PHASE FIELD MODELS FOR HYPERCOOLED SOLIDIFICATION

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Abstract

Properties of the solidification front in a hypercooled liquid, so-called because the temperature of the resulting solid is below the melting temperature, are derived using a phase field (diffuse interface) model. Certain known properties for hypercooled fronts in specific materials are reflected within our theories, such as the presence of thin thermal layers and the trend towards smoother fronts (with less pronounced dendrites) when the undercooling is increased within the hypercooled regime. Both an asymptotic analysis, to derive the relevant free boundary problems, and a rigorous determination of the inner profile of the diffusive interface are given. Of particular interest is the incorporation of anisotropy and general microscale interactions leading to higher order differential operators. These features necessitate a much richer mathematical analysis than previous theories. Anisotropic free boundary problems are derived from our models, the simplest of which involves determining the evolution of a set (a solid particle)

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whose boundary moves with velocity depending on its normal vector. Considerable attention is given to the identification of surface tension, to comparison with previous theories and to questions of stability.

1 Introduction

The process of crystal growth into a hypercooled liquid is examined with the aid of phase field models. Previous theoretical studies of solidification into such a liquid, such as those in [6, 24, 32] have often been done in the setting of the boundary layer model [5], in which the motion of the phase boundary is determined without reference to the temperature field away from the boundary. In [28], a thin thermal layer was also postulated. In [33] a cellular model which does retain the spatial temperature distribution was used. It accounts for the possibility of variable solid/liquid ratio in a cell, and assumes a linear relationship between the temperature and the rate of change of that ratio in any given cell.

We use the phase field model, which has had considerable success in other solidification contexts. In particular, it has been shown to incorporate, within one unified system of PDE's, the Gibbs-Thompson and kinetic undercooling effects at low undercoolings, as well as the conduction of heat and the conservation of energy condition at the phase boundary. This has been done in a variety of settings, but not in that of hypercooled solidification.

We show that in this context as well, asymptotic analysis of the phase field model predicts without extra assumptions certain properties of the interface, listed below. Since the phase-field models are not entirely grounded in fundamental physical principles, we cannot definitively claim that our analysis establishes the listed properties as being characteristic of real materials. The predictions are, however, very suggestive.

- The velocity of a solidification front, if the influence of curvature can be neglected, is larger by a factor ϵ^{-1} than it is when the undercooling is not in the hypercooled range. Here ϵ, a nondimensional surface energy, is our basic small parameter for the asymptotics. This conclusion is compatible with previous theories. For example we give in Sec. 4 an order of magnitude comparison between our prediction and that of Sarocka and Bernoff [28].

  In practice, experiments (e.g. [18]) show that the transition to hypercooling is not accompanied by an abrupt increase of velocity, as one might expect from this. Rather, there is a smooth increase of velocity as the undercooling is increased past the critical value ($\Delta = 1$, in the conventional notation; see (6) below) into the hypercooled region. Part of the reason for this probably lies in the fact that in experiments, propagation does not occur by planar or moderately curved fronts unless the undercooling Δ is sufficiently larger than unity. A discussion of this point is given, e.g., in [32]. Another possible cause is that the coefficient α in (2) below, related to the attachment kinetics, may properly depend on temperature, whereas we take it to be constant.

- The motion of the interface is autonomous, with only small influence from the temperature field elsewhere in the medium. This is true also of most previous theories of hypercooling.

- At lowest order in ϵ, the law of motion is simple, stating that the normal velocity of the interface depends in a specific way on the latter's orientation. This is a stable motion which agrees in part with the fact (e.g. [6, 32]) that planar fronts become more stable and dendrites become angular at higher undercoolings.

- There is no uniquely defined temperature at the interface. Rather, the temperature undergoes a sharp transition there as one passes from the liquid to the solid side. This transition, of course, lends credence to the boundary layer theory and other thermal layer theories. However the ambiguity of interface temperature is not a part of those theories.

- The usual linear Gibbs-Thompson and kinetic undercooling relation at the interface is replaced by a (nonlinear) relation between the velocity of the interface and the temperatures on either side of it. This feature contrasts with most previous theories.

- All phase-field theories involve the concept of a diffuse interface, in which the order parameter changes rather quickly from its liquid to its solid value. This is somewhat akin to one of the features of the model in [33].

In Secs. 7 – 9, the phase-field theory for hypercooled interfaces is established in the case that the relaxation time for the order parameter is increased by a factor $1/\epsilon$. In that case, some of the above features (such as a sharp thermal layer) no longer appear.

Our analysis proceeds through formal asymptotics. We are led to a traveling wave problem for the determination of the dominant order inner profile at the phase boundary, as well as its velocity. A rigorous theory for this problem was given in our companion paper [2]. (A user's guide to the notational differences between that paper and this one is given in the first appendix.)

Our phase field models are partial differential equations for two field variables: a nondimensional temperature variable u and an order parameter variable ϕ. To begin with, we use a simple dimensionless isotropic phase-field model of a general form including those in [27, 15, 35], and elsewhere:

$$u_t + w(\phi)_t = \nabla^2 u, \tag{1}$$

$$\alpha\epsilon^2\phi_t = \epsilon^2\nabla^2\phi + F(\phi, u), \tag{2}$$

where the function $F(\phi, u)$, related to the ϕ-derivative of the bulk free energy density, is bistable in ϕ for each fixed u, and has the equal area property if and only if $u = 0$ (see Figure 1). It has the property that $\int_{h_-(u)}^{h_+(u)} F_u(\phi, u)d\phi > 0$, where $h_\pm(u)$ are the two extreme zeros of F for fixed u (we take $h_+ > h_-$). Two examples of the curves $F(\phi, u) = 0$ in the (ϕ, u) plane are shown in Fig. 2, together with the functions $h_\pm(u)$. These examples are

$$(a)\ F = (1 - \phi^2)(\phi + a(u)),$$

$$(b)\ F = \phi(1 - \phi^2) + u,$$

with $a'(u) > 0$. In example (a), $h_\pm$ are constant. Other examples are given in [27] on the basis of a density-functional theory, and in [22, 35] and elsewhere. An alternate form of the phase field equations, in which the function F in (2) is replaced by $\hat{F}(\phi, \epsilon k)$, in which the dependence on u is weak, has been used in many papers, e.g. [9, 26, 34, 35]. A comparison between the two versions is given in App. C.

In (1), (2), the function $w(\phi)$, which is the nondimensional potential energy part of the internal energy

$$e(\phi, u) \equiv u\ + w(\phi),$$

is concave. The parameter ϵ is a small dimensionless quantity related to the surface tension, and α is a relaxation constant for the order parameter. A discussion of the surface energy and Gibbs-Thompson relation within the

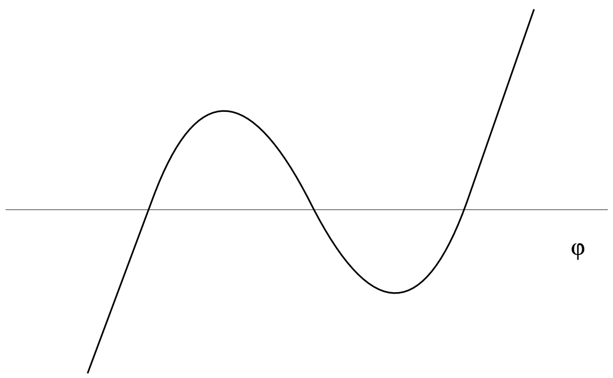

Figure 1: The bistable function $F(\phi, \cdot)$.

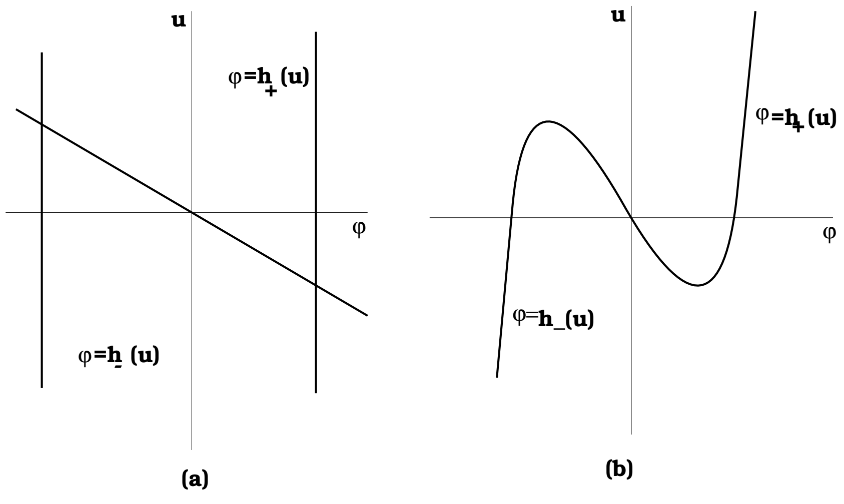

Figure 2: Two examples of the nullset $F(\phi, u) = 0$.

framework of the phase field model is given in section 4 and the second appendix.

In [27, 35], the system (1), (2) is derived as a gradient flow of an entropy functional

$$-S[\phi, e] \equiv \int_\Omega \left[-s(\phi, e) + \bar{K}|\nabla\phi|^2\right] dx, \tag{3}$$

Ω being the spatial domain of interest, in a manner which conserves the total internal energy

$$E[\phi, u] \equiv \int_\Omega e(\phi, u) dx. \tag{4}$$

Here all variables have been nondimensionalized,

$$F(\phi, u(e, \phi)) = \frac{\partial s}{\partial \phi}, \tag{5}$$

and ϵ (assumed to be small) is defined by $\bar{K} = \frac{1}{2}a^2\epsilon^2$, where a is a macrolength of the system. Thus ϵa is a characteristic microlength whose square is a measure of the relative weight assigned to the gradient part of the entropy density in (3), as compared to that assigned to the bulk part.

We generalize this approach in Sec. 6 to the case when the interaction part of the free energy functional is nonlocal. We then introduce a second characteristic microlength, denoted by ρ, which specifies the characteristic interaction distance between spatial locations.

By introducing a nonnegative interaction kernel, and truncating its expansion with respect to a small dimensionless parameter, we obtain a model similar to (1), (2), except that the Laplacian in the second of these equations becomes a higher order operator. This is a convenient vehicle for introducing anisotropy.

To better explain the parameter regime in which our analysis applies, let us mention that it will be shown in Sec. 2 that the phase field equations provide a unique nondimensional latent heat $\ell(u_\ell)$, depending on the liquid temperature u_ℓ. The origin of the temperature variable u is set at the melting temperature. The nondimensional supercooling strength $\Delta(u_\ell)$ is defined by

$$\Delta = \left|\frac{u_\ell}{\ell(u_\ell)}\right|, \tag{6}$$

and the liquid is said to be hypercooled if $\Delta > 1$. In this case we shall explain in Sec. 2 that our companion paper [2] implies the existence of a planar traveling front solution of the phase field equations with constant velocity;

the advancing solid will have temperature $u_s(u_\ell) = u_\ell + \ell(u_\ell) \equiv g(u_\ell)$, so that

$$\frac{u_s}{\ell} = 1 - \Delta < 0.$$

In any case, physical constraints require that the value u_s in the solid must be nonpositive. If (as is typically the case) the melt is not hypercooled, so that $\Delta < 1$, then if the front is planar, the advancing solid will have temperature $u = 0$, and the velocity of the front cannot be constant. This is a well-known fact, and is incorporated into all accepted models.

All of this was concerned with planar fronts, which again may be something of a mathematical abstraction. We shall be concerned with moderately curved fronts with possibly varying velocities.

For background, we review the well-known results of layer analyses of the phase field model (1), (2) in the case $0 < \Delta < 1$. Generally [11], we are led to a Stefan problem with small corrections due to curvature and kinetic undercooling. There are other limiting free boundary problems as well ([9] and other papers). For example, suppose the temperature range being observed is small, of order ϵ, as measured with respect to the melting temperature on the absolute scale. As mentioned before, the nondimensional temperature variable u measures the difference from the melting temperature. Therefore we set $u = \epsilon\bar{u}$ with $\bar{u} = O(1)$. Also, we expect the normal velocity v to be slow, so set $v = \epsilon\bar{v}$. The function $\bar{u}(x,t)$ is formally approximated by the solution $\hat{u}$ of a free boundary problem, commonly called a "Mullins-Sekerka" problem, roughly stated as follows [11] (see also [9]).

FBP1: Given an initial surface Γ_0 embedded in a domain $\mathcal{D}$, find a surface $\Gamma(t)$ separating $\mathcal{D}$ into two regions (solid and liquid) and a function $\hat{u}$, satisfying $\Gamma(0) = \Gamma_0$,

$$\nabla^2\hat{u} = 0 \quad \text{at points not on } \Gamma(t), \text{ no-flux boundary conditions on } \partial\mathcal{D}; \tag{7}$$

$$\hat{u} = -\sigma\kappa; \qquad [\partial_\nu \hat{u}]_\Gamma = -\bar{v}\ell \ \text{ at points on } \Gamma(t). \tag{8}$$

Here κ is the mean curvature of Γ, σ is a positive parameter related to the surface tension of the interface, and the brackets denote the limit as Γ is approached from the liquid side minus the limit from the other side. The various sign conventions here are chosen so that the solid advances into the liquid when there is energy flow away from the interface. This problem arises as the outer limit of a formal approximation, which includes also an inner approximation valid near the interface Γ.

The primary aim in this paper is to examine the "opposite" case, namely the asymptotic free boundary problem for solidification into a hypercooled medium, with $\Delta > 1$ and bounded away from 1. We find that the new free boundary problem, to lowest order, is much simpler in form than the above.

This asymptotics and the resulting free boundary problem for the simplest isotropic model are described in Sec. 3. We rely on the existence result of [2], which is described in Sec. 2. Section 4 is devoted to order of magnitude considerations for some physical parameters of our problem, and to comparing our results with a previous treatment of hypercooled solidification. In Sec. 5, we consider the question of how to alter this simple model to account for anisotropy, and in particular describe the most direct ad hoc approach. The changes necessary in the free boundary problem are clear. Models with nonlocal interaction are considered in Sec. 6. They again yield free boundary problems which incorporate anisotropy .

Also of interest is the case when the relaxation time for the order parameter, which we have called $\alpha\epsilon^2$ above, is slow. In Sec. 7 the problem with a relaxation time of order $O(\epsilon)$ rather than $O(\epsilon^2)$ is considered. We call this the case of slow solidification fronts. Since the anisotropy involves only the spatial terms, its effect in this case on the equations is identical to the case of faster relaxation time. Hence, the analysis of Sec. 6 carries through immediately. However, the slower relaxation leads to a fundamentally different free boundary value problem, which is derived in Sec. 7. Extended to the next order in ϵ, it contains in one of the interface conditions a term proportional to the curvature.

The inner layer equations for the slow solidification front are solved in Sec. 8. This result is then analogous to that given in the companion paper [2] for the faster relaxation time. Thus, the two problems are resolved to the same extent.

A stability analysis for the free boundary problem obtained in Sec. 7 is given in Sec. 9. It is found that planar traveling fronts are unstable to a range of wave numbers, but that the growth rate of these instabilities is bounded independently of wave number, so that the initial value problem with an initial perturbation of a planar front is likely well posed.

This paper generally examines only the lowest order free interface problem in the small parameter ϵ, but equations for the higher order terms can be obtained by standard methods. The higher order terms would, of course, incorporate curvature effects. They are included in the theory of Sarocka and Bernoff [28] and others and curvature effects are also part of the well known boundary layer model [5].

To reiterate, the major difference between our theory and previous treatments of hypercooled solidification is the following. Usually it is assumed that the solidification front is sharp, with well-defined temperature, and that there is a linear relation among the front's temperature, velocity (the usual kinetic undercooling effect) and curvature. We do not assume this, but rather deduce interfacial relations directly from the phase field equations. These equations do imply such a linear relation in the case $\Delta < 1$, but do not in the hypercooled case. There are two things that prevent it from doing so:

- The temperature makes an abrupt transition at the interface, so that the front's temperature itself is not well defined. Of course, the limits of the temperature from the liquid and from the solid both exist, as $\epsilon \to 0$.
- To lowest order, there is an implied relation between the velocity, on the one hand, and the limiting temperatures from the two sides of the interface, on the other hand. But that relation is not linear in general.

In short, the phase field approach suggests that the usual linear kinetic undercooling - curvature relation at the interface breaks down when we enter the hypercooling regime.

2 The traveling wave problem

Let us restrict attention for the moment to traveling wave solutions $u = \hat{u}(x \cdot n - ct)$, $\phi = \hat{\phi}(x \cdot n - ct)$ of (1), (2) moving with velocity $c > 0$ in the direction n, where n is a unit vector, corresponding to planar solidification fronts moving into a hypercooled liquid (the exact definition of this will latter be given below).

It is appropriate to scale the variables in the following way:

$$c = \frac{v}{\epsilon}, \quad \xi = \frac{x \cdot n}{\epsilon} - \frac{vt}{\epsilon^2}, \quad u(x,t) = U(\xi), \quad \phi(x,t) = \Phi(\xi).$$

Then

$$-v(U + w(\Phi))' = U'', \tag{9}$$

$$-\alpha v \Phi' = \Phi'' + F(\Phi, U), \tag{10}$$

$$U(\pm\infty) = u_{\ell,s}, \quad \Phi(\pm\infty) = \phi_{\ell,s}. \tag{11}$$

In (11) and below, the plus (resp. minus) sign goes with the subscript ℓ (resp. s); $u_\ell < 0$ is the temperature of the undercooled liquid, and $u_s < 0$ is the temperature of the solid. Such a solution does not make sense physically unless the melt is hypercooled (u_ℓ is large enough negative). The companion paper [2] is concerned with this traveling wave problem. It is important not just for its independent interest, but also as a crucial ingredient of our treatment of general interfaces in the rest of this paper. We here review the results of [2].

First, it is clear that under natural assumptions, the limit values $\phi_{\ell,s}$ and u_s will be determined uniquely from the knowledge of u_ℓ.

In fact, from (10) and (11), it necessarily follows that the constants in (11) must satisfy

$$F(\phi_{\ell,s}, u_{\ell,s}) = 0. \tag{12}$$

We associate larger values of the order parameter ϕ with liquid and smaller ones with solid. Thus ϕ is really a "disorder parameter", as opposed to its usage in [7], [27] and [15]. Therefore we interpret (12) by saying that the point (ϕ_ℓ, u_ℓ) must lie on the right hand branch $\phi_\ell = h_+(u_\ell)$ of the curve in Fig. 2. In the same way, the state in the solid, at $-\infty$, must lie on the left hand branch $\phi_s = h_-(u_s)$. An important special case is that when both branches are vertical lines; then $\phi_{\ell,s}$ are independent of u_ℓ.

The equation (9), integrated together with boundary conditions (11), implies that

$$u_\ell + w(\phi_\ell) = u_s + w(\phi_s). \tag{13}$$

This equation, together with the two equations (12), will typically determine u_s, ϕ_s, and ϕ_ℓ uniquely as functions of u_ℓ. In fact, as is shown in Figure 3, the two points (ϕ_ℓ, u_ℓ) and (ϕ_s, u_s) are the intersections of the curve $u = u_\ell + (w(\phi_\ell) - w(\phi))$ in the (ϕ, u) plane with the two outer branches of the curve in Fig. 2.

Def. u_ℓ is a hypercooled temperature if these intersections exist, are unique, and result in $u_s < 0$.

If this is the case, we may write

$$u_s = g(u_\ell), \quad \phi_{\ell,s} = h_\pm(u_{\ell,s}).$$

The dimensionless latent heat in such a transition is defined by

$$\ell(u_\ell) = w(h_+(u_\ell)) - w(h_-(g(u_\ell))), \tag{14}$$

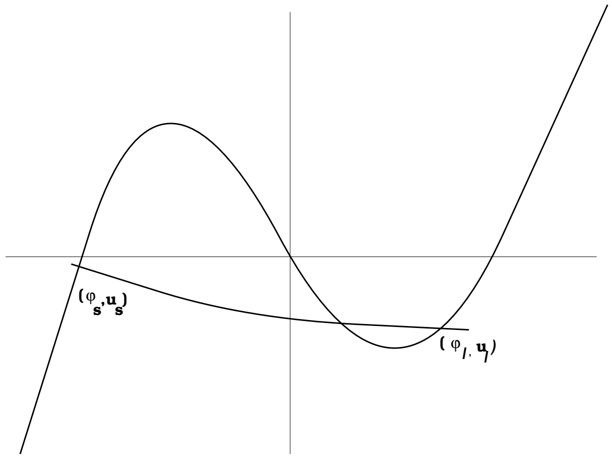

Figure 3: The determination of u_s, $\phi_{\ell,s}$

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so that (13) gives

$$u_s = u_\ell + \ell(u_\ell). \tag{15}$$

If the intersection of the curves exists at a point with a positive value of u, then we set $u_s = 0 = g(u_\ell)$, and the same definition (14) holds, but (15) does not. Recalling (6), we see that u_ℓ is hypercooled if and only if $\Delta > 1$.

In [2], it is shown that under the above assumptions and some other technical assumptions as well, there exists a (traveling wave) solution of (9), (10), (11). The problem of course includes the determination of its velocity v, which is always positive and clearly depends on α and u_ℓ. Its uniqueness (modulo shifts in z) is proved for small enough or large enough values of α. Finally, the α-dependence of v is shown (see Cor. 4.4 of [2]) to satisfy, for some positive constants A_i,

$$A_1\alpha^{-1} < v < A_2\alpha^{-1}. \tag{16}$$

3 Layer asymptotics and the resulting free boundary problem in the hypercooled isotropic case.

We retain the rapid time scaling used implicitly in the traveling wave problem. When the melt is hypercooled, our expectation is that the fronts will move more rapidly, and we choose our time variable to be

$$\tau = \frac{t}{\epsilon}.$$

Our basic equations (1), (2) become

$$u_\tau + w(\phi)_\tau = \epsilon \nabla^2 u, \tag{17}$$

$$\alpha\epsilon\phi_\tau = \epsilon^2 \nabla^2 \phi + F(\phi, u). \tag{18}$$

We shall continue to use the symbol v to denote velocity with respect to this new time variable, but now it will mean normal velocity of the curved solidification front.

We shall pose an initial-value problem which is an analog of the Stefan problem (or of the Mullins-Sekerka problem) with prescribed initial temperature. The analog turns out to be very different. Initially, we prescribe a temperature $u_0(x)$, a phase function $\phi_0(x)$, and a solid-liquid interface $\Gamma(0)$, separating space into two regions $\mathcal{D}_{\ell,s}(0)$. (We consider $\mathcal{D}_\ell$ to be the domain of liquid, and the other to be the solid.) In $\mathcal{D}_\ell$, the initial temperature $u(x,0) = u_0(x)$ will be any negative function which is hypercooled and smooth. The most natural particular case to consider is that in which u_0 is constant in this region, but for the sake of generality we allow u_0 to vary in x. We assume that on $\Gamma(0)$, the limit of $g(u_0(x))$ from $\mathcal{D}_\ell$ equals the limit of $u_0(x)$ from $\mathcal{D}_s$. Other than that, in $\mathcal{D}_s$ $u_0(x)$ is an arbitrary smooth nonpositive function. The interface will evolve in time as a surface $\Gamma(\tau)$ separating the domain into two regions $\mathcal{D}_{\ell,s}(\tau)$. It will always (we shall see) move into $\mathcal{D}_\ell$, so the domain $\mathcal{D}_s(\tau)$ will be growing larger, and $\mathcal{D}_\ell(\tau)$ shrinking. Finally, we choose ϕ_0 to be its local equilibrium value

$$\phi_0(x) = h_\pm(u_0(x)), \quad x \in \mathcal{D}_{\ell,s}(0). \tag{19}$$

To obtain the lowest order approximation $(u^0(x,\tau), \phi^0(x,\tau))$ in the two regions $\mathcal{D}_{\ell,s}$, we set $\epsilon = 0$ in (17), (18). The result is that $u^0 + w(\phi^0)$ is independent of τ, and $F(\phi^0, u^0) = 0$. Putting these two together, we find that

$$u^0(x,\tau) + w(\phi^0(x,\tau)) = u_0(x) + w(\phi_0(x)), \tag{20}$$

$$F(u^0(x,\tau), \phi^0(x,\tau)) = 0 \tag{21}$$

for all τ.

We also require that $u^0(x,\tau)$ be continuous in τ except when $x \in \Gamma(\tau)$. What this implies is simply that for x in $\mathcal{D}_\ell(\tau)$, $u^0(x,\tau)$ and $\phi^0(x,\tau)$ remain equal to $u_0(x)$ and $\phi_0(x)$ until the front passes the point x, after which time $x \in \mathcal{D}_s(\tau)$, u^0 changes to the value $g(u_0(x)) = u_0(x) + \ell(u_0(x))$, and $\phi^0(x,\tau) = h_-(u^0(x)) = h_-(g(u_0(x))$.

In short, the lowest order outer approximation satisfies the following, for $x \in \mathcal{D}_\ell(0)$:

$$\begin{aligned} u^0(x,\tau) = u_0(x), \quad \phi^0(x,\tau) = h_+(u_0(x)) \;\; &\text{for } \tau \text{ such that } x \in \mathcal{D}_\ell(\tau), \\ u^0(x,\tau) = g(u_0(x)), \quad \phi^0(x,\tau) = h_-(g(u_0(x))) \;\; &\text{for } \tau \text{ such that } x \in \mathcal{D}_s(\tau), \end{aligned} \tag{22}$$

and simpler relations hold when $x \in \mathcal{D}_s(0)$.

We still lack the crucial information about the dynamics of $\Gamma(\tau)$. To obtain this, we examine the inner approximations. For the lowest order inner approximation, we use the local coordinates (r,s) as in [11] and other places, r denoting signed distance from $\Gamma(\tau)$ with $r > 0$ in the liquid phase. The stretched variable is $z = \frac{r}{\epsilon}$. We express $u(r,s,\tau;\epsilon) = U(z,s,\tau;\epsilon)$ and the same for ϕ. What we get to lowest order is a system which is identical to our original traveling wave problem (9) and (10), except that derivatives are now with respect to the new stretched coordinate z. The reason for this is that r depends on τ as well as x, so that the derivatives with respect to τ in (17), (18) appear to lowest order in ϵ as $\epsilon^{-1} r_\tau$ times derivatives with respect to z. We then note that $v = -r_\tau$.

Required matching relations between the inner and outer solutions now imply

$$U(\infty,\tau) = u_0(x), \quad \Phi(\infty,\tau) = \phi_0(x) = h_+(u_0(x)), \tag{23}$$

$$U(-\infty,\tau) = g(u_0(x)), \quad \Phi(-\infty,\tau) = h_-(g(u_0(x))). \tag{24}$$

In (23) and (24), x denotes a location on Γ; it appears explicitly only in those boundary conditions and not in (9) or (10).

Since this problem is autonomous, we may shift the z-axis at will. We shall specify the location of the interface by requiring

$$\Phi(0,\tau) = 0. \tag{25}$$

We wish a solution of (9), (10), (23) - (25) for each τ and each $x \in \Gamma(\tau)$. Since τ appears nowhere explicitly, it suffices to have a solution for each

$x \in \mathcal{D}$. As mentioned before, the existence of such a solution, including a positive velocity v, is proved in [2], and its uniqueness as well, for either small or large values of α. We here assume that the velocity v is unique in all cases. Then, as was brought out above, it depends only on x. Therefore $v > 0$ is a function only of x (through the choice of initial data). We denote this function by the symbol V:

$$v = V(x). \tag{26}$$

We thus obtain the following lowest order free boundary problem for the motion of Γ:

FBP2: Find $\Gamma(\tau)$, given its initial value Γ_0 and given that its normal velocity satisfies (26).

Once this FBP is solved, the domains $\mathcal{D}_{\ell,s}(\tau)$ will be known, and the outer approximation to the temperature away from $\Gamma(\tau)$ will be provided by (22). Of course the most important case, sufficient to convey the essential concepts, is the one when the initial data in $\mathcal{D}_\ell$, and therefore the function V as well, are independent of x. The fronts then move, to lowest order, at a constant normal velocity.

4 Dimensional considerations and comparison with previous treatments

Our system (1), (2) is the nondimensional form of a basic pair of dimensional phase field equations [27, 15], which fairly generally can be written in the form

$$\partial_{\bar{t}}(cT + \bar{w}(\phi)) = \nabla \cdot k\nabla T, \tag{27}$$

$$K_0 \partial_{\bar{t}}\phi = K_1 \nabla^2 \phi - \frac{1}{T}\frac{\partial \bar{f}(\phi, T)}{\partial \phi}, \tag{28}$$

where T is absolute temperature, $cT + \bar{w}(\phi) = \bar{e}$ is internal energy density, c is heat capacity, k is the heat conduction coefficient (c and k could depend on ϕ and T; we take them to be constant), and the last term of (28) equals $\bar{s}_0'(\phi) - \frac{1}{T}\bar{w}'(\phi)$, where $\bar{s}_0$ is the temperature-independent part of the entropy density. The function $\bar{f}(\phi, T)$ is the Helmholz free energy density. Finally K_0 and K_1 are dimensional constants related, as we shall see, to the relaxation speed of the order parameter and to the interfacial thickness. The latent heat at melting temperature is defined by

$$\bar{\ell}_0 = \bar{w}(\phi_\ell) - \bar{w}(\phi_s),$$

where $\phi_{\ell,s}$ are the values of the order parameter for solid and liquid, respectively, at the melting temperature $T = T_0$. This is simply the dimensional form of (14) in the special case that $u_\ell = 0 = g(u_\ell)$.

There exist many ways to nondimensionalize the system (27), (28). We describe an approach similar to that in [15].

Space is made dimensionless with a characteristic macrolength a for our system, and time by the characteristic time ca^2/k. The latent heat $\bar{\ell}_0$ is used to nondimensionalize $\bar{w} = \bar{\ell}_0 w$ and $\bar{f} = \bar{\ell}_0 f$, and the dimensionless temperature variable is $u = (T - T_0)c/\bar{\ell}_0$. The nondimensional quantities use the same symbols, with bars removed. Thus

$$t = \frac{\bar{t}k}{ca^2}, \qquad \text{etc.}$$

Let $\beta = \left|\frac{\partial^2 f}{\partial \phi^2}(0,0)\right|$; we normalize f by defining $\tilde{f} = f/\beta$. We consider β to be a fixed number. It should be noted that a parameter $1/a$, similar to β, was been used in other forms of the phase field equations, and coupled to ϵ so that $\beta \to \infty$ as $\epsilon \to 0$. This alternate form is discussed in Appendix C.

Finally, we define dimensionless constants $\epsilon,\ \alpha,\ \nu$ by

$$\nu = \frac{\bar{\ell}_0}{cT_0}, \quad \epsilon^2 = \frac{K_1 T_0}{\beta a^2 \bar{\ell}_0}, \quad \alpha\epsilon^2 = \frac{K_0 k T_0}{\beta c a^2 \bar{\ell}_0},$$

and a dimensionless function (see its connection with entropy following (4))

$$F(\phi, u) = -\frac{1}{1 + \nu u}\frac{\partial \tilde{f}}{\partial \phi}.$$

By choice of β, we have that the bistable function F is normalized so that $F_\phi(0,0) = 1$. Alternatively, we could normalize so that the magnitude of the local maximum of $F(\phi, 0)$ is unity. This normalization factor is related to the maximum possible undercooling of the liquid.

All this yields (1) and (2).

Note the definition (6) of Δ, where ℓ is defined by (14). In the following, we assume that Δ is bounded and bounded away from 1 by fixed numbers which will not be specified.

The constants ϵ and α are closely related to dimensionless forms of the surface energy and kinetic constant at $T = T_0$. In the case of ϵ, this can be done in two ways, with identical results. On the one hand, it will be shown in Appendix B that the surface energy $\bar{\gamma}$ at $T = T_0$ can be calculated directly from its definition and the nature of the interfacial layer profile to be

$$\bar{\gamma} = 2\epsilon a \bar{\ell}_0 \beta p, \tag{29}$$

where p is an $O(1)$ dimensionless quantity depending on the normalized function $\tilde{f}$. If we define the dimensionless surface tension $\gamma = \frac{\bar{\gamma}}{\bar{\ell}_0 a}$, then

$$\gamma = 2\epsilon\beta p. \tag{30}$$

Thus the dimensionless surface tension γ is equal to an $O(1)$ constant times $\beta\epsilon$.

On the other hand, a surface energy enters into the Gibbs-Thompson relation, derivable by formal asymptotics [15] (again see Appendix B) in the case that the liquid is not hypercooled, i.e. $\Delta < 1$. In dimensionless form, this relation is

$$u = 2(\epsilon p \beta/\nu)(\alpha v_{PF} + \kappa), \tag{31}$$

where $v_{PF} = -r_\tau$ is the dimensionless front velocity in our phase-field model and κ is the mean curvature of the interface.

Using (29), we see that the dimensional version of this relation is

$$T - T_0 = \frac{\bar{\gamma} T_0}{\bar{\ell}_0} \left(\alpha \frac{c}{k} \bar{v}_{PF} + \bar{\kappa} \right). \tag{32}$$

The curvature term here gives the physically correct dependence on $\bar{\gamma}$ and $\bar{\ell}_0$, and serves as independent corroboration of (29). At the same time, it identifies α as the ratio of kinetic coefficient to curvature coefficient in the dimensionless Gibbs-Thompson relation (31) (a physical parameter). However, we emphasize that the relation (31) is derived only in the case of lower undercoolings, $\Delta < 1$. As we shall see, it does not apply to the hypercooled case.

It will be useful for us to estimate the front velocity v_{PF} in the hypercooled regime predicted by the phase-field model in terms of the other physical parameters. In the framework of the fast time variable τ as in Sec. 2, we have found a dimensionless velocity v which is the solution of (9), (10) with boundary conditions, and as such depends only on α and $u_0(x)$. The quantity $u_0(x)$ is assumed to be well into the hypercooled range and bounded. However, we wish to consider positive values of α which may be small, moderate, or large, and shall pay attention to how the velocity depends on it. For this we use (16). Let us denote by v_{PF} the nondimensional velocity in the original frame, using t rather than τ as the time variable. Then since $v = \epsilon v_{PF} = O(1)$, we have from (16) and (30)

$$v_{PF} \approx (\alpha\epsilon)^{-1} \approx \frac{\beta}{\gamma\alpha}. \tag{33}$$

Here and later, the approximation symbol means that the ratio of one quantity to the other is bounded and bounded away from 0, independently of ϵ, ν, α, and β.

We now convert this relation to dimensional form, using $\bar{\gamma} = a\bar{\ell}_0\gamma$:

$$\bar{v}_{PF} = v_{PF}\frac{k}{ca} \approx \frac{k}{ca}\frac{a\bar{\ell}_0\beta}{\bar{\gamma}\alpha} = \frac{k\bar{\ell}_0\beta}{c\bar{\gamma}\alpha}. \tag{34}$$

As was brought out in the introduction, other models for hypercooled fronts have been given in the past. We shall make a comparison of our results with some of the lowest order results in the Sarocka-Bernoff theory [28]. They use a different nondimensionalization from the one described above.

In [28], the dimensionless velocity is given by

$$v_{SB} = \frac{\Delta - 1}{\Delta}. \tag{35}$$

If the right side of (35) is an $O(1)$ quantity, then their dimensional velocity will be

$$\bar{v}_{SB} \approx \frac{\bar{\ell}_0\bar{T}}{\rho\bar{\gamma}T_0}, \tag{36}$$

where $\bar{T}$ is the difference between the solid and the liquid temperatures at the front and ρ is the ratio of the kinetic coefficient (of velocity) to the Gibbs-Thompson coefficient (of curvature) in the interface condition. We shall assume that $\bar{T} \approx \bar{\ell}_0/c$, which is the temperature difference at which hypercooling begins. The ratio ρ is a physical constant with dimensions of time/(length)^2. In our phase field model, it is seen from (32) to be related to α by

$$\rho = \frac{c\alpha}{k}.$$

In [28], a parameter m^{-1} is used, which is related to ρ by

$$\rho = \frac{\bar{\ell}_0}{mT_0\bar{\gamma}}.$$

This can be used to identify α as

$$\alpha = \frac{k\bar{\ell}_0}{mcT_0\bar{\gamma}}. \tag{37}$$

We therefore have

$$\bar{v}_{SB} \approx \bar{T}m \approx \frac{\ell_0^2 k}{c^2\bar{\gamma}T_0\alpha}. \tag{38}$$

Taking the quotient, we find that

$$\frac{\bar{v}_{SB}}{\bar{v}_{PF}} \approx \frac{\bar{\ell}_0}{cT_0\beta} = \frac{\nu}{\beta}. \tag{39}$$

The quantity ν is less than unity. If $\tilde{f}$ is given, then β is proportional to the maximum possible undercooling, in units of $\bar{\ell}_0/c$. When the ratio (39) is of order unity, the Sarocka-Bernoff theory and our theory, though based on quite different models, provide hypercooled velocities of the same orders of magnitude.

5 A direct adjustment for anisotropy

The penalty term in (3) for gradients in ϕ depends only on $|\nabla\phi|$, independently of the direction of the gradient. This term may be easily generalized [22, 26] to depend as well on the direction $\boldsymbol{\nu} = \frac{\nabla\phi}{|\nabla\phi|}$, remaining homogeneous of degree 2 in $\nabla\phi$, by replacing ϵ by $\epsilon\hat{\gamma}(\boldsymbol{\nu})$ for some positive function $\hat{\gamma}$. In view of (30), $\hat{\gamma}$ will be a surface tension scaled by ϵ. This way, (3) becomes

$$-S[\phi, e] \equiv \int_\Omega \left[-s(\phi, e) + \frac{1}{2}\epsilon^2\hat{\gamma}^2(\boldsymbol{\nu})|\nabla\phi|^2\right] dx. \tag{40}$$

The motivation for this is that within the layer, the gradient of ϕ, hence $\boldsymbol{\nu}$, will be directed approximately normal to the layer, so that $\boldsymbol{\nu}$-dependence in (40) will, in the sharp interface limit, be translated into the dependence of the velocity of the interface on the latter's normal vector. An obvious disadvantage of this approach is the fact that the integrand in (40) may not be regular at locations where $\nabla\phi = 0$.

In quite the same way, dependence on $\boldsymbol{\nu}$ can be introduced in the kinetic coefficient α, which appears in (2) and (10). Again, in the sharp interface limit, this provides a mechanism for the dependence of velocity on orientation of the interface. Both types of approaches have been pursued in the past. Here, we concentrate on the former: dependence of the scaled surface tension on $\boldsymbol{\nu}$.

The form of the gradient flow on the right of (2) must also be changed: the operator $\nabla^2\phi$ becomes a second order quasilinear operator $M\phi$, with the coefficients of the second derivatives depending on $\boldsymbol{\nu}$. These coefficients are quadratic in $\hat{\gamma}$ and its derivatives up to order two.

In the case of two space dimensions, we may set $\boldsymbol{\nu} = (\cos\theta, \sin\theta)$ and $\hat{\gamma} = \hat{\gamma}(\theta)$, where θ is the angle between $\nabla\phi$ and the x_1-axis. In this case, we may calculate

$$M\phi = \partial_1(\hat{\gamma}^2\partial_1\phi - \hat{\gamma}\hat{\gamma}'\partial_2\phi) + \partial_2(\hat{\gamma}^2\partial_2\phi + \hat{\gamma}\hat{\gamma}'\partial_1\phi). \tag{41}$$

This expression can be written as a combination of second order derivatives of ϕ with coefficients depending on θ. It constitutes an elliptic operator at those values of θ where $\hat{\gamma}''(\theta)+\hat{\gamma}(\theta) > 0$. There always exist such values of θ, for example near those which make $\hat{\gamma}$ minimal, so that $\hat{\gamma}''$ is nonnegative.

On the other hand, there may exist values of the direction θ at which the ellipticity criterion fails. The corresponding statement is of course true in the case of 3 space dimensions. It is important to realize that there will in general exist no persistent layered solutions of (1), (2) (with $\nabla^2\phi$ replaced by $M\phi$) such that the normal to the layer is directed in a nonelliptic direction. In fact, if initial conditions on ϕ and u were given with ϕ possessing a layer structure like this, then the initial value problem would be non-parabolic and ill-posed. Lacking such a persistent layer structure with orientation in these directions, the formal procedure used in obtaining inner and outer expansions for layered solutions would be vacuous and therefore invalid.

The nonelliptic directions are therefore excluded directions when we model the growth of crystals. This statement of course holds not just in the hypercooled situation, but in general. The existence of excluded directions is a feature of other theories of crystal growth, and represents the growth of crystals with facets. As an example, consider the two-dimensional case with $\hat{\gamma}(\theta) = 1 - b\cos 4\theta$, $b > 0$, so that the anisotropy has 4-fold symmetry. The operator M will be elliptic everywhere if $0 < b < \frac{1}{15}$, but if $b > \frac{1}{15}$, there will be excluded values of θ near $\frac{\pi}{4}$.

This anisotropy affects the inner-outer formalism in Sec. 3 in the following way. The lowest order outer solution (22) is unchanged. However, the equations (9), (10) governing the inner profile are altered by having a $\boldsymbol{\nu}$-dependent coefficient $\sigma(\boldsymbol{\nu}) > 0$ multiplying the second derivative Φ_{zz} in (10), where now $\boldsymbol{\nu}(x)$ is the unit normal to $\Gamma(\tau)$ in the direction of $\mathcal{D}_\ell(\tau)$ at the point x, provided that $\boldsymbol{\nu}$ is an allowed direction. Thus no crystal can grow which has an interface with a normal vector in a disallowed direction. However, facets may occur, at whose edges $\boldsymbol{\nu}(x)$ jumps discontinuously between disjoint allowed $\boldsymbol{\nu}$-intervals.

Incorporating this anisotropy into the previous treatment, we obtain

$$v = V(\boldsymbol{\nu}, x). \tag{42}$$

The initial value problem would involve specifying an initial surface Γ_0 and asking how it evolves in accordance with the law (42). Let us consider the case when there is no x-dependence: $V = V(\nu)$. Initially smooth interfaces may well evolve into singular ones for which the normal vector is not uniquely defined, and the notion of the evolution by (42) will then have to be generalized if the motion is to be continued beyond that point. Generalizations for this law and a wide class of others, including motion by curvature, have been studied a great deal in recent years (see e.g. [13, 29]), and the existence of solutions of the generalization established for all positive t.

Especially noteworthy is the connection between this evolution law and the Wulff region W_V corresponding to the function V when the latter is defined and positive for all ν on the unit sphere. W_V is a bounded convex set in R_d whose boundary may have corner points. Except for scaling, it is invariant when its boundary evolves according to (42) in a natural weak sense. In fact, for any $a > 0$, the set $(a+t)W_V$ is a solution of that evolution law.

It was conjectured by Angenent and Gurtin [1], and proved by Soner [29], that any bounded set $E(0) \in R^d$ in a certain general class has a global weak evolution $E(t)$ in a sense similar to that in [13], and that

$$\lim_{t\to\infty} \frac{E(t)}{t} = W_V.$$

6 Higher order phase field equations; anisotropy through microscale interaction

In [27], the self-interaction part of the entropy functional S was postulated to be

$$-\bar{K} \int |\nabla\phi|^2 \, d\bar{\mathbf{x}},$$

as shown in (3) (we now denote space coordinates by $\bar{\mathbf{x}}$). We now introduce a more general quadratic form which is motivated by considering the complete self-interaction of the field ϕ. Such self-interaction expressions are commonplace [21]; see [10, 8] for their use in the phase field context. Let $J : R^d \to R$ be a nonnegative, rapidly decaying function with unit integral and unit standard deviation. We define the Hamiltonian of self interaction as

$$\mathcal{H}_\rho(\phi) = \int\int \rho^{-d-2} J\left(\frac{\bar{\mathbf{x}} - \bar{\mathbf{y}}}{\rho}\right) (\phi(\bar{\mathbf{x}}) - \phi(\bar{\mathbf{y}}))^2 d\bar{\mathbf{x}} d\bar{\mathbf{y}}. \tag{43}$$

Since J has unit standard deviation, ρ is identified as a characteristic interaction distance. This Hamiltonion has the dimensions of $(\text{length})^{d-2}$.

We shall allow J to be anisotropic in general so that self interaction is stronger in certain directions. Note that in $L^2(R^d)$ the gradient of $\mathcal{H}_\rho$ at ϕ is represented by the function $4\rho^{-2}[\phi - J_\rho * \phi]$, where $J_\rho(\mathbf{x}) = \rho^{-d} J\left(\frac{\mathbf{x}}{\rho}\right)$ and $*$ denotes convolution. Thus replacing the integral in (3) involving $|\nabla\phi|^2$ by $M\mathcal{H}_\rho(\phi)$ for some M would result in (2) being replaced by an equation of the form

$$\hat{\alpha}\phi_t = 4M\rho^{-2}[J_\rho * \phi - \phi] + F(\phi, u). \tag{44}$$

The quantity $\rho^{-2}[J_\rho * \phi - \phi]$ appearing in (44) is clearly analogous to $\nabla^2\phi$. For example, the discrete Laplacian on a lattice with spacing ρ, applied to a lattice function ϕ and evaluated at a lattice point x, is the average of ϕ over neighboring points minus the value $\phi(x)$, all this divided by ρ^2. The convolution is another type of average over neighboring points, no longer restricted to a lattice. We obtain the Laplacian formally by taking the limit of $\rho^{-2}[J_\rho * \phi - \phi]$ in the isotropic case as $\rho \to 0$.

The equation (44), for fixed u, can be viewed as an ordinary differential equation in L^2 provided F satisfies certain growth and regularity conditions. The analysis of (44) in that context is interesting in its own right (see [3, 19, 16]; for related issues see [25, 30]). But here we prefer to focus on a "truncated" version of this equation as explained below. (See also [4].)

We shall employ the following notation:
For a vector $\boldsymbol{\xi} \in R^d$ and a d-dimensional multiindex α, let $|\alpha| = \alpha_1 + \cdots + \alpha_d$, $\boldsymbol{\xi}^\alpha = \xi_1^{\alpha_1} \cdots \xi_d^{\alpha_d}$, $\alpha! = \alpha_1! \cdots \alpha_d!$, and $\boldsymbol{\partial}^\alpha = \partial_{x_1}^{\alpha_1} \cdots \partial_{x_d}^{\alpha_d}$, ∂_{x_j} being differentiation with respect to x_j.

In (43) change variables by writing $\mathbf{x} = \frac{\bar{\mathbf{x}} - \bar{\mathbf{y}}}{2}$, $\mathbf{y} = \frac{\bar{\mathbf{x}} + \bar{\mathbf{y}}}{2}$. Furthermore write the formal Taylor series expansions of $\phi(\bar{\mathbf{x}})$ and $\phi(\bar{\mathbf{y}})$ as

$$\begin{aligned}\phi(\bar{\mathbf{x}}) &= \phi(\mathbf{y}+\mathbf{x}) = \sum_{k=0}^{\infty}\sum_{|\alpha|=k}\frac{\boldsymbol{\partial}^{\alpha}\phi(\mathbf{y})}{\alpha!}\mathbf{x}^{\alpha}\\ \phi(\bar{\mathbf{y}}) &= \phi(\mathbf{y}-\mathbf{x}) = \sum_{k=0}^{\infty}(-1)^{k}\sum_{|\alpha|=k}\frac{\boldsymbol{\partial}^{\alpha}\phi(\mathbf{y})}{\alpha!}\mathbf{x}^{\alpha}.\end{aligned}$$

Hence,

$$\phi(\bar{\mathbf{x}})-\phi(\bar{\mathbf{y}}) = 2\sum_{k=1}^{\infty}\sum_{|\alpha|=2k-1}\frac{\boldsymbol{\partial}^{\alpha}\phi(\mathbf{y})}{\alpha!}\mathbf{x}^{\alpha}$$

and

$$(\phi(\bar{\mathbf{x}})-\phi(\bar{\mathbf{y}}))^{2} = 4\sum_{k=1}^{\infty}\sum_{\substack{|\alpha|+|\beta|=2k\\ |\alpha|\ \text{odd}}}\frac{\boldsymbol{\partial}^{\alpha}\phi(\mathbf{y})\boldsymbol{\partial}^{\beta}\phi(\mathbf{y})}{\alpha!\beta!}\mathbf{x}^{\alpha+\beta}.$$

So formally we may write

$$\begin{aligned}\mathcal{H}_{\rho}(\phi) &= 2^{d}\rho^{-2}\int\sum_{k=1}^{\infty}\sum_{\substack{|\alpha|+|\beta|=2k\\ |\alpha|\ \text{odd}}}\left(4\int\frac{J_{\rho}(2\mathbf{x}/\rho)\mathbf{x}^{\alpha+\beta}}{\alpha!\beta!}d(\mathbf{x}/\rho)\right)\boldsymbol{\partial}^{\alpha}\phi(\mathbf{y})\boldsymbol{\partial}^{\beta}\phi(\mathbf{y})d\mathbf{y}\\ &\equiv \int\sum_{k=1}^{\infty}\rho^{2k-2}\sum_{\substack{|\alpha|+|\beta|=2k\\ |\alpha|\ \text{odd}}}b_{\alpha\beta}\boldsymbol{\partial}^{\alpha}\phi(\mathbf{y})\boldsymbol{\partial}^{\beta}\phi(\mathbf{y})d\mathbf{y}, \qquad (45)\end{aligned}$$

where

$$b_{\alpha\beta} = 2^{d+2}\int\frac{J(2\mathbf{z})\mathbf{z}^{\alpha+\beta}}{\alpha!\beta!}d\mathbf{z}. \qquad (46)$$

We shall truncate the infinite sum at $k=m$ and examine the resulting Hamiltonian, $\mathcal{H}_{\rho}^{m}$, as well as the associated PDE derived as a gradient flow. We shall be using the entropy functional (3) with the integral of the gradient term replaced by $K\mathcal{H}_{\rho}^{m}(\phi)$.

Naturally one expects $\mathcal{H}_{\rho}^{m}$ to be a penalty term in the revised entropy functional, i.e. nonnegative for any choice of ϕ. Using Fourier transforms, we express

$$\mathcal{H}_{\rho}^{m} = -\int\left(\sum_{k=1}^{m}\rho^{2k-2}\sum_{\substack{|\alpha|+|\beta|=2k\\ |\alpha|\ \text{odd}}}(-1)^{k}b_{\alpha\beta}\boldsymbol{\xi}^{\alpha}\boldsymbol{\xi}^{\beta}\right)|\hat{\phi}(\boldsymbol{\xi})|^{2}d\boldsymbol{\xi},$$

so that the criterion for $\mathcal{H}_\rho^m$ to be a penalty is

$$\sum_{k=1}^{m}(-1)^k\rho^{2k-2}\sum_{\substack{|\alpha+\beta|=2k\\ |\alpha|\ \text{odd}}} b_{\alpha\beta}\boldsymbol{\xi}^\alpha\boldsymbol{\xi}^\beta < 0 \quad \text{for all} \quad \boldsymbol{\xi}\neq 0. \tag{47}$$

Furthermore, the the differential operator $-\frac{\delta\mathcal{H}_\rho^m}{\delta\phi}$ to be used in place of the expression $4\rho^{-2}[J_\rho*\phi-\phi]$ on the right of (44) should typically be elliptic if the initial value problem is to be well-posed. This operator is given by

$$L_m\phi \equiv 2\sum_{k=1}^{m}\rho^{2k-2}\sum_{\substack{|\alpha+\beta|=2k\\ |\alpha|\ \text{odd}}} b_{\alpha\beta}\boldsymbol{\partial}^{\alpha+\beta}\phi. \tag{48}$$

It is elliptic if and only if

$$(-1)^m\sum_{\substack{|\alpha+\beta|=2m\\ |\alpha|\ \text{odd}}} b_{\alpha\beta}\boldsymbol{\xi}^{\alpha+\beta} < 0 \quad \text{for all} \quad \boldsymbol{\xi}\neq 0. \tag{49}$$

Lemma 6.1. Inequalities (47) and (49) hold for coefficients $b_{\alpha\beta}$ given by (46) for any J described above whenever m is odd. The reverse inequality in (49) holds when m is even.

Proof. First, we show that

$$\sum_{\substack{|\alpha+\beta|=2k\\ |\alpha|\ \text{odd}}} b_{\alpha\beta}\boldsymbol{\xi}^{\alpha+\beta} = 2\int J(\mathbf{x})\frac{(\mathbf{x}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}d\mathbf{x}. \tag{50}$$

For this, note that

$$b_{\alpha\beta}\boldsymbol{\xi}^{\alpha+\beta} = 2^{d+2}\int \frac{J(2\mathbf{x})\mathbf{x}^{\alpha+\beta}}{\alpha!\beta!}d\mathbf{x}\ \boldsymbol{\xi}^{\alpha+\beta},$$

so that

$$\sum_{\substack{|\alpha+\beta|=2k\\ |\alpha|\ \text{odd}}} b_{\alpha\beta}\boldsymbol{\xi}^{\alpha+\beta} = 2^{d+2}\int J(2\mathbf{x})\left[\sum_{\substack{|\alpha+\beta|=2k\\ |\alpha|\ \text{odd}}}\frac{\mathbf{x}^{\alpha+\beta}\boldsymbol{\xi}^{\alpha+\beta}}{\alpha!\beta!}\right]d\mathbf{x}. \tag{51}$$

Recall the multinomial expansion formula

$$\left(\sum_{i=1}^{d} z_i\right)^r = \sum_{|\gamma|=r} \frac{r!}{\gamma!}\mathbf{z}^{\gamma}. \tag{52}$$

Therefore, the term in brackets in (51) may be written

$$\begin{aligned}
& \sum_{r=1}^{k} \sum_{|\alpha|=2r-1} \frac{\mathbf{x}^{\alpha}\boldsymbol{\xi}^{\alpha}}{\alpha!}\left(\sum_{|\beta|=2k-2r+1} \frac{\mathbf{x}^{\beta}\boldsymbol{\xi}^{\beta}}{\beta!}\right) \\
= & \sum_{r=1}^{k}\left(\sum_{|\alpha|=2r-1} \frac{\mathbf{x}^{\alpha}\boldsymbol{\xi}^{\alpha}}{\alpha!}\right)(\mathbf{x}\cdot\boldsymbol{\xi})^{2k-2r+1}/(2k-2r+1)! \\
= & \sum_{r=1}^{k} \frac{(\mathbf{x}\cdot\boldsymbol{\xi})^{2r-1}}{(2r-1)!}\frac{(\mathbf{x}\cdot\boldsymbol{\xi})^{2k-2r+1}}{(2k-2r+1)!} = (\mathbf{x}\cdot\boldsymbol{\xi})^{2k}\sum_{r=1}^{k}\frac{1}{(2r-1)!(2k-2r+1)!} \\
= & \frac{(\mathbf{x}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}\sum_{r=1}^{k}\frac{(2k-1)![(2r-1)+(2k-2r+1)]}{(2r-1)!(2k-2r+1)!} \\
= & \frac{(\mathbf{x}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}\left[\sum_{r=1}^{k}\frac{(2k-1)!}{(2r-2)!(2k-2r+1)!}+\sum_{r=1}^{k}\frac{(2k-1)!}{(2r-1)!(2k-2r)!}\right] \\
= & \frac{(\mathbf{x}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}\sum_{j=0}^{2k-1}\frac{(2k-1)!}{j!(2k-1-j)!} = \frac{(\mathbf{x}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}(1+1)^{2k-1} \\
= & \frac{(2\mathbf{x}\cdot\boldsymbol{\xi})^{2k}}{2(2k)!}.
\end{aligned} \tag{53}$$

Putting this into (51), we find

$$\sum_{\substack{|\alpha|+|\beta|=2k \\ |\alpha| \text{ odd}}} b_{\alpha\beta}\boldsymbol{\xi}^{\alpha+\beta} = 2^{d+1}\int J(2\mathbf{x})\frac{(2\mathbf{x}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}d\mathbf{x} = 2\int J(\mathbf{y})\frac{(\mathbf{y}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}d\mathbf{y},$$

which establishes (50).

Since $J \geq 0$ and is not identically zero, and for fixed $\boldsymbol{\xi} \neq 0, (\mathbf{x}\cdot\boldsymbol{\xi})^{2k} > 0$ a.e., (49) holds when m is odd and the reverse inequality holds when m is even. To establish (47) when m is odd we note the following:

$$\sum_{k=1}^{m}(-1)^k\rho^{2k}\sum_{\substack{|\alpha+\beta|=2k \\ |\alpha| \text{ odd}}} b_{\alpha\beta}\boldsymbol{\xi}^{\alpha+\beta} \quad = \quad 2\sum_{k=1}^{m}(-1)^k\int J(\mathbf{y})\frac{(\rho\mathbf{y}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}\,d\mathbf{y}$$

$$= \quad 2\int J(\mathbf{y})\left[\sum_{k=1}^{m}(-1)^k\frac{(\rho\mathbf{y}\cdot\boldsymbol{\xi})^{2k}}{(2k)!}\right]d\mathbf{y}$$

Now consider the factor in brackets for $m = 2n+1$ and write $b = \rho\mathbf{y}\cdot\boldsymbol{\xi}$. If

$$f_n(b) \equiv \sum_{k=1}^{2n+1}(-1)^k b^{2k}/(2k)!,$$

then $f_n(b)$ approaches $\cos b - 1 \leq 0$ as $n \to \infty$. Furthermore

$$b^{4r}/(4r)! - b^{4r+2}/(4r+2)! > 0$$

if and only if

$$b^2 < (4r+1)(4r+2) \equiv b_r^2.$$

Now fix $|b| > 0$. There exists an integer r such that $b_r^2 < b^2 \leq b_{r+1}^2$(taking $b_{-1} = 0$) and since b_r^2 is strictly increasing,

$$f_r(b) \leq f_{r+1}(b) < \cdots < \cos b - 1 \leq 0$$

while

$$f_r(b) < f_{r-1}(b) < \cdots < f_0(b) \quad = -\frac{b^2}{2} < 0.$$

From these it follows that $f_n(b) < 0$ for each n and the claim is established. This completes the proof of the lemma.

To simplify notation we shall write

$$\bar{L}_k\phi \equiv \sum_{\substack{|\alpha|+|\beta|=2k \\ |\alpha|\ \mathrm{odd}}} b_{\alpha\beta}\boldsymbol{\partial}^{\alpha+\beta}\phi,$$

so that from (48)

$$L_m\phi = 2\sum_{k=1}^{m}\rho^{2k-2}\bar{L}_k\phi.$$

With those preliminary calculations, we now return to formulate the analog of (2). We must pay attention to length scales (of which there are three), but in writing the analog of (3), it will be convenient to assume that $s(\phi, e)$ is nondimensional. That can be arranged by dividing through the dimensional version by the characteristic entropy density $\bar{\ell}_0/T_0$. Then $\bar{K}$ will have dimensions of (length)^2. We therefore write $\bar{K} = Ka^2$, where a is a characteristic macrolength of the system.

To proceed with our generalization, we replace the integral of $\bar{K}|\nabla\phi|^2$ in (3) by $Ka^2\mathcal{H}_\rho^m(\phi)$, where K, as before, is dimensionless. We now have

$$-S[\phi,e] \equiv \int_\Omega (-s(\phi,e))dx + Ka^2\mathcal{H}_\rho^m(\phi). \tag{54}$$

The equation analogous to (2) will be of the form $\hat{\alpha}\phi_t = \frac{\delta S}{\delta\phi}$, where $\hat{\alpha}$ is a relaxation time. Thus in view of (48) and (5), we have

$$\hat{\alpha}\phi_t = 2K\left(\frac{a}{\rho}\right)^2 \sum_{k=1}^{m} \rho^{2k}\bar{L}_k\phi + F(\phi,u). \tag{55}$$

We nondimensionalize space by $x \to a\hat{x}$, so that $\hat{x}$ is dimensionless, then drop the hat. At the same time, we define ϵ as before (following (4)) by $2K = \epsilon^2$, and α by $\hat{\alpha} = \alpha\epsilon^2$, so that (55) becomes

$$\alpha\epsilon^2\phi_t = \epsilon^2 \sum_{k=1}^{m} \left(\frac{\rho}{a}\right)^{2k-2} \bar{L}_k\phi + F(\phi,u). \tag{56}$$

As before, it will turn out that ϵa will be the characteristic thickness of the interface.

In summary, we have introduced three characteristic lengths: a macroscopic one (a) and 2 microscopic ones (ρ and $a\epsilon$). This last one, with ϵ defined above, can be characterized roughly in the following way. Set $\phi = e^{ikx}$ (assuming space is one dimensional). As k increases, the contribution to $-S$ from $\int(-s(\phi,e))dx$ remains bounded, but that of $Ka^2\mathcal{H}_\rho^m$ starts from 0 and increases indefinitely. There is a value of k at which the two contributions to $-S$ are about equal. That characteristic wave number yields a characteristic wave length which is $\approx \epsilon a$.

Finally, define $\mu = \frac{\rho}{a\epsilon}$ (the ratio of the two microlengths). Later, it will be assumed that μ is small enough. That assumption means that the characteristic interaction length ρ is small enough, as compared to the length $a\epsilon = a\sqrt{2K}$ associated with the interaction terms in (54). The assumption that μ is small enough implies that when $a\epsilon$ is small, ρ must be even smaller. The particular case $\rho = \mu = 0$ gives us the second order case (2) again. We can therefore express (56) as

$$\alpha\epsilon^2\phi_t = \sum_{k=1}^{m} \mu^{2k-2}\epsilon^{2k}\bar{L}_k\phi + F(\phi,u). \tag{57}$$

We sketch the construction of the inner expansion corresponding to (57) (see [15, 11], for example) for small ϵ with μ fixed. It will be seen to be valid in a formal sense uniformly for μ sufficiently small. Consider the same local coordinate system (r, s) mentioned in Sec. 3 and used in [11], r denoting signed distance from an interface Γ and s denoting coordinates on Γ.

Let $\boldsymbol{\nu}$ be the vector of direction cosines of the r-axis, i.e. the unit normal at some point on Γ. Derivatives are transformed as follows:

$$\boldsymbol{\partial} = (\partial/\partial x_i) = (\nu_i \partial/\partial r + \; a_i(\boldsymbol{\nu}) \cdot \nabla_s)$$

for some coefficients a_i, where ∇_s is the surface gradient operator on Γ.

We may therefore write

$$\begin{aligned} \bar{L}_k \phi \;\; &= \sum_{\substack{|\alpha+\beta|=2k \\ |\alpha| \text{ odd}}} b_{\alpha\beta} \boldsymbol{\nu}^{\alpha+\beta} \partial_r^{2k} \phi + (\text{terms in } \nabla_s) \\ &+ \;\; (\text{terms of lower order in } \partial_r). \end{aligned}$$

The first part of this we denote by

$$\begin{aligned} \Lambda_k(\boldsymbol{\nu})\phi \;\; &\equiv \sum_{\substack{|\alpha+\beta|=2k \\ |\alpha| \text{ odd}}} b_{\alpha\beta} \boldsymbol{\nu}^{\alpha+\beta} \partial_r^{2k} \phi \\ &\equiv \;\; b_k(\boldsymbol{\nu}) \partial_r^{2k} \phi. \end{aligned} \tag{58}$$

From (50), we see that

$$b_k(\boldsymbol{\nu}) = 2 \int \frac{J(\mathbf{x})(\mathbf{x} \cdot \boldsymbol{\nu})^{2k}}{(2k)!} d\mathbf{x}. \tag{59}$$

With the stretched variable $z = r/\epsilon$, the right side of (57) now becomes

$$\sum_{k=1}^{m} \mu^{2k-2} b_k(\boldsymbol{\nu}) \partial_z^{2k} \Phi + F(\Phi, U) + (\text{terms of higher order in } \epsilon), \tag{60}$$

and (10) becomes

$$-\alpha v \Phi_z = \Lambda(\boldsymbol{\nu}) \Phi + F(\Phi, U), \tag{61}$$

where

$$\Lambda(\boldsymbol{\nu}) = \sum_{k=1}^{m} \mu^{2k-2} b_k(\boldsymbol{\nu}) \partial_z^{2k}. \tag{62}$$

Thus, the main effect of the generalization to higher order equations given in this section is in the lowest order basic system (9), (10) for the layer profile. The first of these equations remains the same, but (10) is to be replaced by (61).

Let us assume that the solution of (9), (61), (23), (24) exists and that it is unique. The existence of a solution of this problem is proved in [2] provided that the parameter μ is sufficiently small. Furthermore it is also proved there that this solution is unique if α is either small or large enough.

Since the operator Λ depends on the normal $\boldsymbol{\nu}$ to the interface, the velocity v will also depend on $\boldsymbol{\nu}$, so that in place of (26), we again obtain an equation of the form (42):

$$v = V(\boldsymbol{\nu}, \mathbf{x}). \tag{63}$$

The function V is not known explicitly; besides its dependence on $\boldsymbol{\nu}$ and x, it depends on α, but not on ϵ. As before, the most important case is when there is no x-dependence.

We shall end this section with a calculation of the operator Λ. We use polar coordinates, expressing

$$\boldsymbol{\nu} = (\cos\psi, \sin\psi), \quad \mathbf{x} = r(\cos\theta, \sin\theta), \quad J(\mathbf{x}) = \sum_{n=-\infty}^{\infty} h_n(r) e^{in\theta}.$$

Then from (59),

$$\mathbf{x}\cdot\boldsymbol{\nu} = r\cos(\psi - \theta),$$

$$b_k(\boldsymbol{\nu}) = \frac{2}{(2k)!}\sum_n \int_0^{2\pi} e^{in\theta}(\cos(\psi-\theta))^{2k} d\theta \int_0^\infty h_n(r) r^{2k+1} dr.$$

The integral here over θ can be expressed as $e^{in\psi}\int e^{in\sigma}(\cos\sigma)^{2k} d\sigma$. If one expresses the cosine in terms of the exponentials $e^{\pm i\sigma}$ and uses the binomial formula to find the $2k$-th power, one sees that the only term contributing to the integral is the one in $e^{-in\sigma}$. Proceeding along these lines, we find that

$$b_k(\boldsymbol{\nu}) = \sum_{\substack{|n|\le 2k \\ n \text{ even}}} q_{n,k} e^{in\psi}, \tag{64}$$

$$q_{n,k} = \frac{2^{2-2k}\pi}{(k-\frac{n}{2})!(k+\frac{n}{2})!}\int_0^\infty h_n(r) r^{2k+1} dr.$$

Let us say that b_k has p-fold anisotropy if its Fourier series expansion in ψ contains nonzero terms in $e^{ip\psi}$, but no higher order ones. Then we can deduce from (64) that b_k has $2k$-fold anisotropy only if J does. Applying this to the expression (62) for the operator Λ, we can likewise say that it has m-fold anisotropy if J does, and in that case only the highest order derivative term in the operator will have that degree of anisotropy. Of course J could have higher order anisotropy, but the truncation erases it.

The above analysis, which is independent of the size of μ, strongly suggests (but it does not prove) that the velocity function V in (63) will retain J's m-fold anisotropy, since it was predicated on our assumption of the existence of a unique traveling wave solution of (9), (61), (23), (24). The latter assumptions were established in [2] under the additional hypotheses that μ is sufficiently small and that α is either sufficiently small or sufficiently large. However, even in this case, the velocity function V is only determined implicitly by the connection problem. An interesting problem would be to calculate the asymptotic expansion of V in the small parameters μ and α (or α^{-1}), both for this connection problem and for the large relaxation regime discussed in the following sections. In this case, it should be possible to see directly how anisotropy in J is encoded into V. For example, for the slow fronts obtained in Thm. 8.2 in which the temperature field is constant, it is anticipated that if $J = h_m(r)(1 + \cos m\psi)$, then $V = V_0 + \mu^{m-2}\cos m\theta + ...$, where V_0 is the wave velocity of the second order connection problem with $\mu = 0$. (When the initial data are constant in the two phases, V_0 will be a constant.) Similarly, expansions for the wave velocity of the system described in Sec. 5 can be calculated for small or large α. These questions, together with the calculation of the evolution of the resulting generalized Hamilton-Jacobi equation, will be explored in a future publication.

7 Slower fronts due to larger relaxation time

As was mentioned before in section 4, the parameter α in (2) is related to a physical parameter in sharp interface models, namely the ratio of the coefficients of velocity and curvature in the interface condition when $\Delta < 1$. It is therefore a given quantity. We explore now (in the hypercooled scenario $\Delta > 1$) the case when α is not of the order unity, as we have assumed in previous sections, but rather large of the order $O(\epsilon^{-1})$. In line with the increase in relaxation time, we expect front velocities to be slower. We therefore change the coefficient of ϕ_t in (2) to $\alpha_1\epsilon$, and stay with the original time variable t, rather than τ as used in (17), (18).

We proceed with the asymptotics as described in section 3. The outer solution to lowest order is the same as (1), namely

$$\partial_t e^0 = \nabla^2 u^0, \tag{65}$$

together with $F(\phi^0, u^0) = 0$ and $e^0 = u^0 + w(\phi^0)$.

The lowest order inner problem becomes the following, in place of (9), (10):

$$U^0_{zz} = 0, \tag{66}$$

$$-\alpha_1 v_0 \Phi^0_z = \Phi^0_{zz} + F(\Phi^0, U^0). \tag{67}$$

The first of these equations implies that the inner variable $U^0(z, s, t)$ is constant in z, which in turn implies that the outer solution for u to lowest order is continuous across the interface. Therefore in this case, it is no longer true that the temperature has a sharp layer. The solution pair (v^0, Φ^0) of (67) depends on the value of $u = U^0$ at the interface (and on α_1 as well). The interface condition therefore takes the form

$$v = Q(u). \tag{68}$$

And, of course, the temperature u is now continuous across the interface. The final determination of the lowest order outer solution comes by proceeding to order $O(\epsilon)$ in the inner problem corresponding to (1). For simplicity, we denote by U and Φ the inner solution up to that order, i.e. that obtained by discarding terms of order ϵ^2 and higher. Then setting $E = U + w(\Phi)$, we obtain

$$U_{zz} = -\epsilon v E_z. \tag{69}$$

Integrate over the z-axis to obtain

$$[U_z]_{z=-\infty}^{z=\infty} = -\epsilon v [E]_{z=-\infty}^{z=\infty}. \tag{70}$$

The matching relations between the inner and outer expansions imply that the left side is $\epsilon[\partial_r u]_\Gamma$ and that $[E]_{z=-\infty}^{z=\infty} = [e]_\Gamma = \ell$. Hence we obtain the Stefan condition

$$[\partial_r u]_\Gamma = -\ell v. \tag{71}$$

Here the bracketed notation indicates the jump in the normal derivative as one crosses Γ.

To lowest order, therefore, this case gives rise to the following free boundary problem:

FBP3: Find a continuous temperature function $u(x,t)$ for $x \in \Omega$ and an interface $\Gamma(t)$ with normal velocity v (depending on the position on the interface) such that

$$\partial_t e = \nabla^2 u, \quad x \notin \Gamma(t),$$

$$e = u + w(\phi),$$

$$v = Q(u(x,t)), \quad x \in \Gamma(t),$$

$$[\partial_r u]_\Gamma = -\ell v.$$

The difference between this and the usual Stefan problem is that u is not required to vanish on the interface or to be a linear function of v and κ. Rather a nonlinear relation holds there between u and v. When the asymptotics is carried to next order in ϵ, the first interface condition assumes the form

$$v = Q(u(x,t)) + \epsilon\gamma\kappa, \quad x \in \Gamma(t),$$

where γ is a constant and κ is the curvature of Γ. Details will not be given.

The stability of planar fronts is examined in Sec. 9 in this model.

Finally, we incorporate anisotropy into this model in the same way as we did in Sec. 6 for the previous model. This amounts to replacing the equation (2) by (57), in which the coefficient $\alpha\epsilon^2$ on the left is changed to $\alpha_1\epsilon$. As a result, (67) becomes (61) with α_1. The meaning of $\Lambda(\boldsymbol{\nu})$, a differential operator of order m, remains the same. The inner profile problem is therefore

$$-\alpha_1 v\Phi_z = \Lambda(\boldsymbol{\nu})\Phi + F(\Phi, U), \tag{72}$$

$$\Phi(\pm\infty) = h_\pm(U), \tag{73}$$

the constant U being given.

The next section will be devoted to proving the existence of a solution of this problem. Once that is known, we obtain v as a function $Q(\boldsymbol{\nu}, u)$ of $\boldsymbol{\nu}$ as well as u. The above free boundary problem **FB3** is generalized by inserting the $\boldsymbol{\nu}$-dependence into the function Q.

8 The higher order interface equations.

In this section we establish the existence of a solution Φ of (72), (73), provided the parameter μ in Λ is sufficiently small. Here it is assumed that U is a constant, such that $h_\pm(U)$ are nondegenerate zeros of $F(\cdot, U)$. We follow the geometric perturbation analysis employed in [17] for the case $m = 3$ (see also [23]).

Suppressing the $\boldsymbol{\nu}$ dependence in (72), we have

$$\alpha_1 v \Phi' + \sum_{k=1}^{m} \mu^{2j-2} b_k \Phi^{(2k)} + F(\Phi, U) = 0. \tag{74}$$

As in the previous section, we take m to be odd. We shall see that the analysis which gave rise to (47) also provides needed spectral information.

We now write (74) as the following system, where $\Phi_1 = \Phi$:

$$\left.\begin{array}{rl} \Phi_1' & = \Phi_2 \\ \Phi_2' & = \Phi_3 \\ \mu\Phi_3' & = \Phi_4 \\ \dots & = \dots \\ \dots & = \dots \\ \mu\Phi_{2m}' & = -\left[\sum_{k=1}^{m-1} b_k \ \Phi_{2k+1} + \alpha_1 v \Phi_2 + F(\Phi_1, U)\right] / b_m \end{array}\right\} \tag{75}$$

Changing variables by putting $\zeta = \mu z$ gives

$$\left.\begin{array}{rcl} \Phi_1' & = & \mu\Phi_2 \\ \Phi_2' & = & \mu\Phi_3 \\ \Phi_3' & = & \Phi_4 \\ \dots & = & \dots \\ \dots & = & \dots \\ \Phi_{2m}' & = & -\left[\displaystyle\sum_{k=1}^{m-1} b_k \ \Phi_{2k+1} + \alpha_1 v \Phi_2 + F(\Phi_1, U)\right] / b_m \end{array}\right\} \tag{76}$$

Setting $\mu = 0$ gives a two dimensional manifold of equilibria

$$M_0 \equiv \{\Phi_4 = \Phi_5 = \cdots = \Phi_{2m} = 0, \Phi_3 = -[\alpha_1 v \Phi_2 + F(\Phi_1, U)]/b_3\}.$$

The strategy is as follows. We will show that the manifold M_0 is normally hyperbolic for (76) with $\mu = 0$. Then we invoke a theorem due to Fenichel [14] which gives the persistence of normally hyperbolic manifolds under small (in C^1) perturbations in the vector field. Thus we will have an invariant manifold M_μ for (76) with $\mu > 0$ but sufficiently small. By understanding the dynamics for (75) on M_0, we will then be able to deduce the existence of our desired solution on M_μ.

In this context, the normal hyperbolicity of M_0 with respect to (76) means that the linearization of the right hand side of (76) at a point of M_0 has precisely two eigenvalues with zero real part.

Clearly, this matrix has at least two zero eigenvalues, corresponding to the dimension of M_0, since M_0 consists of stationary solutions. We claim that all other eigenvalues have nonzero real part, i.e., we claim

Lemma 8.1. The manifold of equilibria, M_0, is normally hyperbolic.

Proof. With $\mu = 0$ the linearization of (76) at a point on M_0 gives an equation of the form $\mathbf{w}' = A\mathbf{w}$ where A is a $2m \times 2m$ matrix with the first two rows being zero. Therefore we need to show that the eigenvalues of the lower right hand $(2m-2) \times (2m-2)$ block have nonzero real part. This block has the form

$$\begin{matrix} 0 & 1 & 0 & 0 & \cdots & \cdot & 0 \\ 0 & 0 & 1 & 0 & \cdots & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdots & 0 & 1 \\ -b_1/b_m & 0 & -b_2/b_m & 0 & \cdots & -b_{m-1}/b_m & 0 \end{matrix}$$

The characteristic polynomial for this matrix evaluated at $i\lambda$, when multiplied by b_m, is

$$\chi(\lambda) = \sum_{k=1}^{m} (-1)^{k-1} \lambda^{2k-2} b_k, \tag{77}$$

as can be determined using column operations to diagonalize the determinant.

From (25) and (77), we have

$$-\lambda^2 \chi(\lambda) = 2 \sum_{k=1}^{m} (-1)^k \int J(\mathbf{x}) \frac{(\lambda \mathbf{x} \cdot \boldsymbol{\nu})^{2k}}{(2k)!} \, d\mathbf{x}.$$

For $\lambda \neq 0$, this is negative when m is odd as shown in section 6 when establishing (47). Since $\chi(0) \neq 0$, the lemma is proved.

Remark. Since χ has real coefficients and has no real zeros, it has $m-1$ roots with positive imaginary part and $m-1$ with negative imaginary parts. Equivalently, the matrix above has exactly $m-1$ eigenvalues with positive real part and $m-1$ with negative real part.

Now we use Fenichel's theorem to deduce the existence of a two dimensional invariant manifold M_μ for (76), provided that $\mu > 0$ is sufficiently small. In fact to do this we should first modify (76) outside a bounded open set containing that part of M_0 which is of interest, mentioned below. This is because Fenichel's theorem applies to normally hyperbolic manifolds which are compact.

With $\mu = 0$, the dynamics of (75) on M_0 is given by

$$\begin{aligned} \Phi_1' &= \Phi_2 \\ \Phi_2' &= -[\alpha_1 v\Phi_2 + F(\Phi_1, U)]/b_1, \end{aligned}$$

and so for $\mu \neq 0$ the dynamics of (75), which is equivalent to (76), on M_μ is given by

$$\left.\begin{aligned} \Phi_1' &= \Phi_2 \\ \Phi_2' &= -[\alpha_1 v\Phi_2 + F(\Phi_1, U)]/b_1 + O(\mu) \end{aligned}\right\} \tag{78}$$

and $\Phi_3, ..., \Phi_{2m}$ are just given by smooth functions of Φ_1 and Φ_2. Note that $(h_\pm(U), 0, 0, ..., 0)$ still lie on M_μ, since they are rest points of (76) for all values of μ. Note also that when $\mu = 0$, there is a unique value $v = v_0$ for which (78) has a solution (Φ_1, Φ_2) with $(\Phi_1, \Phi_2)(\pm\infty) = (h_\pm(U), 0)$. A large ball in M_0 containing this connecting orbit is the region of interest mentioned above. Under usual circumstances, we could not expect this connection to persist for $\mu > 0$. However, we have v at our disposal. We append the equation

$$v' = 0$$

to (75) and (78), finding that $M_\mu \times R$ is then a three dimensional invariant manifold for the $(2m+1)$-dimensional system, and that two dimensional slices $M_\mu \times \{v\}$ are themselves invariant. If we examine (78) with $\mu = 0$, we see that as v passes through the critical value v_0, the unstable manifold of $(h_-(U), 0)$ crosses the stable manifold of $(h_+(U), 0)$ transversely.

When viewed in the three dimensional manifold $M_0 \times R$, the line of stationary solutions $(h_-(U), 0) \times R$ has a two dimensional unstable manifold which has a transverse intersection with the two dimensional stable manifold of the line of stationary solutions $(h_+(U), 0) \times R$ at the level $v = v_0$. These manifolds perturb smoothly for $\mu > 0$ and sufficiently small and so transversality at $\mu = 0$ ensures a transverse intersection at some value $v = v_\mu$ within

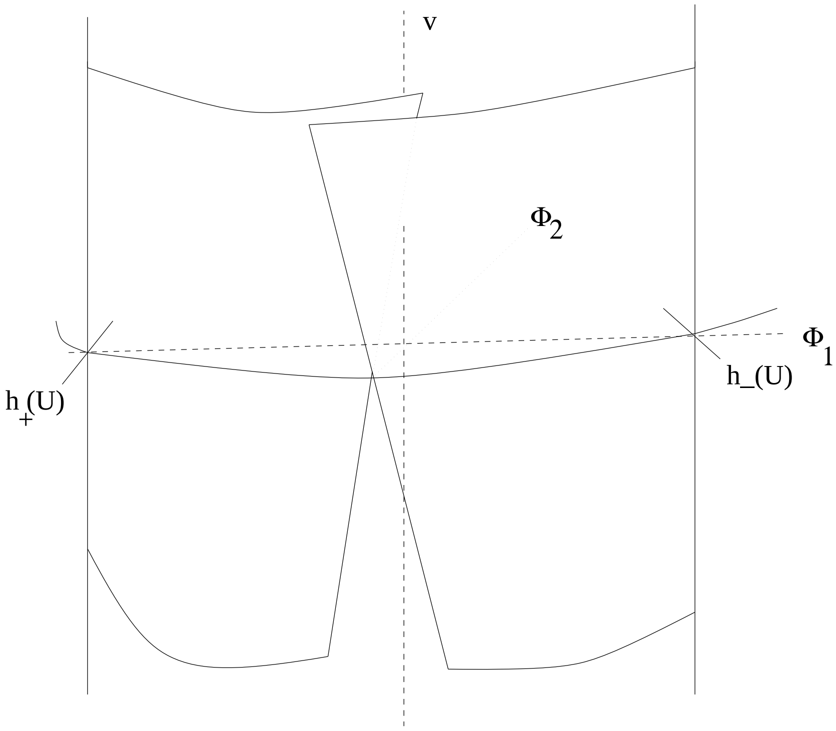

Figure 4: CAPTION

$M_\mu \times R$ for μ sufficiently small. The invariance of the v_μ slice then gives the connection we seek. Note that transversality ensures that the connection and speed are locally unique. We have therefore proved

Theorem 8.2. Let U be such that $F(\cdot, U)$ is bistable with extreme zeros $h_-(U) < h_+(U)$ nondegenerate. Then for $\mu > 0$ and sufficiently small, there exists a locally unique solution ϕ to (72), (73).

We finally remark on the contrast between this technique and that used to prove the existence of the analogous solution in the $O(\epsilon^2)$ relaxation case, as given in the companion paper [2]. In the present case, the basic existence of the unperturbed heteroclinic orbit is guaranteed by virtue of its satisfying a second-order ODE, which is well understood analytically. In contrast, the argument in [2] is topological in nature. One might naturally suspect that the analytic argument that is available in the slow relaxation case offers more information and this is indeed true. If one expands to higher order in the small parameter ϵ, equations for the higher order terms can be calculated in the usual way. Their validity, however, depends upon the satisfaction of solvability conditions. The derivation of these solvability conditions involves the assumption that the kernel of the adjoint of the linearization of (74) at the solution ϕ, guaranteed to exist by Theorem 8.2, is one-dimensional. This is closely related to the stability analysis of this solution and can be proved by the same method as used in this section. Indeed, it closely follows the stability proof given in [17].

9 Stability analysis of FBP3

We include the Gibbs-Thompson correction and write the free boundary problem in the (x, y) plane as follows, where the interface is taken to be $x = X(y, t)$, with solid to the left and liquid to the right. The function $v(y, t) = X_t/\sqrt{1 + (X_y)^2}$ is the normal velocity of the interface and κ is its curvature.

$$\begin{aligned} u_t &= u_{xx} + u_{yy}, \quad x \neq X(y,t), && (79) \\ v(y,t) &= Q(u(X(y,t),y,t)) + \epsilon\gamma\kappa(y,t), && (80) \\ [\partial_n u] &= -\ell v(y,t), \quad x = X(y,t). && (81) \end{aligned}$$

Here bracketing on the left of (81) denotes the jump at the interface, and γ is a constant which will not be specified.

We want to test the stability of the traveling wave solutions, which we parameterize by the value $-\alpha$ of the function u at the interface. Thus $-\alpha$ is the solid temperature. They represent planar solidification fronts, and are given by $u(x, y, t) = u_0(x - v_0 t) = u_0(z)$, $z = x - v_0 t$, where (setting $Q(-\alpha) = q$)

$$u_0(z) = \begin{cases} -\alpha, & z < 0, \\ -\alpha - \ell + \ell e^{-qz}, & z > 0 \end{cases}, \quad v_0 = q. \tag{82}$$

We subject this to a small perturbation as follows, where $|\delta| \ll 1$:
Set

$$z = x - qt - \delta\psi(y, t),$$

$$u = u(z, y, t) = u_0(z) + \delta\hat{u}(z, y, t),$$

$$\hat{u}(z,y,t) = \begin{cases} u_-(z,y,t), & z<0, \\ u_+(z,y,t), & z>0. \end{cases}$$

Thus $X(y,t) = qt + \delta\psi(y,t)$.

We disregard all but first order terms in the small parameter δ. Thus

$$\partial_n u = \partial_x u - X_y \partial_y u = \partial_z u - \delta \Psi_y(y,t)\partial_y u, \tag{83}$$

$$v(y,t) = q + \delta\psi_t(y,t), \quad \kappa(y,t) = \delta\psi_{yy}(y,t). \tag{84}$$

Since we look for functions $\hat{u}$ which are smooth with respect to y, we have $[\partial_y \hat{u}] = 0$, so that from (83),

$$[\partial_n u] = -\ell q + \delta\left[\partial_z \hat{u}\right].$$

In all, we have the following system, based on (79) - (81):

$$\delta\hat{u}_t + (-q-\delta\psi_t)(u_0'(z)+\delta\hat{u}_z) = u_0''(z) + \delta\hat{u}_{zz} + \delta\hat{u}_{yy} - \delta\psi_{yy}u_0'(z), \quad z\neq 0, \tag{85}$$

$$q + \delta\psi_t = Q(-\alpha + \delta\hat{u}(0,y,t)) + \epsilon\gamma\delta\psi_{yy}, \tag{86}$$

$$-\ell q + \delta\left[\partial_z\hat{u}\right] = -\ell q - \delta\ell\psi_t, \tag{87}$$

hence setting $\beta = -Q'(-\alpha) > 0$, we have

$$\hat{u}_t - \psi_t u_0'(z) - q\hat{u}_z = \hat{u}_{zz} - \psi_{yy}u_0'(z) + \hat{u}_{yy}, \quad z \neq 0, \tag{88}$$

$$\psi_t = -\beta\hat{u}(0,y,t) + \epsilon\gamma\psi_{yy}, \tag{89}$$

$$[\partial_z \hat{u}] = -\ell\psi_t. \tag{90}$$

We now set $\hat{u}(z,y,t) = u_-(z,y,t) \ \ (u_+), \ \ z<0 \ \ (z>0)$. Thus

$$\partial_t u_-(z,y,t) - q\partial_z u_- = \partial_z^2 u_- + \partial_y^2 u_-, \quad z<0, \tag{91}$$

$$\partial_t u_+(z,y,t) + \ell q e^{-qz}\psi_t - q\partial_z u_+ = \partial_z^2 u_+ + \partial_y^2 u_+ + \psi_{yy}\ell q e^{-qz}, \quad z>0, \tag{92}$$

$$\psi_t(y,t) - \epsilon\gamma\psi_{yy} = -\beta u_-(0,y,t) = -\beta u_+(0,y,t), \tag{93}$$

$$\partial_z u_+(0,y,t) - \partial_z u_-(0,y,t) = -\ell\psi_t(y,t). \tag{94}$$

We now set $\psi(y,t) = e^{\sigma t + iky}, \ \ u_\pm(z,y,t) = U_\pm(z)e^{\sigma t+iky}$. Thus

$$U_-'' + qU_-' - (k^2+\sigma)U_- = 0, \quad z<0 \tag{95}$$

$$U_+'' + qU_+' - (k^2+\sigma)U_+ = \ell q(\sigma + k^2)e^{-qz}, \quad z>0 \tag{96}$$

$$U_-(0) = U_+(0) = -(\sigma + \epsilon\gamma k^2)/\beta, \tag{97}$$

$$U'_+(0) - U'_-(0) = -\ell\sigma. \tag{98}$$

To solve this system, let $r = \sqrt{q^2 + 4(\sigma + k^2)}$, $\mu = \frac{1}{2}(r - q)$, $\nu = \frac{1}{2}(-r - q)$. We choose the branch of the square root so that $\mathrm{Re}[r] > 0$ when $\mathrm{Re}[\sigma] > 0$. We shall require that

$$\mathrm{Re}[\mu] > 0. \tag{99}$$

Then from (95) - (97) we have

$$U_-(z) = -\frac{\sigma + \epsilon\gamma k^2}{\beta} e^{\mu z}, \quad z < 0, \tag{100}$$

$$U_+(z) = -\ell q e^{-qz} + \left(\ell q - \frac{\sigma + \epsilon\gamma k^2}{\beta}\right) e^{\nu z}, \quad z > 0. \tag{101}$$

We now apply (98) to this to obtain the following equation relating σ, k, and the other parameters.

$$\sqrt{q^2 + 4(\sigma + k^2)} = \frac{\ell(2(\sigma + \epsilon\gamma k^2) + q^2)}{q\ell - (2(\sigma + \epsilon\gamma k^2)/\beta)}. \tag{102}$$

We simplify this expression by setting

$$\bar{\sigma} = \sigma/q^2, \quad \bar{k} = k/q, \quad p = q/\beta\ell \tag{103}$$

to obtain

$$\sqrt{1 + 4(\bar{\sigma} + \bar{k}^2)} = \frac{1}{p}\left[-1 + \frac{1 + p}{1 - 2p(\bar{\sigma} + \epsilon\gamma\bar{k}^2})\right]. \tag{104}$$

Denote the left and right sides of (104) by $L(\bar{\sigma})$ and $R(\bar{\sigma})$. It can be checked that a sufficient condition for $\mathrm{Re}[R(\bar{\sigma})] < 0$ is that

$$\mathrm{Re}[\bar{\sigma}] > \frac{1}{2p} - \epsilon\gamma\bar{k}^2. \tag{105}$$

On the other hand $\mathrm{Re}[L(\bar{\sigma})] > 0$ when $\mathrm{Re}[\bar{\sigma}] > 0$, so that no root of (104) satisfies (105). This shows that

(i) the growth rate $\mathrm{Re}[\bar{\sigma}(\bar{k})]$ is bounded by $1/2p$ independently of k, and

(ii) the planar front is stable to all perturbations with wave number $\bar{k} > O(2p\epsilon\gamma)^{-1/2}$.

In fact, a more careful analysis will show that the front is stable to all wave numbers if $\epsilon\gamma$ is large enough, depending only on p.

The first of these two conclusions holds in fact even if $\gamma = 0$. Moreover, even in that case it is very likely that the initial value problem for this FBP is well posed. This is clear from the fact that the Fourier transform $(\tilde{u}(z,k,t),\ \tilde{\psi}(k,t))$ in y of the solution of the linearized problem (91) - (94) decaying as $|z|\to\infty$ is given by

$$\tilde{u}(z,k,t) = \tilde{u}(z,k,0)e^{\sigma(k)t}, \quad \tilde{\psi}(k,t) = \tilde{\psi}(k,0)e^{\sigma(k)t}$$

with $\mathrm{Re}[\sigma(k)]$ bounded. Thus some or all modes grow exponentially, but not at a rate which increases with k, as it would were (80) replaced by $u(X(y,t),y,t) = 0$. This is an ill-posed problem.

10 Discussion

A theory for hypercooled solidification is given, based on the phase field model. Mathematically, this leads to a rather difficult system of layer equations, treated in the companion paper [2]. The free boundary problem obtained through formal asymptotics also leads to conclusions suggesting physical properties of hypercooled interfaces. It is predicted, consistently with other theories, that the motion of the phase boundary is autonomous and that the temperature undergoes a quick transition there. It also predicts that the linear relation among the temperature, velocity, and curvature at the interface breaks down under hypercooling, and is replaced by another nonlinear relation between the velocity and limiting temperatures from the solid and liquid sides.

Anisotropic and nonlocal variations on the phase field model are also considered, and their effects on the free boundary problem examined. These variations are relevant not only in the hypercooled scenario, but in other solidification contexts as well.

Finally, when the relaxation time of the order parameter is larger by an ϵ-order of magnitude, we recover coupling with the temperature field away from the phase boundary, but the interface condition (68) and its generalizations remain nontraditional.

We have neglected the dependence of the relaxation time on temperature, an effect which may have important consequences in the high undercooling region under consideration. It may, in fact, result in a continuous trend, as the degree of undercooling is increased, from the regime where the model in Sec. 3 is appropriate toward that where the other model is.

Appendix A. Notational comparison with the companion paper

There are some differences in notation between [2] and the present paper. In that paper, the planar solidification fronts move to the left with velocity $c < 0$. In this paper, they move to the right with velocity $v > 0$. This difference implies the correspondance given below between the functions $U(\xi)$ in the two papers. Other differences are as follows:

Companion paper	This paper	Meaning
$\lambda W(\phi)$	$w(\phi)$	Potential energy part of internal energy
$\phi = h_{r,\ell}(u)$	$\phi = h_{\pm}(u)$	Right and left branches of $F(\phi, u) = 0$
u_-	u_ℓ	Liquid temperature
u_+	u_s	Solid temperature
$U(\xi)$	$U(-\xi)$	Temperature profile of traveling wave

Relations analogous to the last three hold also for ϕ and Φ. The parameter λ in the potential energy arises in a physical way (see [15]) from the normalization of the function F and the fact that F and w are related to one another. Conditions on λ are imposed for some results in [2]; but the parameter plays no role in the present paper.

Appendix B. Surface energy

Our purpose here is to derive (29) and (31). First, we give a direct calculation of the surface tension, i.e. the surface density of free energy in the layer. The usual inner analysis for a layer gives an order parameter profile $\psi(z)$ in the layer, where $z = r/a\epsilon$ is the stretched dimensionless spatial coordinate through (normal to) the layer. We use the fact that this profile is such that the bulk free energy and the free energy due to the gradient terms in the order parameter stemming from those in (3) are equal, to lowest order. Therefore we express the surface energy as twice that due to the bulk term:

$$\bar{\gamma} = 2a \int_{-\infty}^{\infty} \bar{f}(\psi(z)) d(\epsilon z).$$

In using this integral, we note that $\epsilon a z = r$, which is the physical space coordinate across the layer. Using our dimensionless free energy density

$\tilde{f} = \bar{f}/(\beta\bar{\ell}_0)$, we obtain

$$\bar{\gamma} = 2a\beta\bar{\ell}_0\epsilon \int_{-\infty}^{\infty} \tilde{f}(\psi(z))dz. \tag{106}$$

Here we recall that the scaled free energy density $\tilde{f}$ has been normalized by β. Neither it nor ψ depend on any of the parameters, so we denote the integral in (106) by p, a dimensionless $O(1)$ quantity, depending only on $\tilde{f}$. Thus

$$\bar{\gamma} = 2a\beta\bar{\ell}_0\epsilon p, \tag{107}$$

which is (29).

Next, we examine the Gibbs-Thompson relation implied by the phase field model for small undercoolings. The usual asymptotic layer analysis of (1) and (2) yields an integrability condition which can be written

$$u|_\Gamma = \epsilon\tilde{\sigma}(\alpha v + \kappa), \tag{108}$$

where

$$\tilde{\sigma} = \frac{\int_{-\infty}^{\infty}(\psi'(x))^2 dz}{-\int_{-\infty}^{\infty} F_u(\psi(z), 0)\psi'(z)dz}. \tag{109}$$

The numerator in (109) is twice the contribution of the gradient terms in the free energy functional, which is $-T$ times the entropy functional (3). By the above observation that the bulk and gradient terms contribute equally when applied to the layer profile, we obtain that the numerator is equal to $2p$.

We now evaluate the denominator. From thermodynamical considerations,

$$\bar{e} = cT + \bar{w}(\phi) = \frac{\partial(\bar{f}/T)}{\partial(1/T)},$$

hence

$$\bar{w}'(\phi) = -T^2 \frac{\partial}{\partial T}\left(\frac{\partial \bar{f}/\partial\phi}{T}\right).$$

By definition, setting $\phi_\pm = h_\pm(0)$,

$$\bar{\ell}_0 = \int_{\phi_-}^{\phi_+} \bar{w}'(\phi)d\phi = -T_0^2\frac{\partial}{\partial T}[\bar{f}(\phi, T)/T]_{\phi_-}^{\phi_+}.$$

Since $\bar{f}(\phi_+, 0) = \bar{f}(\phi_-, 0)$ (definition of critical temperature), we have

$$\bar{\ell}_0 = -T_0\frac{\partial}{\partial T}\left\{\bar{f}(h_+(T), T) - \bar{f}(h_-(T), T)\right\}|_{T=T_0}.$$

Thus setting $T_0\frac{\partial}{\partial T} = \frac{1}{\nu}\frac{\partial}{\partial u}$, $\bar{f} = \beta\bar{\ell}_0\tilde{f}$, we get

$$\frac{\nu}{\beta} = -\frac{\partial}{\partial u}\left\{\tilde{f}(h_+(u), u) - \tilde{f}(h_-(u), u)\right\}_{u=0}.$$

We now use the fact that $\tilde{f}(h_\pm(0), 0) = 0 = \int_{h_-(0)}^{h_+(0)} F(\phi, 0)d\phi$ to obtain

$$\begin{aligned} -\frac{\nu}{\beta} &= \frac{\partial}{\partial u}\int_{h_-(u)}^{h_+(u)} \tilde{f}d\phi|_{u=0} \\ &= \int_{h_-(u)}^{h_+(u)} \frac{\partial\tilde{f}}{\partial u}d\phi|_{u=0} \\ &= \int_{h_-(u)}^{h_+(u)} F_u(\phi, 0)d\phi \\ &= \int_{-\infty}^{\infty} F_u(\psi(z), 0)\psi'(z)dz. \end{aligned}$$

Thus from (108) we have

$$u|_\Gamma = \frac{2\epsilon\beta p}{\nu}(\alpha v + \kappa),$$

which is (31).

Appendix C. A variant of the phase field model

In many uses of the phase field theory, e.g. in [9, 12, 26, 34, 35] an extra parameter a (different from the macrolength "a" used in Sec. 4) is introduced by supposing that the function F has the form

$$F(\phi, u) = \frac{1}{a}G'(\phi) + q(u)r(\phi), \qquad (110)$$

where $G(\phi)$ is a function with two equally deep wells and $g(0) = 0$. From the remark following (28), it is clear that the corresponding dimensional form of G would be $\bar{s}_0$. It is assumed that a is small; in that case, $1/a$ is proportional to the height of the barrier between the two wells, and is also some measure of the theoretical maximum possible undercooling sustainable by the liquid. In fact, for our purposes we may identify a with β^{-1}. The practice is then essentially to define a new small parameter $\hat{\epsilon} = \epsilon^2$, and to introduce a relation between a and ϵ by setting $a = \epsilon^2$ as well. This way, one arrives at the following alternate version of (2) (with $\alpha = \text{const}$):

$$\alpha\hat{\epsilon}^2\phi_t = \hat{\epsilon}^2\nabla^2\phi + G'(\phi) + \hat{\epsilon}q(u)r(\phi). \qquad (111)$$

At this point, it is assumed that $\hat{\epsilon}$ is the small parameter, which of course implies by the above that a is also small of the order $a = O(\hat{\epsilon})$. The effects of this are that (1) the interfacial thickness will be $O(\hat{\epsilon})$, (2) the surface tension will be positive and independent of $\hat{\epsilon}$ as the latter parameter tends to zero, and (3) the phase equation (111) is only weakly coupled to the temperature variable u.

The reason for introducing this variant is in order to have a model for which a positive surface tension is retained in the sharp interface limit. On the other hand, as we have seen in App. B, the original parameter ϵ is a natural measure of the surface tension and can therefore be regarded as a given physical parameter. It can be calculated in each specific case if the surface tension and other properties of the material are known. Typical figures resulting from such a calculation provide a value $\epsilon \approx 10^{-7}$ [15], which is an undisputably small number. In view of this, the advantages of coupling the parameter a with ϵ, other than computational, are unclear. Although in the original formulation surface tension will indeed approach zero if ϵ does, this is not seen as a disadvantage. In any case, we do not need to let ϵ approach zero: it remains small but positive and the asymptotics is very well founded. Finally, it should be pointed out that when a is very small, other physical parameters such as the maximum undercooling become unreasonably large.

In this alternate formulation, if $q(u)$ is linear the phase field equations lead (as a formal approximation for small $\hat{\epsilon}$) to free boundary problems in which the Gibbs-Thompson and kinetic undercooling terms appear as $O(1)$ terms. Such approximating free boundary problems, however, can be obtained within the previous formulation (1), (2) under the assumption that the temperature T is close to the melting temperature, i.e. that u is small. For example in [11] this was done for the Mullins-Sekerka problem. This is a realistic setting in which one might expect the Mullins-Sekerka dynamics to operate.

The problem of hypercooled solidification within the setting of this variant of the phase field equation has been studied theoretically only in [12], where the existence of a traveling wave was proved. Because of the weak coupling of (111) with u, it was possible to use a perturbative argument, in contrast to the nonperturbative approach required for the analogous problem (9) - (25) in our case.

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