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Rapid growth and critical behaviour in phase field models of solidification

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Rapid solidification fronts are studied using a phase field model. Unlike slow moving solutions which approximate the Mullins–Sekerka free boundary problem, different limiting behaviour is obtained for rapidly moving fronts. A time-dependent analysis is carried out for various cases and the leading order behaviour of solidification front solutions is derived to be one of several travelling wave problems. An analysis of these problems is conducted, leading to expressions for front speeds in certain limits. The dynamics leading to these travelling wave solutions is derived, and conclusions about stability are drawn. Finally, a discussion is made of the relationship to other solidification models.

1 Introduction

Rapid solidification processes have become important in many modern manufacturing applications [17, 20, 19]. Modeling of these events is complicated by the fact that at high velocities, solidification fronts may be far from thermodynamic equilibrium. This leads to growth modes different from those of slow solidification processes, and results in the formation of different microstructures.

Many studies of solidification have been done in the context of free boundary problems, which assume the solid-liquid interface is infinitesimally narrow (see [21] for a review). More recently, phase field models have become a popular way of describing the dynamics of solidification [13, 22]. They introduce a continuous order parameter ϕ which takes on (approximately) the values

$$\phi = \begin{cases} 1 & \text{solid} \\ -1 & \text{liquid} \end{cases}$$

corresponding to the two material phases. The phase interface is described implicitly by the zero level set

$$\Gamma = \{\phi(x) | \phi = 0\}.$$

An additional field u represents temperature and is dynamically coupled to ϕ.

Phase field models have been derived from thermodynamic considerations and incorporate many observed features of solidification processes including undercooling, surface tension and kinetic effects. Several authors [16, 26, 32] have suggested a phase field

formulation based upon a free energy functional of the form

$$\mathscr{F}(\phi, u) = \int aF(\phi, u) + \frac{b}{2}|\nabla\phi|^2. \tag{1.1}$$

The first term is the classical free energy density, where a is the dimensional magnitude of this energy, and $F(\phi, u)$ is a nondimensional, $O(1)$ quantity. The second term accounts for energy due to gradients of the order parameter; the constant b sets the scale of this term.

We will choose a scale for u so that the coexistence temperature of the two phases is zero. Letting c_p, L be the heat capacity and latent heat respectively, we may nondimensionalize u by setting

$$u' = c_p u/L.$$

We will drop the prime notation from here on.

The internal energy density e may also be scaled by latent heat, and so in nondimensional form is related to the temperature by

$$e = u - \frac{1}{2}p(\phi),$$

where p is some increasing function for which $p(\pm 1) = \pm 1$ and $p'(\pm 1) = 0$. It will not be essential to specify the exact forms of the constitutive functions described here. It will be convenient at times to regard F as a function of e instead; we will write either $F(\phi, e)$ or $F(\phi, u)$, where the context will remove any ambiguity.

There are two fundamental requirements that F must satisfy. The first is that $F(\phi, u)$ has two wells at $\phi = \pm 1$ for each fixed u, ensuring that at constant temperature, the liquid and solid states are stable to infinitesimal perturbations. The second requirement is that for fixed ϕ, $F(\phi, u)$ is convex in u, which is necessary for well-posedness of the diffusion equation. We will concentrate on the simplest model which satisfies these two requirements, namely

$$F(\phi, u) = g(\phi) + \frac{\lambda}{2}u^2,$$

where g is a double well potential with equal well depths at ± 1. The positive coupling parameter λ is the relative magnitude of bulk free energy in comparison to surface energy.

The free energy may be restated in terms of the more familiar quantities of surface energy and interface width. The equilibrium one dimensional interface profile will solve the Euler–Lagrange equation for (1.1) with $u \equiv 0$:

$$b\phi_{xx} - ag'(\phi) = 0.$$

This may be integrated to give

$$\phi_x = \sqrt{\frac{2ag(\phi)}{b}}$$

which motivates the choice $\epsilon = \sqrt{\frac{b}{a}}$ as the interface width. The surface energy density σ is the free energy if this interface, which may be computed to give

$$\sigma = \sqrt{ab}\int_{-1}^{1} \sqrt{2g(\phi)}\, d\phi.$$

We suppose that the constant a was defined so that the integral in this expression is unity,

so that $\sigma = \sqrt{ab}$. In terms of these new quantities, the free energy is

$$\mathscr{F}(\phi, u) = \sigma \int \frac{1}{\epsilon} F(\phi, u) + \frac{\epsilon}{2} |\nabla \phi|^2 \, dx. \tag{1.2}$$

The dynamics resulting from (1.2) are generated by allowing the free energy to relax, while conserving internal energy [26, 32]. The internal energy satisfies the conservation law

$$e_t + \nabla \cdot j = 0$$

where j is the heat flux. The time derivative of (1.2) is

$$\frac{d\mathscr{F}}{dt} = \frac{\sigma}{\epsilon} \int \left[-\epsilon^2 \Delta \phi + g'(\phi) + \frac{\lambda}{2} \left(e + \frac{1}{2} p(\phi) \right) p'(\phi) \right] \phi_t + \left[e + \frac{1}{2} p(\phi) \right] e_t \, dx. \tag{1.3}$$

To ensure that this quantity is negative, we choose

$$\phi_t = D_\phi \left[-\epsilon^2 \Delta \phi + g'(\phi) + \frac{\lambda}{2} \left(e + \frac{1}{2} p(\phi) \right) p'(\phi) \right],$$
$$j = -D_T \nabla u,$$

where D_ϕ, D_T are phase and thermal mobilities, respectively. The result is the pair of equations

$$\tau \frac{\partial \phi}{\partial t} = \epsilon^2 \Delta \phi - g'(\phi) - \frac{\lambda}{2} u p'(\phi) \equiv \epsilon^2 \Delta \phi + f(\phi, u) \tag{1.4}$$

$$\frac{\partial e}{\partial t} = D_T \Delta u \tag{1.5}$$

where $\tau = D_\phi^{-1}$ is a relaxation timescale and D_T is thermal diffusion.

It is important to point out that phase field models for isothermal alloy growth have the same mathematical structure as the one we describe. The analogy between physical quantities is

$$\text{temperature} \leftrightarrow \text{chemical potential}$$
$$\text{internal energy} \leftrightarrow \text{solute concentration}$$

A discussion of this analogy is given in Lowen *et al.* [24]. We shall occasionally refer to this physical problem as well.

The most studied limit of the phase field model for pure solidification is the Mullins–Sekerka free boundary problem (MS):

$$u_t = D_T \Delta u \quad x \notin \Gamma \tag{1.6}$$

$$V_n = D_T (\nabla u_s - \nabla u_l) \cdot \mathbf{n} \quad \text{on } \Gamma \tag{1.7}$$

$$u = -d_0 \kappa - \beta V_n \quad \text{on } \Gamma. \tag{1.8}$$

Here V_n is the normal velocity of the interface Γ, κ is the geometric curvature of the interface and β is a 'kinetic' undercooling parameter. The limit of (1.4)–(1.5) as $\epsilon \to 0, \tau \sim \epsilon^2$ was investigated first by Caginalp & Fife [8], and later rigorously by Soner [29]. The leading order behaviour was shown to be the above interface motion, and relationships between diffuse and sharp interface parameters were given. Karma & Rappel [18] considered a different limit, one where $\tau \sim \epsilon^3$ and $\lambda \sim \epsilon$. In this limit they showed

that the kinetic coefficient β could be determined arbitrarily. Other limits of the phase field models have been identified by Caginalp [6] and proved by Caginalp & Chen [7].

A crucial aspect of the asymptotics described above was a separation of scales between the interface width ϵ and the diffusion length D_T/V, where V is a characteristic velocity of the interface. This assumes a timescale that is $\mathcal{O}(1)$, which is not necessarily valid for large undercoolings. In this case, the interface temperature may not be well defined, so a different free boundary problem must be sought.

Recently, Bates *et al.* [4, 5] developed a phase field model describing hypercooling, when the far field temperature $-\Delta$ (the negative undercooling) is less than -1. In their paper, they consider dynamics on a timescale of order $\mathcal{O}(\epsilon)$, and the interface velocity is determined solely by the travelling wave problem associated with equations (1.4)–(1.5). A number of studies of this travelling wave problem have been conducted. Caginalp & Nishiura [9] prove existence when the coupling between the two variables is weak. In a more recent study, Bates *et al.* [4] established the existence of waves under the hypothesis of hypercooling, when $\Delta > 1$. Schofield & Oxtoby [28], as well as Löwen *et al.* [23, 24], studied the non-hypercooled situation; they obtain solutions for very specific forms of equations (1.4)–(1.5).

This paper extends the results described above in the following ways:

- A time-dependent analysis of the full equations is carried out, which examines a number of different scaling regimes for both parameters and time, and deduces the resulting leading order behaviour.
- We show by thermodynamic considerations that hypercooling is not necessary to obtain steadily propagating (travelling wave) fronts. In particular, steady solidification fronts may exist when Δ is larger than some critical value Δ^* which depends on the parameters of the model.
- As shown elsewhere [28, 23, 24] for very specific models, the critical value Δ^* is less than 1 when the ratio λ/D is larger than some constant, but is equal to one otherwise. In our study, an asymptotic treatment shows that this is in general the case.
- Quantitative information about front speeds is derived in regimes where the diffusion length is both small and large.
- The approach to travelling wave solutions of the inner problems is systematically analysed by considering motion on very fast time scales. In particular, the one-dimensional stability properties of some solutions are derived.

The layout of the paper is as follows. A formal analysis of the time dependent equations is performed in § 2, leading to several different travelling wave problems. The resulting travelling wave problems are analysed in more detail in § 3–§ 4. In § 5, the transient dynamics of the model is explored, showing how travelling wave solutions are approached in the full, time dependent model. A discussion of the relationship between the phase field model and other solidification models is presented in § 6.

2 Sharp interface limits

We will analyse the time dependent behaviour of the model in the limit of small interface width ϵ. Rather than further non-dimensionalizing the evolution equations, we leave them as they are so that the results of the analysis are not obscured.

In the spirit of Caginalp [6], we shall consider various scales of model parameters, and determine the resulting leading order behaviour. For each combination of parameters, we select a one or more timescales on which to look for solutions. Of course, some combinations of parameters and timescales lead either to scalings which have been encountered previously, or to inconsistencies in the asymptotics. We shall therefore mostly focus only on situations which give new and sensible results.

The following combinations will be considered:

$$\tau \sim \epsilon, \epsilon^2, \epsilon^3$$
$$D_T \sim 1, \epsilon.$$

The scale $D_T = \mathcal{O}(\epsilon)$ is particularly important in the case of alloy growth, since impurity mobility is usually small near the phase interface [33]. The case $\lambda = O(\epsilon)$ or smaller, while of interest in the slow time scale asymptotics, leads to nothing new for rapid dynamics, so we shall always have $\lambda = O(1)$.

A matched asymptotic approach is used (e.g. see Caginalp & Fife [8]), and we work in two space dimensions. For the inner solution (ϕ, u) corresponding to the interfacial layer, an orthogonal curvilinear coordinate system (r, s) is used, where r is the distance from the interface $\Gamma = \{x | \phi(x) = 0\}$ and s is the distance along the interface. We will assume that $r < 0$ corresponds to $\phi > 0$, i.e. solid. The normal coordinate r is rescaled using $z = \epsilon^{-1} r$ reflecting the fact that ϕ varies rapidly near the interface. In this new coordinate system, the time derivative becomes

$$\frac{\partial}{\partial t} + \epsilon^{-1} \frac{dr}{dt} \frac{\partial}{\partial z} + \frac{ds}{dt} \frac{\partial}{\partial s},$$

noting that that dr/dt is to leading order just the normal interface velocity V_n. We shall also rescale time, in such a way as to make V_n an $\mathcal{O}(1)$ quantity. The Laplacian is replaced by

$$\epsilon^{-2} \frac{\partial^2}{\partial z^2} + \epsilon^{-1} \Delta r \frac{\partial}{\partial z} + |\nabla s|^2 \frac{\partial^2}{\partial s^2} + \Delta s \frac{\partial}{\partial s}.$$

It will be assumed throughout that the interface is smooth, and not highly curved, so that $\Delta r, |\nabla s|^2$ and Δs are all $\mathcal{O}(1)$. All quantities are then expanded in an asymptotic series in powers of ϵ, and solutions to each order are sought.

To leading order, the outer solution for ϕ, which we will denote by the capitalized version Φ, satisfies

$$\Phi = +1 \text{ or } \Phi = -1 \tag{2.1}$$

in each outer region. In what follows, we will consider either $D_T = \mathcal{O}(\epsilon)$ or a timescale $t = \mathcal{O}(\epsilon)$, with one noted exception (case V below). Therefore, the leading order temperature in the outer expansion will be constant, determined by the initial data. Notice that this is in sharp contrast to the Mullins-Sekerka limit, where the evolving temperature field away from the interface will affect the interface's dynamics.

The outer solutions are then matched to the inner ones (e.g. see Caginalp & Fife [8])

by the leading order conditions

$$\Phi(0^+) = \lim_{z\to\infty} \phi(z), \quad \Phi(0^-) = \lim_{z\to-\infty} \phi(z)$$
$$U(0^+) = \lim_{z\to\infty} u(z), \quad U(0^-) = \lim_{z\to-\infty} u(z).$$

Although we have been careful about writing the details of the coordinate transformations up to this point, the analysis which follows will only consider the model's leading order behaviour, which generally will not involve curvature effects at leading order. Again, this is different from the Mullins–Sekerka limit, where curvature effects are important, and crucial to obtain a well-posed free boundary problem [25].

Case I: $\tau = \mathcal{O}(\epsilon^2)$, $D_T = \mathcal{O}(1)$

Let $\tau = \alpha\epsilon^2$, where α is assumed to be $\mathcal{O}(1)$. With a timescale $t = \mathcal{O}(1)$, the Fife–Caginalp asymptotics are recovered, and the interface motion is given by the MS problem. When the motion becomes fast, however, we must rescale time so that each of the terms in the expansion remains $\mathcal{O}(1)$.

Bates *et al.* [5] introduced the time scale defined by the new variable

$$\mathscr{T} = \epsilon^{-1}t.$$

For completeness, we summarize their analysis. To lowest order for the inner expansion, one obtains the problem

$$\phi_{zz} + \alpha V_n \phi_z + f(\phi, u) = 0, \tag{2.2}$$

$$D_T u_z + V_n \left(u - \frac{1}{2} p(\phi) - e_\infty \right) = 0, \tag{2.3}$$

where e_∞ is a constant of integration determined by matching to the outer solution as $z \to \infty$:

$$e_\infty = u_L + \frac{1}{2},$$

where u_L is the temperature just on the liquid side of the interface, which we shall call the 'local' undercooling and denote by $-\Delta$. Assuming a solution exists, we may also use the matching condition for $z \to -\infty$ to obtain

$$u_S = e_\infty + \frac{1}{2} = u_L + 1, \tag{2.4}$$

where u_S is the temperature just on the solid side of the interface. The boundary conditions for ϕ are also obtained by the matching conditions:

$$\phi(\pm\infty) = \mp 1. \tag{2.5}$$

We refer to the problem (2.2)–(2.5) as the phase-field travelling wave problem (PF); it will be discussed extensively in § 3.

The interface motion is therefore described by a free boundary problem where the temperature field is discontinuous across the interface, changing by exactly one unit, and the leading order interface motion is given by a simple law of the form

$$V_n = V(u_L; D_T, \lambda). \tag{2.6}$$

The function $V(u_L)$ is given by finding the (stable) velocity to the PF problem. It will

happen that sometimes no solution will exist. This simply means that the initial assumption about motion on the fast timescale was incorrect, and the interfacial motion is therefore described by slow timescale asymptotics.

Case II: $\tau = \mathcal{O}(\epsilon^2)$, $D_T = \mathcal{O}(\epsilon)$
We now consider the situation of small diffusivity, setting $D_T = \epsilon\tilde{D}$. With a timescale now $\mathcal{O}(1)$ again, the leading order inner solution satisfies

$$\phi_{zz} + f(\phi, u) = 0, \tag{2.7}$$

$$\tilde{D}u' + V_n\left(u - \frac{1}{2}p(\phi) - e_\infty\right) = 0, \tag{2.8}$$

which is like the first travelling wave problem, but the $V\phi'$ term has been suppressed in the first equation. This problem has the same boundary conditions as before. We call this the fast relaxation travelling-wave problem (FR problem), and it will be seen that its solutions are unstable.

Now with the fast timescale again, we obtain the leading order problem

$$\phi_{zz} + \alpha V_n\phi_z + f(\phi, u) = 0, \tag{2.9}$$

$$u + \frac{1}{2}p(\phi) = e_\infty, \tag{2.10}$$

where the constant of integration e_∞ has the same value as before. Upon substitution of u into the first equation, we obtain

$$\phi_{zz} + \alpha V_n\phi_z - F'(\phi; e_\infty) = 0, \tag{2.11}$$

where F is the bulk part of the free energy, evaluated at constant internal energy e_∞. This is the well known standard Bistable Travelling-Wave (BTW) problem. The solution to this problem is both unique and stable. We will discuss this problem below as well.

Case III: $\tau = \mathcal{O}(\epsilon^3)$, $D_T = \mathcal{O}(1)$
We now consider the more rapid relaxation rate $\tau = \alpha\epsilon^3$ which has been has been suggested in recent versions of the pure solidification model [2, 18]. This case is actually the same as case II, except that time has been rescaled by a factor of ϵ^{-1}. Therefore, on the timescale $\mathcal{T} = \epsilon^{-2}t$, we obtain the BTW problem (2.11), and on the timescale $\mathcal{T} = \epsilon^{-1}t$ we obtain the FR problem.

Case IV: $\tau = \mathcal{O}(\epsilon^3)$, $D_T = \mathcal{O}(\epsilon)$
This case is similar to Case III, except that the timescales are a factor of ϵ slower. On the $\mathcal{T} = t$ timescale, the FR problem is obtained, and on the $\mathcal{T} = \epsilon^{-1}t$ scale, the BTW problem is obtained.

Case V: $\tau = \mathcal{O}(\epsilon)$, $D_T = \mathcal{O}(1)$
Finally, we consider the case where $\tau = \alpha\epsilon$. On timescales faster than $\mathcal{T} = t$, we find the leading order velocity $V = 0$, which means that motion must be $\mathcal{O}(1)$ or less. This violates the intent of this paper, but we include this case because it yields leading order behaviour similar to that above.

For $D_T = \mathcal{O}(1)$ and motion on the $\mathcal{T} = t$ timescale, the outer temperature solution is no longer a constant, but satisfies a simple diffusion equation in each outer regions:

$$u_t = D_T\Delta u.$$

For the inner solution, we get the leading order problem

$$\phi_{zz} + \alpha V_n \phi_z + f(\phi, u) = 0, \tag{2.12}$$

and u is a constant, determined by matching conditions

$$u = u_L = u_S \equiv u_I.$$

This is a different bistable problem than the one above, which we shall call the alternative Bistable (AB) travelling wave problem.

Case VI: $\tau = \mathcal{O}(\epsilon)$, $D_T = \mathcal{O}(\epsilon)$
This case is really identical to Case I, but time has been rescaled by a factor of ϵ^{-1}. Therefore, now on the (original, slow) $\mathscr{T} = t$ timescale, we obtain the PF problem. For small undercoolings, this problem will not have solutions; we would therefore look for solutions on the (very) slow $\mathscr{T} = \epsilon t$ timescale, which leads to the original MS problem.

3 Solutions to the phase-field travelling wave problem

Of the travelling wave problems derived above, the PF system has the richest behaviour. We will rescale by setting $V := \alpha V_n$ and $D = \alpha D_T$ in equations (2.2)–(2.3), giving

$$\phi_{zz} + V\phi_z + f(\phi, u) = 0, \tag{3.1}$$

$$Du_z + Vu - \frac{1}{2}Vp(\phi) - Ve_\infty = 0. \tag{3.2}$$

with the boundary conditions

$$\phi(-\infty) = 1, \quad \phi(+\infty) = -1, \tag{3.3}$$

$$u(+\infty) = -\Delta\,(= u_L). \tag{3.4}$$

For $\Delta > 1$, existence, and in restricted cases uniqueness, was obtained by Bates *et al.* [4]. A rigorous study of this problem has also been conducted by the present author [14], who considers $\Delta < 1$ as well.

By the gradient flow construction of the model, there are some elementary conditions which travelling wave solutions must satisfy. In one dimensional front propagation, one steady state is being replaced with another. Intuitively, this implies that the free energy of the final state must be smaller than that of the initial state, and internal energy must be the same in both states. Formally, this is

Proposition 1 *Any solution to* (3.1)–(3.2) *for which*

$$\lim_{x \to \pm\infty} \phi, u \text{ exists}$$

must satisfy

$$\left(u - \frac{1}{2}p(\phi)\right)\Big|_{z=-\infty}^{z=\infty} = 0 \tag{3.5}$$

and

$$[F(\phi, e_\infty)]_{z=-\infty}^{z=\infty} = V\int_{-\infty}^{\infty} (\phi_z)^2\,dz + \frac{D\lambda}{V}\int_{-\infty}^{\infty} (u_z)^2\,dz \tag{3.6}$$

The first property is just conservation of internal energy, which simply implies that the the supercooled liquid is warmed by exactly one unit when it changes into solid. The second property (3.6) is just a computation of free energy dissipated as the front moves. For a front to have positive velocity, a necessary condition for existence is that

$$[F(\phi, e_\infty)]_{z=-\infty}^{z=\infty} = \lambda[u(\infty)^2 - u(-\infty)^2] > 0$$

which using (3.4) and (3.5) means one must at least have $\Delta > 1/2$. For fixed values of D, λ, there will be some critical value, Δ^*, a value of the undercooling below which no solutions will exist. It will always be the case that

$$\frac{1}{2} < \Delta^* \leqslant 1.$$

We note that equation (3.6) has analogues for the other travelling wave problems as well.

There are two different limiting cases for which the problem is reasonably tractable: one where the diffusion length D/V is small, the other where it is large. We will carry out an asymptotic analysis in these limits.

3.1 The limit of small diffusion length

Here we find a solution to (3.1)–(3.2) perturbatively when the diffusion length D/V is small in comparison to unity. By examining (3.6), it follows that V must remain finite for this to happen, since the integral of $(u')^2$ remains bounded. Then for small values of D we look for solutions with the asymptotic expansions

$$\phi \sim \phi_0 + D^{1/2}\phi_1 + D\phi_2 + \cdots, \tag{3.7}$$

$$u \sim u_0 + D^{1/2}u_1 + Du_2 + \cdots, \tag{3.8}$$

$$V \sim V_0 + D^{1/2}V_1 + DV_2 + \cdots. \tag{3.9}$$

Furthermore, we choose a new scale for the undercooling by defining

$$\delta \equiv D^{-\frac{1}{2}}\left(\Delta - \frac{1}{2}\right),$$

which is assumed $\mathcal{O}(1)$. These choices of scalings are made so that the three terms in (3.6) balance in the limit $D \to 0$. Inserting these into (3.1) - (3.2), we obtain to lowest order in D that u_0 is "slaved" to ϕ_0:

$$u_0 - \frac{1}{2}p(\phi_0) = 0, \tag{3.10}$$

and ϕ_0 is the solution of

$$(\phi_0)_{zz} + V_0\phi_z + G'(\phi_0) = 0, \tag{3.11}$$

where

$$G(\phi) = g(\phi) + \frac{\lambda}{2}\left(\frac{1}{2}p(\phi)\right)^2.$$

Multiplying equation (3.11) by ϕ_z and integrating gives the solvability condition $V_0 = 0$. The solution of (3.11) is then some monotone decreasing function which represents the phase profile.

We proceed to the next order in D, which gives the linear system

$$\left(\frac{d^2}{dz^2} + f_\phi\right)\phi_1 + f_u u_1 = -V_1\phi_0',$$
$$-\frac{1}{2}p'(\phi_0)\phi_1 + u_1 = -\frac{u_0'}{V_1} + \delta,$$

where derivatives of f are computed at ϕ_0, u_0. Such a problem only has solutions if the right-hand side is orthogonal to solutions of the homogeneous adjoint problem. In our case, it is easy to see that the vector $[(\phi_0)_z, \lambda(u_0)_z]$ is a null vector of the adjoint operator. We obtain the solvability condition

$$-V_1 I + \lambda\delta - \frac{\lambda}{V_1}J = 0, \tag{3.12}$$

where

$$I = \int_{-\infty}^{\infty}(\phi_0)_z^2\,dz, \qquad J = \int_{-\infty}^{\infty}(u_0)_z^2\,dz. \tag{3.13}$$

The quadratic equation (3.12) has the two real positive roots

$$V_1 = \frac{\lambda\delta \pm \sqrt{(\lambda\delta)^2 - 4\lambda IJ}}{2I}, \tag{3.14}$$

as long as

$$\Delta \geqslant \frac{1}{2} + 2\left(\frac{IJD}{\lambda}\right)^{1/2}. \tag{3.15}$$

The interpretation of (3.14) is that travelling wave solutions are possible for undercooling somewhat larger than $1/2$ provided D is small. Furthermore, there are *two* solution branches which emanate from a saddle-node type bifurcation. Equation (3.15) gives a perturbative estimate for the critical value Δ^*.

A simple argument suggests that the faster one is the dynamically preferred, thus stable, solution. Suppose that we are just past the existence point, so that the fast and slow solutions are nearly identical. For any travelling wave solution, one may compute the time derivative of the free energy to be

$$\frac{d\mathscr{F}}{dt} = -V\lambda\left(\Delta - \frac{1}{2}\right).$$

Now consider any initial condition which is near both solutions. Since the dynamics are a gradient flow for $\mathscr{F}$, the initial condition will evolve so that $d\mathscr{F}/dt$ is as large as possible. As a consequence, it is unlikely that the time evolving solution would tend toward the slow front. It is, however, unclear if the fast branch should be globally attracting. In fact, for $\Delta < 1$, hysteresis is quite possible; depending on the initial data, either the fast, steady front will be approached, or the front may slow to the point where the slower scale asymptotics apply instead.

3.2 The limit of large diffusion length

We next examine the case when the diffusion length is large. In contrast to the small-diffusion length situation, we may take D to be fixed and assume that V is getting small,

but not as fast as ϵ is getting small, so that leading order time-dependent asymptotics still yield the PF problem. Taking $V \to 0$ in expression (3.6), after a careful evaluation of the integral we see that

$$[F(\phi, e_\infty)]_{z=-\infty}^{z=\infty} = \frac{\lambda}{2}$$

which means that $\Delta = 1$. In other words, to have small velocities we must be near unit undercooling.

We define a new small quantity

$$\delta = \Delta - 1$$

and expand ϕ, u, V in powers of δ. Since the temperature field varies on a spatial scale of δ^{-1}, a matched asymptotic expansion is necessary. Far in front of the interface ($z >> 1$), we use the rescaled coordinate $\zeta = \delta z$, and denote solutions of various orders using the capital letters Φ, U instead.

Near the interface, the lowest order solution must satisfy

$$(\phi_0)_{zz} + V_0(\phi_0)_z + f(\phi_0, u_0) = 0, \tag{3.16}$$

$$D(u_0)_z = 0. \tag{3.17}$$

Since to leading order $u_0(z) \to 0$ as $z \to -\infty$, we have $u_0 \equiv 0$. This means that V_0 must be zero for (3.16) to have a solution.

The leading order 'outer' problem for $\zeta > 0$ is

$$f(\Phi_0, U_0) = 0, \tag{3.18}$$

$$D(U_0)_\zeta = V_1 \left(-U_0 + \frac{1}{2} p(\Phi_0) - \frac{1}{2} \right). \tag{3.19}$$

Therefore, $\Phi_0 \equiv -1$ and the solution of the second equation is just

$$U_0 = -1 + \exp\left(-\frac{V_1}{D} \zeta \right), \quad \zeta > 0, \tag{3.20}$$

where we have assumed that the interface is at $\zeta = 0$ and the leading order matching condition has been used.

For the next order of solution, the inner problem for u_1 gives

$$D(u_1)_z = V_1 \left(u_0 + \frac{1}{2} p(\phi_0) - \frac{1}{2} \right),$$

which has the general solution

$$u_1(z) = \overline{u_1} + \frac{V_1}{2D} \int_{-\infty}^{z} p(\phi_0(z)) - 1 \, dz,$$

where $\overline{u_1}$ is a constant of integration. Expanding the left-hand boundary condition $u(-\infty) = -\Delta + 1$ in powers of δ, it follows that $\overline{u_1} = -1$. Then ϕ_1 solves the linear equation

$$\left[\frac{d^2}{dz^2} + f_\phi(\phi_0, 0) \right] \phi_1 = -V_1(\phi_0)_z + \frac{\lambda}{2} u_1 p'(\phi_0),$$

which has the solvability condition

$$-V_1 \int_{-\infty}^{\infty} (\phi_0)_z^2 \, dz + \frac{\lambda}{2} \int_{-\infty}^{\infty} u_1 [p(\phi_0)]_z \, dz = 0.$$

As before, we set the integral of $(\phi_0)_z^2$ equal to I, and find that

$$\int_{-\infty}^{\infty} u_1 [p(\phi_0)]_z \, dz \equiv 2 + \frac{V_1}{D} J,$$

where J is the integral

$$J = \int_0^{\infty} 1 - p(\phi_0)^2 \, dz.$$

The solvability condition may then be restated in terms of the leading order velocity:

$$V \sim \delta V_1 = \delta \lambda \left(I - \frac{\lambda}{2D} J \right)^{-1}. \tag{3.21}$$

Condition (3.21) says that when the ratio λ/D is small, then there is a branch of solutions for $\Delta > 1$ where the velocity is roughly proportional to $\Delta - 1$; it will be shown that this branch is stable. However, when the ratio λ/D is larger than $2I/J$, for the leading order velocity to be positive one needs $\Delta < 1$. This is a rather unphysical situation: the velocity decreases with increasing undercooling. It will be demonstrated later on that this branch is actually unstable.

Figure 1 shows numerical computations of V using an elementary shooting method where the particular constitutive functions are

$$g(\phi) = \frac{1}{4}(1 - \phi^2)^2, \quad p(\phi) = \frac{15}{8} \left(\phi - \frac{2}{3}\phi^3 + \frac{1}{5}\phi^5 \right).$$

When λ/D is subcritical (less than about 2.6 in this case), solutions only exist in the hypercooled region (when $\Delta > 1$). But when the ratio is large, solutions are seen to exist for undercoolings which are smaller than 1. Furthermore, we see that the large diffusion length solution branch is simply a continuation of the the unstable branch of solutions in the small diffusion length case.

4 The fast relaxation and bistable travelling wave problems

In the limit of slow diffusion or fast relaxation, two different travelling wave problems arise simultaneously, operating on different timescales: the (slow) FR problem and the (fast) BTW problem. Alternatively, for slow relaxation, we obtain a different bistable travelling wave problem (problem AB). We shall again rescale both V and D_T by α as in the previous section.

We first consider the FR problem (2.7)–(2.8). The analog of the dissipation equality (3.6) in the PF problem is

$$\Delta - \frac{1}{2} = \frac{D}{V} \int_{-\infty}^{\infty} u_z^2 \, dz. \tag{4.1}$$

This means that again one needs $\Delta > \frac{1}{2}$ to obtain forward moving solutions. It turns out that for large diffusion lengths, and most likely in general, solutions are unstable.

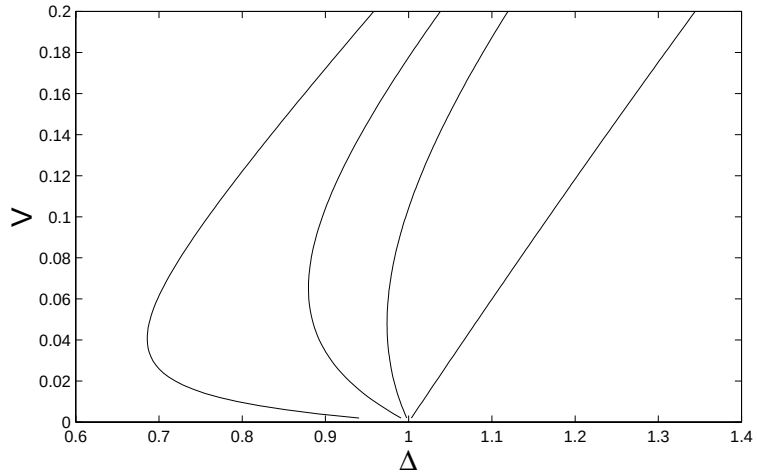

FIGURE 1. Numerical solution of travelling wave velocities as a function of the undercooling. The plots from right to left are for the values $\lambda/D = 0.8, 4.0, 8, 40$. In each case, $\lambda = 0.4$.

Therefore initial data will generically be driven to the alternative faster dynamics, given by the BTW problem.

The BTW problem (2.11) has been extensively studied [12, 11]. This problem has a unique solution and wave speed. The dissipation of free energy for this case is

$$[F(\phi; e_\infty)]_{z=-\infty}^{z=\infty} = V \int_{-\infty}^{\infty} \phi_z^2 \, dz. \tag{4.2}$$

For V to be positive and $O(1)$, the undercooling must necessarily satisfy $\Delta > \frac{1}{2}$. In particular, if V is small, then asymptotically

$$V \approx I^{-1} \, [F(\phi; e_\infty)]_{z=-\infty}^{z=\infty} \tag{4.3}$$

where I is just the integral of $(\phi_0)_z^2$, ϕ_0 being the solution for $V = 0$. In other words, the propagation velocity is roughly proportional to the jump in free energy across the interface.

We finally discuss the AB problem, which is of the same form as the BTW problem, the difference being that temperature, rather than internal energy, is constant across the interface. Multiplying (2.12) by ϕ_z and integrating gives

$$\lambda u_I = -V \int_{-\infty}^{\infty} \phi_z^2 \, dz.$$

To a good approximation, the velocity therefore is proportional to the negative interface temperature.

5 Stability and approach to the travelling wave solutions

For arbitrary initial data, the asymptotic inner solution will only be valid after a very short initial transient time. Even so, there is no guarantee that this travelling wave solution will be approached if it is not stable. Here a time-dependent analysis is presented for

the situation where the diffusion length is small, but large compared to the interface width ϵ. This determines the leading order dynamics of the transient solution and allows conclusions to be drawn about stability.

We introduce a new small variable δ, representing the ratio of interface width to diffusion length which will play the same role as it did in the § 3.2. We will conduct a time-dependent analysis as $\epsilon, \delta \to 0$ with the further assumption that

$$\epsilon = o(\delta^2). \tag{5.1}$$

We will attempt a matched expansion now in some new rescaled spatial coordinate ζ. The coordinate system near the interface for the inner expansion is the same as before. The new spatial scale ζ is defined by

$$\zeta = \delta \epsilon^{-1} r$$

so that the diffusion length measured in terms ζ is exactly unity. We shall look for dynamics on a very fast time scale, namely

$$\mathscr{T} = \delta^2 \epsilon^{-2} t.$$

5.1 The PF problem

In the new coordinate system, the equations pertaining to the inner solution may be written

$$\delta^2 \phi_{\mathscr{T}} = \delta^2 \phi_{\zeta\zeta} + f(\phi, u) + o(\delta^2), \tag{5.2}$$

$$e_{\mathscr{T}} = D_T u_{\zeta\zeta} + o(\delta). \tag{5.3}$$

The outer solutions are the same as before: the temperature field is constant, and $\phi = \pm 1$.

Equations (5.2)–(5.3) are the one-dimensional versions of those considered in the Caginalp–Fife analysis [8], where δ now plays the role of the small parameter. Rather than repeating their somewhat lengthy analysis, we only summarize the resulting free boundary problem. We then examine the stability of fronts for this problem instead.

In the limit $\delta \to 0$, the leading order behaviour of u is $\delta U(\zeta, t)$ where U satisfies the one-dimensional 'Stefan' problem

$$U_{\mathscr{T}} = U_{\zeta\zeta} \quad \text{in } (-\infty, \infty)/\{s(t)\}, \tag{5.4}$$

$$V \equiv s'(\mathscr{T}) = -\beta U(s), \tag{5.5}$$

$$V = D_T [U_\zeta(s+) - U_\zeta(s-)], \tag{5.6}$$

where $s(\mathscr{T})$ denotes the position of the interface and $s+, s-$ are limits from the left and right, respectively. The kinetic coefficient β is given by

$$\beta = \lambda^{-1} \left(I - \frac{\lambda}{2D} J \right). \tag{5.7}$$

where I and J are the same integrals as in § 3.2. Note that the velocity V is defined in terms of the rescaled coordinates; in original coordinates the velocity is actually $\epsilon^{-1}\delta V$. The boundary conditions for U are given by a matching condition:

$$U(-\infty) = u_S = u_L + 1, \quad U(+\infty) = u_L \equiv -\Delta. \tag{5.8}$$

The first remark to be made is that the problem (5.4)–(5.8) has the well known travelling wave solution

$$s(t) = V\mathscr{T}, \tag{5.9}$$

$$U_0(\zeta, \mathscr{T}) = -\Delta + \exp\left[-\frac{V}{D_T}(x - V\mathscr{T})\right], \tag{5.10}$$

with velocity

$$V = \frac{\Delta - 1}{\beta}.$$

Note that V is identical to the velocity derived in equation (3.21). Thus the hypercooled solution branch simply corresponds to $\beta > 0$, whereas the non-hypercooled branch corresponds to $\beta < 0$.

For arbitrary initial conditions, it is known what occurs in the case $\beta > 0$ [10]. For $\Delta > 1$, the travelling wave solution is globally attracting. When $\Delta < 1$, solutions slow down via a $t^{-1/2}$ power law, and approach a self-similar solution originally derived by Zener [34].

The case where $\beta < 0$ has received, on the other hand, little attention. We shall demonstrate here that the travelling wave solution is, as expected, unstable.

Consider a perturbation to the travelling wave solution given by

$$U(\zeta, \mathscr{T}) = U_0(\zeta, \mathscr{T}) + \varepsilon e^{\omega\mathscr{T}} \times \begin{cases} Ae^{-\mu_+(\zeta - V\mathscr{T})}, & \zeta < Vt, \\ Be^{-\mu_-(\zeta - V\mathscr{T})}, & \zeta > Vt, \end{cases} \tag{5.11}$$

and

$$s(\mathscr{T}) = V\mathscr{T} + \varepsilon e^{\omega\mathscr{T}}, \tag{5.12}$$

where ε is some small quantity, and $\mu_- < 0$, $\mu_+ > 0$, ensuring that the perturbation is bounded (Of course, more general perturbations could be considered, but we are only interested in instability). Inserting these into equations (5.4)–(5.8), to leading order in ε we obtain that $A = B$, and ω, μ_-, μ_+ satisfy

$$\omega + \mu_- V = \mu_-^2, \tag{5.13}$$

$$\omega + \mu_+ V = \mu_+^2, \tag{5.14}$$

$$\mu_+ - \mu_- = -\beta^{-1}. \tag{5.15}$$

Equations (5.13)–(5.15) have the real solutions

$$\mu_\pm = \frac{1}{2}(-V \pm \sqrt{V^2 + 4\omega}),$$

where ω is given by

$$\omega = \frac{1}{\beta^2} - V^2 = \frac{1 - (\Delta - 1)^2}{\beta^2}.$$

Provided $\Delta < 1$, ω is positive, proving instability.

5.2 The FR problem

The analysis for the FR problem follows the same lines as what appears above. The only real difference is that the time derivative term in equation (5.2) vanishes. This leads to

Table 1. *Various behaviours of the phase field model in different parameter regimes. The velocity scales are those of the stable solutions. For rapid growth situations, the interface velocity is determined solely by solving the travelling wave problem listed*

τ scale	D_T scale	Velocity scale	Interfacial Motion	Undercooling regime
$\mathcal{O}(\epsilon^2)$	$\mathcal{O}(1)$	$\mathcal{O}(1)$	MS	$\Delta < 1$
$\mathcal{O}(\epsilon^2)$	$\mathcal{O}(1)$	$\mathcal{O}(\epsilon^{-1})$	PF	$\Delta > \Delta^*$
$\mathcal{O}(\epsilon^2)$	$\mathcal{O}(\epsilon)$	$\mathcal{O}(\epsilon^{-1})$	BTW	$\Delta > \frac{1}{2}$
$\mathcal{O}(\epsilon^3)$	$\mathcal{O}(1)$	$\mathcal{O}(\epsilon^{-2})$	BTW	$\Delta > \frac{1}{2}$
$\mathcal{O}(\epsilon^3)$	$\mathcal{O}(\epsilon)$	$\mathcal{O}(\epsilon^{-1})$	BTW	$\Delta > \frac{1}{2}$
$\mathcal{O}(\epsilon)$	$\mathcal{O}(1)$	$\mathcal{O}(1)$	AB	any
$\mathcal{O}(\epsilon)$	$\mathcal{O}(\epsilon)$	$\mathcal{O}(1)$	PF	$\Delta > \Delta^*$
$\mathcal{O}(\epsilon)$	$\mathcal{O}(\epsilon)$	$\mathcal{O}(\epsilon)$	MS	$\Delta < 1$

the same modified Stefan problem as before, except that the I term in equation (5.7) is suppressed, giving instead

$$\beta = -\frac{\delta}{2D} J < 0. \tag{5.16}$$

By virtue of the results above, we may conclude that solutions to the FR problem are always unstable.

6 Discussion; relationship to other models

By considering different scales of variables and parameters in the phase field model, we have classified several possible behaviours the model can have. A summary is given in Table 1. It may be that all of the parameter regimes we have studied are not experimentally accessible, but we have nevertheless included them for completeness. The free boundary problems obtained have a close relationship with existing theories of solidification; we now discuss this.

The most interesting case is that which yields the PF system. When λ/D is supercritical, steady solutions exist without hypercooling. This is not possible in many models of rapid solidification, but it is not clear experimentally if this should always be the case. The experiments of Glicksman & Schaefer [15] on white phosphorus showed a velocity dependence which decreased in a continuous fashion as the undercooling decreased below unity, much as in the left-most curve in Figure 1. It should be pointed out that their solidification fronts in this regime were not strictly planar, however, and therefore cannot be directly compared to our results.

For the subcritical case, rapid dynamics may only exist for the situation of hypercooling. The front velocity is only determined by local conditions, namely the (local) undercooling. This resembles models for hypercooling of Bernoff and Sarocka [27], as well as Umantsev & Davis [31]. Their theories also incorporate dependence on local geometric properties of the interface; we anticipate that proceeding to further orders in the time-dependent asymptotics would produce these features in the phase field model as well.

The other cases which give the BTW problem yield a generalization of many geometric models of crystal growth [30], which assume that the velocity is proportional to the

jump in free energy at the interface. Note that the BTW problem is obtained by the fact that e is constant across the interface. In alloy solidification, where e represents solute concentration, this is an important non-equilibrium effect known as solute trapping [3, 1].

7 Conclusion

A mathematical treatment of rapid dynamics in phase field models has been presented. Interfacial motion different from the usual Mullins–Sekerka problem has been derived. The essential qualitative and quantitative features of front dynamics have also been produced.

We mention that the necessity of using a free-energy functional in constructing the model is only due to the mathematical simplicity which results. For other models which are not based on a variational principle, the qualitative structure of the equations (3.1)–(3.2) is still the same and should produce similar behaviour. The incorporation of other effects such as long range forces and anisotropy of surface energy, however, may be important. In particular, anisotropy could result in fast growth in certain directions but not others due to the critical nature of existence.

Future work should include extending the analysis presented here to models with unequal diffusion scales, such as those encountered in alloy solidification. Additionally, the asymptotics may be carried out to further orders to derive presumably geometric corrections to the interface motion laws.

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