An Analysis of a Phase Field Model of a Free Boundary

GUNDUZ CAGINALP

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Abstract

A mathematical analysis of a new approach to solidification problems is presented. A free boundary arising from a phase transition is assumed to have finite thickness. The physics leads to a system of nonlinear parabolic differential equations. Existence and regularity of solutions are proved. Invariant regions of the solution space lead to physical interpretations of the interface. A rigorous asymptotic analysis leads to the Gibbs-Thompson condition which relates the temperature at the interface to the surface tension and curvature.

Notations in the Order Introduced

Ω	domain containing material
$\mathbb{R}^N$	product space of reals
T_M	melting temperature
$T(t, x)$	temperature as a function of time and space
$u(t, x)$	$T - T_M$
Ω_1, Ω_2	liquid and solid regions
Γ	interface between solid, liquid
K	thermal diffusivity
$\hat{n}, \vec{v}$	unit normal, velocity of Γ
l	latent heat (per unit mass)
u_∂, u_0	boundary and initial temperatures
$H(u), \varphi$	enthalpy, phase-field
R, u_R	radius of sphere, equilibrium temperature for sphere
σ	surface tension
$\varkappa$	sum of principal curvatures
Δs	entropy density difference
$F_u\{\varphi\}$	free energy
ξ	length scale
$u_\partial, \varphi_\partial$	boundary values
u_0, φ_0	initial values

τ	relaxation time
U	$\begin{pmatrix} u \\ \varphi \end{pmatrix}$
A	matrix coefficient of Δ
$F(U)$	source term
U_0, U_∂	initial and boundary data
$\mathscr{B}$, BC	Banach space, bounded uniformly continuous functions
C^∞	infinitely differentiable functions
$\|\cdot\|_{\mathscr{B}}$	norm associated with $\mathscr{B}$
$\|\cdot\|$, $\|\cdot\|_\infty$	norm, L_∞ norm
n	dimension of solution space
Σ	invariant region
δ	end of local time interval
$\mathscr{V}$	region in $\mathbb{R}^n$
w	point in $\mathscr{V}$
η	point in $\mathbb{R}^n$
D, D_i	gradient, derivative
D^2, D_{ij}	second derivatives
q	ratio
G_i	functions defining invariant region
c_i, d_i	constants in definition of G_i
$f(u, \varphi)$	$\frac{1}{2}(\varphi - \varphi^3) + \frac{1}{2} u$
Σ_0	invariant set
$\Sigma_\pm$	invariant set
x'	$x' \equiv x/\xi$
Λ	$\Lambda \equiv \bar{\Omega} \times [0, T]$
$d(P, Q)$	distance between P, Q
$v(t, x)$	function of t, x
α	Hölder exponent
$\|v\|_0^{(\Lambda)}$	sup norm
$H_\alpha^{(\Lambda)}(v)$	Hölder coefficient
$\|v\|_\alpha^{(\Lambda)}$	Hölder norm
$C_{j+\alpha}(\Lambda)$	Hölder spaces
$L^{(\Lambda)}(v)$	Lipschitz coefficient
a_{ij}, b_i, c, L	parabolic operator, coefficient
$\|v\|_{1-0}$, $\|v\|_{2-0}$	Lipschitz norms
$C_{1-0}(\Lambda)$, $C_{2-0}(\Lambda)$	Lipschitz spaces
$g(t, x)$	source term
$\partial\Lambda$, v_∂	parabolic boundary, data
H_0, H_1, H_2, H_3	bounds on ellipticity, *etc.*
V, B, G, (V)	terms in system of parabolic equations
P	matrix of constants
F_1, F_2	components of $F(U)$
$W = (w_1, w_2)$	generic vector-valued function
Ω_0	solid region
Ω_1	domains needed for defining BC on φ
$g(x)$	modification of double-well
$\bar{u}$	scaled temperature
$Q_\xi\varphi$	quasilinear operator for phase field
$O(\xi)$, $o(\xi)$	"order of" symbols
Φ_M, $\varphi_j(x, \xi)$	approximations to φ

$p(s)$	parametric representation for surface $\partial\Omega_0$
$n(s)$	normal to $\partial\Omega_0$
Ω^*	portion of $\Omega\setminus\Omega_0$
$x = p(s)$	parametric representation of $\partial\Omega_0$
r	coefficient of $n(s)$
X_M	outer expansion
χ_j	terms in outer expansion
R_1	remainder for outer expansion
C_M	constant bound
γ_k	expansion coefficient for g^2
Ψ_M, ψ_j	inner expansion
ϱ	$= r/\xi$
L_j	linear part of Q_ξ
R_2	remainder for inner expansion
$\mathscr{F}_k$	remainder terms
$h(\varrho)$	arbitrary function
a	arbitrary constant
$\mathscr{F}(\varrho)$	arbitrary source term
$P(\varrho)$, $Z(\varrho)$	decomposition of $\mathscr{F}$
$\mathscr{S}_k$	exponentially declining functions
p	polynomial
P_j, Z_j	decomposition of $\mathscr{F}_j$
Y_M	inner expansion
$R_{2,\psi}$, $R_{2,\varrho}$	remainder terms
$\zeta(x)$	mollifier
$B_k(x, \xi)$	bounding function
$\tilde{\varphi}_M$	remainder term
f_M	remainder term
$W^0_{k,2}$	Sobolev space
$L_{M,\xi}$, $N_{M,\xi}$, F_M	linear operators related to equation
$\mathscr{L}_{M,\xi}$	linear operator
$\mathscr{S}(u)$	sphere in $C(\overline{\Omega}_0)$
μ	constant
$\xi_*(M)$	critical value of ξ
$\tilde{u}$	$2\xi^{-1}\,u$
$\tilde{\Omega}$, a	portion of Ω within "a" of $\partial\Omega_0$
$\\|\cdot\\|_{2,\alpha}$ $C^{2,\alpha}$	Hölder norm and space
h_1	source term in $\Delta\tilde{\varphi}_1 = \xi^{-1}\,h_1$
L_1	$L_1 = \xi^2\Delta + \frac{1}{2}\,[1 - 3\Phi_0^2]$
$\mathscr{G}(\varphi)$	$\mathscr{G}(\varphi) \equiv \frac{1}{8}\,(\varphi^2 - 1)^2$
A	area of interface
R^*	critical radius
S	entropy
ν	measure $d(\varphi/2)$
C_0, φ^0	minimum and minimizer of $\mathscr{F}(\varphi)$
$\mathscr{F}(\overline{\varphi})$	frree energy functional
λ_0	eigenvalue of Δ
$\varphi^{(n)}$	minimizing sequence
$\tilde{\varphi}$	limit of $\varphi^{(n)}$
$\delta\mathscr{F}(\overline{\varphi})$	first variation of $\mathscr{F}$

1. Introduction

In this paper I present a mathematical analysis of a new approach to free boundary problems arising from phase transitions. In the mathematical literature such problems have been studied for over a century [1–16]. Most of the work is concerned with the classical Stefan problem [1], which incorporates the physics of latent heat and heat diffusion in a homogeneous medium.

We begin by describing the essential variables in such problems along with their physical significance. A material, which may be in either of two phases, *e.g.*, solid or liquid, occupies a region in space, $\Omega \subset \mathbb{R}^N$ [see Figure 1]. One defines $T_M \in \mathbb{R}$ as a constant which is the melting temperature at equilibrium. Physically, this is the temperature at which solid and liquid may coexist in equilibrium separated by a planar interface. One then defines the function $T = T(t, x)$ as the temperature at $(t, x) \in [0, L] \times \Omega$, where $L \in \mathbb{R}$ is an arbitrary time. For convenience, it is customary to let $u(t, x) \equiv T(t, x) - T_M$ be the reduced temperature.

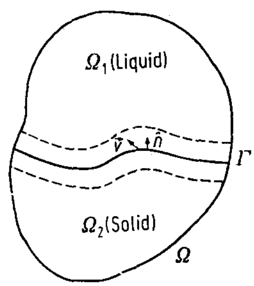


Fig. 1. A material occupying a region Ω exists in two phases: liquid (Ω_1) or solid (Ω_2). The phases are separated by an interface, Γ. The dotted lines indicate possible thickness of interface.

In the classical Stefan problem the temperature of the interface between the solid and liquid is assumed to be T_M, i.e., $u = 0$. Hence, one defines the interface, or transition region, Γ as

$$\Gamma(t) = \{x \in \Omega : u(t, x) = 0\}. \tag{1.1}$$

Furthermore, if $u(t, x) > 0$ the point, $x \in \Omega$ lies in the liquid region, Ω_1, while $u(t, x) < 0$ implies that x is in the solid phase, Ω_2.

The (reduced) temperature $u(t, x)$ must then satisfy the heat diffusion equation

$$u_t = K \Delta u \tag{1.2}$$

in Ω_1 and Ω_2. Here K is the thermal diffusivity, which is thermal conductivity divided by heat capacity per unit volume (we set heat capacity per volume equal to unity) which for simplicity is assumed to be the same constant in the solid and liquid. Introducing two distinct constants does not generally alter the mathematics significantly. In practice, the diffusivities of a typical solid and its melt usually differ by about 10%.

For any interface Γ, one defines a unit normal $\hat{n}$ (in the direction solid to liquid) at each point of Γ as well as a local velocity $\vec{v}(t, x)$. Across the interface Γ, the latent heat of fusion (per unit mass), l, must be balanced by the heat flux, i.e.,

$$l\vec{v} \cdot \hat{n} = K(\overrightarrow{\nabla u_s} - \overrightarrow{\nabla u_L}) \cdot \hat{n}, \qquad x \in \Gamma, \tag{1.3}$$

where $\overrightarrow{\nabla u_L}$ is the limit of the gradient of u at a value $x \in \Gamma$ when approached from Ω_1 (liquid) while $\overrightarrow{\nabla u_s}$ is the limit from Ω_2 (solid). Thus the right hand side of (1.3) is simply the jump in the normal component of the temperature multiplied by the thermal conductivity. The density factor multiplying the $l\vec{v} \cdot \hat{n}$ term in the latent heat equation has been set equal to one.

To complete the mathematical statement of the problem one must specify initial and boundary conditions for $u(t, x)$, e.g.,

$$u(t, x) = u_\partial(t, x) \qquad x \in \partial\Omega, \qquad t > 0, \tag{1.4}$$

$$u(0, x) = u_0(x). \tag{1.5}$$

Thus, the mathematical problem is to find $u(t, x)$ and $\Gamma(t)$ in suitable spaces satisfying equations (1.1)–(1.5). The interface $\Gamma(t)$ is often called the free boundary. One method for studying the classical Stefan problem is the enthalpy or H-method [7]. The basic idea is to introduce the function $H = H(u)$ defined by

$$H(u) \equiv u + \frac{l}{2}\varphi \qquad \varphi = \begin{cases} +1 & u > 0 \\ -1 & u < 0. \end{cases} \tag{1.6}$$

The heat-diffusion equation and the latent heat equation are then a weak formulation [7] equivalent to the single equation

$$\frac{\partial}{\partial t} H(u) = K \Delta u, \tag{1.7}$$

which is a balance of heat equation.

We will not discuss the details of this formulation but will use it as a basis for considering a more detailed model of a free boundary arising from a phase transition. First, however, it will be useful to understand how and why the physics is often more complicated than the description given by equations (1.1)–(1.5). Perhaps the most basic phenomenon one observes is that the liquid is often below its freezing point, which phenomenon is called supercooling. The analogous phenomenon for a solid is called superheating. One should emphasize that supercooling is an equilibrium phenomenon and is not merely a transient effect (altough supercooling may arise from nonequilibrium considerations as well). The origin of this phenomenon for a pure substance is in the finite size effect of the interface between the solid and liquid. The classical Stefan problem neglects the thickness of the interface between a solid and liquid and treats the physics at a purely continuum level. A simple and rough argument for appreciating these equilibrium effects as a first-order correction to the continuum theory is as follows. Suppose that $u = 0$ is the equilibrium temperature between a solid and liquid separated by a planar interface. This means that a certain amount of energy is required in order that a molecule at the surface overcome the binding energy of the crystal lattice and become part of the liquid with lower binding energy. The amount of energy required to produce this transition depends on the number of nearest neighbors in the cyrstal structure and on the number of nearest neighbors of an atom on the surface. Now suppose that the interface between the solid and liquid is curved (*e.g.*, solid protruding into liquid, which we will define as positive curvature). In this case, the molecule on the surface has fewer nearest neighbors, since some are missing due to the curvature. Hence, one expects that it will require less energy to produce the transition. Consequently, if we consider a solid with constant mean curvature, *i.e.*, a sphere, in equilibrium with its melt, then we expect the prevailing temperature to be lower. Namely $u = u_R < 0$ where R is the radius of the sphere. A more detailed version of this argument which is well known to solid state physicists and materials scientists may be found in [17]–[19]. From the nature of these arguments it is clear physically that u_R must be proportional to R^{-1} with the proportionality constant involving the surface tension, σ.

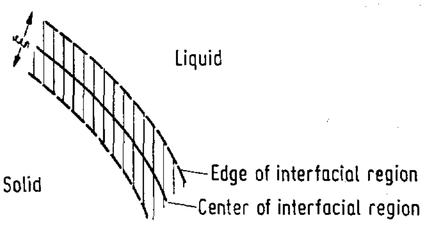
A more satisfying argument leading to the same conclusion (and further generalizations) may be obtained from statistical mechanics [20]–[23]. By equating free energies and chemical potentials of the solid sphere and the liquid surrounding one may obtain the same result. These ideas have led to the assertion that

$$u(t, x) = -(\sigma/\Delta s)\,\varkappa \qquad (t, x) \in \Gamma, \tag{1.8}$$

whenever one has an interface between two phases in equilibrium, where $\varkappa$ is the sum of the principal curvatures, and Δs is the difference in entropy between solid and liquid per unit volume. For simplicity we will choose units of energy and temperature so that $\Delta s = 4$ (unit of energy)/(degree of temperature). We will suppress the dimensions of entropy. Equation (1.8) is known as the Gibbs-Thompson relation for surface tension and will follow mathematically from the analysis of the model we will discuss.

Having accepted the Gibbs-Thompson relation as the condition to be satisfied at the interface, one may consider using equations (1.2) and (1.3) along with (1.8) as a mathematical description of the physics. Although these equations should be a good approximation for most purposes, there is one aspect which is physically unappealing. In patricular, the Gibbs-Thompson relation arises specifically from the finite thickness of the interface. This means that the change of phase is occurring continuously within a finite range [see Figure 2(a), shaded region]. Thus, if the interface is moving, one cannot expect the heat equation for a homogeneous medium to hold exactly within this region [shaded region] as it would for a sharp interface. Viewing this from the H-method formulation makes the sharp interface correspond to a phase function φ which is a step function [eqn. (1.6)]; while the phase function for an interface with finite thickness should have the qualitative behavior shown in Figure 2(b), *i.e.*, a smooth function from $\varphi = -1$ (solid) to $\varphi = +1$ (liquid). Thus the heat balance should have the form (1.7) where φ is no longer the step function but a smooth function to be determined from physical considerations concerning such phase transitions.

The phase field function, φ, within this interpretation, is basically a local average of the phase. In statistical mechanics, a model in which atoms are assumed



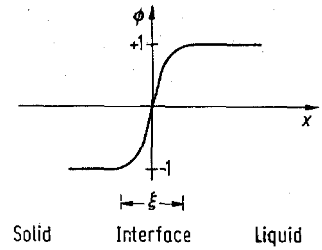


Fig. 2. An interfacial region with finite thickness ξ is shown in (a). A possible phase parameter, φ, for this interface is illustrated in (b).

to interact with a mean field created by the other atoms is known as a mean field theory [24]–[26]. One such theory is the Landau-Ginzburg theory of phase transitions [24]. In this context the free energy may be written as

$$F_u\{\varphi\} \equiv \int d^N x \left[\tfrac{1}{2}\xi^2 (\nabla\varphi)^2 + \tfrac{1}{8}(\varphi^2 - 1)^2 - 2u\varphi\right] \tag{1.9}$$

where ξ is a length scale and, at the microscopic level, is a measure of the strength of the bonding. The term involving $(\nabla\varphi)^2$ is the basic interaction term while $\frac{1}{8}(\varphi^2 - 1)^2$ is a prototype double well potential common to many statistical mechanics and quantum field theory models. This double well potential indicates a lower free energy associated with the values $\varphi = \pm 1$ (pure solid or liquid) than the intermediate values corresponding to transitional states. The double well potential may be modified in many different ways to incorporate different physics while retaining the features necessary for our analysis. The last term in (1.9), which introduces the coupling between u and φ, may be understood best as the part of the free energy which corresponds to the component which is generally written as temperature times change in entropy. The ideas involved in formulating and interpreting such free energies arising from Landau-Ginzburg theory have appeared in several papers in the literature of physics (*e.g.*, see [17]–[29]).

In the context of statistical mechanics, the correct function φ which occurs in equilibrium (*i.e.*, time independent cases in the language of differential equations) is that which minimizes the free energy among some suitable class of functions. The Euler-Lagrange equations imply the identity:

$$0 = \xi^2 \Delta\varphi + \tfrac{1}{2}(\varphi - \varphi^3) + 2u. \tag{1.10}$$

Consequently, in equilibrium, this equation is combined with the time independent heat balance equation (1.7), *i.e.*,

$$0 = \Delta u. \tag{1.11}$$

Thus a system is in equilibrium if (u, φ) satisfies (1.10), (1.11) subject to appropriate boundary conditions, *e.g.*,

$$u(x) = u_\partial(x) \qquad x \in \partial\Omega \tag{1.12}$$

$$\varphi(x) = \varphi_\partial(x) \qquad x \in \partial\Omega. \tag{1.13}$$

For the non-equilibrium or time-dependent situation, φ will not minimize $F_u\{\varphi\}$ but will differ by a term proportional to φ_t. In Landau-Ginzburg theory, this is known as the Model A equation [30]:

$$\tau\varphi_t = \xi^2 \Delta\varphi + \tfrac{1}{2}(\varphi - \varphi^3) + 2u \tag{1.14}$$

where τ is a relaxation time. The right hand side is often expressed as $-\delta F/\delta\varphi$. This equation is now coupled with (1.7)

$$u_t + \tfrac{1}{2}\, l\, \varphi_t = K\Delta u. \tag{1.15}$$

With the initial conditions

$$u(0, x) = u_0(x) \quad x \in \Omega, \tag{1.16}$$

$$\varphi(0, x) = \varphi_0(x) \quad x \in \Omega, \tag{1.17}$$

the system (1.12)–(1.17) specifies the mathematical problem to be studied in the time-dependent case. The subsequent sections will involve a mathematical analysis of these equations as well as the time-independent equations (1.10)–(1.13).

These equations have been studied by numerical computation [31], with physically reasonable results. One of the interesting features of physical systems with supercooling is that they tend to have Mullins-Sekerka shape instabilities or dendritic growth [32]–[35]. These are spikes which occur on spikes, *etc.* A simple way to understand this physically is to imagine a protrusion into the liquid which is supercooled with the temperature decreasing as one moves away from the solid. Assume also that solid temperature is fixed at $u = 0$. If the governing equations are (1.1)–(1.5), *i.e.*, no surface tension is present, then the protrusion will have a larger temperature gradient and by (1.3) will advance faster than neighboring parts of the interface. Thus, protrusions tend to become larger, which is the basis of the instability. A precise quantitative discussion of these ideas may be found in [34].

The effect of surface tension is to act as a stabilizing force. In the phase field model (1.12)–(1.17) the surface tension is proportional to ξ (this is shown in Section 7). Hence by adjusting ξ one may observe the competition between supercooling which tends to promote instabilities and surface tension which tends to suppress them.

Numerical studies of dendritic growth by solving equations (1.2), (1.3) and (1.8) have also been performed [35]. Although physically reasonable results were obtained, the curvature condition resulted in a vague resolution of the boundary. The numerical procedures also included some mathematically *ad hoc*, though physically plausible, features.

Numerical studies of the phase field equations (1.12)–(1.17) avoid the problem of tracking an interface. I hope that these equations will help bridge the gap between a molecular understanding of a material and the properties of the interface between two of its phases. Statistical mechanics currently provides a reasonable procedure to obtain a free energy of the form (1.9). Although such a free energy is not rigorously derived from the basic idea in statistical mechanics, *i.e.*, a partition function over energy states, it is nevertheless widely believed to contain the relevant physics for such problems so long as one avoids subtleties such as the critical temperature. I hope that further rigorous results will eventually strengthen the connection between molecular physics and mean field free energies of the form (1.9). The relationship between a free energy in the form (1.9) and the resulting macroscopic behavior is then basically a mathematical problem. With a combination of rigorous analysis and numerical methods, one may hope to obtain a satisfying understanding of the macroscopic behavior in a broad range of problems in volving solidification.

The outline of the remainder of the paper is as follows. In Section 2 we use invariant set theory to obtain *a priori* bounds on sup $|u|$ and sup $|\varphi|$ in equations (1.12)–(1.17) for suitable values of τ and ξ. When combined with classical methods using integral expression, this leads to a global existence theorem. The ideas about invariant sets also provide insight into the physical situation and the numerical calculations. They provide a criterion for determining the interfacial region, and indicate values of τ, ξ for which various values of φ will be stable points.

In Section 3 we use Schauder-type estimates on equations (1.12)–(1.17) as well as (1.10)–(1.13) to obtain bounds on the derivatives of φ which are of the form

$$\left|\frac{\partial\varphi}{\partial(x/\xi)}\right| < C, \qquad \left|\frac{\partial^2\varphi}{\partial(x/\xi)^2}\right| < C. \tag{1.18}$$

These bounds indicate that the interface does not become increasingly sharper for long times. Estimates (1.18) also provide the basis for studying the behavior of the equations for small ξ.

In Sections 4, 5 and 6 we analyze the time-independent equations (1.10)–(1.13) for small ξ. The basic method is a rigorous matched asymptotic analysis.

In Section 7 we use the results of Sections 4 and 5 to show that the Gibbs-Thompson relation for surface tension (1.8) must be valid in an appropriate asymptotic sense. I also suggest generalizations of this relation under different circumstances.

In Section 8 we apply some variational methods to equations (1.10)–(1.13) in situations for which ξ is not necessarily small.

2. Invariant Regions for Phase Field Equations

Equations (1.14)–(1.15) may be written in a more standard mathematical form by use of a substitution for φ_t such as

$$U_t = A\,\Delta U + F(U) \tag{2.1}$$

where

$$U \equiv \begin{pmatrix} u \\ \varphi \end{pmatrix}, \quad A \equiv \begin{pmatrix} K & -l\xi^2/2\tau \\ 0 & \xi^2/\tau \end{pmatrix},$$
$$F(U) \equiv [\tfrac{1}{2}(\varphi - \varphi^3) + 2u]\frac{1}{\tau}\begin{pmatrix} -l/2 \\ 1 \end{pmatrix}. \tag{2.2}$$

We write the boundary and initial conditions (1.12), (1.13) and (1.16), (1.17) as

$$U(t, x) = U_\partial(x), \quad x \in \partial\Omega, \tag{2.3}$$

$$U(0, x) = U_0(x), \quad x \in \Omega. \tag{2.4}$$

Our first objective is to prove a global existence theorem for equations (2.1)–(2.4) [equivalently, equations (1.12)–(1.17)]. For simplicity we assume Ω is convex and $\partial\Omega$ is C^∞. We let $\mathscr{B}$ be a suitable Banach space with norm $\|\cdot\|_{\mathscr{B}}$, *e.g.*,

$$\mathscr{B} = BC = \{\text{bounded, uniformly continuous functions on } \Omega\}. \tag{2.5}$$

We define $C([0, T]; \mathscr{B})$ as the Banach space of continuous functions on $[0, T]$ with values in $\mathscr{B}$, with norm

$$\|U\| = \sup_{0 \leqq t \leqq T} \|U(t)\|_{\mathscr{B}}. \tag{2.6}$$

Other Banach spaces such as $BC \cap L_p$ $(p \geqq 1)$ are also possible (see [21] for details). In this Banach space and integral representation and an application of BANACH'S fixed-point theorem leads to the following conclusion for small times [21]:

Theorem 2.1 (Existence in small time). *Let* $U_0 \in \mathscr{B}$. *Then there is a positive* t_0, *depending only on* F *and* $|U_0|_\infty$, *such that* (2.1) *has a unique solution* U *in* $C([0, t_0]; \mathscr{B})$ *and* $\|U\| \leqq 2\|U_0\|_{\mathscr{B}}$. □

To prove a global existence theorem, *i.e.*, the existence of a solution on $0 \leqq t \leqq T$ for arbitrary finite time T, one needs to prove an *a priori* bound. Namely, one must show that there is a constant C, depending only on $\|U_0\|_\infty$, such that if U is any solution of (2.1), (2.4) in $0 \leqq t \leqq T$, then $\|U(\cdot, t)\|_\infty \leqq C$. Hence the local solution may be continued for arbitrarily large T if one has an *a priori* bound. More precisely, one has

Lemma 2.2. *Suppose* $U_0 \in \mathscr{B}$. *If the solution in Theorem 2.1 has an* a priori *bound in the* L_∞ *norm on* $0 \leqq t \leqq T$, *then the solution* U *of* (2.1) *and* (2.4) *exists for all* $t \in [0, T]$ *and* $U(\cdot, t) \in \mathscr{B}$ *for* $0 \leqq t \leqq T$. □

To establish an *a priori* bound, we shall use the idea of invariant regions [36]–[41]. The necessary definitions and theorems of invariant regions are as follows. Consider any problem of the form (2.1), (2.3), (2.4). More general boundary conditions may also be considered. We assume that this problem has a local solutoin in time on some set $X: \Omega \to \mathbb{R}^n$. The topology on X should be at least as strong as the compact-open topology (*i.e.*, uniform convergence on compact subsets of Ω).

Definition 2.3. A closed subset $\Sigma \subset \mathbb{R}^n$ is called a (positively) invariant region for the local solution of (2.1), (2.3) and (2.4) in $t \in [0, \delta)$ if any solution having all of its boundary values and initial values in Σ satisfies $U(t, x) \in \Sigma$ for all $(t, x) \in [0, \delta) \times \Omega$. □

The invariant regions may be specified as the intersection of half-spaces, *i.e.*,

$$\Sigma = \bigcap_{i=1}^{m} \{U \in \mathbb{R}^n : G_i(U) \leqq 0\} \tag{2.7}$$

where the $G_i : \mathscr{V} \to \mathbb{R}$ are smooth real-valued functions defined on bounded open subsets $\mathscr{V} \subset \mathbb{R}^n$.

We define DG as the gradient of G; given $w \in \mathscr{V} \subset \mathbb{R}^n$ and $\eta = (\eta_1 \ldots \eta_n) \in \mathbb{R}^n$, we define the inner product:

$$DG_w(\eta) \equiv \sum_{i=1}^{n} D_i G_w \eta_i \tag{2.8}$$

where G_w indicates G is evaluated at w, D_i indicates differentiation with respect to the i^{th} component. Similarly, let D^2 be the matrix $[D_{ij}]$ and define the tensor product

$$D^2 G_w(\eta, \eta) = \sum_{i=1}^{n} \sum_{j=1}^{n} D_{ij} G_w \eta_i \eta_j. \tag{2.9}$$

Definition 2.4. A smooth function $G : \mathbb{R}^n \to \mathbb{R}$ is called quasiconvex at w if $DG_w(\eta) = 0$ implies $D^2 G_w(\eta, \eta) \geqq 0$.

We shall need some kind of continuous dependence of the solutions of (2.1) on the function F. This is expressed in

Definition 2.5. The system (2.1), (2.3), and (2.4) is F-stable if $F_n \to F$ in the C^1 topology on compacta implies that any solution U of (2.1), (2.3) and (2.4) is the limit, in the compact-open topology, of functions U_n which are solutions of equations (2.1), (2.3), and (2.4) with F_n replacing F. □

Remark. Since the matrix A is constant, in our case it is clear that the system (2.1)–(2.4) is F-stable. A simple proof may be constructed by diagonalizing A and using Green's representation [42] on each equation.

The basic idea is to examine the flow in (u, φ) space as a function of time. The aim is to find regions such that the flow at the boundaries of the region is directed inward.

We shall use the following theorem, which is proved in [38]:

Theorem 2.6 (Invariant regions). *Let Σ be defined as in* (2.7), *and let A be a positive definite matrix. Suppose that* (2.1) *is F-stable. Then Σ is an invariant region for* (2.1) *if and only if the following conditions hold at each* $U_0 \in \partial\Sigma$ (i.e., $G_i(U_0) = 0$ *for some* i):

(i) DG_i is a left eigenvector of A (2.10)

(ii) G_i is quasi-convex at U_0 (2.11)

(iii) $DG_i(F) \leqq 0$. (2.12)

□

We proceed to apply this lemma to our problem: equations (2.1) and (2.2). One left eigenvector of A is (0, 1) with eigenvalue ξ^2/τ. The other is $(1, q)$ with eigenvalue K, provided

$$q = \frac{l\xi^2/2\tau}{(\xi^2/\tau) - K} \qquad \left(\frac{\xi^2}{\tau} \neq K\right). \tag{2.13}$$

The functions G_i in Theorem 2.6 must satisfy

$$DG_i = C(0, 1) \quad \text{or} \quad DG_i = C(1, q). \tag{2.14}$$

Thus any invariant region must have a boundary consisting of vertical lines and lines of slope q, and so we let

$$G_1 \equiv c_1\varphi + d_1, \tag{2.15}$$

$$G_2 \equiv c_2(u + q\varphi) + d_2, \tag{2.16}$$

$$G_3 \equiv c_3\varphi + d_3, \tag{2.17}$$

$$G_4 \equiv c_4(u + q\varphi) + d_4, \tag{2.18}$$

thereby satisfying condition (i) of Theorem 2.6. The quasiconvexity condition is trivially satisfied since the G_i are linear in u and φ. To determine the conditions under which (iii) is satisfied, we compute:

$$DG_1(F) = (0, c_1) \cdot F = \frac{c_1}{\tau}\left[\tfrac{1}{2}(\varphi - \varphi^3) + 2u\right], \tag{2.19}$$

$$DG_3(F) = (0, c_3) \cdot F = \frac{c_3}{\tau}\left[\tfrac{1}{2}(\varphi - \varphi^3) + 2u\right], \tag{2.20}$$

$$DG_2(F) = c_2(1, q) \cdot F = \frac{c_2}{\tau}\left[\tfrac{1}{2}(\varphi - \varphi^3) + 2u\right]\left(-\frac{l}{2} + q\right), \tag{2.21}$$

$$DG_4(F) = c_4(1, q) \cdot F = \frac{c_4}{\tau}\left[\tfrac{1}{2}(\varphi - \varphi^3) + 2u\right]\left(-\frac{l}{2} + q\right). \tag{2.22}$$

We consider first the case in which the parameters K, ξ, τ are such that the stability inequality

$$\frac{\xi^2}{\tau} < K \tag{2.23}$$

is satisfied. This implies that the $\left(-\frac{l}{2} + q\right)$ factors in (2.21) and (2.22) are negative.

The function $f(u, \varphi) \equiv \frac{1}{2}(\varphi - \varphi^3) + 2u$ along with the c_i determine the regions of (u, φ) space in which the gradients $DG_i(F)$ are nonpositive [see Figure 2]. Thus, if we take

$$\begin{gathered} c_1 \equiv 1, \quad c_3 \equiv -1, \quad c_2 > 0, \quad c_4 < 0, \\ d_1 < 0, \quad d_3 > 0, \quad d_2 > 0, \quad d_4 < 0, \end{gathered} \tag{2.24}$$

the set Σ defined by (2.7) is a parallelipiped containing the origin.

Definition 2.7. A set Σ_0 defined by (2.7) and (2.15)–(2.18) with constants c_i, d_i satisfying (2.24) is said to be a sufficiently large parallelipiped if the following conditions hold:

(i) The parallelipiped Σ_1 contains the local maximum $(u, \varphi) = 3^{-\frac{1}{2}}(1/6, -1)$ and the local minimum $(u, \varphi) = 3^{-\frac{1}{2}}(-1/6, 1)$ of the curve $f(u, \varphi) = 0$.

(ii) The vertices of Σ_1 in the quadrants $(+, +)$ and $(-, -)$ lie on $f(u, \varphi) = 0$. □

With the G_i, c_i, d_i defined as above, the identities (2.19)–(2.22) imply (2.12) so that a sufficiently large parallelipiped Σ_0 satisfies the hypotheses of Theorem 2.6.

Definition 2.8. A set Σ_+ (Σ_-) is said to be a parallelipiped in the positive (negative) region if it is defined by (2.7), (2.15)–(2.18) and the c_i, d_i are defined in such a way that the following conditions are satisfied:

$$\text{(i) } c_1 \equiv 1, \quad c_3 \equiv -1, \quad d_1 < d_3, \quad d_3 \leqq -3^{-\frac{1}{2}} \tag{2.25}$$

$$(\text{for } \Sigma_-,\ d_1 \geqq 3^{-\frac{1}{2}}, \quad d_3 > d_1).$$

(ii) The upper right and lower left vertices of $\Sigma_\pm$ lie on $f(u, \varphi) = 0$. □

Such regions $\Sigma_\pm$ will once again satisfy (2.12) by virtue of (2.19)–(2.22). Upon examination of identities (2.19)–(2.22) in conjunction with the positive and negative regions of $f(u, \varphi)$ on the (u, φ) plane [see Figure 3], it becomes clear that any parallelipiped (other than $\Sigma_0, \Sigma_\pm$) consisting of vertical lines and lines with slope q will fail to satisfy condition (iii) of Theorem 2.6. These results are summarized in

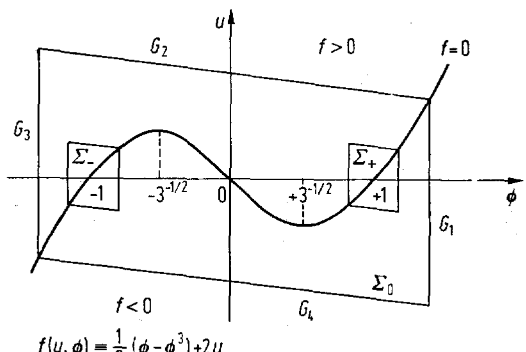


Fig. 3. The (u, φ) plane is illustrated to show invariant regions. The cubic curve, $f = 0$, divides the plane into regions $f > 0$ and $f < 0$. This determines the three types of invariant regions Σ_0, Σ_+, Σ_- as shown.

Theorem 2.9. *A region Σ is an invariant region* [*in the sense of Definition 2.3*] *for the system* (2.1)–(2.4) *if and only if Σ is either a sufficiently large parallelipiped* [*Definition 2.7*] *or a parallelipiped in the positive or negative region* [*Definition 2.9*]. □

One immediate consequence of Theorem 2.9 is the existence of an *a priori* bound for the system (2.1)–(2.4). Given any set of bounded initial and boundary conditions U_∂ and U_0 in (2.3), (2.4) we can choose a parallelipiped Σ_0 sufficiently large as to enclose all values u, φ attained in U_∂ and U_0. Since Σ_0 is a bounded invariant region this implies an *a priori* bound on u and φ. Combining this with Lemma 2.2 one has

Theorem 2.10 (Global existence). *Suppose l, K, ξ, τ are any positive constants subject to the stability inequality* (2.23). *If $U_\partial, U_0 \in \mathscr{B}$ and $T \in (0, \infty)$, then there is a unique solution U of the system* (2.1)–(2.4) *for all $t \in [0, T]$ such that $U(\cdot, t) \in \mathscr{B}$.* □

Remarks. (1) One should note that while the existence of an invariant region is a strong statement, the assertion that such a region does not exist is not so complete. The reason for this is that our definition of an invariant region does not include regions which depend on time. For example, one may not have an invariant region in the sense of Definition 2.3 but still obtain one which oscillates in time. Although this is unlikely for the system (2.1)–(2.4) if one considers directions of flow, the theorems above do not exclude it. With this word of caution we make the following observation.

(2) It is interesting to note that by virtue of Theorem 2.9, the smallest invariant region containing $\varphi = 0$ must contain $\varphi = \pm 1$. This is interesting from a physical and computational point of view. For an invariant region is stable in the sense that values within the region tend to remain there unless they are perturbed out of the region. The absence of such a region for values of φ near 0 (in fact $|\varphi| < 3^{-\frac{1}{2}}$) indicates the physical interface should not have the tendency to dominate the solid and liquid. That is, even if one started with a material which was initially in the interfacial phase (near $\varphi = 0$) one would not expect it would remain in that state indefinitely.

(3) By Theorem 2.9, one can construct invariant regions, Σ_+, which lie entirely in the positive half-plane of φ. The major restriction for such regions is that they lie in the half-plane $\varphi > 3^{-\frac{1}{2}}$. This suggests that an appropriate definition for the liquid phase is the set of points $x \in \Omega$ for which $\varphi(t, x) \geqq 3^{-\frac{1}{2}}$. The solid phase is analogously the set of those points for which $\varphi(t, x) \leqq -3^{-\frac{1}{2}}$, while the region in between ($|\varphi| < 3^{-\frac{1}{2}}$) is the interface. The interface comprises the solid part of the interface ($\varphi < 0$) and the liquid part ($\varphi > 0$). The thickness of the interface is then given by the distance between points for which $\varphi(t, x) = 3^{-\frac{1}{2}}$ and those for which $\varphi(t, x) = -3^{-\frac{1}{2}}$.

The physical basis for this type of definition, as opposed to the definition of $\varphi > 0$ as the liquid $\varphi = 0$ as the interface and $\varphi < 0$ as the solid is the following. The ideas which lead to the Gibbs-Thompson condition (1.8), described briefly in Section 1, imply that a material which is entirely in the liquid state at an arbitrary temperature will not solidify. In practice, of course, this description ceases to be valid at temperatures given by (1.8) which correspond to the curvature of a typical cluster of molecules in a liquid. Nevertheless, within this theory (which is based on ideas about mean fields) we do not expect crystallization of a liquid without a seed (*i.e.*, small solid region at initial time). Consequently, our definition of points in Σ_+ (Σ_-) as liquid (solid) is consistent with physical expectations.

Choosing any criterion other than $|\varphi| \leqq 3^{-\frac{1}{2}}$ for the interface would not yield the same physical interpretation as a material which is entirely liquid (with the alternative definition) could crystallize spontaneously, since the region would not be invariant.

(4) If the stability inequality (2.23) is not valid, it is no longer possible to construct invariant regions in the sense of Definition 2.3, though an existence proof by other means is not excluded.

(5) The invariant regions Σ_0, $\Sigma_\pm$ depend on the ratio ξ^2/τ through q, but not on ξ and τ individually.

This concludes our discussion of invariant regions and basic existence theory. We note that existence has been shown for fixed values of ξ and τ (subject to (2.23)). One of the questions of interest is the behavior of these equations in the limit of small ξ and τ. Remark (5) is one indication that the appropriate scaling limit is one which satisfies

$$C_1 \leqq \xi_i^2/\tau_i \leqq C_2 \tag{2.26}$$

where $\{\xi_i\}$ and $\{\tau_i\}$ are sequences tending to zero.

3. Regularity of Solutions, Schauder-type Estimates and Bounds on Thickness of Interface

Having proved existence of solutions of the systems of equation (2.1)–(2.4), we shall now address some closely related questions. First, we prove some statements of regularity and then use these two prove that in terms of the scaled spatial variable,

$$x' \equiv x/\xi, \tag{3.1}$$

the first and second derivatives of φ are uniformly bounded (in terms of ξ and τ)

$$C_1 \leqq \xi^2/\tau \leqq C_2. \tag{3.2}$$

In practical terms, such a result implies that an interfacial region which is initially of thickness ξ cannot become significantly sharper. This section will thereby establish the connection between the parameter ξ and bounds on derivatives of φ and the interfacial thickness. It will be shown later (Section 7) that the surface tension is asymptotically proportional to ξ. Thus the physical significance of the parameter ξ as well as the connection between interfacial thickness and surface tension will be evident.

We begin by defining the relevant norms and seminorms. Let $\Lambda \equiv \bar{\Omega} \times [0, T]$ where $\Omega \subset \mathbb{R}^N$ is any bounded domain containing a ball of radius ε. We consider the usual distance function

$$d(P, Q) \equiv [|x - \bar{x}|^2 + |t - \bar{t}|]^{\frac{1}{2}} \tag{3.3}$$

between points $P = (t, x)$ and $Q = (\bar{t}, \bar{x})$ in Λ, where $|x|$ is the Euclidean norm $(\Sigma x_i^2)^{\frac{1}{2}}$. We use the notation

$$\|v\|_0^{(\Lambda)} \equiv \sup_{(t,x)\in\Lambda} |v(t, x)| \tag{3.4}$$

$$H_\alpha^{(\Lambda)}(v) \equiv \sup_{P,Q\in\Lambda} \frac{|v(P) - v(Q)|}{[d(P, Q)]^\alpha} \tag{3.5}$$

where α is the Hölder exponent and $H_\alpha^{(\Lambda)}(v)$ is the Hölder coefficient of v. Thus $H_\alpha^{(\Lambda)}(v) < \infty$ if and only if v is Hölder continuous with exponent α. Now we let

$$\|v\|_\alpha^{(\Lambda)} \equiv \|v\|_0^{(\Lambda)} + H_\alpha^{(\Lambda)}(v). \tag{3.6}$$

We denote by D_x^m any partial derivative of order m with respect to the variables $x_1, \ldots, x_N$, and we let D_t be the partial derivative with respect to t. If $D_x v$ exists in Λ, then we define

$$\|v\|_{1+\alpha}^{(\Lambda)} \equiv \|v\|_\alpha^{(\Lambda)} + \Sigma \|D_x v\|_\alpha^{(\Lambda)}, \tag{3.7}$$

and if $D_x^2 v$ and $D_t v$ also exist in Λ, then we let

$$\|v\|_{2+\alpha}^{(\Lambda)} \equiv \|v\|_\alpha^{(\Lambda)} + \Sigma \|D_x v\|_\alpha^{(\Lambda)} + \Sigma \|D_x^2 v\|_\alpha^{(\Lambda)} + \|D_t v\|_\alpha^{(\Lambda)}, \tag{3.8}$$

where the sums in (3.7) and (3.8) are taken over all partial derivatives of indicated order. Letting $C_{j+\alpha}(\Lambda)$ be the set of functions for which $\|v\|_{j+\alpha}^{(\Lambda)} < \infty$ $(j = 0, 1, 2)$, we note that $C_\alpha(\Lambda)$, $C_{1+\alpha}(\Lambda)$ and $C_{2+\alpha}(\Lambda)$ are Banach spaces.

We shall also need the following norms and spaces. Let

$$L^{(\Lambda)}(v) \equiv \sup_{(t,x)\in\Lambda,(\bar{t},\bar{x})\in\Lambda} \frac{|v(t, x) - v(\bar{t}, \bar{x})|}{|x - \bar{x}| + |t - \bar{t}|}, \tag{3.9}$$

$$\|v\|_{1-0}^{(\Lambda)} \equiv \|v\|_0^{(\Lambda)} + L^{(\Lambda)}(v), \tag{3.10}$$

$$\|v\|_{2-0}^{(\Lambda)} \equiv \|v\|_{1-0}^{(\Lambda)} + \Sigma \|D_x v\|_{1-0}^{(\Lambda)}. \tag{3.11}$$

Also, let the spaces $C_{1-0}(\Lambda)$, $C_{2-0}(\Lambda)$ be defined analogously to $C_{j+\alpha}(\Lambda)$. The references to Λ will be omitted when no confusion is likely to arise.

Now let L be a linear parabolic operator,

$$Lv \equiv \sum_{i,j=1}^N a_{ij}(t, x) \frac{\partial^2 v}{\partial x_i \partial x_j} + \sum_{i=1}^N b_i(t, x) \frac{\partial v}{\partial x_i} + c(t, x)\, u - \frac{\partial u}{\partial t}, \tag{3.12}$$

and consider the initial-boundary problem for the single equation

$$Lv = g(t, x) \qquad (t, x) \in \Lambda \tag{3.13}$$

$$v(t, x) = v_\partial(t, x) \qquad (t, x) \in \partial\Lambda \tag{3.14}$$

where $\partial\Lambda \equiv \partial\Omega \cap \{\Lambda \cap \{t = 0\}\}$.

We shall use two basic Schauder-type estimates for this problem. We make the assumptions

(i) L is parabolic in Λ, *i.e.*, there exists a positive constant H_0 such that for every $(t, x) \in \Lambda$ and every real vector $\zeta \in \mathbb{R}^N$,

$$\sum_{i,j=1}^{N} a_{ij}(t, x)\, \zeta_i \zeta_j \geqq H_0 \sum_{i=1}^{N} \zeta_i^2. \tag{3.15}$$

(ii) The coefficients of L are uniformly Hölder continuous (exponent α) in Λ, *i.e.*,

$$\|a_{ij}\|_\alpha \leqq H_1, \qquad \|b_i\|_\alpha \leqq H_1, \qquad \|c\|_\alpha \leqq H_1 \tag{3.16}$$

also, $a_{ij} \in C_{1-0}(\partial\Lambda)$, *i.e.*,

$$\|a_{ij}\|_{1-0}^{(\partial\Lambda)} \leqq H_2. \tag{3.17}$$

(iii) The function g is uniformly Hölder continuous.

(iv) The boundary $\partial\Lambda$ belongs to $C_{2+\alpha}$, by which we mean that each point of $\partial\Lambda$ has a neighborhood in which $\partial\Lambda$ is the graph of a $C_{2+\alpha}$ function of $N-1$ of the coordinates $x_1, \ldots, x_N$ (see [43] for equivalent definitions). The function v_∂ belongs to $C_{2+\alpha}$, *i.e.*,

$$\|v_\partial\|_{2+\alpha}^{(\partial\Lambda)} \geqq H_3. \tag{3.18}$$

For the source function g we shall require the following conditions on the respective estimates.

(v) The function $g(t, x)$ is a bounded, continuous function in Λ.

(v)′ The function $g(t, x)$ is uniformly Hölder continuous (exponent α).

We state first the *a priori* $(1+\delta)$ estimate (see [42, 44, 45] for proof.)

Theorem 3.1. *Assume conditions* (i)–(v), *and let* $v(t, x)$ *be a solution to* (3.13), (3.14). *Then for any* δ $(0 < \delta < 1)$ *there is a constant* C, *depending only upon* δ, H_0, H_1, H_2 *and* Λ, *such that*

$$\|v\|_{1+\delta} \leqq C\{\|g\|_0 + H_3\}. \tag{3.19}$$

□

Next, we need an estimate for $C_{2+\alpha}$ regularity [42].

Theorem 3.2. *Assume conditions* (i)–(iv), (v)′ *and let* v *be a solution to* (3.13) *and* (3.14). *Then there is a constant* C *depending only on* H_0, H_1 *and* Λ *such that*

$$\|v\|_{2+\alpha} \leqq C\{\|g\|_\alpha + H_3\}. \tag{3.20}$$

□

To exploit these estimates, we first rewrite the system (2.1)–(2.4) in diagonalized form

$$V_t = B\Delta V + G(V) \tag{3.21}$$

where we have used the definitions

$$B \equiv \begin{pmatrix} K & 0 \\ 0 & \xi^2/\tau \end{pmatrix} = PAP^{-1}; \qquad P \equiv \begin{pmatrix} 1 & q \\ 0 & 1 \end{pmatrix};$$
$$V \equiv \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} \equiv PU = \begin{pmatrix} u + q\varphi \\ \varphi \end{pmatrix}; \tag{3.22}$$

$$\begin{aligned} G(V) \equiv PF(U) &= \begin{pmatrix} F_1(u, \varphi) + qF_2(u, \varphi) \\ F_2(u, \varphi) \end{pmatrix} \\ &= \begin{pmatrix} F_1(v_1 - pv_2, v_2) + qF(v_1 - pv_2, v_2) \\ F_2(v_1 - pv_2, v_2) \end{pmatrix}; \end{aligned} \tag{3.23}$$

$$V_\partial \equiv PU_\partial; \qquad V_0 \equiv PU_0. \tag{3.24}$$

Note that the constant q is defined by (2.13), while F_1 and F_2 denote components of F, defined by (2.2). We shall say that a vector-valued function belongs to $C_{j+\alpha}$ if each of its components is in $C_{j+\alpha}$. We will also denote for any vector-valued function $W = (w_1, w_2)$

$$\| W \|_{j+\alpha} \equiv \| w_1 \|_{j+\alpha} + \| w_2 \|_{j+\alpha}. \tag{3.25}$$

We can now prove the basic $C_{2+\alpha}$ estimate for the phase field equations (1.12)–(1.17).

Theorem 3.3. *Let* $U \in C([0, T], \mathscr{B})$ *be a solution of the phase field equations* (2.1)–(2.4.) *Suppose* $U_\partial, U_0 \in C_{2+\alpha}$. *Then* $U \in C_{2+\alpha}$, *and*

$$\| U \|_{2+\alpha} \leqq \frac{C}{\tau} \{ \| U_0 \|_{2+\alpha} + \| U_\partial \|_{2+\alpha} \} \tag{3.26}$$

where C *depends on* ξ^2/τ, α, l, K *and* A. □

Proof. The diagonalized system (3.21)–(3.24) enables us to apply theorems about single linear equations. Combining the bounds for the two equations (v_1, v_2), one has the bound (Theorem 3.1)

$$\| V \|_{1+\alpha} \leqq C_1 \{ \| G(V) \|_0 + C_0 \} \tag{3.27}$$

where $C_0 \equiv \| V_\partial \|_{2+\alpha} + \| V_0 \|_{2+\alpha}$. Using Theorem 3.2 as an *a priori* bound for each of the two semilinear equations in (3.21), one has

$$\| V \|_{2+\alpha} \leqq C_2 [\| G(V) \|_\alpha + C_0]. \tag{3.28}$$

The C_α norm for $G(V)$ may be written as:

$$\begin{aligned} \| G(V) \|_\alpha &= \| G(V) \|_0 + H_\alpha[G_1(V)] + H_\alpha[G_2(V)] \\ &\leqq \| G(V) \|_0 + \max \{ \| DG_1 \|_0, \| DG_2 \|_0 \} \| V \|_\alpha. \end{aligned} \tag{3.29}$$

The bounds for $\| DG_1 \|_0$ and $\| DG_2 \|_0$ depend on q, l and (linearly) on τ^{-1}. Combining this with (3.27)–(3.29), one has

$$\| V \|_{2+\alpha} \leqq \frac{C_3}{\tau} [\| V_0 \|_{2+\alpha} + \| V_\partial \|_{2+\alpha}]. \tag{3.30}$$

Setting $U = p^{-1}V$, we transform this estimate into one in terms of U and so obtain the desired conclusion. □

We now apply these estimates to obtain bounds on the phase field φ in terms of the scaled spatial variable x' [see (3.1)].

Theorem 3.4. (Gradient bounds). *Let* (u, φ) *be the solution of the phase field equations* (1.12)–(1.17) *and suppose that the boundary conditions and initial conditions are all* $C_{2+\alpha}$. *Then one has the bounds*

$$\left|\frac{\partial \varphi}{\partial x'}\right| \leqq C[C_1, C_2, l, K, \Lambda, u_0, u_\partial, \varphi_0, \varphi_\partial], \tag{3.31}$$

$$\left|\frac{\partial^2 \varphi}{\partial x'^2}\right| \leqq C[C_1, C_2, l, K, \Lambda, u_0, u, \varphi_0, \varphi_\partial]. \tag{3.32}$$

Proof. Since the Schauder-type estimates involve constants which depend on the size of Ω, one cannot simply obtain a bound of the form (3.31) by rescaling in the obvious way, for the constant would then approach infinity as ξ approaches zero [and volume (Ω) in x' scale approaches infinity].

However, one has from Theorem 3.3 the bounds

$$\left|\frac{\partial^2 \varphi}{\partial x^2}\right| \leqq \frac{C}{\xi^2} \tag{3.33}$$

where C depends on the constants in (3.31), and (3.32), and ξ^2 has been substituted for τ using (3.2). This implies (3.32). The boundedness of φ (Theorem 2.10) along with (3.32) implies (3.31). □

The same conclusions may, of course, be obtained for u, although one expects u to vary more slowly than (3.31)–(3.32) would imply.

The estimates we have obtained for the parabolic equations (1.12)–(1.17) can be obtained directly for the corresponding elliptic equations which will be studied in the next section. Theorems 3.1 and 3.2 may be replaced by the corresponding results in the elliptic theory (*e.g.*, see Theorems 6.15 and 8.24 in [43]). The supremum bound for φ then follows from a variational formulation (see Section 8).

4. A Rigorous Matched Asymptotic Analysis—The Outer Expansion

In the preceding sections we have obtained various results on the existence, regularity and properties of the phase field equations for arbitrary but fixed ξ, τ. However, the invariant regions studied in Section 2 depended on ξ^2/τ and not on ξ and τ individually. Thus, any limit of ξ and τ approaching zero which is consistent with (3.3) preserves the invariant regions. A similar uniformity was evident in the gradient bounds of Theorem 3.4.

In this and the following three sections we shall study explicitly the effect of varying a small parameter. In particular, we shall concentrate on the time-independent (equilibrium) equations (1.10)–(1.13), and analyze the behavior of φ as ξ approaches 0. This will lead (in Section 7) to the Gibbs-Thompson relation (1.8), which refers to equilibrium. The question we address is the following. Given a sequence of materials indexed by $\{i\}$, and characterized by ξ_i (but otherwise identical) we assume that each material occupies a region Ω of which Ω_0 is solid ($\varphi > 0$) and $\Omega \setminus \bar{\Omega}_0$ is liquid ($\varphi < 0$); see Figure 4. Thus we study the scaling and asymptotics as ξ approaches 0 under these conditions. Note that since u satisfies (1.11), specification of u_∂ uniquely determines u in Ω. To specify the boundary conditions for φ, let Ω_1 be a region strictly contained in Ω_0 (see Figure 4). We define boundary conditions for φ by

$$\begin{aligned} \varphi(t, x) &= -1 + O(\xi) \quad & x \in \Omega_1 \\ &= +1 + O(\xi) \quad & x \in \partial\Omega \\ &= 0 \quad & x \in \partial\Omega_0 . \end{aligned} \tag{4.1}$$

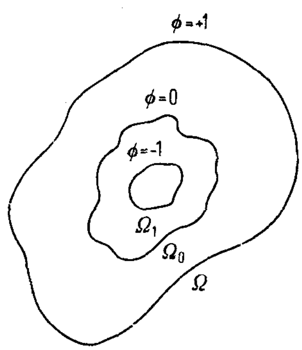


Fig. 4. Shaded area, Ω_1, represents the region in which $\varphi = -1$ is fixed, $\partial\Omega_0$ is the center of the interface ($\varphi = 0$) and $\partial\Omega$ corresponds to $+1$.

One can analogously define situations in which the liquid is surrounded by the solid as well as multiple regions of liquid and solid. Since our analysis is essentially local, the central concern is with a single interface between liquid and solid. The boundary conditions (4.1) may be modified by small terms, *e.g.* $e^{-c/\xi}$, without affecting our asymptotic analysis.

We study the equations (1.10)–(1.13) with the phase field equation (1.10) in slightly more general form by allowing for modifications of the double-well potential $(\varphi^2 - 1)^2$ in (1.9) and also specify the relative order of the boundary conditions on u, which implies the order of u in Ω. Thus we consider the phase field equation (1.10) in the form

$$Q_\xi \varphi = \xi^2 \Delta\varphi + \tfrac{1}{2} [\varphi - g^2(x) \varphi^3] + \xi \bar{u}(x) = 0 \tag{4.2}$$

where $g(x) \in C^\infty$, $\bar{u}(x) \in C^\infty$ and $\bar{u}$ is bounded by a constant independent of ξ ($\bar{u} = 2\xi^{-1} u$). We will concentrate on positive solutions φ in the region $\Omega \setminus \Omega_0$; the analysis of negative solutions in the region $\Omega_0 \setminus \Omega_1$ is similar.

Our asymptotic analysis is based largely on the work of BERGER & FRAENKEL [46], who considered equations similar to (4.2) without the $\bar{u}$ term and under homogeneous boundary conditions. Various other rigorous analyses of this type have been performed (*e.g.*, [47]–[49], see also [50]), although some of the methods are restricted to monotonic functions in place of a term such as $\varphi - \varphi^3$.

We adopt the usual notation of asymptotics. Namely, we say that a function $f(x, \xi)$ is $O(\xi)$ if it satisfies the inequality

$$|f(x, \xi)| \leqq C\xi \tag{4.3}$$

for sufficiently small ξ, where C is a constant independent of ξ and x. A function $f(x, \xi)$ is said to be $o(\xi)$ if

$$\xi^{-1} |f(x, \xi)| \to 0 \quad \text{(uniformly in } x) \tag{4.4}$$

as ξ approaches 0.

A brief sketch of the ideas to be used in the analysis is as follows. For sufficiently small values of ξ, we expect that (4.2) will have a solution $\varphi(x, \xi)$ which tends to $1/g(x)$ as ξ approaches 0 outside a narrow "boundary layer" of width $O(\xi)$ concentrated near $\partial\Omega_0$. This is called the "outer expansion". Within the boundary layer one may rescale the variable normal to $\partial\Omega_0$ by dividing the normal by ξ. The resulting expansion is often called the "inner expansion". The first term in this expansion will be a hyperbolic tangent function of the rescaled variable. The aim is then to construct an approximate solution

$$\Phi_M(x, \xi) \equiv \sum_{j=0}^{M} \xi^j \varphi_j(x, \xi) \tag{4.5}$$

such that

$$\varphi(x, \xi) - \Phi_M(x, \xi) = O(\xi^{M+1}) \tag{4.6}$$

uniformly on $\overline{\Omega \setminus \Omega_0}$. This approximate solution is constructed by "asymptotically matching" the two solutions. This procedure, which is often formal, is made rigorous in this and the following two sections. The basic ideas involve interpretation of the Fréchet derivative of an equation as an operator equation in the proper Sobolev space. The necessary estimates are obtained from explicit analysis of the two expansions, and L_p regularity theory and Sobolev estimates. This analysis is restricted to dimension $N \leqq 3$ for technical reasons at one stage of the analysis.

We begin by defining a new set of coordinates (s, r) where r is a measure of distance from $\partial\Omega_0$ to all points in a fixed neighborhood of $\Omega \setminus \Omega_0$. In each neighborhood, $\partial\Omega_0$ has a parametric representation

$$x = p(s) \qquad s = (s_1, \ldots, s_{N-1}). \tag{4.7}$$

The boundary $\partial\Omega_0$ may be covered by finitely many such neighborhoods. If we restrict attention to that part of the domain $\Omega \setminus \Omega_0$ which is at distance less than r_0 from $\partial\Omega_0$, (denoted by Ω^*), where r_0 is chosen so that normals originating at distinct points of $\partial\Omega_0$ do not intersect for $r < r_0$, then we may write the transformation as

$$x = p(s) + rn(s) \qquad 0 \leqq r \leqq r_0. \tag{4.8}$$

Here $n(s)$ is the unit normal to $\partial\Omega_0$ directed toward the region $\Omega \setminus \Omega_0$. This transformation is one-to-one and infinitely differentiable on Ω^*.

The components of the covariant and contravariant metric tensions are denoted by

$$a_{kl} \equiv \left(\frac{\partial p}{\partial s_k} + r\frac{\partial n}{\partial s_k}\right)\cdot\left(\frac{\partial p}{\partial s_l} + r\frac{\partial n}{\partial s_l}\right) \qquad k, l = 1, \ldots, N-1 \tag{4.9}$$

$$a_{Nl} \equiv \delta_{Nl} \qquad l = 1, \ldots, N$$

$$a^{kl} \equiv a^{-1}\ (\text{cofactor of } a_{kl}) \qquad p, q = 1, \ldots, N \tag{4.10}$$

where a is the determinant of $\{a_{kl}\}$, and δ_{Nl} is the Kronecker delta.

Following the notation of [46], we write the Laplacian operator as

$$\Delta = \frac{\partial^2}{\partial r^2} + b_N\frac{\partial}{\partial r} + \sum_{l=1}^{N-1} b_l\frac{\partial}{\partial s_l} + \sum_{k=1}^{N-1}\sum_{l=1}^{N-1} a^{kl}\frac{\partial^2}{\partial s_k\,\partial s_l},$$

$$b_k \equiv \sum_{l=1}^{N-1} a^{-\frac{1}{2}}\frac{\partial}{\partial s_l}(a^{\frac{1}{2}}a^{kl}), \tag{4.11}$$

$$b_N \equiv a^{-\frac{1}{2}}\frac{\partial a^{\frac{1}{2}}}{\partial r}.$$

We proceed now to analyze the outer expansion

$$X_M(x, \xi) \equiv \sum_{j=0}^{M} \xi^j\chi_j(x) \tag{4.12}$$

in which the χ_j are defined as the solutions of the equations obtained by setting equal to zero the coefficients of ξ^j in (4.2). The first-order equation is

$$\chi_0 - g^2(x)\,\chi_0^3 = 0. \tag{4.13}$$

We choose the positive solution $\chi_0 = 1/g$. The functions χ_j are then determined as:

$$\chi_1 = -\bar{u}, \tag{4.14}$$

$$\chi_2 = \Delta(1/g) + \frac{g}{4}\bar{u}, \tag{4.15}$$

$$\chi_j = \Delta\chi_{j-2} - g^2 \sum\sum\sum_{\substack{p+q+r=j\\ p,q,r\leqq j-1}} \chi_p\chi_q\chi_r \qquad (j \geqq 3). \tag{4.16}$$

By generalizing [46], we may prove the following two lemmas about the outer expansion (4.12).

Lemma 4.1. *In the expansion $X_M(x, \xi)$ the coefficients $\chi_j(x)$ belong to $C^\infty(\overline{\Omega \setminus \Omega_0})$, and*

$$Q_\xi X_M(x, \xi) = -\xi^{M+1}R_1(x, \xi, M) \quad \text{in } \Omega \setminus \Omega_0 \tag{4.17}$$

where $|R_1| \leqq C_M$ independently of x and ξ on $\overline{\Omega \setminus \Omega_0}\times(0, \xi_0]$ for some ξ_0.

Proof. Since g is strictly positive and C^∞ and $\bar{u} \in C^\infty$ it follows that $\chi_j \in C^\infty(\overline{\Omega \setminus \Omega_0})$. The bound (4.17) follows from (4.14)–(4.16) and the boundedness of u. □

Lemma 4.2. *The coefficients χ_j have the expansions*

$$\chi_j(x) = \sum_{k=0}^{M-j} \chi_{j,k}(s)\, r^k + O(r^{M-j+1}) \tag{4.18}$$

as r approaches 0. Furthermore, the sequence $\chi_{0,0}, \ldots, \chi_{0,M}, \ldots, \chi_{M,0}$ is the unique solution of the system of algebraic equations which one obtains by writing $Q_\xi X_M$ as a double power series in ξ and r, equating coefficients of $\xi^j r^j$, and setting $\chi_{0,0} \equiv 1/g(s, 0)$.

Proof. Noting that $\chi_j \in C^\infty$ and $x = x(s, r)$ is one-to-one and infinitely differentiable on $\bar{\Omega}^*$, by use of Taylor's theorem we prove the existence of an expansion of the form (4.18). To compute the coefficients $\chi_{j,k}$ we note that g is C^∞ so it has an expansion

$$g^2(s, r) = \sum_{k=0}^{n} \gamma_k r^k + O(r^{n+1}) \tag{4.19}$$

as r approaches 0. Hence we may compute the $\chi_{0,k}$ by substituting (4.18) and (4.19) into (4.13) and equating coefficients of r^k, and defining $\chi_{0,0}$ as $\gamma_0^{-\frac{1}{2}}$. To obtain the remaining coefficients one must use (4.18) and (4.19) in (4.14)–(4.16) along with the expression (4.11) for the Laplacian. The equations thus obtained are then the same as those which arise from equating to zero the coefficients of $\xi^j r^k$ in the double power series for $Q_\xi X_M$. □

This completes our analysis of the outer expansion which does not vanish on $\partial\Omega_0$.

5. The Inner Expansion

The analysis of this section deals with the behavior of the solution φ near the boundary $\partial\Omega_0$. Our aim is to construct a sequence of functions

$$\Psi_M(s, \varrho, \xi) \equiv \sum_{j=0}^{M} \xi^j \psi_j(s, \varrho) \tag{5.1}$$

where $\varrho \equiv r/\xi$ is a "streched variable". The coefficients ψ_j are obtained by letting $Q_\xi \Psi_M = 0$ and setting coefficients of ξ^j equal to 0. One has

$$\begin{aligned} Q_\xi \Psi_M &= \xi^2 \Delta \Psi_M + \tfrac{1}{2}(\Psi_M - g\Psi_M^3) + \xi\bar{u} \\ &= \sum_{j=0}^{M} \xi^j \left\{ \frac{\partial^2 \psi_j}{\partial \varrho^2} + L_j(\psi_0, \ldots, \psi_{j-1}) + \tfrac{1}{2}\psi_j + \alpha_{j-1}\varrho^{j-1} \right. \\ &\quad \left. - \tfrac{1}{2} \sum\sum\sum_{l+m+n+p=j}\sum \gamma_l \varrho^l \psi_m \psi_n \psi_p \right\} + \xi^{M+1} R_2(s, \varrho, \xi, M) \end{aligned} \tag{5.2}$$

where we have used the expansion

$$
\begin{aligned}
\bar{u}(x) &= \sum_{k=0}^{j} \alpha_k(s)\, r^k + O(\varrho^{j+1}) \\
&= \sum_{k=0}^{j} \xi^k \alpha_k(s)\, \varrho^k + O(\xi^{j+1}\varrho^{j+1})
\end{aligned}
\tag{5.3}
$$

and $\alpha_{-1} \equiv 0$, and we have defined the L_j and R_2 by

$$
\begin{aligned}
L_0 &\equiv 0 \\
L_j(\psi_0, \ldots, \psi_{j-1}) &\equiv \sum\sum_{l+m+1=j} b_l(s)\varrho^l \frac{\partial \psi_m}{\partial \varrho} + \sum_{p=1}^{N-1} \sum\sum_{l+m+2=j} b_l^p(s)\,\varrho^l \frac{\partial \psi_m}{\partial s^p} \\
&\quad + \sum_{p=1}^{N-1} \sum_{q=1}^{N-1} \sum\sum_{l+m+2=j} a_l^{pq}(s)\,\varrho^l \frac{\partial^2 \psi_m}{\partial s^p\, \partial s^q},
\end{aligned}
\tag{5.4}
$$

$$
\begin{aligned}
\xi^{M+1} R_2 \equiv \sum_{k=M+1}^{\infty} \xi^k \Bigg\{ & L_k(\psi_0, \ldots, \psi_M, 0, \ldots, 0) \\
& - \sum_{\substack{l+m+n+p=k \\ m,n,p \leq M}}\sum\sum\sum \tfrac{1}{2} \gamma_l \varrho^l \psi_m \psi_n \psi_p + \alpha_{k-1} \varrho^{k-1} \Bigg\}.
\end{aligned}
\tag{5.5}
$$

The coefficient of unity in the expansion (5.2) is given by

$$
\frac{\partial^2 \psi_0}{\partial \varrho^2} + \tfrac{1}{2}\,(\psi_0 - \gamma_0(s)\, \psi_0^3) = 0 \tag{5.6}
$$

which has the solution

$$
\psi_0 = [\gamma_0(s)]^{-\frac{1}{2}} \tanh \varrho/2. \tag{5.7}
$$

For higher order, i.e., $k = 1, \ldots, M$, one has

$$
\frac{\partial^2 \psi_k}{\partial \varrho^2} + \tfrac{1}{2}\,(1 - 3\gamma_0 \psi_0^2)\, \psi_k = \frac{\partial^2 \psi_k}{\partial \varrho^2} + \left(\tfrac{3}{2}\,\mathrm{sech}^2 \frac{\varrho}{2} - 1\right) = \mathscr{F}_k, \tag{5.8}
$$

$$
\mathscr{F}_k \equiv -L_k(\psi, \ldots, \psi_{k-1}) + \tfrac{1}{2} \sum_{\substack{l+m+n+p=k \\ m,n,p \leq k-1}}\sum\sum \gamma_l \varrho^l \psi_m \psi_n \psi_p - \alpha_{k-1}\varrho^{k-1} \quad (k \geqq 1) \tag{5.9}
$$

which are subject to the boundary conditions

$$
\psi_k(\varrho = 0), \qquad \psi_k = o(e^{2\varrho}). \tag{5.10}
$$

To proceed with the analysis we need further information on the nature of the solutions of (5.8). We consider (5.8) as a special case of the more general problem

$$
\begin{aligned}
Q\psi &\equiv \frac{d^2 \psi}{d\varrho^2} + \{h(\varrho) - a^2\}\, \psi = \mathscr{F}(\varrho), \\
\psi(0) &= c, \qquad \psi(\varrho) = (e^{a\varrho}) \quad \text{as } \varrho \to \infty.
\end{aligned}
\tag{5.11}
$$

The problem (5.11) has been analyzed in [46] (see p. 582) for functions $h(\varrho)$ which are in $C^\infty[0,\infty)$ and are such that h and all of its derivatives are $O(e^{-a\varrho})$.

We summarize the conclusions as follows. The unique solution of (5.11) is

$$\psi(\varrho) \equiv A(\varrho) \int_0^\varrho B(\varrho')\, \mathscr{F}(\varrho')\, d\varrho' + B(\varrho) \int_\varrho^\infty A(\varrho')\, \mathscr{F}(\varrho')\, d\varrho' + cA(\varrho),$$

$$A(\varrho) \equiv \operatorname{sech}^2 \varrho/2, \tag{5.12}$$

$$B(\varrho) \equiv -2 \operatorname{sech}^2 \varrho/2 \int_0^\varrho \cosh^4 \varrho'/2\, d(\varrho'/2).$$

Definition 5.1. A function $f \in C^\infty[0,\infty)$ is in the set of exponentially declining functions, denoted by $\mathscr{S}_k$, if for $\varrho \to \infty$, $f(\varrho)$ and all of its derivatives $f^{(n)}(\varrho)$ are $O(\varrho^k e^{-a\varrho})$.

Lemma 5.1. *Suppose that in* (5.11), $\mathscr{F}(\varrho) = P(\varrho) + Z(\varrho)$ *where* $P(\varrho)$ *is a polynomial of degree* j *and* $Z(\varrho) \in \mathscr{S}_k$. *Let*

$$p(\varrho) \equiv \frac{1}{-a + D^2} P(\varrho) = -\frac{1}{a^2}\left\{1 + \frac{D^2}{a^2} + \dots + \left(\frac{D^2}{a^2}\right)^{[j/2]}\right\} P(\varrho)$$

where D denotes differentiation with respect to ϱ and let $m = \max\{j+1, k+1\}$. *Then the solution of* (5.11) *is* $\psi = p + z$ *where* $z \in \mathscr{S}_m$. □

This lemma may now be applied to our problem.

Theorem 5.3. (i). *In the expansion* (5.1) *for* Ψ_M, *the coefficients* ψ_j *are* C^∞ *and can be written as*

$$\psi_j(s,\varrho) = p_j(s,\varrho) + z_j(s,\varrho) \tag{5.13}$$

where p_j *is a polynomial in* ϱ *of degree* j *and* $z_j \in \mathscr{S}_{2j}$.

(ii) *The polynomial* p_j *in* (5.13) *has coefficients given by*

$$p_j = \sum_{k=0}^{j} \psi_{j,k}(s)\, \varrho^k \tag{5.14}$$

where the $\psi_{j,k}$ *are related to the* $\chi_{l,k}$ *of* (4.18) *by*

$$\psi_{j+l,k} = \chi_{l,k}. \tag{5.15}$$

Proof. Since $\partial\Omega_0$, g and $\bar{u}$ are smooth, the coefficients a_l^{pq}, b_l, b_l^p, γ_l, α_l are also smooth. Therefore, the ψ_k given by the explicit solution (5.12) are infinitely differentiable with respect to s.

To examine the behavior with respect to ϱ we proceed by induction. We may write ψ_0 as

$$\psi_0 = p_0 + z_0,$$

$$p_0 \equiv [\gamma_0(as)]^{-\frac{1}{2}}, \quad z_0 \equiv [\gamma_0(s)]^{-\frac{1}{2}}\, [\tanh \varrho/2 - 1].$$

Now assume that the assertion is true for $\psi_0, \dots, \psi_{j-1}$. Then we may write (5.9) as

$$\mathscr{F}_j(\varrho) = P_j + Z_j,$$

$$P_j \equiv -L_j(p_0, \dots, p_{j-1}) + \sum_{\substack{k+l+m+n=j \\ l,m,n \leq j-1}}\sum\sum\sum \gamma_k \varrho^k p_l p_m p_n - \alpha_{j-1}\varrho^{j-1}, \tag{5.17}$$

$$Z_j \equiv -L_j(z_0, \dots, z_{j-1}) + \sum_{\substack{k+l+m+n=j \\ l,m,n \leq j-1}}\sum\sum\sum \gamma_k \varrho^k \{(p_l + z_l)(p_m + z_m)(p_n + z_n) - p_l p_m p_n\}.$$

The expression P_j is a polynomial of degree j. The terms in Z_j consist of $L_j(z_0, \dots, z_{j-1})$ which is in the set $\mathscr{S}_{2j}$, and terms in the second set of sums of which the dominant term is $\varrho^k \varrho_l p_m p_{j-1} \in \mathscr{S}_{2j-1}$. Hence the quadruple sum belongs to $\mathscr{S}_{2j-1}$, so that $Z_j \in \mathscr{S}_{2j}$.

(iii) To prove the second part of the theorem we claim that the P_j satisfy the differential equations that result from replacing $(\psi_0, \dots, \psi_M)$ by $(p_0, \dots, p_M)$. The ψ_j satisfy (5.6), (5.8), so that $\psi_0 = p_0 + z_0$ satisfies

$$\frac{\partial^2}{\partial \varrho^2}(p_0 + z_0) + \tfrac{1}{2}\{(p_0 + z_0) - \gamma_0(p_0 + z_0)^3\} = 0. \tag{5.18}$$

Since p_0 is a constant (polynomial of degree p) it must satisfy (taking the positive solution once again)

$$p_0(s) = [\gamma_0(s)]^{-\frac{1}{2}}. \tag{5.19}$$

Continuing this process for higher orders one has

$$\sum_{j=0}^{M} \xi^j \left[\frac{\partial^2 p_j}{\partial \varrho^2} + L_j(p_0, \dots, p_{j-1}) + \tfrac{1}{2} p_j - \gamma_{j-1}\varrho^{j-1} + \tfrac{1}{2} \sum_{k+l+m+n=j}\sum\sum\sum \gamma_k \varrho^k p_l p_m p_j\right] = 0. \tag{5.20}$$

Consider now the function

$$Y_M \equiv \sum_{j=0}^{M} \xi^j p_j(s, \varrho) = \sum_{j=0}^{M} \xi^j \sum_{k=0}^{j} \psi_{j,k}(s)\, \varrho^k \tag{5.21}$$

so that $Q_\xi Y_M$ is a double power series in ξ and ϱ. Equation (5.20) implies that the coefficient of $\xi^j \varrho^k$ vanishes for $j = 0, \dots, M$ and $k = 0, \dots, j$. Substituting $r = \xi\varrho$ makes $Q_\xi Y_M$ become a double series in r and ξ, *i.e.*,

$$Y_M = \sum_{j=0}^{M} \xi^j \sum_{k=0}^{M-j} \psi_{j+k,k} r^k. \tag{5.22}$$

The claim then is that the sequence of coefficients $\{\psi_{j+k,k}\}$ satisfies the system of equations described in Lemma 4.2, namely the equations obtained by writing $Q_\xi X_M$ as a double power series in ξ and r. Recalling that this system is unique so long as one chooses the positive solution $\chi_{0,0} = \gamma_0^{-\frac{1}{2}}$, one has the equality asserted in the theorem. $\square$

The next objective is to show that this expansion Y_M is a sufficiently good approximation to Ψ_M.

Theorem 5.4. *The inner expansion* Ψ_M, *defined by* (5.1) *and* (5.2), *and the outer expansion* Y_M, *given by* (5.21), (5.22), (5.15) *satisfy the relationship*

$$Q_\xi \Psi_M - Q_\xi Y_M = O(\xi^{M+1}) \text{ uniformly on } \Omega^*. \tag{5.23}$$

Proof. Let $R_{2,\psi}$ be the remainder terms

$$\xi^{M+1} R_{2,\psi} \equiv \sum_{k=M+1}^{\infty} \xi^k \Big\{ L_k(\psi_0, \ldots, \psi_M, 0, \ldots, 0) - \sum_{\substack{j+l+m+n=k \\ l,m,n \leqq M}} \sum \sum \sum \gamma_j \varrho^j \psi_l \psi_m \psi_n + \alpha_{k-1} \varrho^{k-1} \Big\} \tag{5.24}$$

and let $R_{2,p}$ be defined in the same way with the P_i replacing the ψ_i in (5.24). One has from the definitions,

$$Q_\xi \Psi_M = \xi^{M+1} R_{2,\psi} \tag{5.25}$$

$$Q_\xi Y_M = \xi^{M+1} R_{2,p}. \tag{5.26}$$

The difference between (5.25) and (5.26) is then

$$Q_\xi \Psi_M - Q_\xi Y_M = \sum_{k=M+1}^{\infty} \xi^k \Big\{ L_k(z_0, \ldots, z_M, 0, \ldots, 0) - \sum_{\substack{j+l+m+n=k \\ l,m,n \leqq M}} \sum \sum \sum \gamma_j \varrho^j [(p_l + z_l)(p_m + z_m)(p_n + z_n) - p_l p_m p_n] \Big\}, \tag{5.27}$$

since the L_k are linear in their arguments. The conclusion now follows upon examining the behavior for different values of ϱ. For ϱ bounded, (5.27) is clearly $O(\xi^{M+1})$; for $\varrho \to \infty$, $Z_j \in \mathcal{S}_{2j}$ implies each term is $O(\xi^{M+1} \varrho^{2M} e^{-2\varrho})$. $\square$

We now combine the two expansions we have developed. Given the estimates of the previous two sections, we may utilize some results of BERGER & FRAENKEL [46] with some modification of boundaries. We have the expansion

$$X_M(x, \xi) = \sum_{j=0}^{M} \xi^j \chi_j(x) \tag{5.28}$$

$$= \sum_{j=0}^{M} \xi^j \sum_{k=0}^{M-j} \chi_{j,k}(s)\, r^k + O(r^{M-j+1}) \tag{5.29}$$

from Section 4, and the expansion

$$\begin{aligned} Y_M(s, \varrho, \xi) &= \sum_{j=0}^{M} \xi^j \sum_{k=0}^{j} \psi_{j,k}(s)\, \varrho^k \\ &= \sum_{j=0}^{M} \xi^j \sum_{k=0}^{M-j} \psi_{j+k,k} r^k \end{aligned} \tag{5.30}$$

near the boundary. By Theorem 5.3, one has

$$X_M = Y_M.$$

In order to construct an approximation which is uniform in $\Omega \setminus \Omega_0$, we first define the mollifier

$$\begin{aligned} \zeta(x) &\equiv 1 \quad 0 \leqq t \leqq t^* \\ &\equiv 0 \quad \overline{\Omega \setminus \Omega_0} \setminus \Omega^*. \end{aligned}$$

The approximate solution introduced by (4.5) is defined by

$$\begin{aligned} \Phi_M(x, \xi) &\equiv X_M + \zeta(\Psi_M - Y_M) = \sum_{k=0}^{M} \xi^k \varphi_k(x, \xi) \\ \varphi_k(x, \xi) &\equiv \chi_k + \zeta \left\{ \psi_k(s, \tau) - \sum_{i=0}^{k} \psi_{k,j}(s)\, \varrho^j \right\}. \end{aligned} \tag{5.31}$$

With these definitions one has [46]:

Theorem 5.5. a) *Each function $\varphi_k(x, \xi)$ defined in* (5.31) *has the following pointwise bounds on* $\overline{\Omega \setminus \Omega_0} \times (0, \xi_0]$:

$$|\varphi_k| \leqq c_k \quad |\nabla \varphi_k| \leqq c_k' B_k(x, \xi) \tag{5.32}$$

where c_k and c_k' are independent of x and ξ, and

$$B_k(x, \xi) \equiv 1 + \frac{1}{\xi} (1 + \varrho^{2k})\, e^{-2\varrho}\, \zeta(x). \tag{5.33}$$

Furthermore, $\varphi_k \in C^\infty$ *on* $\overline{\Omega \setminus \Omega_0} \times (0, \xi_0]$.

(b) *The function $\Phi_M(x, \xi)$ defined by* (5.31) *is an approximate solution of*

$$Q_\xi \varphi \equiv \xi^2 \Delta \varphi + \tfrac{1}{2} [\varphi - g^2 \varphi^3] + \xi \bar{u} \quad \text{in } \Omega \tag{5.34}$$

$$u = 0 \quad \text{on } \partial \Omega_0 \tag{5.35}$$

in the sense that

$$Q_\xi \Phi_M = O(\xi^{M+1}) \tag{5.36}$$

uniformly on $\Omega \setminus \Omega_5$ *and*

$$\Phi_M = 0 \quad \text{on } \partial \Omega_0. \tag{5.37}$$

The boundary conditions we are using differ from [46] *in that we do not have homogeneous boundary conditions about the entire region of interest. Since we have*

$\varphi = 0$ *on* $\partial\Omega_0$, *the boundary exhibiting the transition layer, the proof can easily be adapted.* □

One has in the same way:

Theorem 5.6. *The approximate solution* $\Phi_M(x, \xi)$ *defined by* (5.31) *may be written*

$$\Phi_M(x, \xi) = \frac{1}{g(x)}\{\zeta(x)\tanh \varrho/2 + 1 - \zeta(x)\}\,[1 + O(\xi)]. \tag{5.38}$$

Also, Φ_M *is positive on* $\Omega \setminus \Omega_0 \times (0, \xi_0]$ *for* ξ_0 *sufficiently small.* □

6. The Remainder Terms in the Asymptotic Series

The results of the preceding two sections led to a rigorous estimate for the asymptotic solution to our problem. We have been considering positive solutions in the region $\Omega \setminus \Omega_0$. The results are equally valid for negative solutions in the region Ω_0. The iteration then begins with the choice $\chi_0 = -1/g$ in (4.13). We now pursue an analysis of the higher order, or remainder, terms in the asymptotic analysis. At this stage we need homogeneous boundary conditions on the entire boundary under consideration. For the purposes of this section we may apply our analysis to any of the following situations:

(a) Consider the liquid region $(\varphi < 0)\ \Omega_0$, so that $\varphi = 0$ on $\partial\Omega_0$;

(b) Consider the solid region as in the previous sections but define a liquid region sufficiently far from the interface of interest. That is, a region, say Ω_1, encloses Ω such that

$$d(x, y) > C \quad \text{if} \quad x \in \Omega), \quad y \in \mathbb{R}^N \setminus \Omega_1. \tag{6.1}$$

The region $\mathbb{R}^N \setminus \Omega_1$ is defined to be liquid so that $\varphi = 0$ on $\partial\Omega_1$ and $\varphi = 0$ on $\partial\Omega_0$.

(c) Consider a solid region Ω_0 surrounded by liquid in $\Omega \setminus \Omega_0$. This situation and (a) are identical except for sign.

Note that this idea of defining a liquid sufficiently far from the interface of interest [as in (b)] is a technical convenience which cannot change the physical situation significantly except at a critical point. For a critical point, however, the phase field equation itself may not provide a sufficiently good description of the physics.

In the context of these remarks, we consider the problem for the remainder

$$\tilde{\varphi}_M(x, \xi) = \varphi(x, \xi) - \Phi_M(x, \xi) \tag{6.2}$$

which is given by

$$\begin{aligned} \xi^2 \Delta\tilde{\varphi}_M + \tfrac{1}{2}(1 - 3g^2\Phi_M^2) &= -\xi^{M+1} f_M + \tfrac{1}{2} g^2 (3\Phi_M \tilde{\varphi}_M^2 + \tilde{\varphi}_M^3) \quad \text{in } \Omega_0 \\ \tilde{\varphi}_M &= 0 \quad \text{on } \partial\Omega_0 \end{aligned} \tag{6.3}$$

where $Q_\xi \Phi_M \equiv \xi^{M+1} f_M(x, \xi)$ and f_M is a smooth function which is bounded independently of ξ (Theorem 5.5).

The problem (6.3) may be reformulated as an operator equation. We define the Sobolev space $\overset{0}{W}_{k,2}(\Omega_0)$ as the space of all real-valued functions $f(x)$ such that f and all of its generalized derivatives of order k or less are square integrable over Ω_0 and vanish on $\partial\Omega_0$ in the generalized sense. The norm of $f \in \overset{0}{W}_{1,2}$ is

$$\|f\|_{k,2}^2 \equiv \sum_{|\alpha|=k} |D^\alpha f|^2 \tag{6.4}$$

where $D^\alpha f$ is any generalized derivative of order k. The inner product of two functions $f, g \in \overset{0}{W}_{1,2}$ is defined by

$$(f, g) \equiv \int_{\Omega_0} \nabla f \cdot \nabla g. \tag{6.5}$$

The Sobolev spaces $\overset{0}{W}_{k,r}$ are defined analogously, with the norms $\|\cdot\|_{k,r}$.

A generalized solution of (6.3) is defined as a function $\tilde{\varphi} \in \overset{0}{W}_{1,2}(\Omega_0)$ such that

$$-\xi(\tilde{\varphi}, v) + \int_{\Omega_0} \tfrac{1}{2}(1 - 3g^2\Phi_M^2)\,\tilde{\varphi} v = -\xi^{M+1} \int_{\Omega_0} f_M \tilde{\varphi} + \int_{\Omega_0} \tfrac{1}{2} g^2(3\Phi_M\tilde{\varphi} + \tilde{\varphi}^3)\,v \tag{6.6}$$

for all test functions $v \in \overset{0}{W}_{1,2}(\Omega_0)$. The integral identity (6.6) has been used by BERGER & FRAENKEL [46] to define an operator equation.

We list the basic results for this operator equation and refer to [46] for the proofs. For $\tilde{\varphi}$, $v \in \overset{0}{W}_{1,2}(\Omega_0)$ set

$$(L_{M,\xi}\tilde{\varphi}, v) \equiv \int_{\Omega_0} \tfrac{1}{2}(3g^2\Phi_M^2 - 1)\,\tilde{\varphi} v, \tag{6.7}$$

$$(F_M, v) \equiv \int_{\Omega_0} f_M v, \tag{6.8}$$

$$(N_{M,\xi}, v) \equiv -\tfrac{1}{2} \int_{\Omega_0} g^2(3\Phi_M\tilde{\varphi}^2 + \tilde{\varphi}^3)\,v. \tag{6.9}$$

The operators $L_{M,\xi}$ and $N_{M,\xi}$ are mappings of $\overset{0}{W}_{1,2}$ into itself and $F_M \in \overset{0}{W}_{1,2}$ (by the Sobolev and Hölder inequalities). Also, define the operator

$$\mathscr{L}_{M,\xi}\tilde{\varphi} = \xi^2\tilde{\varphi} + L_{M,\xi}\tilde{\varphi}. \tag{6.10}$$

One then has as a consequence of Poincaré's inequality and the Lax-Milgram lemma [46, 51]:

Theoerm 6.1. (a) *The generalized solutions of* (6.3) *are in one-to-one correspondence with the solutions of the operator equation*

$$\xi^2\tilde{\varphi} + L_{M,\xi}\tilde{\varphi} = \xi^{M+1}F_M + N_{M,\xi}\tilde{\varphi}. \tag{6.11}$$

(b) *There are positive numbers* $\nu(M)$ *and* $\xi_0(M)$ *such that, for any* $\tilde{\varphi} \in W_{1,2}$ *and for* $0 < \xi < \xi_0$

$$\begin{aligned} \mathscr{L}_{M,\xi}(\tilde{\varphi}, \tilde{\varphi}) &= \int_{\Omega_0} \{\xi^2(\nabla\tilde{\varphi})^2 + \tfrac{1}{2}(3g^2\Phi_M - 1)\,\tilde{\varphi}^2\} \\ &\geqq \xi^2\nu^2 \int_{\Omega_0} (\nabla\tilde{\varphi})^2. \end{aligned} \tag{6.12}$$

(c) *The operator* $\mathscr{L}_{M,\xi}$ *has a bounded linear inverse* $\mathscr{L}_{M,\xi}^{-1}$ *which maps* $W_{1,2}^{0}$ *into itself and satisfies the inequality*

$$\|\mathscr{L}_{M,\xi}^{-1}\eta\| \leqq \frac{\|\eta\|}{\xi^2\nu^2} \tag{6.13}$$

for all $\eta \in W_{1,2}^{0}$ *and* $\xi \in (0, \xi_0]$. □

As a consequence of the proof of Theorem 6.1(b) one has

$$(\mathscr{L}_{M,\xi}\eta, \eta) \geqq \mu^2 \int \eta^2 \qquad \xi \in (0, \xi_0] \tag{6.14}$$

for all $\eta \in W_{1,2}^{0}$. One may then define the open sphere in $C(\bar{\Omega}_0)$:

$$\mathscr{S}(\mu) \equiv \left\{\eta \,|\, \sup_{\Omega_0} |\eta| < \mu^2 \,|\, \sup_{\Omega_0} 6g^2\Phi_M\right\} \tag{6.15}$$

We may then utilize the two theorems proved in Section 4 of [46].

Theorem 6.2. *Given any integer M and any* $\xi \in (0, \xi(M))$ *where* $\xi(M)$ *is sufficiently small, the equation* (6.3) *has a solution* $\tilde{\varphi}_M(x, \xi)$ (*in the pointwise sense*). *This solution satisfies the bound*

$$\sup_{\Omega_0} |\tilde{\varphi}_M| = O(\xi^{M+1}) \tag{6.16}$$

and is the unique solution of (6.3) *in the sphere* $\mathscr{S}(\mu)$.

Theorem 6.3. Given a positive integer $M \in \{0, \ldots, M_*\}$ and $\xi \in (0, \xi_*(M_*))$ for some $\xi_*(M_*)$, the function

$$\varphi \equiv \Phi_M + \tilde{\varphi}_M \tag{6.17}$$

is a solution of (4.2) with homogeneous boundary conditions [see remarks (a)–(c) at the beginning of this Section], is independent of M and is positive in Ω_0. □

Note that the solution constructed in this way is the unique solution of (4.2) such that

$$\|\varphi - \Phi_M\| = O(\xi^{M+1}). \tag{6.18}$$

We summarize the physical aspects of the conclusions. Given a boundary separating the liquid and solid phases of a material in equilibrium, we have analyzed it under the following technical assumptions. First, we have assumed that the boundary is fixed as ξ approaches zero. The physical interpretation of this is given at the beginning of Section 4. Second, we supposed that the solid is ultimately surrounded by liquid (or vice-versa). This is a technical restriction to ensure homogeneous boundary conditions (as discussed in the beginning of this section), which should not have a significant effect on the physical situation. These two restrictions are currently needed at this stage but are probably not intrinsic to the underlying physics. I conjecture that if one considers a free boundary in the mathematical sense and allows more general boundary conditions, further mathematical analysis will show that the asymptotic solution will be of the same form, with a hyperbolic tangent term leading the series.

The assumption of equilibrium is more significant as a physical restriction. An asymptotic analysis of non-equilibrium situations would involve the parabolic equations (1.14) and (1.15) and would depend on the velocity of the interface as well as ξ and τ.

7. Surface Tension and the Gibbs-Thompson Relation

We consider now one of the physically most interesting questions about this model; namely the relation between the temperature at the interface, the curvature of interface and the surface tension. We prove that within the context of our model and assumptions, the Gibbs-Thompson relation (1.8) is a necessary condition for the existence of an appropriate solution.

For simplicity, consider a solid region Ω_0 ($\varphi < 0$) surrounded by a liquid region $\Omega \setminus \Omega_0$ ($\varphi > 0$); the situation is similar for any other topology since the analysis is essentially local. We continue to assume that $\partial\Omega_0$ and $\partial\Omega$ are C^∞. Let $\varphi \in C^2(\Omega)$ be a function which satisfies (1.10), (1.13) and (6.18) for $M = 0$, and let $2u(x, \xi) \equiv \xi\tilde{u}(x)$ be a $C^2(\Omega)$ function. The function u is determined completely by the boundary conditions as discussed in Section 3. The results of the present section are not restricted to $N \leqq 3$ provided there exists function $\varphi \in C^2(\Omega)$ which satisfies (6.18) at least for $M = 0$. With some technical modifications the proof may be extended to weak solutions φ.

Consider the region $\tilde{\Omega} \equiv \{x \in \Omega \mid d(x, \partial\Omega_0) < a\}$ for some number a for which the normals do not intersect. A coordinate system (s, r) may be defined in any neighborhood of a point on $\partial\Omega_0$ by extending the transformation (4.8) to negative values of r.

Recalling from Section 5 that

$$\Phi_0 \equiv \tanh \varrho/2 \qquad \varrho \equiv r/\xi \tag{7.1}$$

solves

$$\xi^2 \frac{d^2\Phi_0}{dr^2} + \tfrac{1}{2}(\Phi_0 - \Phi_0^3) = 0, \tag{7.2}$$

we subtract this from the full equation

$$\xi^2 \Delta\varphi + \tfrac{1}{2}(\varphi - \varphi^3) + \xi\tilde{u} = 0. \tag{7.3}$$

Use of (4.11) shows that the remainder $\tilde{\varphi}_1(x, \xi)$ [see (6.2)] is

$$\xi^2 \Delta\tilde{\varphi}_1 + \tfrac{1}{2}[\tilde{\varphi}_1 - 3\Phi_0^2\tilde{\varphi}_1 - 3\Phi_0\tilde{\varphi}_1^2 - \tilde{\varphi}_1^3] + \xi b_N \frac{d\Phi_0}{d\varrho} + \xi\tilde{u} = O^2(\xi) \tag{7.4}$$

in the region $\tilde{\Omega}$.

To proceed further, we need stronger bounds on derivatives of $\tilde{\varphi}_1$. We define the Hölder norm $\|\cdot\|_{2,\alpha}$ and the associated space $C^{2,\alpha}(\tilde{\Omega})$ as in (3.8) except that we use the Euclidean metric in place of (3.3).

Lemma 7.1. *If* $\tilde{\varphi}_1 \in C^2$ *is a solution of* (7.4) *in* $\tilde{\Omega}$ $(a > \xi)$ *with* $\bar{u}$ *bounded independently of* ξ *and satisfies* (6.18) *for* $M = 0$, *then*

$$\|\tilde{\varphi}_1\|_{2,\alpha} \leqq C/\xi, \tag{7.5}$$

$$\left|\frac{\partial \tilde{\varphi}_1}{\partial r}\right| \leqq C \tag{7.6}$$

for a constant C which is independent of ξ.

Proof. From (6.18) and explicit differentiation of Φ_0 one has the bounds:

$$|\tilde{\varphi}_1| \leqq C_1 \xi, \tag{7.7}$$

$$\left|\frac{d\Phi_0}{d\varrho}\right| \leqq C_2. \tag{7.8}$$

One then has from (7.4), (7.7), (7.8) and the bound on $\bar{u}$:

$$\Delta \tilde{\varphi}_1 = -\tfrac{1}{2}[1 - 3\Phi_0^2]\frac{\tilde{\varphi}_1}{\xi_2} - \frac{\bar{u}}{\xi} - \frac{b_N}{\xi}\frac{d\Phi_0}{d\varrho} + O(\xi) = \xi^{-1} h_1(\tilde{\varphi}_{11}; r, s) \tag{7.9}$$

where h_1 is bounded by a constant C_3 independently of ξ. Now applying regularity theorems for elliptic equations (in particular Theorems 6.15 and 8.24 of [43]), one has the bound (7.5). Hence

$$\left|\frac{\partial^2 \tilde{\varphi}_1}{\partial \varrho^2}\right| \leqq C\xi. \tag{7.10}$$

If one considers the function $\tilde{\varphi}_1/\xi$, inequalities (7.7) and (7.10) imply that this function and its second derivative are bounded. Hence the first derivative is bounded (as a function of ϱ), so (7.6) follows. □

Next, we wish to show that the significant part of $\xi^2 \Delta \tilde{\varphi}_1$ to the appropriate order is, in some sense, just $\partial^2 \tilde{\varphi}_1/\partial \varrho^2$. Let Ω' be any domain contained in $\tilde{\Omega}$ and let Φ_0' denote $d\Phi_0/d\varrho$. Then by Green's second identity

$$\int_{\Omega'} \Phi_0' \Delta \tilde{\varphi}_1 dx = \int_{\Omega'} \tilde{\varphi}_1 \Delta \Phi_0' + \int_{\partial\Omega'} \left(\Phi_0' \frac{\partial \tilde{\varphi}_1}{\partial \nu} - \tilde{\varphi}_1 \frac{\partial \Phi_0'}{\partial \nu}\right) ds \tag{7.11}$$

where ν is the (outward) normal to the surface and ds is the surface element of integration. Using the bounds of Lemma 7.1 along with (7.8), one may bound the surface term by a constant (independent of ξ), yielding the estimate

$$\xi^2 \int_{\Omega'} \Phi_0' \Delta \tilde{\varphi}_1 dx = \xi^2 \int_{\Omega'} \tilde{\varphi}_1 \Delta \Phi_0' \, dx + O(\xi^2) = \int_{\Omega_1'} \tilde{\varphi}_1 \frac{d^2 \Phi_0'}{d\varrho^2} dx + O(\xi^2). \tag{7.12}$$

The function Φ_0' satisfies the differential equation

$$\frac{d^2 \Phi_0'}{d\varrho^2} + \tfrac{1}{2}[1 - 3\Phi_0^2]\, \Phi_0' = 0. \tag{7.13}$$

Hence, if we multiply the equation

$$L_1\tilde{\varphi}_1 \equiv \xi^2 \Delta\tilde{\varphi}_1 + \tfrac{1}{2}[1 - 3\Phi_0^2]\,\tilde{\varphi}_1 = -\xi\{\tilde{u} + b_N\Phi_0'\} + O(\xi^2)$$

by Φ_0' and integrate over Ω', we obtain, upon using (7.12) and (7.13) the equation

$$\xi \int_{\Omega'} \bar{u}\Phi_0'\,dx = -\xi \int_{\Omega'} b_N(\Phi_0')^2\,dx + O(\xi^2). \tag{7.14}$$

In order to use (7.14) to determine $\bar{u}$ on $\partial\Omega_0$ we choose Ω' to be a small sphere centered about a point $x \in \partial\Omega_0$:

$$\Omega' \equiv \{y \in \Omega \mid d(x, y) < \xi^p\} \tag{7.15}$$

where $p: 0 < p < 1$ is arbitrary. Using the mean value theorem for $\bar{u}$ and b_N, one has

$$\xi\tilde{u}(x) = \xi b_N(x)\frac{\int_{\Omega'}(\Phi_0')^2\,dx}{\int_{\Omega'}\Phi_0'\,dx} + O(\xi^{p+1}). \tag{7.16}$$

Noting that

$$|\Phi_0'(r = \xi^p/2)| \leqq C\xi^{-p}e^{-\xi^{p-1}}, \tag{7.17}$$

and that b_N is the sum of the principal curvatures [52], we have proved the Gibbs-Thompson relation [see (1.8)]:

Theorem 7.2. *If (u, φ) is a solution of (1.10)–(1.13) satisfying the hypotheses stated in the beginning of this section and those of Lemma 7.1, then $u(x)$ satisfies the Gibbs-Thompson relation*

$$u(x) = -\frac{\sigma_0\varkappa}{4} + o(\xi) \qquad x \in \partial\Omega_0 \tag{7.18}$$

where $\varkappa$ is the sum of the principal curvatures $\varkappa_1 + \ldots + \varkappa_N$, and the constant σ_0 is defined by

$$\sigma_0 = \xi^2 \int_{-\infty}^{\infty}\left(\frac{d\Phi_0}{dr}\right)^2 dr = \tfrac{2}{3}\,\xi. \tag{7.19}$$

□

It remains to prove that this constant σ_0 (which we have defined above) is equal to the surface tension as determined by the original free energy F_u defined by (1.9). Also, we must show that the entropy density difference between solid and liquid is indeed 4. Using our bounds on φ and $\tilde{\varphi}_1$, we can establish this rigorously.

We define the potential

$$\mathscr{G}(\varphi) \equiv \tfrac{1}{8}(\varphi^2 - 1)^2 \tag{7.20}$$

in agreement with the potential in the free energy $F_u\{\varphi\}$ in (1.9). The function Φ_0 satisfies the differential equation

$$\xi^2\frac{d^2\Phi_0}{dr^2} - \mathscr{G}'(\Phi_0) = 0 \tag{7.21}$$

with boundary conditions

$$\Phi_0(r = \pm a) = \pm 1 + O(e^{-a/\xi}). \tag{7.22}$$

Multiplying (7.21) by $d\Phi_0/dr$ and integrating the resulting exact differential implies

$$\frac{\xi^2}{2}\left(\frac{d\Phi_0}{dr}\right)^2 = \mathscr{G}(\Phi_0) + C + (Oe^{-a/\xi}). \tag{7.23}$$

The constant C is seen to be $O(e^{-a/\xi})$ by considering $r = a$.

The surface tension σ is generally defined [17]–[19] in terms of the difference between the free energy of the system with an interface of cross-sectional area A and an average of the homogeneous free energies, *i.e.*,

$$\sigma \equiv \frac{F_u\{\varphi\} - \frac{1}{2}F_u\{\varphi = +1\} - \frac{1}{2}F_u\{\varphi = -1\}}{A}. \tag{7.24}$$

In the domain $\tilde{\Omega}$, *i.e.*, within a of $\partial\Omega_0$, one may write the free energy $F_u\{\Phi_0\}$ as

$$\begin{aligned} F_u\{\Phi_0\} &= A \int_{-a}^{a} dr \left\{\frac{\xi^2}{2}\left(\frac{d\Phi_0}{dr}\right)^2 + \mathscr{G}(\Phi_0) + 2u\Phi_0\right\} + O(e^{-a/\xi}) \\ &= A \int_{-a}^{a} dr \left\{\xi^2\left(\frac{d\Phi_0}{dr}\right)^2 + 2u\Phi_0\right\} + O(e^{-a/\xi}) \end{aligned} \tag{7.25}$$

using (7.23). Also, with the assumption that $2u = \xi\bar{u}(x)$ [in fact it suffices to assume $|\nabla u| \leqq c\xi^p$, $p < 1$] one has

$$F_u\{\Phi_0\} = A \int_{-\infty}^{\infty} dr\, \xi^2 \left(\frac{d\Phi_0}{dr}\right)^2 + O(\xi^2). \tag{7.26}$$

Also, one has

$$\tfrac{1}{2}F_u\{\varphi = +1\} + \tfrac{1}{2}F_u\{\varphi = -1\} = 0 \tag{7.27}$$

for any $\mathscr{G}(\varphi)$ such that $\mathscr{G}(+1) = \mathscr{G}(-1)$.

Hence, one has

$$\frac{F_u\{\Phi_0\} - \frac{1}{2}F_u\{\varphi = +1\} - \frac{1}{2}F_u\{\varphi = -1\}}{A} = \xi^2 \int_{-\infty}^{\infty} \left(\frac{d\Phi_0}{dr}\right)^2 dr + O(\xi^2). \tag{7.28}$$

In order to assert the equality of expressions (7.24) and (7.28) to $O(\xi^2)$ we appeal to the bounds established in Lemma 7.1 and the arguments leading to Theorem 7.2. With these we have the result:

Theorem 7.3. *Under the hypotheses of Theorem 7.2 the surface tension* σ [*defined by* (7.24)] *satisfies*

$$\sigma = \sigma_0 + O(\xi^2) = \xi \int_{-\infty}^{\infty} \left(\frac{d\Phi_0}{d\varrho}\right)^2 d\varrho + O(\xi^2) = \tfrac{4}{3}\xi + O(\xi^2). \tag{7.29}$$

□

Finally, we need to verify that the entropy densities of the solid and the liquid differ by 4. Using the thermodynamic identity

$$\frac{\partial F_u}{\partial u}\{\varphi\} = -s \tag{7.30}$$

one has from the definition (1.9) of $F_u\{\varphi\}$

$$\Delta s = -\frac{\partial F_u}{\partial u}\{\varphi = +1\} + \frac{\partial F_u}{\partial u}\{\varphi = -1\} = 4\times \text{Volume}. \tag{7.31}$$

Hence the constants in Theorem 7.2 are the correct physical quantities for our model.

Remarks. (1) A well known concept in solidification [17] is the notion of a critical radius R^*, defined as the radius of a solid sphere which is in equilibrium with its melt at a fixed temperature u. For three dimensions this is given by (7.18) as

$$R^* = -\frac{\sigma_0}{2u}. \tag{7.32}$$

This equilibrium is, of course, an unstable one since a slight increase in temperature would mean that the elliptic equation (1.10) would not be satisfied. Instead, the parabolic equation (1.14) would imply a negative φ_t, *i.e.* melting. The coupled equation (1.15) then suggests that u_t is positive (the rate of increase depending on the magnitude of the diffusivity K), *i.e.*, temperature increases causing further melting. This cycle persists until the entire solid has melted.

The reverse procedure, *i.e.*, a slight drop in temperature (under conditions of spherical symmetry and initially critical radius), lead to complete solidification in the same manner.

(2) Theorems 7.2 and 7.3 may be interpreted as the following statement in equilibrium statistical mechanics: given a system which obeys the physics of a Landau-Ginzburg model of a phase transition, then any reasonable solution (the precise conditions are stated at the beginning of this section) will satisfy the Gibbs-Thompson relation.

(3) We have been considering $u = O(\xi)$ throughout this section. This provides the correct scaling for a curvature $\varkappa$ which is bounded independently of ξ. This is implicit in our assumptions since Ω_0 is fixed. If we were to let $\varkappa$ increase as ξ^{-1} and let $u = O(1)$ then formally we would expect a relation similar to (7.18), except that u would now be varying too rapidly to allow appropriate use of the mean value theorem as in (7.16). Formally, the Gibbs-Thompson relation may be generalized as follows. We define the measure

$$dv_\xi = d(\varphi/2). \tag{7.33}$$

Then

$$\int_{\Omega'} u(x)\, dv(x)_\xi = -\frac{\sigma_0 \varkappa}{\Delta s} + O(\xi) \tag{7.34}$$

should be the correct generalization for Ω' a sufficiently small domain containing x.

(4) For the time dependent equations (1.14)–(1.17), the Gibbs-Thompson relation (7.18) would remain valid if the terms u_t and φ_t are sufficiently small, *e.g.*, $O(\xi^2)$. If these terms are $O(1)$, for example, then one expects dynamical terms which dominate the surface tension effect.

8. Variational Methods for Phase Field Equations

In this section, we apply variational methods to the (equilibrium) phase field equations

$$\xi^2 \Delta\varphi + \tfrac{1}{2}[\varphi - g^2(x)\varphi^3] + \xi\bar{u}(x) = 0 \qquad x \in \Omega_0 \tag{8.1}$$

$$\varphi = 0 \quad \text{on } \partial\Omega_0.$$

The primary objective is to obtain results for values of ξ which are not necessarily very small. In addition, we may relax the restrictions on $g(x)$ and $\partial\Omega_0$ (previously required to be C^∞) to $C^{0,\alpha}(\bar{\Omega}_0)$ $(\alpha > 0)$ and $C^{2,\gamma}$ $(\gamma > 0)$, respectively. The restriction $N \leqq 3$ may also be eliminiated [see Remark 8.3].

These results are simple generalizations of [46].

We define the analog of the free energy (1.9):

$$\mathscr{F}(\varphi) \equiv \int_{\Omega_0} \left\{\xi(\nabla\varphi)^2 - \tfrac{1}{2}\left(\varphi^2 - \frac{g^2}{2}\varphi^4\right) - \xi\bar{u}\varphi\right\}. \tag{8.2}$$

Suppose φ is a critical point of the functional $\mathscr{F}(\varphi)$ over the class $W^0_{1,2}(\Omega_0)$. The Euler-Lagrange equation for (8.2) is (8.1), so that φ is at least a generalized solution to (8.1). The elliptic regularity theory then implies that φ is a pointwise solution (see Chapter 8 of [43]). One has the supremum bound:

Lemma 8.1. *If* φ *satisfies* (8.1),

$$|\varphi(x)| \leqq \sup_{\Omega_0} \frac{1}{g(x)} + \xi C(g) \sup_{\Omega_0} |\bar{u}(x)|. \tag{8.3}$$

Proof. Suppose $x_0 \in \Omega_0$ is a positive local maximum. Then $\Delta\varphi(x_0) \leqq 0$ so that (8.1) implies

$$\varphi - g^2(x_0)\varphi^3 + \xi\bar{u}(x_0) \geqq 0. \tag{8.4}$$

Hence

$$\varphi[1 - g^2(x)\varphi^2] \geqq -\xi \sup_{\Omega_0} \bar{u}(x). \tag{8.5}$$

For sufficiently small ξ, then, the upper bound part of (8.3) follows. The lower bound is obtained in a similar way. □

Next, we show that a critical point of (8.2) is in fact attained.

Theorem 8.2. *Let* $C_0 \equiv \inf \mathscr{F}(\varphi)$, *and let* λ_0 *denote the smallest eigenvalue of the Laplacian on* Ω_0 *subject to homogeneous boundary conditions. Then* $|C_0| < \infty$

and C_0 determines a critical value of the functional $\mathscr{F}(\varphi)$. Furthermore, there is a function $\varphi^0 \in W^0_{1,2}$ such that $\mathscr{F}(\varphi^0) = C_0$. If $\bar{u} \geqq 0$ then $\varphi^0 \geqq 0$.

Proof. We first show that $C_0 > -\infty$. By Lemma 8.1

$$|\varphi| \leqq C'(g)$$

for some C' depending only on g; hence

$$\mathscr{F}(\varphi) \geqq -\int_{\Omega_0} \{\varphi^2 - \tfrac{1}{2} g^2 \varphi^4\} \geqq -\mathrm{Vol}\,(\Omega_0)\,[C'(g)]^2. \tag{8.6}$$

Next we show the existence of a function $\varphi^0 \in W^0_{1,2}$ such that $\mathscr{F}(\varphi^0) = C_0$. Since $C_0 > -\infty$, there is a sequence $\varphi^{(n)} \in W^0_{1,2}$ such that $\mathscr{F}(\varphi^{(n)})$ approaches C_0 as $n \to \infty$. Hence, for sufficiently large n,

$$\mathscr{F}(\varphi^{(n)}) \leqq C_0 + 1. \tag{8.7}$$

Hence

$$\begin{aligned} \xi^2 \int_{\Omega_0} [\nabla \varphi^{(n)}]^2 &\leqq C_0 + 1 + \int_{\Omega_0} \{\tfrac{1}{2} [\varphi^{(n)}]^2 - \tfrac{1}{4} g^2 [\varphi^{(n)}]^4 - 2\xi \bar{u} \varphi^{(n)}\} \\ &\leqq C_0 + 1 + C'\,\mathrm{Vol}\,(\Omega_0). \end{aligned} \tag{8.8}$$

Inequality (8.8) then allows us to use the analysis of [46]. In particular one has the following.

(i) By (8.8) $\|\varphi^{(n)}\|_{1,2} \leqq C$, in which C is independent of n. Since $W^0_{1,2}$ is a Hilbert-space, $\{\varphi^{(n)}\}$ has a weakly convergent subsequence. Denoting this subsequence by $\varphi^{(n)}$ also, we call its weak limit $\bar{\varphi}$.

(ii) Since $\varphi^{(n)}$ converges weakly to $\bar{\varphi}$ in $W^0_{1,2}$, one has [51]

$$\int_{\Omega_0} (\nabla \bar{\varphi})^2 \leqq \liminf_{n \to \infty} \int_{\Omega_0} (\nabla \varphi^{(n)})^2. \tag{8.9}$$

(iii) Noting that $\{\varphi^{(n)}\}$ converges strongly in $L_1(\Omega_0)$, $L_2(\Omega_0)$ and $L_4(\Omega_0)$ for $N \leqq 3$ one has

$$\int_{\Omega_0} \{\tfrac{1}{2} [\varphi^{(n)}]^2 - \tfrac{1}{4} g^2 [\varphi^{(n)}]^4 - 2\xi \bar{u} \varphi^{(n)}\} \to \int_{\Omega_0} \{\tfrac{1}{2} \bar{\varphi}^2 - \tfrac{1}{4} g^2 \bar{\varphi}^4 - 2\xi \bar{u} \bar{\varphi}\}. \tag{8.10}$$

Thus (ii) and (iii) imply

$$\mathscr{F}(\bar{\varphi}) \leqq \liminf_{n \to \infty} \mathscr{F}(\varphi^{(n)}) \equiv C. \tag{8.11}$$

Since $\inf \mathscr{F}(\varphi) \equiv C_0$ one has $\mathscr{F}(\bar{\varphi}) = C_0$.

One can show by explicit computation that the first variation vanishes at $\bar{\varphi}$, *i.e.*,

$$\delta \mathscr{F}(\bar{\varphi}) \equiv \lim_{t \to 0} \frac{\mathscr{F}(\bar{\varphi} + tv) - \mathscr{F}(\bar{\varphi})}{t} = 0 \tag{8.12}$$

for all $v \in W^0_{1,2}(\Omega_0)$.

Finally, we show that if $\bar{u} \geqq 0$ then $\varphi^0 \geqq 0$. If $\varphi^{(n)} \in W^0_{1,2}(\Omega_0)$ then $|\varphi^{(n)}| \in W^0_{1,2}(\Omega_0)$. Also,

$$\mathscr{F}(|\varphi^{(n)}|) \leqq \mathscr{F}(\varphi^{(n)}). \tag{8.13}$$

Hence we can choose $\{|\varphi^{(n)}|\}$ as the minimizing sequence. By Rellich's lemma and the completeness of L_2, one then has $|\varphi^{(n)}| \to \bar{\bar{\varphi}}$ in L_2. The function $\bar{\bar{\varphi}}$ is nonnegative almost everywhere. By redefining on a set of measure zero one then has the desired result. □

Remark 8.3. By using an appropriate truncation of $u - g^2u^3$ the results of this section may be extended to $N \geqq 4$.

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Department of Mathematics and Statistics
University of Pittsburgh
Pittsburgh, Pennsylvania

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