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Abstract.

This paper develops a macroscopic theory that includes Ostwald ripening, a process occurring in solid-liquid phase mixtures whereby the size scale of the solid phase tends to grow so as to decrease interfacial energy. The dynamic mixture theory presented is also capable of dealing with transport phenomena and phase redistribution effects that arise from relative flow between the phases. The presence of the interfacial energy means that the pressures of the liquid and solid in the phase mixture are not equal and the ripening process is directly related to the relaxation of the system to a state of local thermodynamic equilibrium with a common pressure for the phases.

1. Introduction.

It is often found that a first-order phase transition results in a region of mixed phase with a structure that generally can be of one of two types. When the solid phase is in the form of fine particles suspended in the liquid phase, the region is usually termed a slurry. Then, belying its name, the solid phase has a fluid-like character with the granular "rain" being free to ascend or sediment according to buoyancy. In the other type of structure, a mush or mushy zone, the solid has a higher degree of rigidity and forms a matrix of crystals or dendrites through which the liquid phase percolates. Interest in modelling these regions has significantly increased during the past few years, fuelled in part by an associated experimental activity but prompted also by a myriad of industrial applications. While mixed phase regions are commonplace in alloy solidification, they occur more rarely for pure substances and their formation usually requires a special experimental configuration as in, for example, volumetric heating. Despite their comparative paucity, in this paper we shall nevertheless concentrate on a phase mixture of pure substance since this is undoubtedly the clearest theoretical environment in which to discuss features that are common to both pure material and the considerably more complex systems of alloys.

To model a two-phase region of a pure material Hills & Roberts [1] proposed a mixture theory that was formulated in terms of a concentration $c(\mathbf{x}, t)$ for the liquid phase at time t at a point \mathbf{x} within the region. This field can take values in $[0, 1]$ and, since it defines the extent of the deviation of the system from the pure solid state ($c = 0$), we may regard it as being a possible order parameter of the system. It is clearly a mean field variable since, according to the usual view, it results from some averaging process over a small physical element of volume centred at \mathbf{x} and containing many solid particles. Within any volume there will be a spectrum of particle sizes and shapes but the details of their evolution is beyond the sensitivity of the measure c . In the same spirit, in [1] and [2] it was assumed that local thermodynamic equilibrium prevailed. This requires that at any point \mathbf{x} at time t the temperatures and pressures of the two phases adjust to equality very rapidly on the time scale of the evolution of the system as a whole so that the thermodynamic state can be reflected by a common temperature, T , and pressure p , both of which are functions of \mathbf{x} and t (see Roberts and Loper [3]). The mixture theory then followed along conventional lines: at every point it is supposed there are two interpenetrating continua

each with smoothly varying fields of density ρ^L, ρ^S , velocity $\mathbf{u}^L, \mathbf{u}^S$ etc. The governing equations result from conservation principles associated with mass, momentum and energy and the constitutive theory is made consistent with an entropy growth postulate. In [1] the liquid phase was assumed linearly viscous while the solid granular phase was viscoelastic being essentially elastic to high frequency disturbances but fluid-like at low frequencies so that the theory could apply equally well to a slurry or a mushy zone.

One of the more unusual aspects of the theory [1] was the way in which the melting/freezing process was modelled. From thermostatics we know that, when microstructure and surface energy effects are ignored, the phase coexistence curve in pT -space is obtained by solving the condition $\Phi^L(p, T) = \Phi^S(p, T)$ where Φ^α denotes the specific Gibbs energy of the phase α . The total Gibbs energy is given by the lever rule

$$\Phi = c\Phi^L + (1 - c)\Phi^S \quad (1.1)$$

and the theory must predict that the concentration $c(\mathbf{x}, t)$ is an arbitrary (possibly discontinuous in \mathbf{x}) function restricted only by $0 \leq c \leq 1$. There should be no physical process that will even out $c(\mathbf{x}, t)$ for a system on the phase line (see [4]). If the system is artificially moved off that line, however, the melting/freezing process will immediately ensue and only cease when the system has either relaxed back to the phase line or else become a single phase of either liquid or solid. This suggests that the rate of production of liquid from solid per unit volume, m^L , should be proportional to the difference in Gibbs functions, *viz.*

$$m^L = -\Lambda(\Phi^L - \Phi^S), \quad \Lambda \geq 0. \quad (1.2)$$

(The actual postulate adopted in [1] is slightly more general due to the presence of viscoelastic stresses in the solid which we shall ignore in this discussion.) Then, for example, if $\Phi^L > \Phi^S$, the system is on the solid side of the phase curve and the liquid will freeze ($m^L < 0$). On the coexistence curve itself m^L properly vanishes.

It is perhaps not surprising that the mean-field approach such as [1], that attempts to model the complex morphology of the solid phase by a single field $c(\mathbf{x}, t)$, thereby disregards microscopic processes of significance. Particularly disturbing is the omission of the interfacial tension between solid grains and the fluid that surrounds them. This is especially crucial when the grains are small. Only when the mixed phase is

‘mature’, that is, when its microscale structure is on such a large length scale that the surface energy is small compared with the volumetric energy, can one expect a theory that is thermodynamically based on p , T and c alone to perform satisfactorily, and for the phase-coexistence curve derived from $\Phi^L = \Phi^S$ to define mixed phase regions. In other cases a more complete description of the morphology of the mixed phase region is required. At one extreme, one might follow Lifshitz and Slezov [5] and later workers by introducing a distribution function specifying the probable number of grains whose mean radius lies between R and $R + dR$, and to derive a Boltzmann-like equation incorporating the processes of growth and decay of each particle size. The complexities of solving any but the simplest model situations are then very great. At the other extreme lies the theory developed here, in which we incorporate only a single moment of Lifshitz and Slezov’s distribution function, namely the mean radius of the grains. In this way we develop a model that hopefully both incorporates the essential physics while being simple enough to be broadly applicable.

Before attempting to develop such a theory it may be useful to review the rôle of interfacial tension. It is well known that a pure liquid phase can exist below the melting temperature for long periods of time; this is known as ‘supercooling’. It arises because interfacial tension creates an energy barrier that solid phase must cross if it is to persist. For the given p and T ‘below’ the phase line, there exists a critical grain radius, R_c given by

$$\Phi^S(p + 2\sigma/R_c, T) = \Phi^L(p, T), \quad (1.5)$$

where σ is the coefficient of interfacial tension. This defines the ‘top’ of the barrier. Equation (1.5) represents phase equilibrium between the liquid in state (p, T) and a solid at the same temperature, but at the greater pressure

$$p^S = p + 2\sigma/R_c, \quad (1.6)$$

that exists within the grain. This state at the top of the barrier is unstable in the sense that particles of radius greater than R_c will grow even larger as new material freezes onto their surfaces, while particles of radius less than R_c will dissolve back into the liquid. A supercooled system continually attempts through thermal fluctuations to create solid particles of all sizes, but (when the system is only slightly below the phase line) thermal fluctuations energetic enough to create particles of mean radius larger than R_c are rare, and so the liquid remains in its

supercooled state for a considerable time. The greater the degree of supercooling, the lower the energy barrier, and nucleation of solid phase once initiated then often proceeds so rapidly as to be experimentally impossible to monitor; see for example Chalmers [6].

In an isolated system, the latent heat released in this sudden nucleation raises the ambient temperature closer to that of the (bulk) melting curve ($R = \infty$), but the solid phase that has been so rapidly created tends to be of small scale crystals. A slower process of morphological change ensues in which the mean grain size increases secularly, with a concomitant rise in temperature towards the bulk melting curve. This process, known as 'Ostwald ripening' or 'phase coarsening', is often viewed as a long-time relaxation process. The distribution of grain sizes broadens as the slurry becomes more mature. The latent heat released from the surfaces of the larger grains as they freeze tends to impede the freezing of smaller grains which, in their turn, inhibit the growth of still smaller grains. It is these processes that Lifshitz and Slezov [5] incorporate in their Boltzmann-like equation governing the distribution function of sizes. In the limit of very large times, in which the system approaches the bulk melting curve, they predict that the distribution of sizes approaches a universal self-similar form with the mean particle radius increasing as $t^{1/3}$.

Much careful experimental work has been performed that confirms both the temporal law and a long-time self-similar behaviour although not precisely of the form predicted by Lifshitz and Slezov; see for example [7]. For practical reasons, the actual conditions envisaged by Lifshitz and Slezov are not attempted: their solution supposes that c is held constant, so that the ripening process is exhibited in its clearest form, unobscured by additional freezing effects. In the experiments of [8] however, it is the ambient temperature that is held fixed, so that ripening is accompanied by additional freezing. One further point should be made. Although our discussion is expressed in terms of a slurry of solid grains, it is also applicable to the mush of dendritic structures generally seen experimentally [9]. Of course, the interpretation is different. The increasing R of the slurry grains corresponds to enlargement and coarsening of the crystal structure in the mush.

A recent theory of phase mixtures that employs continuum concepts is the so-called phase fluid model (see [10]–[11]). Essentially this theory relates to static systems and has two fundamental variables: a non-dimensional temperature and an order parameter ϕ that takes values

-1 and 1 for pure solid and liquid respectively. The free energy of the system contains a contribution that, although non-convex in ϕ , nevertheless seeks to drive the system to a state where either $\phi = -1$ or $\phi = 1$. There is also a contribution proportional to $(\nabla\phi)^2$ that is intended to reflect surface energies and whose rôle is to smooth out inhomogeneities and send the system to one of uniform ϕ . By this approach the advent of a phase mixture is inextricably related to the non-convex part of the free energy in the manner of spinodal decomposition in alloys (see Cahn [12]).

There is clearly the need for a dynamic macroscopic theory that is capable of dealing with the transport phenomena and phase redistribution effects that arise from the relative flow between the phases. There is also the need for a theory capable of reflecting ripening phenomena in the transient or short-time regime, since for many systems it may not be possible to reach the long-time regime in any experimentally realistic time. The successes of the Lifshitz-Slezov theory and of the subsequent experiments set obvious objectives for our simpler model of ripening phenomenon. Although our approach is evidently incapable of determining the distribution function of grain sizes, it should be capable of reproducing the long-time $t^{1/3}$ power law of mean grain size. This evidently should be a prime objective of our work. We shall however not formulate our theory in terms of the field, $R(\mathbf{x}, t)$, representing the mean grain size at the point \mathbf{x} at time t . Instead we shall find it more convenient to work with two pressures, that of the liquid, $p(\mathbf{x}, t)$, and that of the solid, $p^S(\mathbf{x}, t)$. From the difference between them we can, if we wish, at any time reinterpret our results in terms of the average grain curvature (i.e. the mean of R^{-1}), by invoking Laplace's formula

$$p^S = p + 2\sigma/R. \quad (1.7)$$

The decrease in R^{-1} will be regarded as a process of stress relaxation in which p^S comes into equality with p .

The governing equations and constitutive model for a two phase mixture theory with unequal thermodynamic pressures is set down in Section 2. For simplicity, we assume that the time scale for the equilibrium of the phase temperatures is so short that we may assume a common temperature field T . (A two-temperature phase mixture theory was adumbrated in [3] but with equal pressures.) We shall principally have in mind slurries where the 'solid' phase is in the form of small particles that

have fluid-like behaviour and this is reflected in the constitutive theory of Section 2. The resulting general theory contains an abundance of physical effects and, in Section 3, we obtain a reduced theory by retaining only the interesting dominant ones. To demonstrate some of the implications of the present theory we investigate the coarsening of a static homogeneous system in the cases when (i) the liquid pressure and (ii) the ambient temperature remain constant. We show that in both cases, as the system moves towards local thermodynamic equilibrium, the liquid concentration decreases.

2. Basic theory and constitutive model.

The two phase system is modelled by a binary reactive mixture theory with partial densities ρ^L , ρ^S for liquid and solid that move with velocities \mathbf{u}^L , \mathbf{u}^S . The governing equations are (see [1])

$$\dot{\rho} + \rho \nabla \cdot \mathbf{u} = 0, \quad (2.1)$$

$$\rho^L \frac{D^L u_i^L}{Dt} + \frac{1}{2} m^L w_i = \rho^L F_i^L + \sigma_{ki,k}^L + g_i, \quad (2.2)$$

$$\rho^S \frac{D^S u_i^S}{Dt} + \frac{1}{2} m^L w_i = \rho^S F_i^S + \sigma_{ki,k}^S - g_i, \quad (2.3)$$

$$\rho r - \rho \dot{U} - q_{i,i} - g_i w_i + \sigma_{ij}^L d_{ij}^L + \sigma_{ij}^S d_{ij}^S = 0. \quad (2.4)$$

Here ρ is the total mass density, U is the internal energy per unit mass of the mixture as a whole and r is the heat supply to the mixture per unit mass per unit time. The vectors \mathbf{q} , \mathbf{g} , and \mathbf{F}^α are respectively the heat flux vector, a diffusive force between the phases and the applied body force to the α -phase ($\alpha = L$ or S). The relative velocity, \mathbf{w} , and barycentric velocity \mathbf{u} are defined by

$$\mathbf{w} = \mathbf{u}^L - \mathbf{u}^S, \quad \rho \mathbf{u} = \rho^L \mathbf{u}^L + \rho^S \mathbf{u}^S. \quad (2.5)$$

The stress tensors σ_{ij}^α are individually assumed symmetric and d_{ij}^α denote the rate of deformation tensors. The motional derivatives D^α/Dt are calculated using the velocity \mathbf{u}^α . A superposed dot denotes the motional derivative following the barycentric velocity as does $D/Dt = D^S/Dt + (\rho^L/\rho) \mathbf{w} \cdot \nabla$, etc.

The liquid phase conversion rate, m^L , is

$$m^L = \partial_t \rho^L + \nabla \cdot (\rho^L \mathbf{u}^L), \quad (2.6)$$

where ∂_t denotes time differentiation holding the spatial variable fixed, and this equation can be recast as

$$\rho \dot{c} + \nabla \cdot [\rho c(1-c) \mathbf{w}] = m^L, \quad (2.7)$$

where $c = \rho^L/\rho$ is the fluid mass concentration. Equation (2.7) is a tautological consequence of the definition (2.6) but the usual approach of phase mixtures is to postulate a constitutive equation for m^L and

then the status of (2.7) is raised to that of an evolution equation for the concentration c (see [13]). The simplest such postulate is the $m^L = 0$ of non-reactive mixtures. We shall, however, be more interested in laws such as (1.2).

Phase mixtures are usually described in thermostatics by the intensive fields of temperature and pressure with the Gibbs free energy acting as the fundamental thermodynamic potential. For two phases to be in equilibrium, their specific Gibbs energies must be equal. Pressure is there unambiguous but this is not the case in dynamic situations (see [1]). For evolving systems, it was supposed in [1] that the thermodynamic specification of a system required, in addition to T and c , a single scalar field \wp . Although at the outset this pseudo-pressure \wp was a formal parameter, later in the analysis it was related to other pressure fields that occur in the theory. The coarsening system that is the subject of this paper has an extra degree of freedom over and above that of [1]. This freedom arises from the non-equality of the solid and liquid pressures. Thus we assume that the specification of the thermodynamic state for the present case will require two pseudo-pressures, \wp , \wp^S . We can formally introduce a Gibbs potential $\Phi = U - ST + \wp/\rho$ and we shall assume that Φ , and related variables such as S and ρ , depend only on \wp , \wp^S , T and c :

$$\Phi = \Phi(\wp, \wp^S, T, c). \quad (2.8)$$

The fields \wp , \wp^S will subsequently be related to both the actual pressure fields p , p^S of the liquid and solid and to the mechanical partial pressures of the phases. Throughout we shall regard the pressure of the liquid as being the ambient field (hence no superscript L) and, as the system approaches equilibrium, the pressure excess $p^S - p$, often called the surface pressure (see [14]), relaxes to zero. We shall require an evolution equation to govern this relaxation process and must expect that it will be intimately related to the constitutive theory for the melting/freezing process. For this reason we postpone introducing our final balance law until we have made some preliminary discussions of entropy growth.

We adopt as our entropy postulate the inequality

$$\rho T \dot{S} + T \nabla \cdot \mathbf{k} - \rho r \geq 0, \quad (2.9)$$

where S is the entropy per unit mass of the mixture and \mathbf{k} is an entropy

flux vector. Using (2.4) we can rewrite this inequality as

$$\begin{aligned}
-\rho(\dot{\Phi} + S\dot{T}) + \dot{\rho} + \rho \nabla \cdot [c\mathbf{u}^L + (1-c)\mathbf{u}^S] \\
+ T \nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{q} - \mathbf{g} \cdot \mathbf{w} + \boldsymbol{\sigma}^L : \mathbf{d}^L + \boldsymbol{\sigma}^S : \mathbf{d}^S \geq 0,
\end{aligned} \tag{2.10}$$

where $\boldsymbol{\sigma}^\alpha : \mathbf{d}^\alpha$ denotes the inner product $\sigma_{ij}^\alpha d_{ij}^\alpha$.

Since S and ρ depend on the argument set of (2.8), equation (2.1) yields

$$\begin{aligned}
\left[\frac{\partial \rho}{\partial \wp} + \frac{\partial \rho}{\partial \wp^S} \right] \dot{\rho} + \frac{\partial \rho}{\partial T} \dot{T} + \frac{\partial \rho}{\partial c} \dot{c} + \frac{\partial \rho}{\partial \wp^S} \overline{(\wp^S - \wp)} \\
+ \rho \nabla \cdot [c\mathbf{u}^L + (1-c)\mathbf{u}^S] = 0.
\end{aligned} \tag{2.11}$$

In our discussion of the entropy inequality, equation (2.11) represents a constraint and this is most easily accommodated by use of a Lagrangian multiplier, λ . Using (2.7), the inequality (2.10) becomes

$$a_\wp \dot{\rho} + a_T \dot{T} + a_D \overline{(\wp^S - \wp)} - \mu m^L + T \nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{q} - \mathbf{w} \cdot \mathbf{G} + \boldsymbol{\Sigma}^L : \mathbf{d}^L + \boldsymbol{\Sigma}^S : \mathbf{d}^S \geq 0, \tag{2.12}$$

where the coefficients a_β , μ , the vector \mathbf{G} and the tensors $\boldsymbol{\Sigma}_{ij}^\alpha$ are defined by

$$\begin{aligned}
a_\wp &= -\rho \left[\frac{\partial \Phi}{\partial \wp} + \frac{\partial \Phi}{\partial \wp^S} - \frac{1}{\rho} + \frac{\lambda}{\rho} \left(\frac{\partial \rho}{\partial \wp} + \frac{\partial \rho}{\partial \wp^S} \right) \right], \\
a_T &= -\rho \left[\frac{\partial \Phi}{\partial T} + S + \frac{\lambda}{\rho} \frac{\partial \rho}{\partial T} \right], \quad a_D = -\rho \left[\frac{\partial \Phi}{\partial \wp^S} + \frac{\lambda}{\rho} \frac{\partial \rho}{\partial \wp^S} \right], \\
\mu &= \left[\frac{\partial \Phi}{\partial c} + \frac{\lambda}{\rho} \frac{\partial \rho}{\partial c} \right], \\
\mathbf{G} &= \mathbf{g} - (\wp - \lambda\rho) \nabla c - \mu \nabla [\rho c(1-c)], \\
\boldsymbol{\Sigma}_{ij}^L &= \sigma_{ij}^L + c[\wp - \lambda\rho + \mu\rho(1-c)] \delta_{ij}, \\
\boldsymbol{\Sigma}_{ij}^S &= \sigma_{ij}^S + (1-c)[\wp - \lambda\rho - \mu\rho c] \delta_{ij}.
\end{aligned} \tag{2.13}$$

Assuming that the evolution equation for the surface pressure and the constitutive theory for m^L , g_i , q_i , k_i and σ_{ij}^α do not introduce any further motional derivatives of \wp and T , we deduce in the usual way that $a_\wp = a_T = 0$, so that $\lambda = \lambda(\wp, \wp^S, T, c)$.

If we introduce the pressure fields $\hat{p} = \wp - \lambda\rho$ and $\hat{p}^S = \wp^S - \lambda\rho$ together with a Gibbs energy $\hat{\Phi} = \Phi - \lambda$ then we find that

$$\hat{\Phi} = \hat{\Phi}(\hat{p}, \hat{p}^S, T, c),$$

$$\frac{\partial \hat{\Phi}}{\partial \hat{p}} + \frac{\partial \hat{\Phi}}{\partial \hat{p}^S} = \frac{1}{\rho}, \quad \frac{\partial \hat{\Phi}}{\partial T} = -S, \quad \frac{\partial \hat{\Phi}}{\partial c} = \mu, \quad (2.14)$$

and throughout we can eliminate Φ , \wp , \wp^S , λ in favour of $\hat{\Phi}$, \hat{p} , \hat{p}^S . Henceforth we shall drop the caret $\hat{}$ over Φ , etc.. We shall see that p , p^S are properly the thermodynamic pressures of liquid and solid.

The principal interest of this paper is with the coarsening phenomenon and its relationship to both the pressure field relaxation and to the melting/freezing process. We, therefore, simplify as much as possible those aspects of the constitutive theory that have only a peripheral bearing on the main issue. In particular we concentrate on the case of slurries where the 'solid' phase is in the form of a loose assemblage of fine particles that can easily be deformed and so has fluid-like characteristics. With this in mind, the stress tensors of both phases are assumed to follow a linear viscous model, viz:

$$\sigma_{ij}^\alpha = -\tilde{p}^\alpha \delta_{ij} + \lambda_1^\alpha d_{rr}^\alpha \delta_{ij} + 2\lambda_2^\alpha d_{ij}^\alpha, \quad (2.15)$$

where λ_β^α are the phase viscosities and \tilde{p}^α are the mechanical pressures, assumed functions of p , p^S , T and c . It is clearly possible to make the solid phase viscoelastic in the manner of [1] and [2], whereby it would exhibit Maxwellian characteristics but the concomitant complexity would obscure our main purpose. Again, for simplicity we assume the fluxes of heat and entropy have the forms

$$\mathbf{q} = T\mathbf{k} + \theta^q \mathbf{w}, \quad \mathbf{k} = -(\kappa/T)\nabla T + \theta^k \mathbf{w}, \quad (2.16)$$

where the thermal conductivity, κ , and the coefficients θ^β are functions of \wp , \wp^S , T , c . We shall see that through θ^q we have the ability to modify the partial pressures \tilde{p}^α without affecting the final governing equations. The significance of the transport coefficient θ^k is illuminated in the subsequent section where coarsening in a slurry confined between two horizontal flat plates is considered.

Next we turn to the evolution equation for the surface pressure $p^S - p$. First and foremost, this equation must predict relaxation to

an equilibrium state where this imbalance vanishes. Being associated with the solid, the motional derivative should clearly be taken using the solid velocity \mathbf{u}^S and one of the simplest possible choices is a generalized 'power law'

$$\frac{D^S}{Dt}(p^S - p) = -\alpha(p^S - p)^N - \pi^L v_{k,k}^L - \pi^S v_{k,k}^S, \quad (2.17)$$

where N is an integer. We expect the coefficients π^α to vanish with $p^S - p$ so that the equation imposes no restriction on the velocity fields for local thermodynamic equilibrium. It will emerge that the coefficient α appears as a prefactor of a temporal law for the ripening phenomenon. The precise determination of the prefactor by experimental means has not yet been possible although it does appear that there may be a volume fraction dependence [15]. We assume quite generally that $\alpha = \alpha(p, p^S, T, c)$.

The diffusive force g_i reflects the nature of the interaction between the phases and undoubtedly its most significant contribution will be a term proportional to the relative velocity. This term gives rise to the 'Darcy friction' that can often dominate other contributions to the linear momentum equations, such as the inertia or viscous terms. The specific form we adopt for \mathbf{g} is suggested in part by the inequality (2.12) when (2.14)–(2.17) are substituted, viz:

$$g_i = pc_{,i} + \mu[\rho c(1 - c)]_{,i} - \rho c(\partial\Phi/\partial p^S)[p^S - p]_{,i} - \theta^k T_{,i} - \theta_{,i}^q - \eta w_i. \quad (2.18)$$

With this form for g_i the dissipation associated with the relative velocity \mathbf{w} from such terms as $-\mathbf{w} \cdot \mathbf{G}$ in (2.12) and other sources becomes simply ηw^2 and the inequality reduces to

$$\alpha(\rho\partial\Phi/\partial p^S)(p^S - p)^N - m_i^L(\Phi^L - \Phi^S) + b^L v_{k,k}^L + b^S v_{k,k}^S + D \geq 0, \quad (2.19)$$

where

$$\begin{aligned} D &= \eta w^2 + (\kappa/T)T_{,i}T_{,i} + \lambda_1^L d_{pp}^L d_{qq}^L + 2\lambda_2^L d_{ij}^L d_{ij}^L \\ &\quad + \lambda_1^S d_{pp}^S d_{qq}^S + 2\lambda_2^S d_{ij}^S d_{ij}^S, \\ b^L &= cp + \rho\mu c(1 - c) + \rho(\partial\Phi/\partial p^S)\pi^L - \theta^q - \tilde{p}^L, \\ b^S &= (1 - c)p - \rho\mu c(1 - c) + \rho(\partial\Phi/\partial p^S)\pi^S + \theta^q - \tilde{p}^S. \end{aligned} \quad (2.20)$$

We expect that it should be possible for the melting/freezing processes to cease in a static isothermal system without the pressures p , p^S being equal. Thus, anticipating that $\partial\Phi/\partial p^S > 0$ [see (2.26) below], we require

$$\alpha \geq 0, \quad N = 2n, \quad (2.21)$$

where n is a positive integer. To ensure that (2.17) has the right properties, let us consider the evolution of a stagnant system with an existing small surface pressure so that to leading order we may take α constant. We find

$$(p^S - p)^{-(2n-1)} = (p^S - p)_0^{-(2n-1)} + (2n - 1)\alpha t, \quad (2.22)$$

where the suffix 0 indicates an initial value. By appealing to the Laplace formula (1.7) for a single grain of solid, we can relate the solution (2.22) to the theory of coarsening developed by Lifshitz & Slezov [5]. They showed that the average particle radius R of an isolated spherical grain satisfied

$$R^3 = R_0^3 + Kt, \quad (2.23)$$

where $K (> 0)$ is constant. All the weight of experimental work has confirmed the veracity of this law and this evidence suggests we take $n = 2$ and henceforth we shall adopt this value.

It is worth noting that the simpler choice $n = 1$ is physically implausible. In terms of the evolution of R , (1.7) and (2.17) give (in the simplest case $\pi^L = \pi^S = 0$)

$$\frac{D^S R}{Dt} = \frac{\alpha\sigma^{2n-1}}{R^{2n-2}},$$

which predicts, in the case $n = 1$, that the mean grain radius increases at a constant rate even when the system approaches bulk equilibrium ($R = \infty$). This unrealism makes $n = 2$ the simplest plausible choice of n .

If we assume, as we shall in (2.27) below, that the constitutive postulate for m^L is independent of velocity gradients then (2.19) gives $b^L = b^S = 0$ and (2.20)_{2,3} determine the mechanical pressures \tilde{p}^L , \tilde{p}^S :

$$\begin{aligned} \tilde{p}^L &= cp + \rho\mu c(1 - c) - a_D\pi^L - \theta^q, \\ \tilde{p}^S &= (1 - c)p - \rho\mu c(1 - c) - a_D\pi^S + \theta^q. \end{aligned}$$

We note that $\pi^L = \pi^S = 0$ by assumption when local thermodynamic equilibrium prevails, and then the sum of the pressures \tilde{p}^α properly

equals the common phase pressure p . We can now see that θ^q reflects an arbitrariness in the pressures \tilde{p}^α , but it does not affect the sum of these pressures nor does it appear in either of the final momentum balance equations (2.2)–(2.3) being removed from \tilde{p}^α by the penultimate term of (2.18). The inclusion of the θ^q terms has, in fact, no physical consequences and may be omitted.

To make further progress we need to make more explicit the assumption (2.14)₁. It is well known that in local thermodynamic equilibrium the Gibbs energy satisfies the lever rule and is, therefore, linear in the concentration c . As a direct consequence of this linearity the phase coexistence curve is independent of c and any concentration is possible for a pT -state lying on that curve. We shall soon find that for the coarsening slurry there is a whole family of curves on which the melting/freezing process ceases. We shall likewise require that any distribution of concentration is possible on each member of this family. This requires that the Φ of the present theory be linear in c also. The partial Gibbs energies of the phases are assumed functions of the common temperature and their respective thermodynamic pressures so that

$$\Phi(p, p^S, T, c) = c\Phi^L(p, T) + (1 - c)\Phi^S(p^S, T). \quad (2.24)$$

By rewriting this equation as

$$\Phi = c\Phi^L(p, T) + (1 - c)\Phi^S(p, T) + (1 - c)[\Phi^S(p^S, T) - \Phi^S(p, T)], \quad (2.25)$$

we can see that the lever rule of local thermodynamic equilibrium has been generalized by the addition of the last term of (2.25) which reflects a contribution of the microstructure and which properly vanishes when $p^S = p$. If we introduce the *actual* densities ρ_*^α , specific volumes v_*^α and entropies S_*^α by

$$\frac{1}{\rho_*^\alpha} = v_*^\alpha = \frac{\partial \Phi^\alpha}{\partial p^\alpha}, \quad S_*^\alpha = -\frac{\partial \Phi^\alpha}{\partial T}, \quad (2.26)$$

then (2.13)_{1,2} can be written as

$$cv_*^L + (1 - c)v_*^S = 1/\rho, \quad S = cS_*^L + (1 - c)S_*^S,$$

which are also generalized lever rules. It is perhaps worth emphasizing that the densities ρ_*^α should not be confused with the partial densities

ρ^α : the 'starred' variables are the mass of a unit volume were it totally filled with the α -phase at pressure p^α and temperature T . We note that $\rho^S v_*^S$ is the volume fraction, f , of the solid present.

Finally, we consider the melting/freezing process. In [1] the driving 'force' of this process was essentially the difference in Gibbs energies and here we take the simplest possible generalization, viz:

$$m^L = -\Lambda [\Phi^L(p, T) - \Phi^S(p^S, T)], \quad (2.27)$$

where $\Lambda = \Lambda(p, p^S, T, c)$. With these constitutive assumptions the entropy inequality becomes

$$\hat{D} \equiv \Lambda(\Phi^L - \Phi^S)^2 + f\alpha(p^S - p)^4 + D \geq 0, \quad (2.28)$$

so that we require

$$\Lambda \geq 0, \quad \eta \geq 0, \quad \kappa \geq 0, \quad \lambda_2^\alpha \geq 0, \quad \lambda_1^\alpha + \frac{2}{3}\lambda_2^\alpha \geq 0. \quad (2.29)$$

The energy equation reduces to

$$\rho T \dot{S} = \rho r - T \nabla \cdot \mathbf{k} + \hat{D}, \quad (2.30)$$

with the entropy flux \mathbf{k} being given by (2.16).

3. Simplifications and simple solutions.

For convenience, we first collect together the governing equations of the preceding section. In addition to the mass conservation equation (2.1), there are (2.2), (2.3), (2.30), (2.7) and (2.17) which we re-express as

$$\rho^L \frac{D^L u_i^L}{Dt} + \frac{1}{2} m^L w_i = \rho^L F_i^L - c[1 + \rho(1 - c)\delta]p_{,i} - (f\pi^L)_{,i} - \Theta T_{,i} - \eta w_i + s_{ji,j}^L, \quad (3.1)$$

$$\rho^S \frac{D^S u_i^S}{Dt} + \frac{1}{2} m^L w_i = \rho^S F_i^S - (1 - c)(1 - \rho c \delta)p_{,i} - (f\pi^S)_{,i} + \Theta T_{,i} + \eta w_i + s_{ji,j}^S, \quad (3.2)$$

$$- \alpha_p T \dot{p} + \rho c_p \dot{T} + L [\rho \dot{c} + (T/L)(\theta^k w_i)_{,i}] - f \alpha_p^S T \overline{(p^S - p)} = \rho r + (\kappa T_{,i})_{,i} + \widehat{D}, \quad (3.3)$$

$$\rho \dot{c} + [\rho c(1 - c)w_i]_{,i} + \Lambda [\Phi^L(p, T) - \Phi^S(p^S, T)] = 0, \quad (3.4)$$

$$D^S(p^S - p)/Dt = -\alpha(p^S - p)^4 - \pi^L v_{k,k}^L - \pi^S v_{k,k}^S, \quad (3.5)$$

where

$$s_{ij}^\alpha = \lambda_1^\alpha d_{pp}^\alpha \delta_{ij} + 2\lambda_2^\alpha d_{ij}^\alpha. \quad (3.6)$$

In (3.1)–(3.3) δ is an expansion coefficient with $\delta = v_*^L - v_*^S$, L is the latent heat given by $L = T(S_*^L - S_*^S)$ and $\Theta = \theta^k - \rho c(1 - c)L/T$. The other thermodynamic material parameters, such as the isothermal compressibilities κ_T^α , κ_T , the thermal expansion coefficients α_p^α , α_p , and the specific heats c_T^α , c_T , are best expressed by the differential forms

$$\begin{aligned} d\Phi^\alpha &= v_*^\alpha dp^\alpha - S^\alpha dT, & dv_*^\alpha &= -v_*^\alpha \kappa_T^\alpha dp^\alpha + v_*^\alpha \alpha_p^\alpha dT, \\ dS^\alpha &= -v_*^\alpha \alpha_p^\alpha dp^\alpha + T^{-1} c_p^\alpha dT, \end{aligned} \quad (3.7)$$

and

$$\begin{aligned} d\Phi &= v dp - S dT + \mu dc + (1 - c)v_*^S d(p^S - p), \\ dv &= -v \kappa_T dp + v \alpha_p dT + \delta dc - (1 - c)v_*^S \kappa_p^S d(p^S - p), \\ dS &= -v \alpha_p dp + T^{-1} c_p dT + LT^{-1} dc - (1 - c)v_*^S \alpha_p^S d(p^S - p), \\ d\mu &= \delta dp - LT^{-1} dT - v_*^S d(p^S - p), \end{aligned} \quad (3.8)$$

where the 'total' mixture parameters are determined by

$$\begin{aligned} v\kappa_T &= cv_*^L\kappa_T^L + (1-c)v_*^S\kappa_T^S, & v\alpha_p &= cv_*^L\alpha_p^L + (1-c)v_*^S\alpha_p^S, \\ c_p &= cc_p^L + (1-c)c_p^S. \end{aligned} \quad (3.9)$$

It is to be expected that the physical effects contained in (3.1)–(3.9) do not all have the same importance. Unless the slurry is extremely dense, the individual particles do not interact strongly and the viscous stresses are negligible. For slow flows the inertial forces are small compared with the Stokes' drag on the particle that enters equation (3.2) via the penultimate term. The solid momentum equation becomes

$$0 = \rho^S F_i - (1-c)(1-\rho c\delta)p_{,i} - (f\pi^S)_{,i} + \Theta T_{,i} + \eta w_i, \quad (3.10)$$

where we have set the applied force $F_i^S = F_i$. The mechanical pressure \tilde{p}^L is expected to be not much altered by the presence of surface energy so that we take $\pi^L = 0$. For slow flows of the liquid phase under the action of the body force F_i we obtain

$$0 = \rho^L F_i - c(1-\rho c\delta)p_{,i} - \Theta T_{,i} - \eta w_i + s_{ij,j}^L. \quad (3.11)$$

Consider now a slurry contained between two horizontal planes $z = \text{constant}$ with the liquid in a hydrostatic state, $\mathbf{u}^L = 0$, but subject to a uniform body force $\mathbf{F} = F\hat{\mathbf{z}}$. Adding (3.11) and (3.10) we get $\nabla(p + f\pi^S) = \rho\mathbf{F}$. When this result is substituted into (3.10) we find

$$\eta w_i = -\rho c(1-c)\delta p_{,i} + c(f\pi^S)_{,i} + \Theta T_{,i}. \quad (3.12)$$

We might expect that solid particles will move predominantly in response to gradients of p and $f\pi^S$ rather than ∇T . It follows that $\Theta = 0$ so

$$\theta^k = \rho c(1-c)L/T. \quad (3.13)$$

Reverting to general flows, (3.10) gives

$$(\rho\mu^L/\rho^S\gamma)w_i = (1-\rho^L\delta)p_{,i} - (f\pi^S)_{,i} - \rho F_i, \quad (3.14)$$

which is a modified Darcy law with γ being a Darcy coefficient that is directly proportional to the square of a typical length between elements of the solid phase and π^S vanishes with the surface pressure.

In the energy balance (3.3) we may usually discard as being small many of the entropy producing terms connected with the dissipation due to viscosity and Darcy friction and with the relaxation processes of melting/freezing and surface pressure. For simplicity we can assume that L/T is a constant so that (3.3) becomes

$$\rho c_p \dot{T} - \alpha_p T \dot{p} - f \alpha_p^S T [D^S(p^S - p)/Dt + c w_i (p^S - p)_{,i}] = \rho r + L \Lambda \mu \quad (3.15)$$

and equation (3.5) gives

$$D^S(p^S - p)/Dt = -\alpha(p^S - p)^4 - \pi^S \nabla \cdot \mathbf{v}^S. \quad (3.16)$$

Next we investigate phase coarsening in some particular environments. First, from (2.27), we see that the melting/freezing process ceases whenever

$$\Phi^S(p^S, T) = \Phi^L(p, T). \quad (3.17)$$

This equation defines a family of curves in the pT -plane each labelled by the surface pressure $\Pi \equiv p^S - p$. Let (p_0, T_E) be some point, E , on the bulk equilibrium curve $\Pi = 0$; see Figure 1. Then for nearby states, (3.17) may be written as

$$(v_*^S)_E (p^S - p) - \delta_E (p - p_0) - L_E (1 - T/T_E) = 0, \quad (3.18)$$

where the suffix E denotes evaluation at (p_0, T_E) . The curves of constant Π are, in this approximation, the straight lines

$$T = T_E - (T v_*^S / L)_E \Pi + (T \delta / L)_E (p - p_0), \quad (3.19)$$

which is essentially the Gibbs-Thompson relation. Equation (2.27) is, to the same order,

$$m^L = (\Lambda v_*^S)_E [p^S - p - (\rho_*^S \delta)_E (p - p_0) - (\rho_*^S L)_E (1 - T/T_E)]. \quad (3.20)$$

Some insight into the implications of the present theory may be gained from the following simple examples, both of which concern the evolution of a static homogeneous system towards equilibrium. In such a case (3.16) integrates to give [cf. (2.22)]

$$(p^S - p)^{-3} = (p^S - p)_0^{-3} + 3\alpha t. \quad (3.21)$$

When (2.27) reduces to (3.20), we have by (3.4)

$$\rho_E \partial_t c = (\Lambda v_*^S)_E [p^S - p - (\rho_*^S \delta)_E (p - p_0) - (\rho_*^S L)_E (1 - T/T_E)]. \quad (3.22)$$

We shall, for simplicity, suppose that the phase balance adjusts continuously and instantaneously to (3.17). This implies that $\Lambda = \infty$ but, by (3.17), the product on the right-hand side of (2.27) is in general finite and non zero, as therefore is m^L . Evolutionary states near E now continuously satisfy (3.18), but the product of zero and infinity in (3.22) is non zero, as is therefore \dot{c} . We shall see in fact that $\partial_t c < 0$ in our two examples.

Since homogeneity eliminates entropy flux, then from (2.30) we see that in the absence of volumetric heating ($r = 0$) the initial entropy will be preserved, i.e. $S = S_0$ where

$$S = cS^L(p, T) + (1 - c)S^S(p^S, T). \quad (3.23)$$

Consider the system evolving from its initial state (p_0, T_0) which is sufficiently close to the bulk phase line $\Pi = 0$ and is represented by A in Figure 1. Since the entropy is constant, we can deduce from (3.8)₃ that

$$c = c_0 + \left(\frac{T\alpha_p}{\rho L} \right)_A (p - p_0) - \left(\frac{c_p}{L} \right)_A (T - T_0) + \left(\frac{f\alpha_p^S T}{\rho L} \right)_A (\Pi - \Pi_0). \quad (3.24)$$

The first example is close in spirit to the situation envisaged by Lifshitz & Slezov [5]. We suppose that the (liquid) pressure is held constant ($p = p_0$) and the system evolves along the path \overrightarrow{AE} . As Π decreases from Π_0 in obedience to (3.21), T increases from T_0 towards T_E , as determined from the $p = p_0$ form of (3.19):

$$T_0 = T_E - (Tv_*^S/L)_E \Pi_0, \quad T = T_E - (Tv_*^S/L)_E \Pi, \quad (3.25)$$

so that, by (3.24),

$$c = c_0 + \left[(f\alpha_p^S T/\rho L)_A + (\rho c_p/L)_A (Tv_*^S/L)_E \right] (\Pi - \Pi_0). \quad (3.26)$$

The final mass fraction of liquid is

$$c_E = c_0 - \left[(f\alpha_p^S T/\rho L)_A + (\rho c_p/L)_A (Tv_*^S/L)_E \right] \Pi_0, \quad (3.27)$$

i.e. $c_E < c_0$.

In the second example, the temperature is held constant ($T = T_0$) and the system is allowed to release pressure as it evolves along the path \overrightarrow{AB} . As Π decreases from Π_0 in obedience to (3.21), so does p according to the $T = T_0$ form of (3.19):

$$p - p_0 = (v_*^S/\delta)_E (\Pi - \Pi_0). \quad (3.28)$$

By (3.24)

$$c = c_0 + (T/\rho L)_A \left[(f\alpha_p^S)_A + (\alpha_p)_A (v_*^S/\delta)_E \right] (\Pi - \Pi_0), \quad (3.29)$$

so that the final mass fraction of the liquid at the point B on the bulk equilibrium curve is

$$c_B = c_0 - (T/\rho L)_A \left[(f\alpha_p^S)_A + (\alpha_p)_A (v_*^S/\delta)_E \right] \Pi_0, \quad (3.30)$$

i.e. $c_B < c_0$.

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Figure Caption.

Figure 1. A phase diagram illustrating how the melting/freezing curve depends on the surface pressure Π . The curve $\Pi = 0$ corresponds to local thermodynamic equilibrium where solid and liquid phases share a common temperature and pressure.

