Macroscopic models for melting derived from averaging microscopic Stefan problems
I: Simple geometries with kinetic undercooling or surface tension

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A mushy region is assumed to consist of a fine mixture of two distinct phases separated by free boundaries. For simplicity, the fine structure is here taken to be periodic, first in one dimension, and then a lattice of squares in two dimensions. A method of multiple scales is employed, with a classical free-boundary problem being used to model the evolution of the two-phase microstructure. Then a macroscopic model for the mush is obtained by an averaging procedure. The free-boundary temperature is taken to vary according to Gibbs–Thomson and/or kinetic-undercooling effects.

1 Introduction

A classical model for the change of phase of a material regards it as consisting of two distinct regions, one occupied by the low-temperature phase (say a solid) and the other by the high-temperature phase (say liquid). The two regions are separated by a distinct interface which moves in a way governed by the temperature field. The temperature at the interface may be taken to be the equilibrium phase-change temperature (the melting point of the material) if it is reasonably flat and slowly moving but if it has a large curvature or high speed then the temperature can vary (through the *Gibbs–Thomson* effect and *kinetic undercooling*, respectively).

In certain cases, including when the medium is not a pure substance but instead a mixture or solution, or when there is body heating, which can result from Ohmic or radiative heating in the material [1], this type of *Stefan problem* can fail as a model. The free boundary can become unstable and the mathematical model might even, in the absence of the Gibbs–Thomson effect and kinetic undercooling, get to be ill posed [7, 5]. A more appropriate model, in such circumstances, allows for a third region, between the liquid and solid zones, in place of the sharp interface, which is some kind of mush, such as a fine mixture of the two phases.

In the work of Atthey [1], such a mushy zone was characterized by its heat content:

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if this were between that of solid at the melting point and that for liquid at the same temperature, then the material would be mush (and thinking of it as a mixture, the composition would be determined by mass fraction of solid, φ, being given by heat content $= \varphi \times$ heat in unit mass of solid $+ (1-\varphi) \times$ heat in unit mass of liquid, both at the phase-change temperature). The mush can be thought of as being formed by an amount of heat being added to solid at its melting point, this amount being insufficient to provide complete melting.

In the work of Lacey & Tayler [6], a very simple model for the fine internal structure of some mush was considered and employed to recover, after averaging, the macroscopic problem used by Atthey. With a suitable scaling, this averaged model for temperature θ and heat content, or enthalpy, h, can be written as

$$\frac{\partial h}{\partial t} = \nabla^2 \theta + 1, \tag{1.1}$$

with $\theta = h$ for $h \leqslant 0$, $\quad \theta = 0$ for $0 \leqslant h \leqslant 1$, $\quad \theta = h - 1$ for $h \geqslant 1$.

Here $\theta = 0$ corresponds to the melting/freezing point, while the 1 on the right-hand side of (1.1) represents the internal body heating and the fact that 1 is a special value of h means that the dimensionless latent heat is 1. This single, degenerate, heat equation can be replaced by linear differential equations in the three regions corresponding to the two pure phases and the mushy region, with two free boundaries:

$$\frac{\partial \theta}{\partial t} = \nabla^2 \theta + 1 \text{ in the solid and in the liquid}; \tag{1.2}$$

$$\theta = 0 \text{ and } \frac{\partial h}{\partial t} = 1 \text{ in the mush}; \tag{1.3}$$

$$\theta = 0 \text{ and } h = 0 \text{ at the solid/mush boundary}; \tag{1.4}$$

$$\theta = 0 \text{ and } (1-h)V = -\left.\frac{\partial \theta}{\partial n}\right|_{\ell} \text{ at the mush/liquid boundary.} \tag{1.5}$$

Here V represents the speed of mush/liquid boundary, directed out of the liquid region, h is the enthalpy just inside the mushy region, and $\frac{\partial \theta}{\partial n}|_{\ell}$ is the normal derivative (again directed out of the liquid region) of the liquid temperature. The last of these free boundary conditions only differs from the standard Stefan condition in that the jump in heat content at the interface is not constant.

The model analysed by Lacey & Tayler [6] took a one-dimensional situation with regularly spaced nucleation sites in an initially cold solid. When the temperature θ reached 0 at these points a pair of free boundaries and a small region of liquid would form. The boundaries would move towards the solid parts as the liquid fraction increased according to the usual Stefan condition

$$\rho L V = \left[\kappa \frac{\partial \theta}{\partial n}\right]_{\ell}^{s} \text{ with } \theta = 0 \tag{1.6}$$

($\frac{\partial}{\partial n}$ is the normal derivative out of the liquid, L is latent heat, ρ is density, κ is the

thermal conductivity, and the *s* denotes quantities on the solid side of the free boundary). An equation like (1.1) holds in the liquid and solid parts of the mush as well as the pure-phase regions. Because of the fine structure, θ remains close to 0 in the mush and the average heat content is, approximately, proportional to the liquid fraction. The present work extends the simple model of Lacey & Tayler [6], varying the conditions on the free boundary. The effects included are 'kinetic undercooling' – when liquid freezes the free-boundary temperature is depressed in proportion to the speed of the interface – and the 'Gibbs–Thomson effect' – any curvature of the free boundary also results in a change of its temperature, and in such a way as tends to cause its flattening. Emphasis is not put on body heating and the consequences of this are only mentioned in passing. For 'small' speeds of the interface, kinetic undercooling results in the free-boundary temperature

$$\theta = AV, \tag{1.7}$$

for A a positive constant, V the normal velocity measured away from the liquid, and taking the equilibrium phase-change temperature to be $\theta = 0$. (Of course for rapid melting (1.7) would predict temperature less than absolute zero. This linear law clearly fails for V sufficiently large. Here it is assumed that (1.7) is satisfactory, but it can be noted that the present analysis is easily modified for more general laws for kinetic undercooling.) The Gibbs–Thomson effect (sometimes referred to as 'surface tension') results in a free-boundary temperature

$$\theta = C\sigma, \tag{1.8}$$

where C is a positive constant and σ is the mean curvature, taken to be positive if the liquid region is convex (the interface is curved towards the liquid).

Using either (1.7) or (1.8), or their combination,

$$\theta = AV + C\sigma, \tag{1.9}$$

together with the Stefan condition (1.6) at the free boundary, a local problem for the temperature within a cell of an assumed periodic lattice can be obtained. With some extra simplifying assumptions, that the lattice is one-dimensional (like that discussed by Lacey & Tayler [6]) or two-dimensional and formed by squares of one size, and also that the free boundary exhibits certain configurations, it is possible to solve this local problem. The temperature and composition can then be averaged (over a region containing a large number of cells but which is small in comparison with the macroscopic length scale) and a macroscopic model is obtained.

2 One dimension with kinetic undercooling

This most idealized case is a one-dimensional medium with nucleation sites, at which melting can initiate, spaced regularly, the separation of neighbouring sites being $2d$. (Alternatively, the medium could be a layered region in three dimensions, with nucleation planes $2d$ apart, and qualities such as temperature varying only with time and the spatial co-ordinate perpendicular to the planes.)

Away from any phase-change points (free boundaries), the temperature satisfies the

one-dimensional heat equation:

$$\rho c \frac{\partial \theta}{\partial t} = \kappa \frac{\partial^2 \theta}{\partial x^2}. \tag{2.1}$$

Throughout this work, we shall assume that density ρ, specific heat c, and thermal conductivity κ are all constant. Although the analysis can easily be adapted to allow c and κ to depend upon phase and/or temperature, allowing ρ to change would result in motion of the material and this would affect the models significantly.

For the purposes of the present paper we shall be thinking of a temperature which is generally increasing: material starts solid (either purely or nearly so) and eventually becomes entirely liquid, possibly progressing through a mush when there are significant amounts of both phases. As we are supposing that body heating is absent this increase of temperature is driven by some boundary condition(s) and at any typical time there can be expected to be a solid region and a liquid region, or three regions, one each of solid, mush and liquid.

Where the material is still fully solid $\theta < 0$ everywhere. Melting starts at nucleation sites when θ reaches the critical temperature 0 at these points, and a mush forms. When free boundaries which have originated from neighbouring sites meet, the material is entirely liquid and now $\theta > 0$ everywhere. It is clear that (2.1) serves as a macroscopic model in the pure-phase regions but the mushy region must be considered more carefully. To do this a method of multiple scales is used.

Taking ℓ to be a typical macroscopic length, say the width of the piece of material or of one of the phases, it is appropriate to scale distance according to

$$x = \ell y.$$

On the other hand, d, the half spacing of sites (i.e. half the lattice period) is a microscopic length scale, and it is also sensible to write

$$x = dz. \tag{2.2}$$

To balance the heat capacity and conduction terms in (2.1), when applied to the liquid and solid regions, time is scaled according to

$$t = \rho c \ell^2 \tau / \kappa.$$

Looking at a local problem, the position of each liquid/solid interface should be scaled like (2.2),

$$s = dS.$$

Considering one period in the mush, this can be taken, without loss of generality, to extend from the location of one nucleation site, $z = 0$, to the next, $z = 2$. There will be two free boundaries in this interval, one having started at each end:

$$0 < S_1 < S_2 < 2.$$

The region (S_1, S_2) is occupied by solid and the rest by liquid. To get what we shall see is an appropriate balance in the Stefan equation, (1.6), we put

$$\theta = \frac{L}{c} u \tag{2.3}$$

(making the Stefan number, $c \times$ typical temperature change$/L$, equal to 1).

Using the method of multiple scales, the dimensionless temperature u is regarded as a function of both dimensionless distances, y and z, as well as of time τ, $u = u(y, z, \tau)$. Then, away from the free boundaries,

$$\frac{\partial u}{\partial \tau} = \delta^{-2} \frac{\partial^2 u}{\partial z^2} + 2\delta^{-1} \frac{\partial^2 u}{\partial z \partial y} + \frac{\partial^2 u}{\partial y^2}, \tag{2.4}$$

where $\delta = d/\ell \ll 1$, assuming that the microstructure is fine, that is, there are many nucleation sites in a macroscopic region. The free-boundary conditions are, from (1.7) (or (1.9) with $\sigma = 0$) and (1.6)

$$u = (-1)^{j-1} \alpha \frac{dS}{d\tau}, \text{ at } z = S = S_j, \ j = 1, 2, \tag{2.5}$$

$$\delta^2 \frac{dS}{d\tau} = \left[\frac{\partial u}{\partial z} + \delta \frac{\partial u}{\partial y} \right]_\ell^s \text{ at } z = S = S_j, \ j = 1, 2, \tag{2.6}$$

where $\alpha = Ad\kappa/L\rho\ell^2$.

To complete this local (or microscopic) problem, boundary conditions must be imposed at $z = 0, 2$. To eliminate secularity u and its z derivative must be the same at each end. Thus periodic boundary conditions apply:

$$[u]_{z=0}^{z=2} = 0; \tag{2.7}$$

$$\left[\frac{\partial u}{\partial z} + \delta \frac{\partial u}{\partial y} \right]_{z=0}^{z=2} = 0. \tag{2.8}$$

Because of the small parameter δ appearing in (2.4) and (2.6), an asymptotic series solution for u can be sought:

$$u \sim u_0 + \delta u_1 + \delta^2 u_2 + \dots \text{ for } \delta \ll 1. \tag{2.9}$$

Substituting (2.9) into (2.4), (2.6), (2.7) first yields

$$\frac{\partial^2 u_0}{\partial z^2} = 0 \text{ and } \frac{\partial u_0}{\partial z} = 0.$$

Hence, $u_0 = u_0(y, \tau)$. Similarly $u_1 = u_1(y, \tau)$ (and could be absorbed into u_0). Now, looking at the δ^2 terms gives

$$\int_0^{s_1} + \int_{s_1}^{s_2} + \int_{s_2}^2 \left(\frac{\partial u_0}{\partial \tau} - \frac{\partial^2 u_0}{\partial y^2} \right) dz$$

$$= \left. \frac{\partial u_2}{\partial z} \right|_{s_1-} - \left. \frac{\partial u_2}{\partial z} \right|_0 + \left. \frac{\partial u_2}{\partial z} \right|_{s_2-} - \left. \frac{\partial u_2}{\partial z} \right|_{s_1+} + \left. \frac{\partial u_2}{\partial z} \right|_2 - \left. \frac{\partial u_2}{\partial z} \right|_{s_2+}$$

from (2.4),

$$\frac{dS_1}{dz} = \left. \frac{\partial u_2}{\partial z} \right|_{s_1+} - \left. \frac{\partial u_2}{\partial z} \right|_{s_1-} \text{ and } \frac{dS_2}{dz} = \left. \frac{\partial u_2}{\partial z} \right|_{s_2-} - \left. \frac{\partial u_2}{\partial z} \right|_{s_2+}$$

from (2.6), and

$$\left. \frac{\partial u_2}{\partial z} \right|_0 = \left. \frac{\partial u_2}{\partial z} \right|_2$$

from (2.8).

Combining these equations gives the compatability condition

$$\int_0^2 \left(\frac{\partial u_0}{\partial \tau} - \frac{\partial^2 u_0}{\partial y^2} \right) dz = 2 \left(\frac{\partial u_0}{\partial \tau} - \frac{\partial^2 u_0}{\partial y^2} \right) = \frac{dS_2}{d\tau} - \frac{dS_1}{d\tau}. \tag{2.10}$$

Considering next (2.5),

$$\alpha \frac{dS_1}{d\tau} = -\alpha \frac{dS_2}{d\tau} = u_0.$$

Because S_1 starts at $z = 0$ and S_2 starts at $z = 2$ at the same time (to leading order), it is possible to write

$$S_1 = 1 - R, \quad S_2 = 1 + R, \tag{2.11}$$

where $2R$ is the dimensionless width of the remaining solid and $R = R(y, \tau)$ is the solid fraction. (Ideally S and R should also be obtained as asymptotic series for $\delta \to 0$ but for the present discussion only their leading-order approximations are of interest.) Of course, the symmetry shown by (2.11) might have been expected. Corresponding symmetry will be used in simplifying the calculations in later sections.

Now, to leading order, $u \sim u_0(y, \tau)$ satisfies

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial y^2} + \frac{\partial R}{\partial \tau}, \tag{2.12}$$

$$\alpha \frac{\partial R}{\partial \tau} = -u \tag{2.13}$$

in the mush. Of course, R can be eliminated to give

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial y^2} - \frac{u}{\alpha}. \tag{2.14}$$

This just expresses normal heat conduction with a sink term representing latent heat being taken up by melting.

To model the material completely, the equations for the purely solid and liquid regions must also be taken into account. These are

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial y^2}, \quad u < 0, \quad R = 1 \text{ in the solid}$$

and

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial y^2}, \quad R = 0 \text{ in the liquid}.$$

The three regions can be considered together by using (2.12) together with

$$\frac{\partial R}{\partial \tau} = \begin{cases} 0 & \text{where } R = 0 \text{ or, where } R = 1 \text{ and } u < 0, \\ -u/\alpha & \text{where } 0 < R < 1 \text{ and, where } R = 1 \text{ and } u > 0. \end{cases}$$

Equivalently,

$$\frac{\partial u}{\partial \tau} - \frac{\partial^2 u}{\partial y^2} = \begin{cases} 0 & \text{where } u < 0 \text{ or, } u > 0 \text{ with } \int_{\omega(y)}^\tau u\, d\tau \geqslant \alpha, \\ -u/\alpha & \text{where } u > 0 \text{ and } \int_{\omega(y)}^\tau u\, d\tau < \alpha, \end{cases}$$

where $\omega(y) = \tau$ is the macroscopic free boundary separating the solid region from the mushy region. (This time τ is when u first reaches 0 at y.)

One easy generalization of this model is to suppose that the material is N-dimensional, with $N = 2$ or 3, and that the nucleation points are replaced by nucleation lines for $N = 2$ and planes for $N = 3$. Again the separation is $2d$. A simple geometry for one cell of the mush, and satisfying the symmetry requirement, has the solid occupying a square ($N = 2$) or cube ($N = 3$) of side $2R$. Now (2.13) still holds but, since the solid fraction is R^N (note that since $\rho = $ constant there is no need to distinguish volume and mass fractions),

$$\frac{\partial u}{\partial \tau} = \nabla_y^2 u + \frac{\partial}{\partial \tau} R^N. \tag{2.15}$$

Here ∇_y denotes the gradient using the variable $y = \ell^{-1} x$. The alternative form of the energy equation is also easily changed. Thus, (2.14) becomes

$$\frac{\partial u}{\partial \tau} = \nabla_y^2 u - \frac{N}{\alpha} u \left(1 - \frac{1}{\alpha} \int_{\omega(y)}^{\tau} u \, d\tau \right)^{N-1}$$

and holds for $\int_{\omega(y)}^{\tau} u \, d\tau < \alpha$, where $\omega(y)$ is the time at which the mush/solid boundary crosses y.

Clearly, these results can be extended to allow for other geometries, giving a different 'sink' term in (2.15), variable conductivity and variable specific heat, nonlinear kinetic undercooling laws, and inclusion of body heating. For example, if there is nondimensional internal heat generation at a rate of q per unit volume, the dimensionless thermal conductivity is $k_\ell(u)$ in the liquid and $k_s(u)$ in the solid, scalings are done using a 'typical' value of the conductivity, and the kinetic undercooling law is $\frac{\partial R}{\partial \tau} = -g(u)$, (2.14) becomes

$$\frac{\partial u}{\partial \tau} = \frac{\partial}{\partial y} \left(\frac{k_\ell(u) k_s(u)}{R k_s(u) + (1 - R) k_\ell(u)} \frac{\partial u}{\partial y} \right) - g(u) + q.$$

It should be noted that (2.12), (2.13) constitute a phase-field model, with R, the solid fraction, playing the role of the order parameter. It is seen that diffusion only applies to heat. It should also be emphasized that this model holds for rising temperature. Should the points $z = 0, \pm 2d, \ldots$ continue to act as nucleation sites, it is clear that having $\frac{\partial \theta}{\partial t} < 0$, starting with pure liquid, the model is essentially the same. If, instead, the material starts as solid with $\theta < 0$, is warmed so that θ becomes positive, and then the temperature is reduced back below 0 before melting is complete, extra free boundaries will be formed and, still regarding R as the solid fraction, $\alpha \frac{\partial R}{\partial \tau} = -2u$ in the mushy region. The model is seen to depend upon the history of the material – if the temperature at some point y has crossed zero n times since the material was a pure phase, then $\alpha \frac{\partial R}{\partial \tau} = -nu$.

3 Two-dimensional models

The remainder of the paper is focused on two-dimensional problems, for which, because of the geometry, surface tension has some influence. To keep things simple, it is assumed that the material has a square-lattice structure, the sides of the squares having length $2d$ (d being small compared with the macroscopic scale ℓ). Either nucleation occurs, this might be at the corners of the squares or along their sides (c.f. the generalizations in § 2), or, even for low temperatures, some residue of liquid remains in small regions around the corners. The square, Ω, may be thought of as a crystal or grain.

In this section, the basic model is introduced and analysed as far as possible in its full generality. In the following sections, extra assumptions, which are possibly physically unrealistic, are applied to be able to solve the local problem, and hence derive a macroscopic model.

The usual heat equation

$$\rho c \frac{\partial \theta}{\partial t} = \kappa \nabla^2 \theta \tag{3.1}$$

applies both in the pure-phase regions and in each phase within the microstructure of the mushy region. At the (microscopic) free boundaries within the mush the conditions (1.9) and (1.6) are taken to hold. The same normalization in each cell as in the previous section ($x = \ell y = dz$, etc.) is done to give, for the local problem,

$$\delta^2 \frac{\partial u}{\partial \tau} = \nabla_z^2 u + 2\delta \nabla_z \cdot \nabla_y u + \delta^2 \nabla_y^2 u, \quad \text{away from } \Gamma \tag{3.2}$$

$$u = \alpha v + \beta K, \quad \text{on } \Gamma \tag{3.3}$$

$$\delta^2 v = \left[\frac{\partial u}{\partial n} \right]_\ell^s = \boldsymbol{n} \cdot [\nabla_z u + \delta \nabla_y u]_\ell^s, \quad \text{on } \Gamma, \tag{3.4}$$

where Γ is the liquid/solid interface, v and K are the dimensionless normal velocity and curvature, respectively, of Γ, using the microscale, $\beta = cC/dL$, and $\boldsymbol{n}$ is the outward unit normal, also on the microscale. Periodic conditions hold around the boundary of the cell:

$$\begin{aligned} u(\boldsymbol{y}, z_1, -1, \tau) &= u(\boldsymbol{y}, z_1, 1, \tau) \text{ for } -1 \leqslant z_1 \leqslant 1, \\ u(\boldsymbol{y}, -1, z_2, \tau) &= u(\boldsymbol{y}, 1, z_2, \tau) \text{ for } -1 \leqslant z_2 \leqslant 1; \end{aligned} \tag{3.5}$$

and

$$\begin{aligned} \frac{\partial u}{\partial z_2}(\boldsymbol{y}, z_1, -1, \tau) &= \frac{\partial u}{\partial z}(\boldsymbol{y}, z_1, 1, \tau) \text{ for } -1 \leqslant z_1 \leqslant 1, \\ \frac{\partial u}{\partial z_1}(\boldsymbol{y}, -1, z_2, \tau) &= \frac{\partial u}{\partial z_1}(\boldsymbol{y}, 1, z_2, \tau) \text{ for } -1 \leqslant z_2 \leqslant 1; \end{aligned} \tag{3.6}$$

here (3.5) has been used to eliminate y derivatives from (3.6).

If we only consider situations for which the cell is symmetric, i.e. $u(\boldsymbol{y}, z_1, z_2, \tau) = u(\boldsymbol{y}, z_1, -z_2, \tau) = u(\boldsymbol{y}, -z_1, z_2, \tau)$, then (3.5) is automatically satisfied and (3.6) can be replaced by

$$\frac{\partial u}{\partial n} = 0 \text{ on the cell boundary.} \tag{3.7}$$

The local problem is then (3.2) away from the free boundary Γ, subject to (3.3) and (3.4) on Γ, and the boundary condition (3.7) on $\partial \Omega$ (plus symmetry) – see Figure 1.

Again, it is appropriate to look for an asymptotic solution in the form of (2.9). The leading approximation now satisfies

$$\nabla^2 u_0 = 0 \text{ in } \Omega \text{ away from } \Gamma_0, \tag{3.8}$$

$$u_0 = \alpha v_0 + \beta K_0 \text{ on } \Gamma_0, \tag{3.9}$$

$$\boldsymbol{n}_0 \cdot [\nabla_z u_0]_\ell^s = 0 \text{ on } \Gamma_0, \tag{3.10}$$

$$\frac{\partial u_0}{\partial n} = 0 \text{ on } \partial \Omega, \tag{3.11}$$
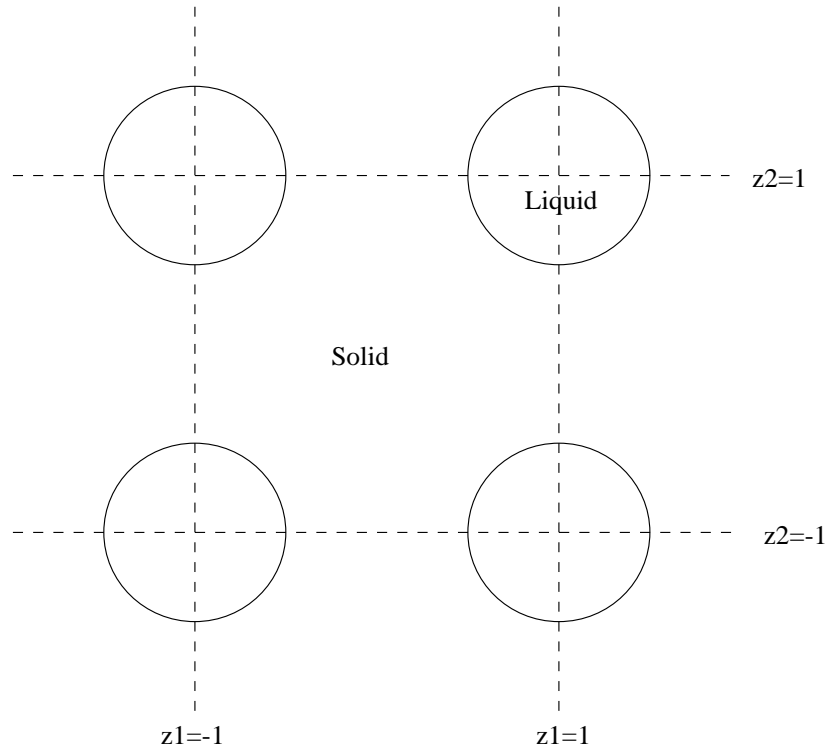
FIGURE 1. The local problem for symmetric microstructure. The broken line is the cell boundary $\partial\Omega$: $\partial u/\partial n = 0$. The solid line is the free boundary Γ: $u = \alpha v + \beta K$, $\delta^2 v = [\partial u/\partial n]$. Also $\delta^2 \partial u/\partial \tau = \nabla_z^2 u + 2\delta \nabla_z \cdot \nabla_y u + \delta^2 \nabla_y^2 u$ away from Γ.

where the velocity v, curvature K, and location of Γ should also be determined asymptotically. (The time derivative has been neglected and a quasi-steady state is being sought.) Since u_0 is harmonic its maximum must be achieved on $\Gamma_0 \cup \partial\Omega$ and, unless it is identically constant (as a function of z), at this maximum its normal derivative (directed from the region towards the boundary) is positive (ignoring difficulties due to the boundary not being smooth at the corners of Ω and any points where Γ meets $\partial\Omega$). This would violate (3.10) or (3.11), as appropriate, and constancy of u_0 is indicated:

$$u_0 = u_0(\boldsymbol{y}, \tau). \tag{3.12}$$

Since $[\nabla_y u_0]_s^\ell = 0$ the $O(\delta)$ correction u_1 can be taken to vanish (and likewise v_1, etc.). The δ^2 terms then give

$$\frac{\partial u_0}{\partial \tau} = \nabla_z^2 u_2 + \nabla_y^2 u_0 \text{ in } \Omega \backslash \Gamma,$$

$$v_0 = \boldsymbol{n}_0 \cdot [\nabla_z u_2]_\ell^s \text{ at } \Gamma,$$

$$\frac{\partial u_2}{\partial n} = 0 \text{ on } \partial\Omega,$$

where u_0, v_0 and K_0 are related by (3.9). Integration over $\Omega \backslash \Gamma$ and application of the

boundary conditions yield the consistency condition

$$\frac{\partial u_0}{\partial \tau} = \nabla_y^2 u_0 - \frac{1}{4} \int_\Gamma v_0 dz, \tag{3.13}$$

which should be expected, since $\int_\Gamma v_0 dz$ is rate of increase of area of the liquid part of Ω, and hence the rate of take up of heat, and Ω has area 4. Equation (3.13) forms part of an average and macroscopic model for temperature u and solid fraction φ ($=\frac{1}{4}$ area of solid part of Ω), where $4\frac{\partial \varphi}{\partial t} = -\int_\Gamma v_0 dz$. In principle, (3.9) gives the evolution of Γ, and consequently of v and K, in terms of u. (It is a type of flow by mean curvature, including an *a priori* unknown function of time.) The difficulty lies in the way this variation depends upon the history of u so (3.9) cannot, in general, be replaced by a simple equation involving u and φ. For this reason, in the following two sections, special types of Γ are considered. These require, probably unrealistic, assumptions on how Γ meets $\partial\Omega$. One particular example is the case of $\beta = 0$ and taking nucleation right round $\partial\Omega$ so Γ is a contracting square; this was a case mentioned in § 2.

We emphasize that the general, and most realistic, problem involves finding $u(\boldsymbol{y}, \tau)$, $\Gamma(\boldsymbol{y}, \tau)$ (or equivalently u and v) satisfying (3.9), (3.13), and whatever condition holds where the free boundary Γ meets the grain boundary $\partial\Omega$. Given such a condition, we know, in principle, how u and Γ evolve: *the evolution is given by a coupled macroscopic heat equation,* (3.13)*, and microscopic mean-curvature flow,* (3.9). It is only in special, and possibly contrived, circumstances, i.e. particular conditions on the way Γ and $\partial\Omega$ interact, that (3.9) can effectively be solved, and a purely macroscopic model, taking the form of a system of partial differential equations, obtained. Having said that, we might expect the properties of the more general problems to be rather similar to those of the special ones, even if the former cannot be posed so simply. We should also note that information regarding the melting of metals and alloys, as opposed to their freezing, is limited [2]. This means that in trying to build a truly realistic model, there is an added difficulty of not knowing precisely what should be imposed at the grain boundary.

Before finishing this section, the possiblity of faster changes should be considered. On writing $\tau = \delta^2 \hat{\tau}$ and $v = \delta^{-2}\hat{v}$, the problem (3.2), (3.3), (3.4), (3.7) becomes, to leading order,

$$\left.\begin{array}{c} \dfrac{\partial u}{\partial \hat{\tau}} = \nabla_z^2 u \text{ in } \Omega\backslash\Gamma, \\[2mm] (\delta^2/\alpha)u - (\beta\delta^2/\alpha)K = \hat{v} \text{ and } \hat{v} = \left[\dfrac{\partial u}{\partial u}\right]_\ell^s \text{ on } \Gamma. \end{array}\right\} \tag{3.14}$$

Three cases need to be looked at.

(a) $\alpha = O(1)$

Here $\hat{v} = 0$, Γ is stationary, and $[u]_\ell^s = [\frac{\partial u}{\partial n}]_\ell^s = 0$ on Γ. The temperature u satisfies the heat equation in Ω and approaches some constant as $\hat{\tau}$ gets large; starting with quite general initial data this short-time solution eventually matches with the longer-time solution.

(b) $\alpha = O(\delta^2)$

We now have a full problem. To get an idea of the stability of a solution to (3.8), (3.9) with the v term absent, (3.10), (3.11), i.e. a steady state of (3.14), we consider the energy. Because
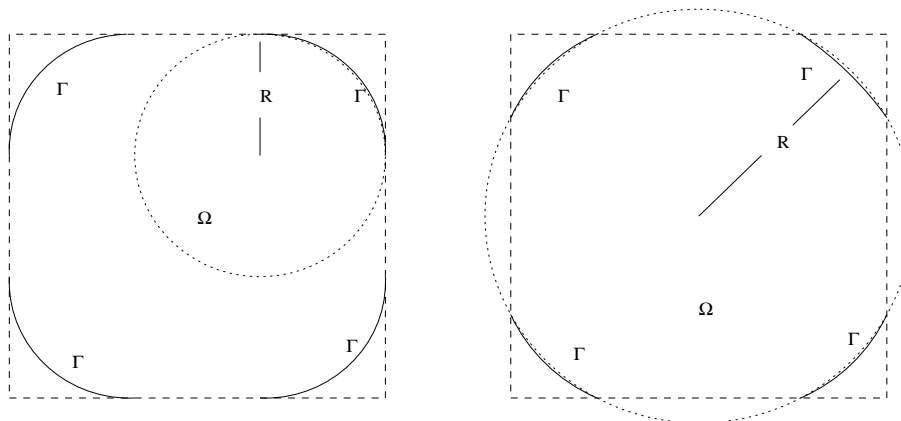
FIGURE 2. Configurations considered for solid fraction $\varphi \geqslant \pi/4$. Left, configuration A. Right, configuration B.

of (3.12) and (3.9), $K =$ constant in this steady situation. For symmetry, Γ is either a circle of radius $R \leqslant 1$ or has four components, one in each corner, each component being a circular arc. With Γ a circle, $u = -\beta/R$ (the solid is inside and the liquid outside) so the heat in Γ is

$$h = 4 - 4\beta/R - \pi R^2 \tag{3.15}$$

(liquid area $= 4 - \pi R^2$ and dimensionless latent heat $=$ dimensionless specific heat $= 1$), or $h = 4 + 4u - \pi\beta^2/u^2$. For $u < -(\pi\beta^2/2)^{\frac{1}{3}}$ $(R < (2\beta/\pi)^{\frac{1}{3}})$ the heat content increases with temperature but for $u > (-\pi\beta^2/2)^{\frac{1}{3}}$ $(R > (2\beta\pi)^{\frac{1}{3}})$ it decreases. This might be thought to suggest stability for small R (low temperature) and instability for larger R (higher temperature). However, the opposite is easily seen to be the case, at least for a radially symmetric problem. Taking, for example, an initial perturbation of a steady state making temperature greater, but with the same radius R_0, the radius decreases and lowers the free-boundary temperature. The lowest temperature continues to be on Γ, by the maximum principle, and R is monotonic decreasing. As the energy has been made larger, if $R_0 \leqslant (2\beta/\pi)^{\frac{1}{3}}$, there is no value of R satisfying (3.15), and R must decrease to 0. If on the other hand $R_0 > (2\beta/\pi)^{\frac{1}{3}}$, R has to be bounded below by the solution to (3.15), since u is greater than $-\beta/R$ for $\hat{\tau} < \infty$, and R remains near to R_0.

When Γ is made up of four circular areas the configuration is not unique. Two cases are discussed here: A $- \Gamma$ consists of four quarter circles of radius $R \leqslant 1$, each of which touches $\partial\Omega$ (see Figure 2 (left)); B $- \Gamma$ consists of four arcs of a single circle centred on $z = 0$, of radius $1 \leqslant R \leqslant \sqrt{2}$ (see Figure 2 (right)).

We should stress that the latter, B, is only included here as an example which can be discussed relatively easily, while still retaining the effect of kinetic undercooling. It could only be a representation of real material in the extremely unlikely event of the angle between Γ and $\partial\Omega$, which would depend upon some quantity such as the local speed, being just right for Γ to be made up of circular arcs.

Considering these two families we find that:

Configuration A

$h = (4-\pi)R^2 - 4\beta/R = 4u + (4-\pi)\beta^2/u^2$, $\frac{dh}{du} = 4 - 2(4-\pi)\beta^2/u^3 > 0$ $(u < 0)$. Now there is stability (within this family of configurations) – addition of heat causes melting, and increase of both R and free-boundary temperature $-\beta/R$.

Configuration B

$h = 4 - R^2(\pi - 4\cos^{-1}\frac{1}{R}) - \sqrt{R^2-1} - 4\beta/R$, $\frac{dh}{dR} = 4\beta/R^2 - 2R(\pi - 4\cos^{-1}\frac{1}{R})$ with $\frac{du}{dR} = \beta/R^2 > 0$. Then $\frac{dh}{dR} > 0$ but (using reasoning like that for the circle) there is instability for $R^3(\pi - 4\cos^{-1}\frac{1}{R}) < 2\beta$, while $\frac{dh}{dR} < 0$ and there is stability for

$$R^3\left(\pi - 4\cos^{-1}\frac{1}{R}\right) > 2\beta \tag{3.16}$$

(in this family of configurations).

(c) $\delta^2 \ll \alpha \ll 1$

Like case (a), taking $\hat{\tau} = O(1)$ gives the heat equation and u becomes uniform in z for large $\hat{\tau}$. However, another time scale is relevant. Using the intermediate time value $\tilde{\tau}$ with $\tau = \alpha\tilde{\tau}$ ($\hat{\tau} = \delta^{-2}\alpha\tilde{\tau}$) and writing $v = \alpha^{-1}\tilde{v}$, u is uniform in z and a mean-curvature flow governs the motion of Γ:

$$\tilde{v} = u - \beta K.$$

Also conservation of heat (equivalently looking for u as an asymptotic series $u \sim u_0 + \alpha u_1 + \ldots$ and finding the condition for u_1 to exist), gives $\frac{\partial u}{\partial\tilde{\tau}} = -\frac{1}{4}\int_\Gamma \tilde{v}\,dz = -\frac{1}{4}\frac{\partial}{\partial\tilde{\tau}}$ (liquid area) and $u = \text{const.} - \frac{1}{4}$ liquid area.

To get some indication of stability, the three configurations discussed in (b) may be examined.

The circle of radius R

Here $K = -1/R$, $\tilde{v} = -\frac{\partial R}{\partial\tilde{\tau}}$ so

$$\frac{\partial R}{\partial\tilde{\tau}} = -u - \frac{\beta}{R}, \quad \frac{\partial u}{\partial\tilde{\tau}} = \frac{\pi}{2}R\frac{\partial R}{\partial\tilde{\tau}}.$$

Then $u = \text{const.} + \frac{\pi R^2}{4}$, $\frac{\partial R}{\partial\tilde{\tau}} = -\text{const.} - \frac{\beta}{R} - \frac{\pi R^2}{4}$ and the same stability criterion as for (b) applies.

Configuration A

Taking a perturbation $u_0 = -\beta/R_0 + \epsilon$ from the steady state $u = -\beta/R_0$, $R = R_0$, then Γ has to lie between the two curves given by $R = R_0$ and $R = R^*$ with $\beta/R^* = \beta/R_0 - \epsilon$ $(R^* > R_0)$. The steady state is stable and, assuming that the perturbed solution approaches a new equilibrium, Γ approaches the steady boundary with $-4\beta/R + (4-\pi)R^2 = -4\beta/R_0 + (4-\pi)R_0^2 + 4\epsilon$ $(R_0 < R < R^*)$.

Configuration B

Here $K = -1/R$,

$$u = \text{const.} + \frac{1}{4}\left(\pi - 4\cos^{-1}\frac{1}{R}\right)R^2 + \sqrt{R^2 - 1} \tag{3.17}$$

so

$$\frac{\partial R}{\partial\tilde{\tau}} = -\tilde{v} = -\text{const.} - \frac{1}{4}\left(\pi - 4\cos^{-1}\frac{1}{R}\right)R^2 - \sqrt{R^2 - 1} - \frac{\beta}{R}$$

and the stability criterion is the same as for the $\alpha = O(\delta^2)$ case.

This primitive stability analysis over the shorter time scales indicates that if α is significant ($\alpha = O(1)$), then we can use the quasi-steady, local problem (3.8), (3.9), (3.10), (3.11) with (3.13) in obtaining macroscopic behaviour. The same applies if $\alpha \ll 1$ for configuration A and for the circular Γ or configuration B, with $R > (2\beta/\pi)^{\frac{1}{3}}$ or (3.16), respectively. However, if these conditions fail to apply, there is instability, rapid collapse of one or other phase is to be expected, and the quasi-steady theory cannot be applied.

4 Macroscopic model for configuration B

We now want to use the general theory to obtain macroscopic models. We take configuration B first as it is more generally applicable, although it requires that the free and grain boundaries intersect at an angle consistent with the radius of the circular arcs.

When the material is cold, i.e. $u < -\beta\sqrt{2}$, it is entirely solid and $\frac{\partial u}{\partial\tau} = \nabla_y^2 u$.

Once u exceeds $-\beta\sqrt{2}$ a mush can form. It is possible to have a Γ of the conjectured form made up of circular arcs with radius R, and having velocity, from (3.9), given by

$$\alpha\frac{\partial R}{\partial\tau} = -\left(\frac{\beta}{R} + u\right). \tag{4.1}$$

This equation (for what might be thought of as an order parameter) is coupled with a heat equation from (3.13) (or using the relation between liquid area and R),

$$\begin{aligned}
\frac{\partial u}{\partial\tau} &= \nabla_y^2 u + \frac{\partial}{\partial\tau}\left(\frac{1}{4}\left(\pi - 4\cos^{-1}\frac{1}{R}\right)R^2 + \sqrt{R^2 - 1}\right) \\
&= \nabla_y^2 u + \left(\frac{\pi}{2} - 2\cos^{-1}\frac{1}{R}\right)R\frac{\partial R}{\partial\tau} \qquad \text{for } 1 < R < \sqrt{2}.
\end{aligned} \tag{4.2}$$

(Note that the homogeneous problem, with the $\nabla_y^2 u$ term absent, has the stability properties noted in the previous section.)

Once R reaches 1 the microscopic free boundary Γ becomes circular and from then on it evolves as a closed curve. With Γ a circle of radius less than 1, (4.1) still applies but (4.2) must be replaced by

$$\frac{\partial u}{\partial\tau} = \nabla_y^2 u + \frac{\partial}{\partial\tau}\left(\frac{\pi}{4}R^2\right) = \nabla_y^2 u + \frac{\pi}{2}R\frac{\partial R}{\partial\tau} \text{ for } 0 < R < 1. \tag{4.3}$$

(Again the stability of the homogenous problem is as in § 3.)

The pair of equations (4.1), with (4.2) for $1 < R < \sqrt{2}$, and (4.3) for $0 < R < 1$, form another phase-field model; again there is no diffusion of the order parameter, which is the volume fraction of liquid φ ($= \pi R^2/4$ for $R \leqslant 1$, $(\pi/4 - \cos^{-1}\frac{1}{R})R^2 + \sqrt{R^2 - 1}$ for

$1 \leqslant R \leqslant \sqrt{2}$). Of course, u can be eliminated between (4.1) and (4.2) or (4.3) to give an equation of the form

$$\alpha \frac{\partial^2 R}{\partial \tau^2} + \beta \frac{\partial}{\partial \tau}\left(\frac{1}{R}\right) = \alpha \nabla_y^2 \frac{\partial R}{\partial \tau} + \beta \nabla_y^2 \frac{1}{R} + \frac{\partial}{\partial \tau} f(R).$$

Once R has reached 0, the mush has been turned entirely liquid and the simple heat equation can again model the temperature u.

As with the one-dimensional model, this representation of the mush can be generalised to allow for various physical quantities changing with temperature and depending upon phase (excluding of course density as a change of this quantity would result in deformation of the material on both macro and microscopic scales). It should be noted that although variable thermal conductivity can in principle be taken into account, the more complicated geometry makes it more difficult in practice. These remarks apply equally well to the modelling in the following section.

Before leaving configuration B, the limiting case of $0 \leqslant \alpha \ll 1$ can be briefly considered, bearing in mind the earlier comments and applicability of the model in the light of stability. (For $\alpha \gg 1$ or $\beta \gg 1$ some rescaling should be done. If $\beta \ll 1$ we recover another simple generalization of the model of §2.)

Neglecting the kinetic undercooling would give

$$u = -\beta/R \tag{4.4}$$

with (4.2) or (4.3) as appropriate. Now u can be eliminated to give a single nonlinear heat equation:

$$\frac{\partial}{\partial \tau}\left\{\frac{1}{4}\left(\pi - 4\cos^{-1}\frac{1}{4}\right)R^2 + \sqrt{R^2-1} + \frac{\beta}{R}\right\} = \beta\nabla^2\frac{1}{R} \quad \text{for } 1 < R < \sqrt{2};$$

$$\frac{\partial}{\partial \tau}\left\{\frac{\pi}{4}R^2 + \frac{\beta}{R}\right\} = \beta\nabla^2\frac{1}{R} \quad \text{for } 0 < R < 1.$$

This can only be a reasonable model if the term being differentiated with respect to time is a decreasing function of R, so that the equation is a forward not a backward heat equation. This criterion is, unfortunately, simply that h, enthalpy per cell, is an increasing function of R and u. This corresponds exactly to the short-time instability of the local problem and inapplicability of the quasi-steady theory.

Further consideration of the stability criterion, $\frac{dh}{dR} > 0$ means instability and $\frac{dh}{dR} < 0$ means stability, and the formulae for h,

$$h = \begin{cases} 4 - \pi R^2 - 4\beta/R & 0 < R \leqslant 1 \\ 4 - \left(\pi - 4\cos^{-1}\frac{1}{R}\right)R^2 - 4\sqrt{R^2-1} - 4\beta/R & 1 \leqslant R \leqslant \sqrt{2} \end{cases}$$

leads to instability where

$$h' = \begin{cases} 4\beta/R^2 - 2\pi R & 0 < R \leqslant 1 \\ 4\beta/R^2 - 2\left(\pi - 4\cos^{-1}\frac{1}{R}\right)R & 1 \leqslant R < \sqrt{2} \end{cases}$$

is positive. From this it can be seen that for β sufficiently large, say $\beta \geqslant \beta^*$, $h(R)$ is strictly increasing but if $\beta < \beta^*$ then $h(R)$ has a local maximum in $(0, \sqrt{2})$. ($h' \sim 4\beta/R^2$

for $R \to 0$, $h'(1) = 4\beta - 2\pi$, $h'(\sqrt{2}) = 2\beta$ so $\beta^* \geqslant \pi/2$.) Indeed, a local maximum must be greater than the value taken at $\sqrt{2}$, $h(\sqrt{2}) = -2\sqrt{2}\beta$, for small enough β, $0 < \beta < \beta_*$, where $\beta_* < \beta^*$. ($h(1) = 4 - \pi - 4\beta$ so $\beta_* \geqslant (4 - \pi)/(4 - 2\sqrt{2})$.)

With $\beta > \beta_*$ it seems likely that as soon as R starts to decrease from $\sqrt{2}$ it should rapidly go to zero: the macroscopic problem would then again be a free-boundary problem. Assuming that this process leaves h unchanged, u would change from $-\beta/\sqrt{2}$ on the solid side to the lower value $-\beta/\sqrt{2} - 1$ on the liquid side. This process would take place in a time of $O(\delta^2)$, compared with a time for the macroscopic free boundaries to move from one cell to the next of order δ. The temperature can then change back to $-\beta/\sqrt{2}$, which is the temperature nearby, in this larger time. The macroscopic problem is simply a Stefan problem, with free-boundary temperature $u = -\beta/\sqrt{2}$, and negligible surface tension.

For $\beta < \beta_*$ the situation is even less clear. Now there are some $R < \sqrt{2}$ for which $h(R) = -2\sqrt{2}\beta$. However, h is a decreasing function near the largest such R and a backward heat equation would be indicated. One might speculate that a free-boundary problem, along the lines suggested for $\beta > \beta_*$, could be an appropriate macroscopic model.

5 Macroscopic model for configuration A

This case might be slightly more physically realistic, in that the angle between the phase interface (free boundary Γ) and the grain boundary (cell boundary $\partial\Omega$) is a constant, namely zero. Unfortunately, Γ must have different normal speeds at different positions so kinetic undercooling would prevent the free boundary from remaining as circular arcs. Therefore in this section, only the Gibbs–Thomson effect is taken to be significant.

The appropriate free-boundary condition (from (3.3) or (1.8)) is then

$$u = -\beta/R.$$

It should be observed that now $u \to -\infty$ as $R \to 0$: no matter how cold it is the material remains as mush (albeit effectively solid) with small amounts of liquid at the grain corners. From (3.13) (or relating heat content to liquid area),

$$\frac{\partial u}{\partial \tau} = \nabla_y^2 u - \left(1 - \frac{\pi}{4}\right) \frac{\partial}{\partial \tau} R^2.$$

Combining these two equations gives a single nonlinear heat equation:

$$\frac{\partial}{\partial \tau} \left(u + \beta^2 \left(1 - \frac{\pi}{4}\right) / u^2\right) = \nabla^2 u \tag{5.1}$$

for $u < -\beta < 0$ ($R < 1$); this equation is a forward heat equation.

When u reaches $-\beta$, R becomes 1, and Γ forms a single circle. Taking $u > -\beta$, the earlier difficulties appear: the isolated-circle model leads to either a backward heat equation or instability of the macroscopic model. We then conjecture that the full macroscopic model should be another Stefan problem. The two, macroscopic, phases are a mush, where $u < -\beta$ and (5.1) holds, and a liquid, where $u > -\beta$ and the heat equation is satisfied. Now $u = -\beta$ on the macroscopic free boundary where the Stefan condition is $[\frac{\partial u}{\partial n}] =$ normal velocity$\times(1 - \frac{\pi}{4})$.

6 Discussion

Using a microscopic model for a phase change in the form of a Stefan problem, with kinetic undercooling and/or a Gibbs–Thomson effect, and taking very simple geometry, a macroscopic phase-field model for a mushy region has been derived. There is no diffusion of the 'order parameter', in this case the solid fraction. With both effects and more general, and probably more physically realistic, geometry of the 'local' free boundary, a macroscopic heat equation remains coupled to a local problem of mean-curvature flow. In some limiting cases the phase-field model is replaced by (nonlinear) heat equations in a liquid region and in a mushy or solid region, with a macroscopic free boundary between the two zones. This macroscopic free-boundary problem is of conventional Stefan type (temperature = constant on the free boundary).

Should the problem be generalized by the inclusion of body heating, then no major changes are expected in the behaviour of the derived phase-field models – although there is rapid variation of phase on the microscale, averaged quantities, for example the order parameter should vary smoothly. This is unlike the solutions found by Fife & Gill [3, 4], where the phase-field problem – with diffusion of the order parameter – exhibited a mush, not with the order parameter taking a value intermediate between the phases in some region, but rather with rapid variation of order parameter: the material segregates into the two separate phases. Exceptions to the smooth behaviour might be for the special cases of negligible kinetic undercooling, where macroscopic free-boundary problems are obtained in the absence of body heating. In these cases a different type of mushy region might be conjectured to appear when body heating is introduced. Once the critical temperature ($-\beta$ for configuration A, $-\beta/\sqrt{2}$ for configuration B) is reached, individual cells could rapidly melt, the proportion purely molten, χ, in some averaging region determining average enthalpy (for A, $u = -\beta$, $h = -\beta + 1 - \pi/4 + \pi\chi/4$; for B, $u = -\beta/\sqrt{2}$, $h = -\beta/\sqrt{2} + \chi$).

A number of minor modifications are easily incorporated into the model. For instance, taking specific heat or thermal conductivity to vary with temperature leads to extra nonlinearity in the final model. Phase dependancy of the specific heat is also easily taken into account but if the thermal conductivity takes a different value in the liquid from that in the solid, the effective, macroscopic, conductivity will not be simply determined in the two-dimensional problems, due to the effects of the geometry. Other laws relating free-boundary temperature with curvature and speed can be easily used, and a surface energy can be simply included.

In a later paper we shall discuss the effects of composition as well as taking different geometry for the cells (or grains), and three-dimensional problems. We finish by noting once again that the present work attempts to indicate what sort of macroscopic model might be obtained as an average of problems on a crystal scale, and is not expected to give a good quantative representation of such situations.

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