DYNAMICS OF LAYERED INTERFACES ARISING FROM PHASE BOUNDARIES

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Abstract. The dynamics of a material in two phases is studied in the context of phase-field models based on a Landau–Ginzburg free energy functional. They consist of a system of two nonlinear diffusion equations for the temperature and order parameter. The interface between the two phases is treated as a moving internal layer in two space dimensions, with thickness $O(\varepsilon)$, $\varepsilon$ being a naturally occurring small parameter. Among other things, a dynamical interfacial relation is derived.

Key words. phase field, phase change, phase interface, Stefan problem, nonlinear parabolic systems, matched asymptotics, internal layer

AMS(MOS) subject classifications. 80A20, 35K55, 82A25

1. Introduction. Consider a substance which may be in either of two phases, e.g., liquid or solid, in a region $\Omega$ of space. We look at mathematical models for the dynamics of such a material, including the motion, shape, and internal structure of the interface $\Gamma(t)$ between the two phases.

The simplest such model is the classical Stefan formulation, in which the interface is considered to be infinitesimally thin, the temperature $T(x, t)$ satisfies the usual heat diffusion equation in each of the two phases, $T$ vanishes at the interface $\Gamma(t)$ between solid and liquid, and an energy balance condition is imposed on $\Gamma$. The latter relates the normal speed of $\Gamma$, the heat flux there, and the latent heat of the material.

The Stefan model does not accommodate various other physical realities which may be relevant. One approach to remedy this situation is based on a Landau–Ginzburg free energy functional [10], [13], [11], [4], [2], [12], where, in addition to the temperature, an order parameter is also envisaged as a field quantity. The resulting equations are known as phase field models. The free energy functionals can be derived in a formal way from discrete lattice models with assumed interactions among the nodes (e.g., [3], [4]). The appropriate Model A field equations can then be analyzed. In so doing, it is possible to connect lattice concepts such as correlation length and anisotropy in lattice interactions with properties of the continuum model which are left out of the Stefan formulation [3]. The latter include: (1) an equilibrium Gibbs–Thompson relation between the temperature at the interface and its curvature ([12], for example); (2) anisotropy in growth velocities [4]; (3) finiteness of the interface thickness; (4) certain supercooling and superheating effects; and (5) interaction of the material and its interface with the boundary of the containing vessel [5].

The phase field models automatically incorporate these phenomena which otherwise may have to be added to existing models in an ad hoc manner. Moreover, successful numerical methods for these models have been developed and used [14], [8].

The field equations generally assume the form

$$
\tau \frac{\partial \phi}{\partial t} = L_{\varepsilon} \phi + J(\phi) + \sigma T.
$$

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* Received by the editors December 15, 1986; accepted for publication (in revised form) July 7, 1987.
This research was supported by National Science Foundation grants DMS-8601764 and DMS-8503007.
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\[
\frac{\partial T}{\partial t} + \frac{1}{2} \frac{\partial \phi}{\partial t} = K \Delta T,
\]

where \( T \) is the temperature; \( \phi \) is the order parameter; \( t' \) is dimensional time; \( \tilde{f} \) is a sigmooidal function of \( \phi \) (derivative of a double-well potential) vanishing with negative derivative at \( \tilde{f} = \pm 1 \) (an example being \( \frac{1}{2}(\phi - \phi^3) \)); \( \xi \) is a small interaction length figuring into the basic lattice model; \( L_{\xi} \) is an elliptic operator depending on the length \( \xi \) in such a way as to make the operator dimensionless; \( \sigma \) is an "entropy" coefficient having the dimension of inverse temperature; \( l \) is the product of latent heat and heat capacity of the material; \( K \) is the diffusivity of heat, and the small parameter \( \tau \) is a relaxation time. Only the simplest example for \( L \) will be considered here, namely

\[
L_{\xi} = \xi^2 \Delta,
\]

\( \Delta \) being the Laplace operator. Generalizations of these equations and of this operator will be mentioned later in § 5. Moreover, \( \tilde{f} \) will be assumed to be odd. Again, extensions are immediately possible.

Existence, uniqueness, and regularity theorems were proved for these equations in [1]. The equilibrium problem for (1.1), (1.2) was studied in several papers [6], [7], [9]; of course, the Gibbs–Thompson relation plays an essential role in these (rigorous) results.

In the present paper, we consider the nonequilibrium situation and focus especially on the structure and laws of motion of the interface. For simplicity we consider two-dimensional space. The basic method involves a formal asymptotic analysis in which the dynamics are understood by considering an "inner" solution describing the region near the moving interface, and an "outer" solution describing the regions away from it. The solutions are matched by the usual rules of asymptotic analysis (derived in the Appendix). One result of this analysis is an equation which must be satisfied at the interface in addition to the Stefan energy balance relation. It is a dynamic Gibbs–Thompson condition relating the temperature at the interface with its curvature, its normal velocity, the relaxation time \( \tau \), and the latent heat \( l \). The coefficients in this relationship are explicitly calculated in terms of the sigmooidal function \( \tilde{f} \) appearing in (1.1). Its physical meaning is discussed in § 4.

Section 5 brings out various generalizations of the basic system (1.1), (1.2), involving the heat source term (second on the left in (1.2)) and the elliptic operator \( L_{\xi} \).

Whereas § 3 deals with a refinement, in some sense, of the Stefan problem, in which the nondimensional temperature is \( O(1) \), a different asymptotic treatment is given in § 6 for the case when the temperature is near 0 and the front moves slowly. In that case, the equilibrium Gibbs–Thompson relation is always valid and solutions may not be approximated by those of the Stefan problem.

2. The dimensionless form of the problem. Our special concern will be with the dependence of the results on the various parameters of the problem, and so it is essential to parameterize it carefully.

Our unit of temperature will be the difference \( T^* \) between the melting temperature (which we are taking to be 0) and the least supercooling temperature (or greatest superheating temperature). This means that (1.1), (1.2) admit constant solutions \((T_0, \phi_0)\) with \( \phi_0 > 0 \) for \( T_0 \geq -T^* \), but not for \( T_0 < -T^* \). Thus the function \( \tilde{f}(\phi) \) has a positive maximum equal to \( \sigma T^* \), and a negative minimum of \( -\sigma T^* \).

As basic unit \( L^* \) of length, we take the maximum diameter of the domain of interest or the minimum radius of curvature of the initial interface. (For planar problems
in all space, we may choose a characteristic length associated with the spatial distribution of the initial temperature.)

Dimensionless parameters and functions will be defined as follows. Here we denote by \( x' \) and \( t' \)-dimensional space and time variables—the same ones that were used in (1.1) and (1.2):

\[
x = \frac{x'}{L^*}, \quad t = \frac{t'K}{(L^*)^2}, \quad u = \frac{T}{T^*},
\]

\[
f = \frac{\tilde{f}}{\sigma T^*}, \quad \varepsilon = \frac{\xi}{\sqrt{\sigma T^* L^*}}, \quad \alpha = \frac{\tau K}{\xi^2}, \quad \lambda = \frac{l}{2T^*}.
\]

In this way, (1.1), (1.2) become

\[
(2.1) \quad u_t + \lambda \phi_x = \Delta u,
\]

\[
(2.2) \quad \alpha \varepsilon^2 \phi_t = \varepsilon^2 \Delta \phi + f(\phi) + u.
\]

By the above construction, the positive maximum of the function \( f \) is equal to 1, and the negative minimum to \(-1\); other than that and the fact that \( f \) is odd and has only three zeros at 0 and \( \pm 1 \), it is unspecified.

3. Interface dynamics in two space dimensions. An asymptotic analysis for \( \varepsilon \ll 1 \) will be carried out for layered solutions of the system (2.1), (2.2), under the assumption that \( \alpha \) and \( \lambda \) are \( O(1) \) quantities. Analogous results could be obtained when this latter is not the case. A complete determination of the solution will involve initial and boundary conditions; however, they will be left unspecified here, as our primary attention is rather on the laws of motion of the interface. Our analysis treats it as a moving internal layer of width \( O(\varepsilon) \).

The appropriate matching rules for the nonuniform motion of such a layer are well known, at least to flame theorists, but for completeness are derived in the Appendix.

The interfacial curve \( \Gamma \) is defined as the set of points in \( \Omega \) at which \( \phi = 0 \). Setting \( x = (x_1, x_2) \), we define \( r(x, t, \varepsilon) \) in a neighborhood of \( \Gamma \) to be \( \pm \) the distance from \( x \) to \( \Gamma \), with the convention that \( + \) is the direction of positive \( \phi \) (which will be the liquid side) and \( - \) is the direction of negative \( \phi \). (We do not require at this point that the temperature \( u \) be predominantly positive on the liquid side or negative on the solid side, although the solutions will no doubt be very unstable otherwise.) Basic regularity results [1] imply that it is reasonable to suppose that \( \Gamma \) is a smooth curve for each \( t \). Therefore \( r \) is a smooth function in a sufficiently small neighborhood of \( \Gamma \). The interface \( \Gamma \) itself may be described by the equation

\[
(3.1) \quad r(x, t, \varepsilon) = 0.
\]

On \( \Gamma \) we have

\[
(3.2) \quad |\nabla r| = 1 \quad \text{and} \quad \Delta r = \kappa,
\]

where \( \nabla \) and \( \Delta \) refer only to the spatial variable \( x \), and \( \kappa \) is the curvature of \( \Gamma \), counted as positive if \( \Gamma \) is concave as seen from the solid. The first equation in (3.2), in fact, holds in the entire neighborhood where \( r \) is defined. We now define a function \( s(x, t, \varepsilon) \) so that \( (s, r) \) is a local orthogonal coordinate system near \( \Gamma \), and such that on \( \Gamma \), \( s \) measures arclength from some point depending smoothly on \( t \).

We set up outer and inner expansions for the functions \( u, \phi, r, \) and \( s \). Thus

\[
(3.3) \quad u = u(x, t, \varepsilon) = u^0(x, t) + \varepsilon u^1(x, t) + \cdots,
\]
with similar expressions for $\phi$, $r$, and $s$. (Note that knowledge of the function $r$ determines $s$, in view of the orthogonality condition and the fact that $s$ measures arclength on $\Gamma$.) The terms on the right of these expansions may be discontinuous at $r = 0$; otherwise they are smooth.

The inner expansion proceeds by defining $z = r/\varepsilon$ and thinking of $u$ and $\phi$ as depending in a regular manner on the variables $z$, $s$, and $t$ near $\Gamma$:

\begin{align*}
(3.4a) \quad u &= U(z, s, t, \varepsilon) = U^0(z, s, t) + \varepsilon U^1(z, s, t) + \cdots, \\
(3.4b) \quad \phi &= \Phi(z, s, t, \varepsilon) = \text{(similar)}. 
\end{align*}

By definition of $r$, we require

\begin{equation}
(3.5) \quad \Phi(0, s, t, \varepsilon) = 0.
\end{equation}

For any function $g$ of the outer variables $x$, $t$, we use the notation $g|_{r=\varepsilon}$ to mean the limiting values of $g$ as $\Gamma$ is approached from the side where $r > 0$ or $r < 0$, respectively; i.e., as $r \downarrow 0$ or $r \uparrow 0$. Similarly, the symbol $g_r|_{r=\varepsilon}$ will denote the limiting values of the normal derivative.

**Outer expansion.** Setting (3.3) into (2.1) and (2.2) and equating coefficients of corresponding powers of $\varepsilon$, we obtain a sequence of outer problems:

\begin{align*}
O(1). & \quad (3.6) \quad u_0^r + \lambda \phi_0^r = \Delta u_0 \\
(3.7) & \quad f(\phi^0) + u_0^s = 0.
\end{align*}

\begin{align*}
O(\varepsilon). & \quad (3.8) \quad u_1^r + \lambda \phi_1^r = \Delta u_1 \\
(3.9) & \quad f'(\phi^0)\phi^1 + u_1^s = 0.
\end{align*}

\begin{align*}
O(\varepsilon^2). & \quad (3.10) \quad u_2^r + \lambda \phi_2^r = \Delta u_2 \\
(3.11) & \quad f''(\phi^0)\phi^2 + u_2^s = -\frac{1}{2}f''(\phi^0)(\phi^1)^2 + \alpha \phi_0^r - \Delta \phi^0,
\end{align*}

etc.

It will be assumed that (3.7) can be solved for $\phi^0$ in a neighborhood of $+1$ as a function of $u^0$, for $u^0$ in the anticipated temperature range in the liquid, and that $f'(\phi^0) < 0$. In particular, this is the case if $f(\phi) = k(\phi - \phi^1)$ and $|u^0|$ is not too large. This is then substituted into (3.6) to obtain an equation for $u^0$ alone, of the form

\[ (u^0 + \lambda f^{-1}(u^0)), = \Delta u^0, \]

which should hold on the liquid side of the layer ($r > 0$). This gives a nonlinear heat conduction law in the material, but a linear one can be readily obtained by one of two possible elementary modifications of the model discussed in § 5.

Similarly, it is assumed that (3.7) can be solved with $\phi^0$ in a neighborhood of $-1$; this will generate an equation for $u^0$ valid for $r < 0$. The higher order equations (3.8), (3.9), etc. likewise reduce to equations for $u^k$ alone. To complete the solution, interface conditions at $r = 0$ will be derived later, and boundary and initial conditions may be imposed.

**Inner expansion.** A standard calculation with use of (3.2) and the orthogonality of the coordinate system $(r, s)$ shows that in terms of that system,

\[ \Delta u = u_{rr} + u_{ss} |\nabla s|^2 + u_r \Delta r + u_s \Delta s. \]
The time derivative \( u_t \) in those coordinates is transformed into the expression
\[
u_t + u_t r_t + u_t s_t.
\]
In terms of \( z, s, \) and \( t, (2.1) \) and (2.2) become
\[
U_{zz} + \varepsilon (-r, U_z - \lambda r, \Phi_z + \Delta r U_z) \\
- \varepsilon^2 (U_t + U_z s_t + \lambda \Phi_t + \lambda \Phi s_t - (U_{ss} |\nabla s|^2 + U_t \Delta s)) = 0,
\]
(3.12)
\[
\Phi_{zz} + f(\Phi) + U - \varepsilon \alpha r, \Phi_z + \varepsilon \Phi, \Delta r + \varepsilon^2 (\Phi_{ss} |\nabla s|^2 + \Phi_t \Delta s - \alpha \Phi_t - \alpha \Phi s_t) = 0.
\]
(3.13)

We shall now proceed to examine the various orders of approximation of (3.12) and (3.13) obtained by substituting (3.4), (3.5) therein.

\[
O(1).
\]
(3.14)
\[
U^0_{zz} = 0,
\]
(3.15)
\[
\Phi^0_{zz} + f(\Phi^0) + U^0 = 0.
\]

We want bounded solutions, so from (3.14), \( U^0 = \text{const} \), and the existence of a bounded solution of (3.15) with distinct limits at \( \pm \infty \) requires \( U^0 = 0 \). From this and matching condition (A.8a) we obtain

\[
U^0 = u^0_{|_{\Gamma \pm}} = 0,
\]
(3.16)

and

\[
\Phi^0 = \Phi^0(z) \equiv \psi(z),
\]
(3.17)

\( \psi(z) \) being the unique solution of
\[
\psi'' + f(\psi) = 0, \quad \psi(\pm \infty) = \pm 1, \quad \psi(0) = 0.
\]
(3.18)

Now (A.8a), applied to \( \phi, \) yields

\[
\phi^0_{|_{\Gamma \pm}} = \pm 1,
\]
which is also evident from (3.7) and (3.16).

\[
O(\varepsilon).
\]
(3.19)
\[
U^1_{zz} = r^0_t U^0_z + \lambda r^0_t \Phi^0 z - \Delta r^0 U^0_z = \lambda r^0_t \psi(z).
\]

The latter equality is a consequence of (3.16) and (3.17). Integrating, we obtain

\[
U^1_z = \lambda r^0_t \psi(z) + c_t(s, t).
\]
(3.20)

But (A.8b) applies, and we let \( z \to \pm \infty \) in (3.20) to obtain

\[
[u^0_t]_{|_{\Gamma \pm}} = \pm \lambda r^0 + c_t(s, t).
\]
(3.21)

Since the normal velocity of \( \Gamma \) in the direction of positive \( \phi \) (liquid) is given by \( v = -r, \) we shall replace \( r^0_t \) in (3.21) and subsequent equations by \( -v^0, \) and similarly for \( r^1 \) and \( v^1. \)

Subtracting this equation with the \( - \) sign from the same equation with the \( + \) sign yields
\[
[u^0_t]_{|_{\Gamma}} = -2 \lambda v^0,
\]
(3.22)

which is the Stefan condition for the lowest order approximation. If we are interested in solving an initial-boundary value problem, then with appropriate initial conditions (3.6), (3.7), (3.16), and (3.22) may be solved to give a unique value for \( u^0(x, t), r^0(x, t) \) and \( \phi^0(x, t). \)
Once \( u^0 \) and \( r^0 \) are found this way, they can be used in (3.21) to determine \( c_1(s, t) \). We now proceed toward the determination of \( U^1 \). Integrate (3.20) to obtain

\[
U^1(z, s, t) = -\lambda v^0 \Psi(z) + c_1(s, t)z + c_2(s, t),
\]

where

\[
\Psi(z) = \int_0^z \psi(z') \, dz'.
\]

Thus we obtain the expression

\[
U^1(z, s, t) = \lambda v^0 \int_0^z (\text{sgn} \, z' - \psi(z')) \, dz' - \lambda v^0 |z| + c_1(s, t)z + c_2(s, t).
\]

Now let \( z \to \infty \) and use (A.8b) to obtain (3.21) again and also

\[
u^1|_{\Gamma_{\pm}} = c_2(s, t) + \lambda v^0 \int_0^{\pm \infty} (\text{sgn} \, z - \psi(z)) \, dz.
\]

The final determination of \( u^1 \) and \( c_2 \) (hence \( U^1 \)) will be done later.

The \( O(\varepsilon) \) terms in (3.13) are

\[
\Phi^1_{zz} + f'(\Phi^0)\Phi^1 + U^1 = -\alpha v^0 \psi'(z) - \kappa^0 \psi'(z),
\]

where we have used the expression (3.2) for \( \kappa \). Let \( \Lambda = (\partial_z)^2 + f'(\psi(z)) \); then this becomes

\[
\Lambda \Phi^1 = -U^1 - \alpha v^0 \psi'(z) - \kappa^0 \psi'(z).
\]

As an operator on \( L^2(-\infty, +\infty) \), \( \Lambda \) has an eigenvalue at the origin, with eigenfunction \( \psi'(z) \). Moreover, it will be simple, so that the solvability condition for \( \Lambda \Phi = g \in L^2 \) is orthogonality of \( g \) to this same eigenfunction, which we denote by \( \psi' \) for short. We know from (A.8a), however, that it can be expected that \( \Phi^1 \) may be unbounded (growing linearly in \( z \) at \( \pm \infty \)). Nevertheless the solvability condition for (3.27) remains the same:

\[
\int \Phi^1 \psi' \, dz + (\alpha v^0 + \kappa^0) \int (\psi')^2 \, dz = 0.
\]

Now the substitution of (3.23) into (3.28) gives the function \( c_2(s, t) \) uniquely, hence \( U^1 \), since everything else in (3.24) is known. Specifically, we use the oddness of \( \psi \) (which follows from the oddness of \( f' \)) to obtain

\[
c_2 = v^0 \left[ \frac{\Lambda}{2} \int_{-\infty}^{\infty} \Psi(z) \psi'(z) \, dz - \frac{1}{2} \alpha A \right] - \frac{1}{2} \kappa^0 A,
\]

where \( A = \int_{-\infty}^{\infty} (\psi')^2 \, dz \). From this and (3.25), we calculate that

\[
u^1|_{\Gamma_{\pm}} = v^0 \left[ \Lambda B - \frac{1}{2} \alpha A \right] - \frac{1}{2} A \kappa^0,
\]

where

\[
B = \int_0^{\infty} (1 - \psi(z))^2 \, dz.
\]

If \( f \) is not odd, then a similar formula is obtained; in that case it is interesting to note that in general \( u^1_{\pm} \neq u^1_{\pm} \), i.e., the outer temperature is discontinuous.

This formula (3.30) is our most important conclusion; it is the dynamic analogue of the Gibbs–Thompson relation. The significance of the various terms will be discussed in the next section. For now we proceed with the asymptotic development.
The right side of (3.30) is a known function of \( s \) and \( t \), \( v^0 \) and \( \kappa^0 \) having been determined at the stage of the zeroth order Stefan problem. It provides the needed boundary conditions at the interface to be used with (3.8), (3.9), and the imposed boundary and initial conditions in the unique determination of \( u^1(x, t) \) on both sides of the interface. If the imposed initial and boundary conditions do not depend on \( \varepsilon \), then those conditions for \( u^1 \) are homogeneous.

Since \( U^1 \) is now known, the function \( \Phi^1 \) can be found uniquely from (3.27), the condition (from (3.6)) that it vanish when \( z = 0 \), and that it satisfy the required behavior at \( \pm \infty \). The latter, obtained from (A.8b) applied to \( \Phi \), turns out to be the same as we obtain directly from (3.27), letting \( z \to \pm \infty \), \( \Phi_{zz} \to 0 \), and using the known asymptotic properties of \( U^1 \). The orthogonality condition having been imposed, we obtain a unique solution \( \Phi^1 \).

We now have the functions \( u, \phi, U, \Phi \) to orders 0 and 1, and \( r \) to order 0.

Equations (3.12) and (3.16) imply that

\[
U^2_{zz} = -v^0(U^1 + \lambda \Phi^1)_z - v^1 \lambda \psi - \kappa^0 U^1_z,
\]

use having been made of the fact that \( U^0 = 0 \) and \( \Phi^0 \) depends only on \( z \). Hence we obtain

\[
U^2_z = -v^0(U^1 + \lambda \Phi^1) - v^1 \lambda \psi - \kappa^0 U^1 + c^*_i(s, t).
\]

The terms on the right of (3.33) not involving \( v^1 \) or \( c^*_i \) were previously determined and have known linear behavior as \( z \to \pm \infty \). Let us call the behavior of the sum of these terms \( A_\pm + B_\pm z \). Thus for large \( z \)

\[
U^2_z = A_\pm + B_\pm z \pm v^1 \lambda + c^*_i.
\]

But from (A.8c), we know that the left side has asymptotic behavior

\[
((u^1_r + u^0_r r^1) + zu^0_r)_{z=\pm} \quad (z \to \pm \infty).
\]

In particular,

\[
(u^1_r + u^0_r r^1)_{z=\pm} = A_\pm \pm v^1 \lambda + c^*_i
\]

and

\[
u^0_r|_{z=\pm} = B_\pm.
\]

It turns out that (3.37) can be obtained independently by evaluating (3.6), (3.7) at \( r = 0 \), so it imposes no additional constraints. On the other hand, (3.36) serves to specify \( r^1(x, t) \) and \( c^*_i \). Namely, taking differences between the + and the − equation and using the fact that \( v^1 = -\partial r^1 / \partial t \) eliminates \( c^*_i \) and gives a first order differential equation for \( r^1 \), which can be solved, given the initial condition \( r^1(x, 0) = 0 \). Then \( c^*_i(s, t) \) is obtained from (3.36). After that, (3.33) is integrated to obtain \( U^2(z, s, t) \), modulo an integration constant \( c^*_i(s, t) \). The latter is obtained by writing the equation for \( \Phi^1 \) and applying the usual solvability condition. This completes the determination of \( U^2(z, s, t) \).

The higher order terms are found in a similar fashion.

4. The dynamical Gibbs–Thompson relation. Equation (3.30) relates the temperature \( u = \varepsilon u^1 \) at the interface to its normal velocity and curvature. It represents an \( O(\varepsilon) \) correction to the Stefan model, for which the temperature is zero there. It reduces to the static Gibbs–Thompson relation when \( v^0 = 0 \).

The terms in that equation have a clear meaning. In phase field models, a change of state is interpreted as a transition from one potential well to another when some stimulus enables the barrier between them to be surmounted. The relaxation parameter
\(\alpha\) (rather than \(\tau\), which is proportional to \(\alpha\)) is roughly a measure of the time it takes to reach the new state once its domain of attraction has been penetrated. On the other hand, the ease of penetration of that domain depends on the temperature. Consider now a planar solidification front advancing into the liquid region in a material with zero latent heat \((\lambda = 0)\). Suppose the temperature is constant. Consider space to be one-dimensional (in the direction of the advancing front). A subzero interfacial temperature is necessary and sufficient in order for a solidification event occurring at one site to be able to stimulate a similar change at nearby locations, and so by the domino effect to produce the chain reaction responsible for the advancing front. In this sense, the temperature induces a tendency to change state. The velocity of the front will increase when the temperature is lowered further from zero, and will be reduced when the relaxation parameter \(\alpha\) is increased. These effects are in fact simple proportionality relations in our approximation: the velocity of the front is proportional to the temperature and inversely proportional to \(\alpha\). This relation is precisely \((3.30)\) when \(\lambda = \kappa = 0:\)

\[ u^1 = -C_1 v^0 \alpha \quad (C_1 = \frac{1}{2} A). \]

Next, consider the same situation, except that the front is curved. Then in a circular neighborhood of a point on \(\Gamma\), there will be slightly more material in one phase than in the other, and so there will be unequal influences from the two phases at nearby locations. The effect of this discrepancy is to shift the temperature influence in the above mentioned relations: what was true for a planar front at temperature \(u^1\) is now true of a curved front at the temperature \(u^1 + C_2 \kappa\), where in fact \(C_2 = \frac{1}{2} A\). We thus have

\[ u^1 + C_2 \kappa^0 = -C_1 v^0 \alpha. \]

This accounts for the last term in \((3.30)\).

Finally, we consider the case when there is nonzero latent heat \((\lambda \neq 0)\). Then the Stefan condition \((3.22)\), which governs the interface at leading order, specifies a discontinuity in the normal derivative of \(u\) across \(\Gamma\). This means in particular that \(u\) is not constant there. Then the correct temperature \(u^1\) to use in \((4.1)\) is a certain local weighted average of temperature across \(\Gamma\), which has finite thickness of order \(\varepsilon\). (In fact, the weighting function is seen from \((3.28)\) to be \(\psi'\).) Moreover, in the next approximation \((O(\varepsilon))\), the Stefan discontinuity in \(u\) is smoothed out across \(\Gamma\) into a convex temperature profile, as a function of the normal coordinate \(z\). The degree of convexity is proportional to the discontinuity \(\lceil u_r \rceil\), hence by \((3.22)\) to \(\lambda \nu^0\). As a result, the actual local average temperature does not coincide with the limit of the macroscopic (outer) temperature as the interface is approached from either side (see Fig. 1). This
discrepancy is $O(\varepsilon)$ and, as mentioned, is proportional to $\lambda v^0$. As a result, if in (4.1) we interpret the symbol $u^1$ as the limit of the macroscopic temperature as the interface is approached, then the formula must be modified by a term as just described, so that now (4.1) is replaced by

$$u^1 + C_2 \kappa^0 - C_3 v^0 \lambda = -C_1 v^0 \alpha \quad (C_3 = B).$$

This reconstitutes and explains all the terms in (3.30). Of course, these effects depend to some extent on the particular form of the double well term $f$. But to this approximation, that influence is seen only through the constants $A$ and $B$.

It should be noted that there is a definite competition between the effect of the latent heat ($\lambda$) and that of the relaxation time $\tau$ seen on the right side of (3.30). In the planar case, for example, the coefficient in the linear relationship between $u^1$ at the interface and $v^0$ may be of either sign, depending on the relative magnitudes of those two parameters.

5. Generalizations of the model. Recall that the leading order outer problem (3.6), (3.7) was handled by first solving (3.7):

$$\phi^0 = -f^{-1}(u^0),$$

the inverse functions here denoting the branch near $\phi^0 = 1$, and then substituting into (3.7) to obtain

$$(u^0 - \lambda f^{-1}(u^0)) = \Delta u^0,$$

which is a nonlinear diffusion equation for the heat distribution in the liquid region. A similar equation holds in the solid region. Note that the nonlinearity here comes from the supposition that changes in temperature induce changes in $\phi$ through (3.7), which in turn act as heat sources or sinks through the second term on the left of (3.6) or (2.1).

It may be objected that the material should support an approximately linear law of heat transport. Certainly such a linear law has been the usual way to model this transport. Irrespective of whether the correct law is linear or nonlinear, it should be pointed out here that minor generalizations of the basic formalism can be designed to provide practically any law that we desire. That procedure will now be described.

The heat source term $\phi$, in (2.1) has been written so that the heat produced or absorbed by changes in $\phi$ depends linearly on that change:

$$dq = \lambda \, d\phi.$$

There is a no a priori reason why this should be true. Equally well, one could posit

$$dq = \lambda \, dp(\phi)$$

for some monotone increasing function $p$, satisfying

$$p(1) = 1, \quad p(-1) = -1.$$  

Then (2.1) would be replaced by

$$u_r + \lambda p(\phi)_r = \Delta u,$$

and (5.1) replaced by

$$(u^0 - \lambda p(f^{-1}(u^0))) = \Delta u^0.$$  

Now the function $p$ can be chosen to produce a wide variety of composed functions $pf^{-1}$, for example, it is easy to choose $p$ and $f$ so that $pf^{-1}$ is a linear function. Moreover, if $p$ is constant or almost constant in neighborhoods of $\phi = \pm 1$, then the nonlinear term in (5.6) vanishes altogether.
This generalization has no qualitative effect on the other results in § 3. For example, in (3.25), \( \psi \) would be replaced by \( p(\psi) \), and in (3.30) only the definitions of the constants \( A \) and \( B \) would change.

Another modeling approach to ensuring the outer problem is nearly linear involves requiring that the function \( f \) be very steep near \( \phi = \pm 1 \). Then \( f^{-1}(\phi) \) is very small.

As mentioned before, the phase field equations can be derived formally from discrete lattice models. Retaining only the lowest order interaction terms in those models results in a second order elliptic operator for \( L_\varepsilon \) in (1.1); it is the Laplacian in the isotropic case. Keeping higher order terms gives higher order operators, as is seen in [4]. Most of the analysis in § 3 may be done for such appropriate higher order operators. Analogous inner and outer approximations may be set up. Difficulties, however, arise in connection with (3.15). Although there is a complete theory of that equation, an analogous theory for the higher order analogues is nonexistent. To continue the analysis of § 3, we must assume a solution \( \psi \) exists to the analogue of (3.18), and moreover assume that the zero eigenvalue of the analogue of the operator \( \Lambda \) in (3.27) is simple.

These are the only places that the development of § 3 cannot be immediately generalized to the higher order case, and with those assumptions the final results are essentially the same as before.

6. Slowly moving interfaces. The development in § 3 changes somewhat when the temperature \( u \) is assumed to be everywhere small of order \( \varepsilon \). Specifically, suppose that the initial and boundary conditions are such that the leading order outer function \( u^0 = 0 \). Then from (3.22), \( v^0 \) is zero as well, so that \( v = O(\varepsilon) \). It is then appropriate to look for solutions which vary slowly in time.

Accordingly, we introduce a slow time variable

\[ t' = \varepsilon t \]

and assume that all time dependences are on that time scale. Thus the time derivatives in (2.1) and (2.2) are to be replaced by \( \varepsilon \partial / \partial t' \).

From (3.7), we have

\[ \phi^0 = \pm 1, \]

and (3.8), (3.9) now become

\[ \Delta u^1 = 0, \quad \phi^1 = -u^1(f'(\pm 1))^{-1}. \]

The first of these equations is to be solved in both outer regions under the imposed boundary conditions, and also under the interface condition obtained from (3.30) with \( v^0 = 0 \):

\[ u^1|_{\Gamma} = -\frac{1}{2}A\kappa^0, \quad (6.1) \]

which is the stationary Gibbs–Thompson relation. To first order, therefore, the outer problem is the stationary problem considered in [6]. As for the inner problem, \( \phi^0 \) is the same as before.

The slow motion of the interface is found only at the \( O(\varepsilon^2) \) stage, from (3.36) in which \( u^0 = 0 \). This in fact provides \( v^1 \) in terms of the jump discontinuity in the normal derivative \( u^1_i \).

The picture which emerges is a slowly moving interface \( \Gamma \) whose velocity at each instant of time is found by solving a Dirichlet problem for the temperature \( u^1 \) in the two regions on either side of \( \Gamma \), the Dirichlet condition on \( \Gamma \) being of Gibbs–Thompson type, then finding \( [u^1_i] \), and calculating the velocity from that.
The motion can be reduced to quadratures in the special case of a radially symmetric problem in an annulus. Let \( r \) now denote distance from the origin in the annulus \( \Omega = \{ r_1 < r < r_2 \} \). Let the boundary conditions be 
\[
    u(r_1) = \varepsilon u_1(r_1) = \varepsilon a, \quad u(r_2) = \varepsilon u_1'(r_2) = \varepsilon b.
\]
Let \( \rho(t') \) be the position of the interface. Then from (6.1) we have 
\[
    u_1'(\rho) = -\frac{1}{2} \mathcal{A} \rho^{-1}.
\]

The solution of the Laplace equation under these boundary conditions is, for each fixed \( \rho \),
\[
    u_1(\rho) = C_1 + C_2 \ln r, \quad r \leq \rho, \quad u_1(\rho) = C_1' + C_2' \ln r, \quad r \geq \rho,
\]
where
\[
    C_1(\rho) = \frac{a \ln \rho}{\ln \rho/r_1} + \frac{A \ln r_1}{4 \rho \ln \rho/r_1}
\]
and \( C_2(\rho), C_1'(\rho), C_2'(\rho) \) are similar expressions. Now
\[
    [u_1'(\rho)] = \rho^{-1}(C_2(\rho) - C_2'(\rho)) = M(\rho).
\]
In (3.36) in the present case we have \( u^0 = 0 \) and \( A_+ = A_- \), so taking differences,
\[
    v_1 = \frac{\partial \rho(t')}{\partial t'} = \frac{1}{2\lambda}[u_1'] = \frac{M(\rho)}{2\lambda}.
\]

This differential equation may now be integrated to determine the trajectory \( \rho(t') \).

**Appendix: Matched asymptotics for a moving internal layer.** The matching conditions are with respect to only the coordinate normal to the layer, and it suffices to treat the one-dimensional case. The relations are exactly the same for a layer moving in several dimensions. So let \( x \) be one-dimensional, and let \( u(x, t, \varepsilon)(\varepsilon \ll 0) \) be a function with internal transition layer with width \( O(\varepsilon) \) at \( x = Y(t, \varepsilon) \). This may possibly be defined as the location where \( u = 0 \), for example.

**Outer expansion.** For \( x \neq Y \), we set 
\[
    u(x, t, \varepsilon) = u^0(x, t) + \varepsilon u_1(x, t) + \cdots.
\]
We allow the terms on the right side, or their derivatives, to be discontinuous at \( x = Y \), but require them to be smooth otherwise. We employ symbols + and − to denote limits of various functions (or their derivatives) as \( x \) approaches \( Y \) from the right or left, respectively.

**Inner expansion.** We define
\[
    u = U(z, t, \varepsilon),
\]
where \( z = (x - Y(t))/\varepsilon \). Expand
\[
    U(z, t, \varepsilon) = U^0(z, t) + \varepsilon U_1(z, t) + \cdots,
\]
\[
    Y(t, \varepsilon) = Y^0(t) + \varepsilon Y_1(t) + \cdots.
\]

**Matching relations.** Near the layer, we formally equate the two expansions:
\[
    U(z, t, \varepsilon) = u(Y(t, \varepsilon) + \varepsilon z, t, \varepsilon)
\]
and expand the right side in Taylor series in \( \varepsilon \). There results:
\[
    U(z, t, \varepsilon) = \sum_{n=0}^{N} \varepsilon^n P_n(z, t) + \varepsilon^{N+1} R_N,
\]
where

\begin{equation}
P_n(z, t) = \frac{1}{n!} \frac{\partial^n}{\partial \varepsilon^n} u(Y(t, \varepsilon) + \varepsilon z, t, \varepsilon)_{\varepsilon=0},
\end{equation}

and $R_N = \text{(similar expression, with } n = N + 1 \text{ and evaluated at some } \varepsilon \text{ rather than } \varepsilon = 0)$. It is clear from (A.6) that for $z > 0$, $P_n$ is a polynomial in $z$ of degree $n$ with coefficients depending on the $Y^m(t)$ and their derivatives, and (linearly) on the $u^k(Y^0(t)+, t)$, $u^k_+(Y^0(t)+, t)$, $u^k_+(Y^0(t)+, t)$, etc. A similar statement holds when $z < 0$. Therefore, the functions $P_n$ will in general be discontinuous at $z = 0$, being polynomials on either side. To make this clear, we may on occasion write them as $P_n^\pm(z, t)$.

We now pass to the limit $z \to \pm \infty$, with $\varepsilon$ related to $z$ so that $\varepsilon z^{N+1} \to 0$, but otherwise in an arbitrary manner. On the assumption that the x-derivatives of the outer function $u$ up to order $N - 1$ are all bounded in the domain $\{x \neq Y(t)\}$, we have that the remainder term in (A.5) is of lower order than any of the preceding terms in (A.5).

On the left of (A.5), expand in the formal series (A.2). In view of the distinguished limit under consideration, and the arbitrariness of the relation between $\varepsilon$ and $z$ subject to the above restriction, we identify the behavior, for large $z$, of the functions $U^n(z, t)$ with the polynomials $P_n(z, t)$:

\begin{equation}
U^n(z, t) = P_n^\pm(z, t) + o(1) \quad (z \to \pm \infty).
\end{equation}

In particular, it follows that the large $z$ behavior of $U^n$ must be that of a polynomial in $z$ of degree $n$. The following gives the specific results on this large-$z$ behavior for $n = 1, 2,$ and $3$. They were obtained by calculating $P_1$, $P_2$, and $P_3$ explicitly:

\begin{align}
U^0(\pm \infty, t) &= u^0(Y^0\pm, t), \\
U^1(z, t) &= u^1(Y^0\pm, t) + z u^0_+(Y^0\pm, t) + Y^1(t)u^0_+(Y^0\pm, t) \quad (z \to \pm \infty), \\
U^2(z, t) &= (u^2(Y^0\pm, t) + \frac{1}{2} Y^1(t)u^1_+ + Y^2 u^0_+ + \frac{1}{2} (Y^1)^2 u^0_{xx}) \\
&\quad + z(\frac{1}{2} u^1_+ + u^0_{xx} Y^1) + \frac{1}{2} z^2 u^0_{xx} \quad (z \to \pm \infty).
\end{align}

Here the arguments of the $u^l$ and their derivatives are the same as in (A.8b), and that of the $Y$'s is $t$.

REFERENCES


