mathbf{h}_0 , then the actual velocities \mathbf{v}_1^S , \mathbf{v}_2^S of the solid need not explicitly enter the theory but, once a particular problem is solved, the fields \mathbf{v}_1^S , \mathbf{v}_2^S can be found using the determined \mathbf{h}_0 , the barycentric velocity \mathbf{v}^S and (2.9)₂. As we shall see, the choice of which of the equations are to have their status changed crucially influences the resulting theory.

Next we consider the restrictions imposed by a postulate of entropy growth. The correct form is given in Hills, Loper and Roberts [4, equation 2.11], *viz*:

$$\begin{aligned} -\rho \left(\frac{D\Phi}{Dt} + S \frac{DT}{Dt} - \frac{1}{\rho} \frac{D\rho}{Dt} + \frac{p}{\rho^2} \frac{D\rho}{Dt} \right) + T\nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{q} \\ - \mathbf{g} \cdot \mathbf{w} + \sigma^S : \mathbf{D}^S + \sigma^L : \mathbf{D}^L \geq 0. \end{aligned} \quad (2.13)$$

Here, Φ is the total Gibbs free energy for the phase mixture and S the entropy, both measured per unit mass; p is the pressure; \mathbf{k} , \mathbf{q} are the flux of entropy and heat; \mathbf{g} is a diffusive force that acts between the phases; and σ_{ij}^α , D_{ij}^α are the stress and rate of deformation tensors. The inequality (2.13) is appropriate to the case of a general mixture of two diffusive phases. For the case of a diffusive mixture in a slurry the last three terms are simply replaced by the total stress power. This distinction will affect the details but not the general conclusion of this paper.

An important consideration is that, since we are discussing a phase mixture of the same material, the free energy must satisfy the lever rule between the partial energies of each phase, *viz.*:

$$\Phi = \phi\Phi^S(p, T, \bar{\xi}^S) + (1 - \phi)\Phi^L(p, T, \bar{\xi}^L). \quad (2.14)$$

Since $\phi(\mathbf{x})$ can take any value in equilibrium, equation (2.14) expresses the energetic indifference of how much of each phase is present in a slurry/mush.

3. Discussion of theories.

We are now in a position to illuminate some of the underlying concepts and their implementation for existing theories and to go further by suggesting ways in which new theories may be constructed to model physical situations.

(a) *The completely fast melting theory of a mush.*

The fast melting theory of Hills, Loper and Roberts [4] assumes that $\bar{\xi}^S$, $\bar{\xi}^L$ lie on the phase curves so that these concentrations are completely determined within the mush from the pressure and temperature fields. The field $\phi(\mathbf{x})$ remains as the only unknown concentration. In view of (2.6) and (1.2) a completely equivalent variable is ξ^M . In [4] ξ^M was adopted as the primitive variable; its evolution is governed by (2.11) with a constitutive postulate for i . For a mush, the relative velocity \mathbf{w} is an independent variable and the model was constructed employing a general mixture theory. Since $\bar{\xi}^S$, $\bar{\xi}^L$ lie on the phase curves, equations (2.8), (2.9), (2.12) are no longer necessary (see discussion in sub-section (d)). It is equally straightforward to derive a theory based on ϕ rather than ξ^M but using (2.12) instead of (2.11)₁. The first two terms on the left-hand side of (2.12) are of course known in view of (1.2), and again (2.9), (2.11) and, interestingly, (2.8) are discarded. In either approach it is not necessary to postulate for the rates m^S , m_1^S : they are determinable immediately from ϕ using definitions (2.5). Although equation (2.9) was not needed in [4], it was nevertheless tacitly assumed that $\mathbf{h}_0 = \mathbf{0}$ so that $\mathbf{v}_1^S = \mathbf{v}_2^S = \mathbf{v}^S$ and the solid phase effectively has no mechanism to even out differences in chemical composition caused by the solidification process. Thus $\mathbf{h}_0 = \mathbf{0}$ and the fast melting approximation are strictly incompatible assumptions except possibly in the idealized case when $\xi^S = 0$ and solidification always produces pure material. This observation led to the development of the theory of the next sub-section

(b) *The generalized Scheil-Pfann theory*

The fundamental assumption of this theory is that the diffusion and convection properties of the liquid are sufficiently rapid that the concentration of the liquid $\bar{\xi}^L$ remains on the liquidus but by contrast the

solid composition $\bar{\xi}^S$ moves away from the phase curve. The lethargic material diffusion processes within the solid are unable to even out the onion-structure discussed in the introduction. Although the material that freezes onto a grain has the composition given by the solidus, the mean value of $\bar{\xi}^S$ (which is the variable of the mixture theory) will be less than this surface value due to the smaller $\bar{\xi}^S$ in the interior. Recognition that, in static conditions, the material always solidifies with the solidus composition, clearly identifies the combination $M \equiv m_1^S - \xi^S m^S$ as important and suggests that (2.9) be recast as

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

$$\mathbf{h} = \mathbf{h}_0 + \rho\phi(1-\phi)(\xi^S - \bar{\xi}^S)\mathbf{w}.$$

This equation forms the foundation of the theory of [5]. The evolution of ϕ is governed by (2.12) which is, in essence, a generalized Scheil-Pfann equation¹. The entropy inequality suggested that, at least in static conditions, the 'driving potential' for M was

$$\chi = [\xi^L - \xi^S]^{-1} [\Phi^S - \Phi^L + \bar{\mu}^S(\xi^L - \bar{\xi}^S)], \quad (3.1)$$

and that then $M = -\Lambda \chi$, with Λ proportional to a relaxation rate. (There is also a further dynamic contribution to M proportional to $\mathbf{w} \cdot \nabla \chi$. The need for this term stems from equilibrium considerations.) In complete thermodynamic equilibrium, while the field ϕ can be non-uniform, the pressure and temperature will be constant across the system and hence, by (1.2), so will be the light constituent concentrations ξ^S and ξ^L . But, if diffusion processes within the solid are slow, an astronomically long time may elapse before this maximum entropy state is reached. On a more practical timescale the system will attain a 'quasi-equilibrium' state in which the temperature field is uniform but $\bar{\xi}^S$ (and the pressure distribution) are not. In other words, on the timescales of

¹A related but *ad-hoc* attempt to incorporate a Scheil-Pfann type equation into a dynamic theory was made by Fowler [6] but without any discussion of the aspects of thermodynamic dissipation.

the laboratory, the diffusionless solid should be able to sustain differences in chemical composition (and associated non-uniformities in the pressure field) without any discernible dissipation or tendency to change. Attention was focussed on quasi-equilibrium by arranging that \mathbf{h}_0 and M are identically zero.

(c) *Fully non-equilibrium theory for a slurry*

The earliest dynamic theory of a two phase region given by Loper and Roberts [3] tackled the physically more complex situation of non-equilibrium conditions but, since the discussion was of a slurry, a diffusive theory for the phase mixture was used. Constitutive equations were presented for the fluxes \mathbf{i} and \mathbf{j} and again it was assumed that in the solid there was no relative motion so that the flux \mathbf{h}_0 vanished. The relative velocity \mathbf{w} entered the theory as a dependent variable via (2.8)₂, and (2.8)₁ became the evolution equation for the mass concentration ϕ . The light constituent concentrations $\bar{\xi}^S$, $\bar{\xi}^L$ were given equal priority. The evolution of $\bar{\xi}^S$ was governed by (2.9) and the equation for $\bar{\xi}^L$ followed by using (2.8), (2.9) and (2.12),

$$\rho(1 - \phi) \frac{D\bar{\xi}^L}{Dt} = \bar{\xi}^L m^S - m_1^S - \bar{\xi}^L \nabla \cdot \mathbf{j} + \nabla \cdot (\mathbf{h}_0 + \bar{\xi}^S \mathbf{j} - \mathbf{i}), \quad (3.2)$$

and then setting $\mathbf{h}_0 = \mathbf{0}$. Later this theory was specialized using the fast melting approximation and, in view of the assumption of no solid diffusion, is therefore subject to the same criticism as that levelled in sub-section (a).

(d) *Non-equilibrium dominant rate theories*

In this final sub-section we consider the formation of theories in which $\bar{\xi}^L$ and $\bar{\xi}^S$ take non-equilibrium values but in which there are one or more dominant rate processes. As in the previous sub-section, $\bar{\xi}^S$ and $\bar{\xi}^L$ are treated on an equal footing but their evolution equations are intimately related to the dominant characteristic rate processes. In all cases, the evolution of the solid concentration, ϕ , is determined by (2.8). We retain the expression (2.8)₂ for the flux \mathbf{j} rather than adopt the Loper and Roberts [3] approach of postulating for \mathbf{j} and of using a diffusive two-phase theory. Employing the lever rule (2.14) and the equations (2.9)

and (3.2)², we can express the entropy growth postulate (2.13) as

$$\mathfrak{R} \equiv -\mu^S \{m_1^S - \bar{\xi}^S m^S\} - \mu^L \{\bar{\xi}^L m^S - m_1^S\} - (\Phi^S - \Phi^L) m^S + Q \geq 0, \quad (3.3)$$

where

$$\begin{aligned} Q = & -\rho a_p \frac{Dp}{Dt} - \rho a_T \frac{DT}{Dt} - \mu^S \rho \phi (1 - \phi) \mathbf{w} \cdot \nabla \bar{\xi}^S \\ & + \mu^S \nabla \cdot \mathbf{h}_0 - \mu^L \nabla \cdot (\mathbf{h}_0 - \mathbf{i} - \rho \phi (1 - \phi) \bar{\xi}^S \mathbf{w}) + T \nabla \cdot \mathbf{k} \\ & - \nabla \cdot \mathbf{q} - \mathbf{g} \cdot \mathbf{w} - (\Phi^S - \Phi^L + \mu^L \bar{\xi}^L) \nabla \cdot (\rho \phi (1 - \phi) \mathbf{w}) \\ & + \boldsymbol{\sigma}^S : \mathbf{D}^S + \boldsymbol{\sigma}^L : \mathbf{D}^L, \end{aligned} \quad (3.4)$$

and

$$\begin{aligned} \mu^\gamma &= \frac{\partial \Phi^\gamma}{\partial \bar{\xi}^\gamma}, \quad (\gamma = S \text{ or } L), \\ a_p &= \phi \frac{\partial \Phi^S}{\partial p} + (1 - \phi) \frac{\partial \Phi^L}{\partial p} - \frac{1}{\rho}, \\ a_T &= \phi \frac{\partial \Phi^S}{\partial T} + (1 - \phi) \frac{\partial \Phi^L}{\partial T} + S. \end{aligned}$$

The expression (3.3) clearly shows that constitutive equations are required not only for the fluxes and stresses, but also for the rates m^S and m_1^S . Such equations should properly reflect the intrinsic time scales associated with the solidification process for a particular situation. There are various ways in which we might proceed, but one particularly appealing course is to follow Gibbs [7] and introduce the chemical potential $\tilde{\mu}_\alpha^\gamma(p, T, \bar{\xi}^\gamma)$ per unit mass of constituent α in phase γ by the definitions

$$\begin{aligned} \Phi^\gamma &= \tilde{\mu}_1^\gamma \tilde{\xi}_1^\gamma + \tilde{\mu}_2^\gamma \tilde{\xi}_2^\gamma, \quad \tilde{\xi}_1^\gamma = \bar{\xi}^\gamma, \quad \tilde{\xi}_2^\gamma = 1 - \bar{\xi}^\gamma, \\ \mu^\gamma &= \tilde{\mu}_1^\gamma - \tilde{\mu}_2^\gamma. \end{aligned} \quad (3.5)$$

² At this stage we consider (2.9) and (3.2) as identities. The forms of the evolution equations are determined as a result of the discussion to follow.

The Gibbs–Duhem relationship,

$$\tilde{\xi}_1^S \frac{\partial \tilde{\mu}_1^S}{\partial \tilde{\xi}_1^S} = \tilde{\xi}_2^S \frac{\partial \tilde{\mu}_2^S}{\partial \tilde{\xi}_2^S},$$

is a natural consequence of these definitions. In terms of these variables, the entropy inequality becomes

$$\mathfrak{R} \equiv \mathfrak{R}_0 + Q \geq 0, \quad (3.6)$$

with

$$\begin{aligned} \mathfrak{R}_0 &\equiv -m_1^S \tilde{\mu}_1^S - m_2^S \tilde{\mu}_2^S - m_1^L \tilde{\mu}_1^L - m_2^L \tilde{\mu}_2^L, \\ &\equiv m_1^S (\tilde{\mu}_1^L - \tilde{\mu}_1^S) + m_2^S (\tilde{\mu}_2^L - \tilde{\mu}_2^S), \end{aligned} \quad (3.7)$$

since

$$m_\alpha^S + m_\alpha^L = 0, \quad m_1^\gamma + m_2^\gamma = m^\gamma, \quad m^S + m^L = 0.$$

Making the reasonable assumption that all fluxes and stresses will vanish in static conditions with spatially uniform independent fields, we see that

$$\mathfrak{R}_0 \geq 0. \quad (3.8)$$

Restricting our attention to linear constitutive relations, we may postulate

$$\begin{aligned} m_1^S &= \lambda_{11} (\tilde{\mu}_1^L - \tilde{\mu}_1^S) + \lambda_{12} (\tilde{\mu}_2^L - \tilde{\mu}_2^S), \\ m_2^S &= \lambda_{21} (\tilde{\mu}_1^L - \tilde{\mu}_1^S) + \lambda_{22} (\tilde{\mu}_2^L - \tilde{\mu}_2^S), \end{aligned} \quad (3.9)$$

where, according to Onsager's symmetry principle,

$$\lambda_{12} = \lambda_{21}. \quad (3.10)$$

From (3.7) and (3.9) we have

$$\mathfrak{R}_0 = \lambda_{11} (\tilde{\mu}_1^L - \tilde{\mu}_1^S)^2 + 2\lambda_{12} (\tilde{\mu}_1^L - \tilde{\mu}_1^S) (\tilde{\mu}_2^L - \tilde{\mu}_2^S) + \lambda_{22} (\tilde{\mu}_2^L - \tilde{\mu}_2^S)^2, \quad (3.11)$$

and (3.8) requires

$$\lambda_{11} \geq 0, \quad \lambda_{11}\lambda_{22} \geq \lambda_{12}^2. \quad (3.12)$$

The positivity of the quadratic form (3.11) tells us that an isolated system will evolve towards the maximum entropy state in which $\bar{\xi}^S$, $\bar{\xi}^L$ achieve the form (1.2), since these phase curves result from solving (1.3).

The arguments given earlier, if correct, imply that the rate constants $\lambda_{\alpha\beta}$ may be very different in order of magnitude, and this invites us to simplify the theory by going to the extreme case when one or more of the $\lambda_{\alpha\beta}$ are infinite and the remainder are finite. As an example, we may expose the fast melting approximation by letting all the $\lambda_{\alpha\beta}$ be infinite. It then follows from (3.9) that (1.3) holds, *i.e.* that $\tilde{\mu}_1^L - \tilde{\mu}_1^S$ and $\tilde{\mu}_2^L - \tilde{\mu}_2^S$ are zero, but in such a manner that the products $\lambda_{\alpha 1} (\tilde{\mu}_1^L - \tilde{\mu}_1^S)$ and $\lambda_{\alpha 2} (\tilde{\mu}_2^L - \tilde{\mu}_2^S)$ are finite in the limit — *there is no suggestion that m_1^S and m_2^S should be zero or infinite*. The actual values of $\lambda_{\alpha 1} (\tilde{\mu}_1^L - \tilde{\mu}_1^S)$ and $\lambda_{\alpha 2} (\tilde{\mu}_2^L - \tilde{\mu}_2^S)$ are whatever are necessary to maintain (1.3). Thus, the equations (2.9) and (3.2) are not adopted for the determination of $\bar{\xi}^S$ and $\bar{\xi}^L$, which are already known to be ξ^S and ξ^L : the equations have become indeterminate. Thus in the fast melting theory (1.2) simply replaces (2.9), (3.2) and the entropy production rate, \mathfrak{R}_0 , is zero in this limit.

The next simplest possibility is suggested by a metallurgical example. It is found in the solidification of Fe–C–M steels where carbon and molybdenum are mixed with iron, that the carbon moves freely between the two phases. In our binary alloy such a process would suggest a limited form of the fast melting approximation for constituent 1 (say), in which $\tilde{\mu}_1^S$, $\tilde{\mu}_1^L$ maintain an approximate equality³. Such a situation would be modelled by taking the limit $\lambda_{11} \rightarrow \infty$. Then (1.3)₁ would hold, and would replace (3.9)₁ in the evolutionary theory with the entropy production rate \mathfrak{R}_0 reducing to $\lambda_{22} (\tilde{\mu}_2^L - \tilde{\mu}_2^S)^2$. The variable m_1^S is ‘downgraded’ from requiring a constitutive equation to being determined from its definition (2.5)₂. It is important to realize that (1.2)₁

³ Metallurgists sometimes refer to this situation as ‘para-equilibrium’. It is a similar, but not identical, concept to the quasi-equilibrium introduced in sub-section (b)

does not follow from (1.3)₁; (1.3)₁ does, however, imply a relationship (usually 1-1) between $\bar{\xi}^S$ and $\bar{\xi}^L$ for a given p, T . In view of the change of status of m_1^S , equation (2.9) no longer has relevance to the evolution equation for $\bar{\xi}^S$. To obtain the requisite equation we reformulate the definition for m_2^S in terms of the barycentric velocity \mathbf{v} as

$$\rho \frac{D [\phi(1 - \bar{\xi}^S)]}{Dt} = \nabla \cdot [\rho \phi(1 - \phi)(1 - \bar{\xi}^S) \mathbf{w}] + \nabla \cdot \mathbf{h}_0 + m_2^S, \quad (3.13)$$

where \mathbf{h}_0 is again given by (2.9)₂. The form (3.13) no longer contains m_1^S and so is appropriate for our purposes. The equation (3.2) is abandoned, with $\bar{\xi}^L$ being determined from (1.3)₁.

An infinite number of other such limiting theories is possible. To illustrate this, we cast (3.7), (3.9), (3.10) in matrix form by writing

$$\mathfrak{R}_0 = \boldsymbol{\eta}^T \mathbf{m} = \boldsymbol{\eta}^T \boldsymbol{\lambda} \boldsymbol{\eta}, \quad \mathbf{m} = \boldsymbol{\lambda} \boldsymbol{\eta}, \quad \boldsymbol{\lambda}^T = \boldsymbol{\lambda}, \quad (3.14)$$

where T denotes transposed matrices and $\boldsymbol{\eta}, \mathbf{m}, \boldsymbol{\lambda}$ are defined by

$$\boldsymbol{\eta} = \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix} \equiv \begin{pmatrix} \tilde{\mu}_1^L - \tilde{\mu}_1^S \\ \tilde{\mu}_2^L - \tilde{\mu}_2^S \end{pmatrix}, \quad \mathbf{m} = \begin{pmatrix} m_1^S \\ m_2^S \end{pmatrix}, \quad \boldsymbol{\lambda} = \begin{pmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{21} & \lambda_{22} \end{pmatrix}. \quad (3.15)$$

Corresponding to the new variable $\boldsymbol{\nu}$, linearly related to $\boldsymbol{\eta}$ by

$$\boldsymbol{\eta} = \mathbf{L} \boldsymbol{\nu}, \quad \det \mathbf{L} \neq 0, \quad (3.16)$$

we have

$$\mathfrak{R}_0 = \boldsymbol{\nu}^T \mathbf{n} = \boldsymbol{\nu}^T \boldsymbol{\omega} \boldsymbol{\nu} \geq 0, \quad \mathbf{n} = \boldsymbol{\omega} \boldsymbol{\nu}, \quad \boldsymbol{\omega}^T = \boldsymbol{\omega}, \quad (3.17)$$

where

$$\mathbf{n} = \mathbf{L}^T \mathbf{m}, \quad \boldsymbol{\omega} = \mathbf{L}^T \boldsymbol{\lambda} \mathbf{L}. \quad (3.18)$$

Let us suppose that $\omega_{11} \equiv M$, and consider the limit $M \rightarrow \infty$; evidently $\nu_1 = O(M^{-1}) \rightarrow 0$ in this limit. Effectively $n_2 = \Lambda \nu_2$ and $\mathfrak{R}_0 = \Lambda \nu_2^2$, where $\Lambda = \omega_{22}$.

Translating back to variables $\boldsymbol{\eta}, \mathbf{m}, \boldsymbol{\lambda}$, we find the following. To leading order in M , the rank of $\boldsymbol{\lambda}$ is one, and for $M \rightarrow \infty$,

$$L_{22} \eta_1 - L_{12} \eta_2 = 0, \quad (3.19)$$

$$L_{12}m_1^S + L_{22}m_2^S = -\frac{\wedge}{\det \mathbf{L}} (L_{21}\eta_1 - L_{11}\eta_2). \quad (3.20)$$

One of the governing equations that replace (2.9), (3.2) is

$$L_{22} (\tilde{\mu}_1^S - \tilde{\mu}_1^L) - L_{12} (\tilde{\mu}_2^S - \tilde{\mu}_2^L) = 0, \quad (3.21)$$

and the other is obtained by reformulating (3.20) using the barycentric velocity \mathbf{v}

$$\begin{aligned} & \rho \left\{ L_{12} \frac{D(\phi \bar{\xi}^S)}{Dt} + L_{22} \frac{D[\phi(1 - \bar{\xi}^S)]}{Dt} \right\} \\ &= (L_{22} - L_{12}) \nabla \cdot \mathbf{h}_0 + (L_{12} + L_{22}) \nabla \cdot (\rho \bar{\xi}^S \phi(1 - \phi) \mathbf{w}) \\ & \quad - \frac{\wedge}{\det \mathbf{L}} [L_{21}(\tilde{\mu}_1^S - \tilde{\mu}_1^L) - L_{11}(\tilde{\mu}_2^S - \tilde{\mu}_2^L)]. \end{aligned} \quad (3.22)$$

The particular case

$$\mathbf{L} = \begin{pmatrix} 1 & -(1 - \xi^S) \\ 1 & \xi^S \end{pmatrix}, \quad (3.23)$$

is interesting. In terms of the variables

$$\Phi^\gamma = \bar{\xi}^\gamma \tilde{\mu}_1^\gamma + (1 - \bar{\xi}^\gamma) \tilde{\mu}_2^\gamma, \quad \mu^\gamma = \tilde{\mu}_1^\gamma - \tilde{\mu}_2^\gamma, \quad (3.24)$$

that arise naturally in the dynamic theory, equations (3.19) and (3.20) are simply

$$\Phi^S - \Phi^L - \bar{\mu}^S (\bar{\xi}^S - \xi^S) - \bar{\mu}^L (\xi^S - \bar{\xi}^L) = 0, \quad (3.25)$$

$$m_1^S - \xi^S m^S = \wedge (\bar{\mu}^S - \bar{\mu}^L). \quad (3.26)$$

When $\wedge = \infty$, (3.25-26) recover the fast melting relations (1.3) leading to (1.2). It may be noticed that ξ^S and not $\bar{\xi}^S$ appears in (3.23) and (3.26). The idea, as adumbrated in Section 1, is that when $\wedge = 0$ the material that freezes onto the surface of the grain has, according to (3.26), the solidus composition appropriate to the p , T at the time that the freezing takes place. Although by taking $\wedge = 0$ we have a physically

reasonable way of adding solidus composition to the surface of the grain, equation (3.25), which can be thought of defining $\bar{\xi}^L$ for given $\bar{\xi}^S$, p , T , will give a non-liquidus composition for the melt. One would have naturally expected, however, that the mobility of ξ^L in the liquid, being so much greater than that in the solid, would have maintained ξ^L on L_0L_1 in Figure I. The theory of [5] shows that it is possible to formulate a theory that replaces (3.25) simply by

$$\xi^L = \bar{\xi}^L \quad (3.27)$$

and at the same time both maintains the positivity of \mathfrak{R}_0 and retains the property that material freezing on the surface of a grain has the current solidus composition, although a slightly different driving potential, χ , (see eqn. (3.1)) replaces the one on the right-hand side of (3.26).

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FIGURE CAPTION

Figure I. A typical *equilibrium* 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 liquidus and solidus are respectively OL and OS and the region between these curves corresponds to a phase mixture that is either a slurry or a mushy zone.

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