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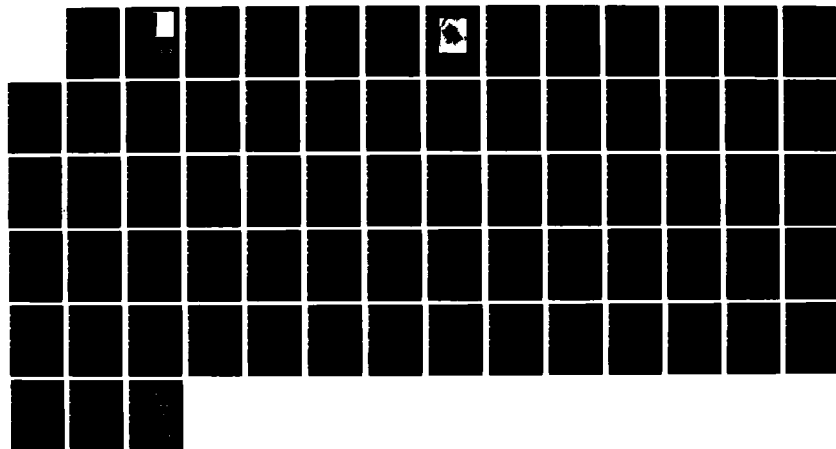
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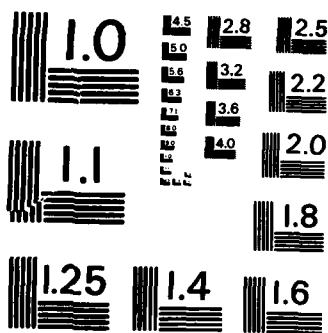
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ON THE TWO-PHASE STEFAN PROBLEM WITH
INTERFACIAL ENERGY AND ENTROPY

Morton E. Gurtin

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UNIVERSITY OF WISCONSIN-MADISON
MATHEMATICS RESEARCH CENTER

ON THE TWO-PHASE STEFAN PROBLEM WITH
INTERFACIAL ENERGY AND ENTROPY

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ABSTRACT

The classical Stefan theory for the melting of a solid or the freezing of a liquid is too simplistic to describe phenomena such as supercooling, in which a liquid supports temperatures below its freezing point, or superheating, the analog for solids, or dendritic growth, in which simple shapes evolve to complicated tree-like structures. In this paper we develop a general theory for two-phase phenomena of this type starting from general thermodynamical laws which are appropriate to a continuum and which include contributions of energy and entropy for the interface between phases. We show that the interfacial temperature is generally not equal to the melting temperature, but depends in a prescribed manner on the curvature of the interface. We describe appropriate initial-boundary-value problems, at various levels of approximation, and deduce corresponding Liapunov functions. We also present a general theory of equilibria, and show that - for an unbounded domain in isothermal equilibrium - there are no stable states in which the bounded phase is solid and the unbounded phase supercooled liquid. We show further that corresponding minimizing sequences for the free-energy are consistent with the formation of dendrites.

AMS (MOS) Subject Classifications: 35K05, 80A15

Key Words: Stefan problem, melting, solidification, dendritic growth

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SIGNIFICANCE AND EXPLANATION

The classical Stefan theory for the melting of a solid or the freezing of a liquid is too simplistic to describe phenomena such as supercooling, in which a liquid supports temperatures below its freezing point, or superheating, the analog for solids, or dendritic growth, in which simple shapes evolve to complicated tree-like structures. In this paper we develop a general theory for two-phase phenomena of this type. We develop partial differential equations satisfied in the phase regions and free-boundary conditions satisfied on the interface between phases, and give arguments which indicate that the resulting boundary-value problems predict the formation of dendrites.

Keywords: equilibrium; Liapunov functions; mathematical physics.



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TABLE OF CONTENTS

1. Introduction.	1
Part I. Equilibrium Theory.	7
2. Assumptions. Terminology.	7
2.1. Constitutive assumptions.	7
2.2. Frequently used moduli.	13
3. Stability.	14
3.1. Isothermal boundary.	14
3.2. Unbounded body under isothermal conditions. Interfacial instabilities.	16
3.3. Isolated body.	22
Part II. General Theory.	27
4. Preliminaries.	27
5. First two laws. Additional constitutive assumptions.	30
6. Partial-differential equations. Jump conditions.	33
7. Boundary conditions. A bound on interfacial area.	37
8. Quasi-static theory.	39
8.1. Basic equations. Growth conditions.	39
8.2. Equilibrium in the quasi-static theory.	43
8.3. Quasi-static theory with B unbounded.	45
8.4. Equilibrium with B unbounded.	47
Part III. Theories Based on the Capillarity Relation.	49
9. Approximations. The capillarity relation.	49
10. Quasi-linear theory.	51
10.1. Basic equations. Growth conditions.	51
10.2. Equilibrium in the quasi-linear theory.	55
11. Quasi-static theory.	57
11.1. Basic equations. Growth conditions.	57
11.2. Equilibrium in the quasi-static theory.	59
11.3. Quasi-static theory when one phase does not conduct heat.	60
Appendix. Some variational problems involving interfaces.	61
Appendix. Scaling the quasi-linear theory. Discussion.	63
References.	65

Morton E. Gurtin

1. Introduction.

A classical problem of mathematical physics is the Stefan problem for the melting of a solid or the freezing of a liquid. The underlying theory, however, is too simplistic to describe phenomena such as supercooling, in which a liquid supports temperatures below its freezing point, or superheating, the analogous phenomenon for solids, or dendrite formation (cf. Figure 1), in which simple shapes, such as spheres, evolve to complicated tree-like structures.¹ The past two decades have seen the development of more general theories² for phenomena of this type, a critical ingredient being a free-boundary condition at the solid-liquid interface $I = I(t)$ in which the temperature depends on the curvature of I . In these theories questions arise as to what are the interface conditions;³ in fact, it is not clear which of the interface conditions are constitutive assumptions and which follow directly from the underlying balance laws.

It is the purpose of this paper to develop a theoretical framework for theories of this type starting from general thermodynamical laws which are appropriate to a continuum and which include interfacial contributions for both energy and entropy. We do not, however, seek the broadest possible theory, but rather, to focus our attention on the thermodynamics and to keep the underlying relations transparent, we limit our discussion to *rigid* heat conductors.⁴

Our chief assumptions - apart from general equations of state for the bulk and interfacial quantities - are that the interface I produce no entropy and that the temperature be continuous across I . Among our main results are the interface conditions

$$\begin{aligned} [q] \cdot m &= v[E] - v\bar{k}e - e^\Delta && \text{on } I, \\ T &= ([E] - \bar{k}e)/([S] - \bar{k}s) && \text{on } I, \\ v m \cdot n &= 0 && \text{on } \partial I, \end{aligned} \quad (1.1)$$

in which T is the temperature; $[E]$, $[S]$, and $[q]$ are the jumps⁵ in energy, entropy, and heat flux across the interface; e and s are the interfacial values of energy and entropy; $\bar{k}$, v , and m , respectively, are, for the interface, the sum of principal curvatures, the normal velocity, and a unit normal vector (with sign convention explained in the text); e^Δ is

¹Cf. Chalmers [1964] and Delves [1974] for discussions of these phenomena.

²Mullins and Sekerka [1963, 1964], Voronkov [1965]. See also the review articles by Sekerka [1968, 1973, 1984], Chernov [1972], Delves [1974], and Langer [1980].

³Cf. Rogers [1983] for a discussion of some of the inconsistencies in the literature.

⁴A future paper will discuss the effect of varying concentration.

⁵Our convention for jumps and for the latent heat L is "phase 2 minus phase 1", with phases labeled so that $L \geq 0$. Thus for a solid-liquid system phase 2 would denote the liquid, and for that reason we will often refer to phases 1 and 2, respectively, as the solid and liquid phases.



Figure 1. Picture of dendritic ice crystal
(Fujioka [1978]).

the time derivative of e following the interface; $\mathbf{n}$ is the outward unit normal on the boundary of the region B occupied by the body.

The first of (1.1) is essentially the first law of thermodynamics at the interface. The second - derived within the fully dynamical theory - is a condition of local equilibrium expressing balance of free-energy across the interface. The third is a contact condition for that portion of the interface¹ which intersects the boundary of B ; it asserts that - where the interface meets ∂B - it is orthogonal to ∂B or stationary.

We discuss two types of boundary conditions: an isolated boundary on which $\mathbf{q} \cdot \mathbf{n} = 0$; an isothermal boundary on which T is constant. We show that, for either of these boundary conditions,

$$\text{interfacial area is uniformly bounded in time,} \quad (1.2)$$

at least when B is *bounded*

We also discuss the *equilibrium* theory under isothermal boundary conditions, and define stable states as minimizers of a global free-energy. We consider a material for which the bulk free-energies cross at a single temperature T_M , and show - for *bounded* B - that stable states are always single phase,² the stable phase being the phase with lower free-energy. T_M therefore represents the temperature at which a change in stable phase occurs, and, for that reason, we refer to T_M as the transition temperature.

The question of stability for *unbounded* B is far more interesting. Here our results, expressed in terms of a solid-liquid system in isothermal equilibrium, assert that:³

1. There are no stable states in which the bounded phase is solid and the unbounded phase supercooled liquid.
2. Under the conditions of (1), minimizing sequences of the free-energy are consistent with interfacial instabilities such as the formation of complicated arrays of thin spikes, behavior indicative of *dendritic growth*.

Next, we introduce a quasi-static model for situations in which the interface moves slowly compared with the time scale for heat conduction. The chief constitutive hypothesis underlying this model is that - in each of the phases - both the bulk energy and the bulk entropy are constant. We also assume that the conductivities k_i , the interfacial energy e , and the

¹Here it is tacit that $\partial I \subset \partial B$.

²Here it is important to emphasize that the boundary is held at constant temperature; two-phase solutions are possible when, for example, the body is isolated and the total energy constrained (cf. Section 3.3).

³In their pioneering paper of [1963], Mullins and Sekerka, working within the *dynamical* theory described by (1.13), established the instability of the interface for infinitesimal perturbations of a sphere solidifying in a supercooled melt. The assertions (1) and (2) are analogs, within the equilibrium theory, of the Mullins-Sekerka instability.

interfacial entropy s are constant. Let $B_i(t)$ denote the subregion of B occupied by phase i ($i = 1, 2$), and let

$$u = T - T_M.$$

Then these assumptions lead to the system¹

$$\begin{aligned} \Delta u &= 0, & q &= -k_i \text{grad} u & \text{in } B_i, \\ u &= -h e / (1 - a e), & [q] \cdot m &= (L - k e) v & \text{on } I, \\ v m \cdot n &= 0 & & & \text{on } \partial I, \end{aligned} \quad (1.3)$$

where

$$h = T_M f(T_M) / L, \quad a = T_M s / L \quad (1.4)$$

with $f(\cdot)$ the interfacial free-energy and L the latent heat. We are able to establish global growth-conditions for (1.3) under the two types of boundary conditions discussed previously. In particular, letting

$$\mu = T_M f(T_0) / L, \quad B = e / L,$$

we show that:

(i) for an isolated boundary,

$$\text{vol}(B_2)^* + B \text{area}(I)^* = 0, \quad \text{area}(I)^* \leq 0; \quad (1.5)$$

(ii) for an isothermal boundary,

$$u_0 \text{vol}(B_2)^* + \mu \text{area}(I)^* \leq 0. \quad (1.6)$$

A detailed analysis of (1.5) and (1.6) is beyond the scope of this paper. We do, however, give a lengthy discussion and indicate several results assuming the stability of solutions as $t \rightarrow \infty$. In particular, we give arguments in support of the interfacial instabilities described in (1) and (2) above. The result (1.5) seems also to indicate an instability characterized by a solid phase whose volume tends to zero, but whose interfacial area does not. We shall refer to this phenomenon as the

¹We use the following notation: grad, div, and Δ are the gradient, divergence, and Laplacian operators; for $F = F(t)$ and $f = f(x, t)$, $F^* = dF/dt$ and $f^* = \partial f / \partial t$; $\text{vol}(\cdot)$ and $\text{area}(\cdot)$ denote the volume and area measures.

formation of a dendrite with null volume.

Thus far we have made no assumptions concerning the size of the interfacial quantities. Moreover, even though the hypotheses underlying (1.3) are strong, the theory is exact in the sense that the underlying equations are fully compatible with the first two laws of thermodynamics.

Next, we return to the general relations (1.1), but in situations for which interfacial energy and entropy are small. We show that to within terms of higher order in these quantities,

$$[q] \cdot m \approx Lv, \quad (1.7)$$

$$u \approx -h\kappa,$$

with h as defined in (1.4). The relations (1.7) are central to the modern work on solidification.¹

We discuss a model based on the interface conditions (1.7) in conjunction with assumptions of constant specific heats and constant conductivities. These assumptions lead to the equations

$$\begin{aligned} C_1 u^* &= -\operatorname{div} q, & q &= -k_1 \operatorname{grad} u && \text{in } B_1, \\ u &= -h\kappa, & [q] \cdot m &= Lv && \text{on } I, \\ v m \cdot n &= 0 &&&& \text{on } \partial I. \end{aligned} \quad (1.8)$$

The assumption

$$C_1 = C_2 \quad (1.9)$$

is common in the literature; granted (1.9), we are able to establish the following growth conditions for (1.8):

(i) for an isolated boundary,

$$\begin{aligned} \{\operatorname{vol}(B_2) + C V u_m^*\}^* &= 0, \\ \{h \operatorname{area}(I) - u_m^* \operatorname{vol}(B_2) + (C/2) \int_B (u - u_m^*)^2\}^* &\leq 0; \end{aligned} \quad (1.10)$$

(ii) for an isothermal boundary,

$$\{h \operatorname{area}(I) - u_0 \operatorname{vol}(B_2) + (C/2) \int_B (u - u_0)^2\}^* \leq 0. \quad (1.11)$$

¹Cr. the references cited in Footnote 1 on page 1.

Here $V = \text{vol}(B)$; $C = C_i/L$; u_m is the mean value of u ; in Case (ii) u_0 is the constant boundary-value of u .

A standard model for solidification follows from (1.8) when the terms $C_i u^*$ are neglected:

$$\begin{aligned} \Delta u &= 0, & q &= -k_1 \text{grad} u & \text{in } B_i, \\ u &= -h_1, & [q] \cdot m &= Lv & \text{on } I, \\ v m \cdot n &= 0 & & & \text{on } \partial I. \end{aligned} \quad (1.12)$$

Here, in place of (1.10) and (1.11), we have the conditions:

(i) for an isolated boundary,

$$\text{vol}(B_i)^* = 0, \quad \text{area}(I)^* \leq 0; \quad (1.13)$$

(ii) for an isothermal boundary,

$$u_0 \text{vol}(B_i)^* + h \text{area}(I)^* \leq 0. \quad (1.14)$$

We discuss consequences of the relations (1.10) and (1.11) and of the relations (1.13) and (1.14).

Because of space limitations, I do not discuss the related theory which allows for variable concentration. As would be expected, the theory and results are, for the most part, completely analogous to those presented here.

I do not list any but the most basic hypotheses of smoothness, since such hypotheses tend to obscure the main ideas, and since at this stage of the theory they are academic: it is not at all clear what are appropriate function spaces in which to analyze the underlying partial-differential equations.

PART I. EQUILIBRIUM THEORY.

2. Assumptions. Terminology.

2.1. Constitutive assumptions.

We consider a body B consisting of two phases separated by an interface I , and write B_i for the subregion of B occupied by phase i ($i=1,2$). (Cf. Figure 2). We assume that:

(A1) B is a closed, regular region with

B *bounded unless stated otherwise*;

(A2) the B_i are closed, regular regions with disjoint interiors, and with

$$B = B_1 \cup B_2, \quad I = \partial B_1 \cap \partial B_2,$$

so that B_1 and B_2 partition B .

We consider bodies whose behavior in equilibrium is described by five fields:

$E(x)$, the bulk internal energy per unit volume;

$S(x)$, the bulk entropy per unit volume;

$T(x)$, the temperature;

$e(x)$, the interfacial energy per unit area;

$s(x)$, the interfacial entropy per unit area.

We assume that in each of the phase regions B_i the material is governed by constitutive equations

$$E = E_i(T), \quad S = S_i(T), \quad (2.1)$$

with¹

$$S_i(T) = -F_i'(T), \quad F_i(T) = E_i(T) - T S_i(T), \quad (2.2)$$

$F_i(T)$ being the free energy of phase i . We assume further that:

(A3) the specific heats

$$C_i(T) = E_i'(T) \quad (2.3)$$

are strictly positive;

¹The prime denotes differentiation with respect to temperature.

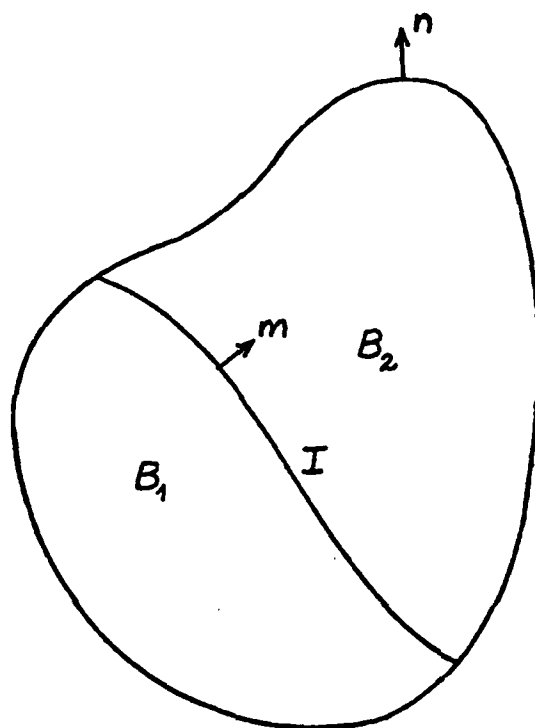


Figure 2. The phase regions B_1 and the interface I .

(A4) the free energies $F_i(T)$ coincide at a *unique* temperature $T = T_M$ called the transition temperature:

$$F_1(T_M) = F_2(T_M). \quad (2.4)$$

The **latent heat** L is the difference in energy between phases at the transition temperature:

$$L = E_2(T_M) - E_1(T_M), \quad (2.5)$$

and a third assumption we shall make is that $L \neq 0$; by labelling phases so that

phase 2 has higher (internal) energy at the transition temperature, (2.6)

we may, without loss in generality, write this assumption as:

$$(A5) \quad L > 0. \quad (2.7)$$

Then, by (2.2)₂, (2.4), and (2.5),

$$S_2(T_M) - S_1(T_M) = L/T_M > 0. \quad (2.8)$$

In view of the agreement (2.6), we shall adopt the following

Convention. We will refer to phase 1 as the **solid phase**, phase 2 as the **liquid phase**.

We do this for convenience only; *the theory is equally valid for liquid-liquid systems, liquid-vapor systems, etc.*

The next result, a direct consequence of the our assumptions, shows that the bulk free-energies have the form shown in Figure 3.

Properties of the bulk free-energies.

(i) *The bulk free-energies are strictly concave: for $T \neq T_0$,*

$$F_i(T) < F_i(T_0) + F_i'(T_0)(T - T_0). \quad (2.9)$$

(ii) *The bulk free-energies cross at $T = T_M$; in fact,*

$$F_1(T) < F_2(T) \text{ for } T < T_M; \quad F_1(T) > F_2(T) \text{ for } T > T_M. \quad (2.10)$$

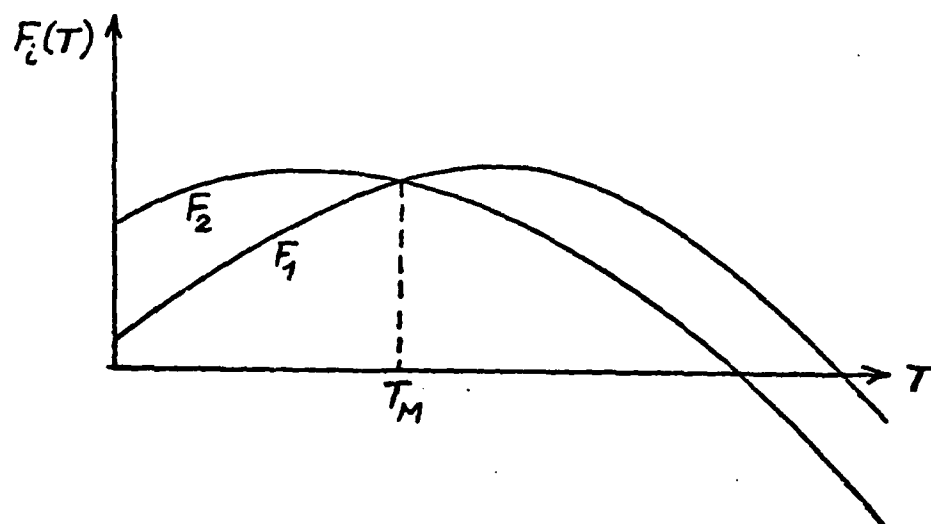


Figure 3. Free-energies $F_i(T)$ as functions of temperature T . T_M is the transition temperature.

(iii) Let $u = 1 - u_M$. Then, as $u \rightarrow 0$,

$$F_1(T) - F_2(T) = Lu/T_M + O(u^2). \quad (2.11)$$

Proof. By (2.2) and (2.3),

$$F_i''(T) = -C_i(T)/T < 0,$$

which implies (i). Further, (2.2)₁ and (2.8) imply that

$$F_1'(T_M) - F_2'(T_M) = L/T_M > 0,$$

which with (A4) yield (ii) and (iii). $\square$

The last result shows that the solid phase has lower free-energy at temperatures below transition, the liquid phase has lower free-energy at temperatures above transition. Even so, it is possible to have the liquid phase at temperatures $T < T_M$, or the solid phase at temperatures $T > T_M$; in the former case the liquid is **supercooled**; in the latter the solid is **superheated**.¹ Generally, we will use the term **superthermal** to designate either of these two situations. Precisely: phase i is **superthermal** at temperature T if, for k the other phase,

$$F_k(T) < F_i(T).$$

We write constitutive equations for I analogous to those for the individual phases. In particular, we assume that

$$e = e(T), \quad s = s(T), \quad (2.12)$$

$$s(T) = -f'(T), \quad f(T) = e(T) - Ts(T), \quad (2.13)$$

and that the interfacial free-energy $f(T)$ and the interfacial specific-heat

$$c(T) = e'(T) \quad (2.14)$$

obey the following hypothesis for all $T > 0$:

$$(A6) \quad f(T) > 0, \quad c(T) \geq 0. \quad (2.15)$$

Then, arguing as above, we see that

¹ Cf. the interesting discussion by Delves [1974], Section 3.2.

$$f \text{ is concave} \quad (2.16)$$

(although not necessarily strictly concave).

It is convenient to introduce the Gibbs functions:

$$W_i(T, T_0) = E_i(T) - T_0 S_i(T), \quad w(T, T_0) = e(T) - T_0 s(T). \quad (2.17)$$

Clearly,

$$F_i(T_0) = W_i(T_0, T_0), \quad f(T_0) = w(T_0, T_0). \quad (2.18)$$

In addition, we have the following less trivial

Properties of the Gibbs functions.

(i) For $T = T_0$,

$$F_i(T_0) < W_i(T, T_0), \quad 0 < f(T_0) \leq w(T, T_0). \quad (2.19)$$

(ii) For each fixed T_0 , each of the Gibbs functions (2.17): has a minimum at $T = T_0$; is monotone decreasing on $(0, T_0)$; is monotone increasing on (T_0, ∞) . Moreover, for W_i the minimum and monotonicity are strict.

Proof. We will establish (i) and (ii) for W_i only; the proof for w is strictly analogous. The inequality (2.19)₁ follows from (2.2) and (2.9) (with the roles of T and T_0 reversed). Also, by (2.2), (2.3), and (2.17),

$$(\partial/\partial T)W_i(T, T_0) = (T - T_0)C_i(T)/T,$$

which yields (ii) for W_i . $\square$

Another consequence of the strict positivity of the bulk specific-heats, obtained by combining (2.2) and (2.9), is the inequality

$$E_i(T) - E_i(T_0) > T_0[S_i(T) - S_i(T_0)] \quad (2.20)$$

for $T \neq T_0$; (2.20) expresses the strict convexity of the bulk energies as functions of the corresponding bulk entropies.

2.2. Frequently used moduli.

In this section we list constitutive moduli that are used repeatedly throughout the paper.

Modulus	Section
$F^*(T_0)$ = bulk free-energy of the bounded phase minus the bulk free-energy of the unbounded phase	3.2
$b = -f(T_0)/F^*(T_0)$	3.2
$h = T_M f(T_M)/L$	8.1
$a = T_M s/L$	8.1
$\mu = T_M f(T_0)/L$	8.1
$\beta = e/L$	8.1
$A = h(C_1 - C_2) - e$	10.1

3. Stability.

3.1. Isothermal boundary.

Given a state of B , that is, a temperature field $T(x)$ and a partition (B_1, B_2) of B with interface $I = \partial B_1 \cap \partial B_2$, the quantities¹

$$\begin{aligned} E(T, B_1, B_2) &= \sum_{B_i} E_i(T) + \int_I e(T), \\ S(T, B_1, B_2) &= \sum_{B_i} S_i(T) + \int_I s(T), \end{aligned} \quad (3.1)$$

represent, respectively, the corresponding **total energy** and **total entropy**.

Remark. We will consider as the underlying class of temperature fields *all* functions $T(x) > 0$ on B with the understanding that the total energy is $+\infty$ and the total entropy $-\infty$ if any of the integrals in (3.1) fail to exist. Further, many of our statements concerning such fields will be modulo a rearrangement on a set of measure zero; the measure, either volume or interfacial area, will be clear from the context.

We assume (for the remainder of the section) that

the boundary is held at (constant) temperature T_0 .

The functional

$$F(T, B_1, B_2) = E(T, B_1, B_2) - T_0 S(T, B_1, B_2) \quad (3.2)$$

then represents the **total free-energy** that would be "recorded" by an experimenter not having access to the detailed temperature distribution in the interior of B . We define as **stable** those states of B that

$$\text{minimize } F(T, B_1, B_2). \quad (3.3)$$

Combining (3.1) and (3.2) we arrive at integrals over B_i and I with integrands equal to the Gibbs functions $W_i(T, T_0)$ and $w(T, T_0)$, respectively. Thus, by (2.18) and (2.19), a necessary and sufficient condition for a minimizer is that $T \equiv T_0$, that $I = \emptyset$, and that B be occupied by the phase with lower free-energy. Thus, by (2.10) and the convention introduced in Section 2, we have the following, physically obvious,

¹Here and in what follows, Σ denotes summation over $i = 1, 2$.

Transition Theorem. *Assume that ∂B is held at the constant temperature T_0 . Then the stable states are single phase with temperature everywhere constant and equal to T_0 . Moreover: if $T_0 < T_M$, the solid phase is the stable phase; if $T_0 > T_M$, the liquid phase is the stable phase; if $T_0 = T_M$, then both phases are stable.*

3.2. Unbounded body under isothermal conditions. Interfacial instabilities.

As we shall show in this section, the theory is more interesting when B is unbounded. In particular, we assume that:

B is all of space.

We are, in effect, modelling a large region whose boundary is held at the constant temperature T_0 , and it would therefore seem appropriate to define stable states through (3.3). The problem with this definition is that, since B is unbounded, the integrals appearing in (3.1) will generally fail to exist. However, for any partition (B_1, B_2) of B and temperature field $T(x)$ we can consider, in place of $F(T, B_1, B_2)$, the approximate free-energy $F_\Omega(T, B_1, B_2)$ obtained by replacing B_i and I by their intersections with a large ball Ω . Then, in view of the discussion leading to the Transition Theorem, for any such Ω ,

$$F_\Omega(T_0, B_1, B_2) < F_\Omega(T, B_1, B_2)$$

for T not identically equal to T_0 .

Thus we are led to consider the problem (3.3) with the **body isothermal** at temperature T_0 . In this case (3.2) takes the form

$$F(T_0, B_1, B_2) = \sum_{B_i} F_i(T_0) + \int_I f(T_0). \quad (3.4)$$

We still have the problem of nonexistent integrals, but this can be circumvented provided we limit our discussion to situations in which

one of the phase regions is bounded,

and this we shall do. Then, by subtracting the same constant K from both bulk free-energies we can give the problem (3.3) meaning; indeed, if we take K to be the bulk free-energy of the unbounded phase at T_0 and normalize the free energies in this manner, we are led to consider, in place of (3.4), the functional

$$F(D) = F^*(T_0)\text{vol}(D) + f(T_0)\text{area}(\partial D),$$

where D is the bounded phase region, while $F^*(T_0)$ is the bulk free-energy of the bounded phase minus the bulk free-energy of the unbounded phase, both evaluated at T_0 . In view of the discussion above,

we define as **stable** those bounded phase regions D that

$$\text{minimize } F(D). \quad (3.5)$$

Problem (3.5) is trivial when $F^*(T_0) \geq 0$: the solution is $D = \emptyset$. Thus assume:

$$F^*(T_0) < 0.$$

Let $b > 0$ be defined by

$$b = -f(T_0)/F^*(T_0), \quad (3.6)$$

so that (3.5) has the form

$$\text{minimize } -\text{vol}(D) + b \text{ area}(\partial D); \quad (3.7)$$

By considering a sequence of balls with radii tending to infinity, it is clear that the infimum of the functional in (3.7) is $-\infty$, and *there are no stable phase regions*. However, even though (3.7) has no solution, we can study the types of instabilities compatible with our model by studying **minimizing sequences**; that is, sequences $\{D_n\}$ on which the functional in (3.7) tends to $-\infty$. Let

$$v_n = \text{vol}(D_n), \quad a_n = \text{area}(\partial D_n).$$

Then $\{D_n\}$ is a minimizing sequence if and only if $\{D_n\}$ is consistent with the **area-volume limit**:

$$v_n - ba_n \rightarrow \infty \text{ as } n \rightarrow \infty.$$

Since $b > 0$, an immediate consequence of this condition is

$$v_n \rightarrow \infty \text{ as } n \rightarrow \infty.$$

Remark. By (2.11), the modulus b has the following approximate form for $u_0 = T_0 - T_M$ small:

$$b \approx T_M f(T_0) / L |u_0|. \quad (3.8)$$

Mullins and Sekerka [1963] estimate that $f(T_M)/L$ has 10^{-7} cm. as order-of-magnitude. Taking this as an estimate of $f(T_0)/L$, and using the value 10^{-2} given by Delves ([1974], p. 80) as a "small value" of $|u_0|/T_M$, we are led to the estimate of 10^{-5} cm. as a reasonable "large value" of b . (Of course, b can be as large as we wish; we simply take T_0 sufficiently close to T_M .)

The area-volume limit restricts the growth-rate of interfacial area, but even so it is possible to construct minimizing sequences in which the interface exhibits interesting behavior. We now give some examples (cf. Figure 4).

1. Dendrite spike.

Let D_n be a right circular cylinder of radius r and height n , with r independent of n and $r > 2b$ (cf. the Remark). Then

$$v_n - ba_n = O(n) \quad (3.9)$$

and the area-volume limit is satisfied. Thus $\{D_n\}$ is a minimizing sequence. We could let $r = r_n$ depend on n , as long as $\inf r_n > 2b$.

2. Dendrite star.

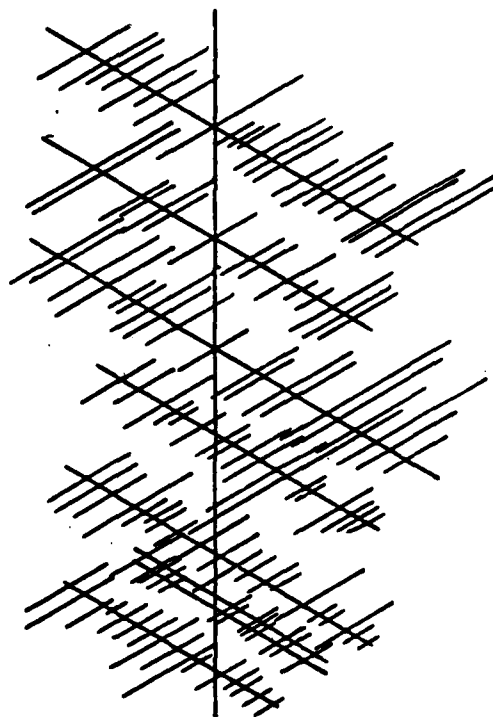
Let D_n be the union of $N(n)$ spikes, all of height n and radius $r > 2b$, where $N(n)$ is finite, but arbitrary. Then (3.9) remains valid and $\{D_n\}$ is a minimizing sequence.

3. Simple dendrite tree.

Let D_n consist of $N(n)$ spikes, each of radius r , but with varying heights which total $l(n)$, where $l(n) \rightarrow \infty$ as $n \rightarrow \infty$. Then, for large n ,

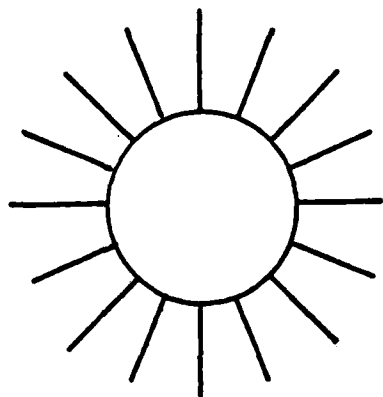
$$v_n = \pi r^2 l(n) + O(1), \quad a_n = 2\pi r l(n) + O(1),$$

and the area-volume limit is again satisfied.



$N(n)$ spikes of
total length $l(n)$;
 $l(n) \rightarrow \infty$

simple dendrite tree



$o(n^2)$ spikes of length n
covering a sphere of
radius n

prickly ball

Figure 4. Some examples of minimizing sequences for (3.5) when the unbounded phase is superthermal.

4. Dendrite tree with branches of varying radii.

Let D_n consist of a stalk, a dendrite spike of radius r_n and height n , and, growing from it, np spikes arranged as follows: for each m , $m = 1, 2, \dots, n$, there are

p spikes of radius r_n/m and height n/m .

Then

$$v_n = \pi r_n^2 np(p^{-1} + 2^{-3} + 3^{-3} + \dots + n^{-3}) + O(1),$$

$$a_n = 2\pi r_n np(p^{-1} + 2^{-2} + 3^{-2} + \dots + n^{-2}) + O(1).$$

For $k = 2, 3$,

$$A_k = p^{-1} + \sum_{m=2}^{\infty} m^{-k}$$

is well defined. Let $r_n \rightarrow r$, with r finite or $+\infty$. Then, if

$$rA_3/A_2 > 2b,$$

the area-volume limit is satisfied.

5. Prickly ball.

Here D_n consists of a sphere of radius n covered with $o(n^2)$ spikes of length n and radius r . Then,

$$v_n = (4/3)\pi n^3 + o(n^3), \quad a_n = o(n^3)$$

and the area-volume limit is satisfied.

The sequences described above furnish simple examples of minimizing sequences and display the richness of the underlying theory; less trivial examples which more closely resemble dendritic behavior are easily constructed.

To state the results of this section succinctly, recall that, in the terminology of Section 2,

$F^*(T_0) < 0$ if and only if the unbounded phase is superthermal;

$F^*(T_0) > 0$ if and only if the bounded phase is superthermal.

Theorem. Assume that the body is isothermal at temperature T_0 .

(i) Consider (3.5) with the unbounded phase superthermal. Then (3.5) has no solution.¹ A sequence $\{D_n\}$ is a minimizing sequence if and only if it obeys the area-volume limit and therefore has corresponding volumes tending to infinity. These conditions allow for interfacial instabilities such as those exhibited by the sequences described above.

(ii) Consider (3.5) with $T_0 = T_M$, or with the bounded phase superthermal. Then the only solution is $D = \emptyset$.

Remarks.

(i) It would be interesting if one could, in some sense, geometrically classify the sequences consistent with the area-volume limit.

(ii) By definition, a phase is superthermal if it has higher free-energy at the underlying temperature. In this sense the superthermal phase is unstable, and, as the theorem shows, the other phase ultimately occupies the entire body.

(iii) Mullins and Sekerka [1963], working within the *dynamical* theory discussed in Section 11, have established the instability of the interface for (infinitesimal perturbations) of a sphere solidifying in a supercooled melt. Assertion (i) of the theorem, with $\{D_n\}$ the prickly ball, gives an analog of the Mullins-Sekerka instability within the framework of the equilibrium theory.

(iv) The Transition Theorem and the theorem above show exactly what is needed for the interface to be unstable, namely:

- (a) an infinite region, for otherwise the boundary captures the instability;
- (b) the unbounded region in a superthermal state, so that it is enveloped by the more-stable bounded region.

¹ Actually, in this case the empty set is a *local* minimum of (3.5), since (3.5) is positive for all D of sufficiently small volume.

3.3. Isolated body.

As a consequence of the transition theorem, stable states are necessarily single phase when the boundary is held at constant temperature. We now show that coexistent phases are possible when, instead, the body is isolated. For convenience, we return to our original assumption that B be *bounded*.

For an **isolated body** the total energy is fixed. Writing E_0 for the value of this energy, the corresponding **stable states** are, by definition, those that

$$\text{maximize } S(T, B_1, B_2) \text{ subject to } E(T, B_1, B_2) = E_0. \quad (3.10)$$

To solve the problem (3.10) we assume that the bulk and interfacial specific heats are strictly positive, and that

$$E_i(0+) \text{ is finite, } E_i(\infty) = +\infty; \quad S_i(0+) = -\infty. \quad (3.11)$$

Also, to insure that the constraint equation in (3.10) has a solution, we assume that

$$E_0 > E_i(0+)V \text{ for at least one value of } i. \quad (3.12)$$

Our next result shows that (3.10) has a solution; in the statement and proof of this theorem we use terminology introduced in the Appendix. Also, for convenience, we write

$$J_M = (E_1(T_M)V, E_2(T_M)V). \quad (3.13)$$

Theorem. *Consider an isolated body. Then there exist stable states corresponding to any E_0 consistent with (3.12). Moreover:*

- (i) *Each stable state has constant temperature.*
- (ii) *Each two-phase stable state has minimal interface; hence the interface is a surface of constant mean curvature which meets ∂B orthogonally.*
- (iii) *For $f(T_M)$ sufficiently small there is a nonempty interval $J \subset J_M$ such that for $E_0 \in J$ all stable states are two phase.*

Proof. Our proof will proceed in three steps.

Step 1: Proof of (i). Fix B_1, B_2 (and hence I), let

$$v_i = \text{vol}(B_i), \quad a = \text{area}(I),$$

and consider (3.10) as a problem for T . Let us agree to call a temperature field T : *admissible* if T is consistent with the energy constraint in (3.10); *phasewise constant* if T is constant on B_1 , constant on B_2 , and constant on I . Further, for each temperature field T define numbers $T_1 > 0$ and $T_2 > 0$ by

$$E(T_1)v_1 = \int_{B_1} E_i(T), \quad e(T_2)a = \int_I e(T).$$

(Because of the strict monotonicity of $E_i(T)$ and $e(T)$, this definition is valid.) Then, in view of (2.20),

$$\int_{B_1} (S_i(T) - S_i(T_1)) = \int_{B_1} (S_i(T) - S_i(T_1) - T_1^{-1}(E_i(T) - E_i(T_1))) < 0$$

if T is not identically equal to T_1 on B_1 ; a similar argument applies to $s(T)$ on I . Assume that T is admissible, but not phasewise constant. Then, by the above inequalities, the phasewise-constant field with values T_1 on B_1 and T_2 on I is admissible and has total entropy strictly larger than that for T . Thus

the set of stable states is contained in the set of states with phasewise-constant temperature fields. (3.14)

Continue to hold B_1, B_2 (and hence I) fixed. Consider the problem, motivated by (3.14), of finding numbers $T_1 > 0$ and $T_2 > 0$ that

$$\begin{aligned} &\text{maximize} \quad S_1(T_1)v_1 + S_2(T_2)v_2 + s(T_2)a \\ &\text{subject to} \quad E_1(T_1)v_1 + E_2(T_2)v_2 + e(T_2)a = E_0. \end{aligned} \quad (3.15)$$

In view of (3.11) and the continuity of the functions appearing in (3.15), this problem has a solution and, using a Lagrange-multiplier, it is a simple matter to verify that solutions have $T_1 = T_2 = T_1$. Thus

the set of stable states is contained in the set of states with constant temperature fields, (3.16)

which establishes assertion (i) of the theorem.

Step 2: Existence of stable states and proof of (ii). Consider the problem of finding numbers

$$T > 0, \quad 0 \leq v \leq V, \quad a \geq a_{\min}(v) \quad (3.17)$$

that solve the problem

$$\begin{aligned} \text{minimize} \quad & W(a, v, T; T_0) = W_1(T, T_0)v + W_2(T, T_0)(1-v) + w(T, T_0)a \\ & (3.18) \end{aligned}$$

$$\text{subject to} \quad E_1(T)v + E_2(T)(1-v) + e(T)a = E_0,$$

where $a_{\min}(v)$ is the minimal-area function defined in the Appendix, W_1 and w are the Gibbs functions (2.17), and $T_0 > 0$ is arbitrary, but fixed. Because of (2.17) and (3.16), every stable state (T, B_1, B_2) yields a solution (a, v, T) of (3.18) with

$$v = \text{vol}(B_1), \quad a = \text{area}(I); \quad (3.19)$$

conversely, every solution (a, v, T) of (3.18) generates - in the obvious sense - a stable state provided we can find a partition of B consistent with (3.19). But by Theorem 1 of the Appendix, such a partition can always be found if

$$a = a_{\min}(v). \quad (3.20)$$

Thus to complete Step 2, it suffices to show that (3.18) has a solution, and that every solution obeys (3.20).

Because of (2.17) and (3.11), $w(T, T_0)$ is bounded below, while

$$W_1(0+, T_0) = +\infty, \quad W_1(+\infty, T_0) = +\infty;$$

thus (3.18) has a solution. Let (a, v, T) be such a solution. Then (a, v, T) is a solution for any $T_0 > 0$. Choose $T_0 > T$. Assume that $a > a_{\min}(v)$. Then, because of the strict monotonicity of the internal energies, we can find numbers a^* and T^* such that $T < T^* < T_0$ and $a_{\min}(v) < a^* < a$; and such that (a^*, v, T^*) satisfies the constraint equation in (3.18). Further, because of (ii) of the theorem containing (2.19),

$$W(a^*, v, T^*; T_0) < W(a, v, T; T_0),$$

which contradicts our assumption that (a, v, T) solve (3.18). Thus (a, v, T) obeys (3.20).

Step 3: Proof of (iii). Let

$$W_M = W_1(T_M, T_M) = W_2(T_M, T_M), \quad a_{\max} = \sup \{a_{\min}(v): 0 \leq v \leq V\},$$

and let $T_i = T_i(E_0)$ be the unique solution of

$$E_i(T_i)V = E_0.$$

Then, as is clear from Figure 5 and the properties of the Gibbs functions, there is a nonempty interval $J \subset J_M$ such that for $E_0 \in J$,

$$W_1(T_i(E_0), T_M) > W_M + f(T_M)a_{\max} \geq W(a_{\min}(v), v, T_M, T_M). \quad (3.21)$$

The left side of this inequality is the total Gibbs-energy (3.18)₁ (with $T_0 = T_M$) for the two admissible single-phase states. On the other hand, for $0 < v < V$ the right side is the total Gibbs-energy for a (not necessarily admissible) two-phase state at temperature $T = T_M$. Thus, if we can find a $v \in (0, V)$ that satisfies the energy constraint (3.18)₂ with $T = T_M$, we will have exhibited an admissible two-phase state with lower total Gibbs-energy than the two admissible single-phase states, so that the solution of (3.18) is necessarily two phase. Thus to complete the proof we have only to find a $v \in (0, V)$ such that

$$E_1(T_M)v + E_2(T_M)(1-v) + e(T)a_{\min}(v) = E_0. \quad (3.22)$$

But since $E_0 \in J_M$, and since the left side of (3.22) varies continuously from $E_2(T_M)V$ at $v = 0$ to $E_1(T_M)V$ at $v = V$, we may use (3.13) to conclude that such a v exists. $\square$

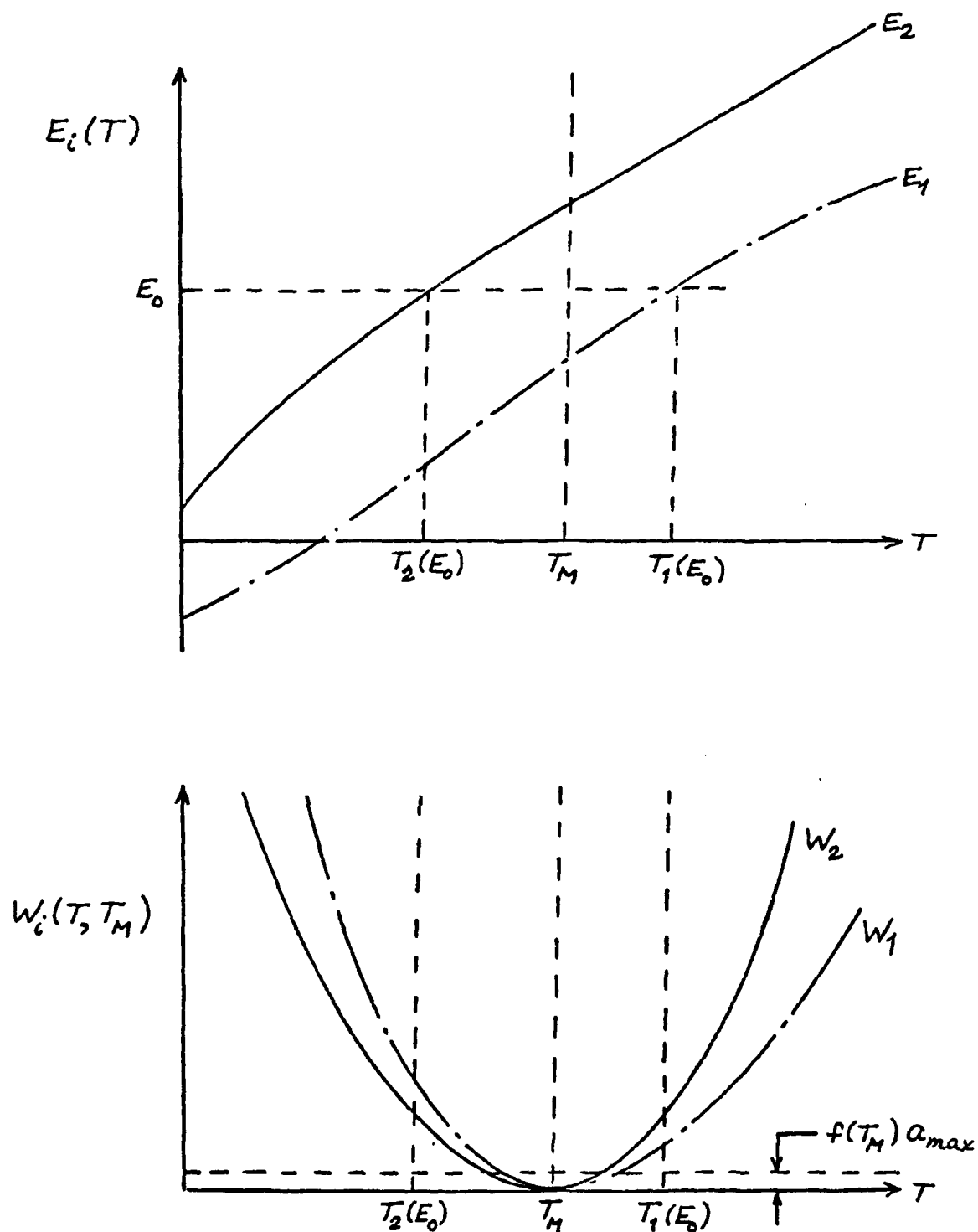


Figure 5. Internal energies $E_i(T)$ and Gibbs functions $W_i(T, T_M)$ as functions of temperature T .

PART II. GENERAL THEORY.

4. Preliminaries.

We now allow the interface $I(t)$ and (hence also) the phase regions $B_i(t)$ to depend on the time t . We use the following notation (Figure 2): $n(x)$ is the outward unit normal to ∂B ; $m(x,t)$ is the outward unit normal to $B_i(t)$ on $I(t)$; $v(x,t)$ is the **normal velocity** of the interface in the direction $m(x,t)$; $\kappa(x,t)$ is the **sum of principal curvatures** of $I(t)$ with $\kappa > 0$ when the center of curvature lies toward B_i ; $\cot(m,n)$ is the cotangent of the angle between m and n :

$$\cot(m,n) = p/(1-p^2)^{1/2}, \quad p = m \cdot n. \quad (4.1)$$

For any field $g(x,t)$, let $g_{(i)}$ denote the limit of g as the interface is approached from points of B_i , and let

$$[g] = g_{(2)} - g_{(1)} \quad (4.2)$$

denote the jump in g across I . We then have the standard identity

$$\left(\int_B g \right)' = \int_{B_1} g' + \int_{B_2} g' - \int_I [g]v. \quad (4.3)$$

A less trivial result holds for integrals over the interface. Let $g(x,t)$ be defined for each x in $I(t)$ and all t . Choose a time β and a point y in $I(\beta)$, and let $x(t)$ denote the curve that passes through y at time β and has

$$x'(t) = v(x(t),t)m(x(t),t)$$

for all t . Then

$$g^A(y,\beta) = (d/dt)g(x(t),t)|_{t=\beta} \quad (4.4)$$

represents the time-derivative of g following I .

Transport Theorem.¹

$$(\int g)^* = \int g_k v + \int g^A - \int_{\partial I} g v \cot(m \cdot n). \quad (4.5)$$

The first term on the right side of (4.5) represents a change in the integral of g due to the curvature of the interface, the second term gives the change due to changes in g , the third term represents a flux of g across the boundary of B .

An immediate consequence of (4.5) is the transport theorem for area:

$$\text{area}(I)^* = \int k v - \int_{\partial I} v \cot(m \cdot n). \quad (4.6)$$

Remark. By (4.1), $\cot(m \cdot n) = \infty$ when $m = \pm n$. Thus for (4.5) and (4.6) to be valid it is necessary that

$$\text{on } \partial I: v = 0 \text{ when } m = \pm n, \quad (4.7)$$

and that this limiting value of v be approached sufficiently rapidly from the interior of I . This condition will be a tacit assumption in what follows.

Let S denote an arbitrary subsurface of ∂B , let $r > 0$, and let

$$D_r = \{x: x = y - Bn(y), y \in S, 0 \leq B \leq r\},$$

$$S_r = \{x: x = y - rn(y), y \in S\}.$$

Then D_r and S_r , respectively, are the region and surface obtained by r -transporting S along the normal. Here we will always write n_r for the outward unit normal to D_r on S_r (Figure 6).

¹Williams [1985]. In this connection see also Scriven [1960], Moockel [1975].

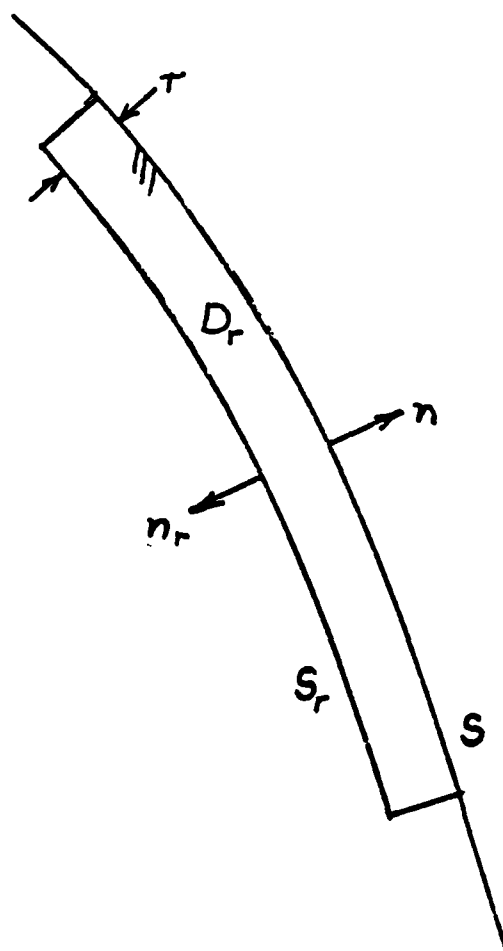


Figure 6. The region D_r and surface S_r obtained by r -transporting S along the normal.

5. First two laws. Additional constitutive assumptions.

To discuss the thermodynamics of B we allow the functions $E(x,t)$, $S(x,t)$, $T(x,t)$, $e(x,t)$, and $s(x,t)$ to depend on the time t , and we introduce a new field: $q(x,t)$, the heat flux per unit area.

Let D be an arbitrary fixed subregion of B , and let

$$I_D = I \cap D; \quad c_D = \partial I_D \setminus \partial B, \quad (5.1)$$

so that ∂I_D is the closed curve which marks the intersection of I with ∂D , while c_D is the portion of this curve which lies in the interior of B .

The internal energy of D is given by

$$\int_D E + \int_{I_D} e,$$

Also, because of the (possible) motion of the interface relative to D , there is a flux of interfacial energy across the boundary of D (and out of D) of amount

$$\int_{c_D} \gamma \cot(m \cdot n),$$

where n is the outward unit normal to ∂D , while $\cot(m \cdot n)$ is defined in (4.1) (cf. Figure 7). We integrate over c_D , rather than ∂I_D , since there is no loss of interfacial energy across the boundary of B . Finally, there is a flux of heat into D of amount

$$- \int_{\partial D} q \cdot n.$$

In view of the above discussion, the first law for D takes the form:

$$\left(\int_D E + \int_{I_D} e \right)' + \int_{c_D} \gamma \cot(m \cdot n) = - \int_{\partial D} q \cdot n. \quad (5.2)^{1,2}$$

Similarly, D has internal entropy and there is a flux of interfacial entropy across the boundary of D . Also, the flow of heat is accompanied by a flux of entropy of amount

¹Fernandez-Diaz and Williams [1979]. An earlier version is contained in the work of and Moeckel [1975], but Moeckel introduces a somewhat artificial material description of the interface. Other discussions of the first law are given by Fisher and Leitman [1968], Murdoch [1976], Wollkind [1979], and Rogers [1983].

²Surface tension, in our theory equal to the interfacial free-energy, does not enter the first law; indeed, since our model is rigid, bulk and interface forces do no work.

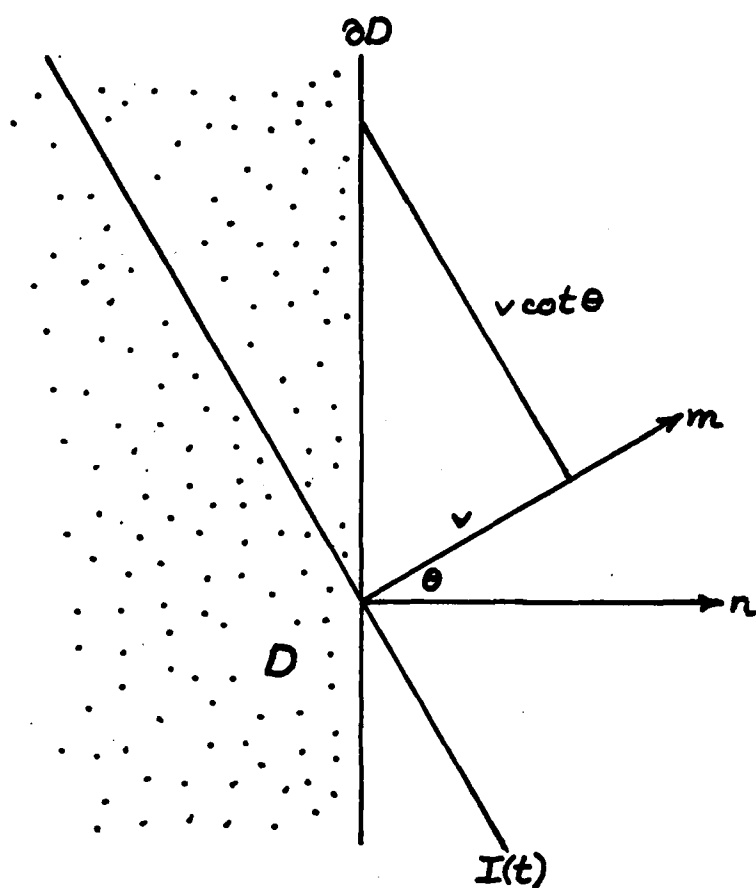


Figure 7. Behavior of the interface $I(t)$ near ∂D ; $v \cot \theta$ is the rate at which interfacial area leaves D , per unit length of ∂I_D .

$$-\int_{\partial D} T^{-1} q \cdot n.$$

We therefore write the second law for D as

$$\left(\int_D S + \int_{\partial D} S \right)' + \int_{\partial D} s v \cot(m \cdot n) \geq - \int_{\partial D} T^{-1} q \cdot n. \quad (5.3)$$

The term

$$P(D) = \left(\int_D S + \int_{\partial D} S \right)' + \int_{\partial D} s v \cot(m \cdot n) + \int_{\partial D} T^{-1} q \cdot n \quad (5.4)$$

represents the entropy production in D, and the second law (5.3) is simply the requirement that $P(D) \geq 0$.

In addition to the constitutive assumptions introduced in Section 2.1, we assume that the heat flux q is governed by the constitutive equation

$$q = -k_j(T) \text{grad} T \quad (5.5)$$

in each phase region B_j , with

(A7) conductivities $k_j(T) > 0$.

Concerning the interface I, we assume that

(A8) T is continuous across the interface, (5.6)

so that the interfacial temperature is defined unambiguously. In addition, we assume that *the interface produce no entropy*:

(A9) if the volume of D tends to zero, then $P(D)$ tends to zero. (5.7)

6. Partial-differential equations. Jump conditions.

In this section we derive consequences of the requirement that the first two laws (5.2) and (5.3) be satisfied in every subregion D of B .

We assume that the fields E , S , and T are smooth away from the interface I . Then (5.2) applied to an arbitrary region D lying in B_1 in conjunction with the constitutive equations (2.1) and (5.5), lead to the classical partial-differential equations

$$E_1(T)^* = -\text{div} q, \quad q = -k_1(T) \text{grad} T, \quad (6.1)$$

or equivalently, by (2.3),

$$C_1(T) T^* = \text{div}(k_1(T) \text{grad} T) \quad (6.2)$$

in B_1 for all time.

Our next step is to derive appropriate jump conditions across the interface. Although the temperature is continuous, the fields E , S , and q will generally suffer jump discontinuities across the interface. We also allow $q(x,t)$ to become infinite as x approaches $\partial I(t)$; in fact, we assume the existence of a scalar function $Q(x,t)$ on $\partial I(t)$ such that: given any suburface S of ∂B , if S_r is obtained from S by r -transporting S along the normal, then

$$\int_{S_r} q \cdot n_r \rightarrow \int_S q \cdot n + \int_{S \cap \partial I} Q, \quad \int_{S_r} T^{-1} q \cdot n_r \rightarrow \int_S T^{-1} q \cdot n + \int_{S \cap \partial I} T^{-1} Q \quad (6.3)$$

as $r \rightarrow 0$.

The next result is central to our investigation.

Interface Theorem. *The interfacial balance laws*

$$-v[E] + v k_e + e^\Delta = -[q] \cdot m, \quad (6.4)^1$$

$$-v[S] + v k_s + s^\Delta = -T^{-1}[q] \cdot m \quad (6.5)$$

hold on I for all time. The contact condition

$$v m \cdot n = 0. \quad (6.6)$$

holds on ∂I for all time.

Proof. Note first that, by (6.1) and the identity $E_1(T)^* = T S_1(T)^*$,

¹Cf. Moeckel [1975], Fernandez-Diaz and Williams [1979].

$$S_i(T)^* = -\operatorname{div}(T^{-1}\mathbf{q}) + r, \quad r = -T^{-2}\mathbf{q} \cdot \operatorname{grad} T \quad (6.7)$$

in B_i for all time.

Next, the laws (5.2) and (5.4), for an arbitrary subregion D of B , have the form

$$\left(\int_D G + \int_{I_D} g \right)^* + \int_{\partial D} g v \cot(\mathbf{m} \cdot \mathbf{n}) = - \int_{\partial D} \mathbf{p} \cdot \mathbf{n} + R(D), \quad (6.8)$$

with $R=0$ for (5.2) and $R=P$ for (5.4), so that in either case R is consistent with (5.7). By (4.3) and (4.5), the left side of (6.8) is equal to

$$\int_{D_1} G^* + \int_{D_2} G^* + \int_{I_D} (g^* v + g^A - [G]v) - \int_{s_D} g v \cot(\mathbf{m} \cdot \mathbf{n}), \quad (6.9)$$

where D_i is the portion of D in B_i , while

$$s_D = \partial I_D \cap \partial B$$

is the portion of ∂I_D in contact with ∂B .

Assume first that ∂D does not touch ∂B . Then we may use (6.1), (6.7), and the divergence theorem to conclude that

$$\int_{D_i} G^* = - \int_{\partial D_i} \mathbf{p} \cdot \mathbf{n} + Z(D_i), \quad (6.10)$$

where $Z(D_i)$ tends to zero with the volume of D_i . Further,

$$\int_{I_D} [\mathbf{p}] \cdot \mathbf{m} = \left(\int_{\partial D} - \int_{\partial D_1} - \int_{\partial D_2} \right) (\mathbf{p} \cdot \mathbf{n}), \quad (6.11)$$

and, since s_D is empty, if we combine (6.7)-(6.11) we find that

$$\int_{I_D} (g^* v + g^A - [G]v + [\mathbf{p}] \cdot \mathbf{m}) = R(D) - Z(D_1) - Z(D_2). \quad (6.12)$$

By (5.7), if we shrink D to the interface, the right side of (6.12) tends to zero; since I_D is essentially arbitrary, this yields (6.4) and (6.5).

Now choose a subsurface S of ∂B , apply (6.8) and (6.9) to the region D_r obtained from S by r -transporting S along the normal, and let r approach zero; by (5.7), (6.3), and the fact that S is arbitrary, the result is

$$\operatorname{evcot}(\mathbf{m} \cdot \mathbf{n}) = Q, \quad \operatorname{svcot}(\mathbf{m} \cdot \mathbf{n}) = T^{-1}Q, \quad (6.13)$$

so that, by (2.13),

$$f(T) \operatorname{vcot}(\mathbf{m} \cdot \mathbf{n}) = 0,$$

which yields (6.6), since $f > 0$. $\square$

Remarks.

(i) It is clear from (6.6) and (6.13) that $Q = 0$, so that (apart from a possible jump discontinuity) the *heat flux is nonsingular* along ∂I .

(ii) We could also allow for surface energies e_i and surface entropies s_i between the phases and ∂B . Were we to do this, then, assuming e_i and s_i are constant, (6.6) would be replaced by the more general condition

$$v(f_1(T) - f_2(T) - (m \cdot n)f(T)) = 0, \quad f_i(T) = e_i - Ts_i$$

on ∂I . Moreover, in this case the *heat flux is generally singular* on ∂I with

$$Q = -v(e_1 - e_2 - (m \cdot n)e(T))\{1 - (m \cdot n)^2\}^{-1/2}.$$

As an immediate corollary of (6.4) and (6.5) we have, for $v \neq 0$,

Balance of free energy. On I , for all time,

$$[F] = k_f, \tag{6.14}$$

or equivalently

$$T = ([E] - k_e)/([S] - k_s). \tag{6.15}$$

Proof. By (2.13) and (4.4), $e^\Delta = Ts^\Delta$; thus if we eliminate the heat flux from (6.4) and (6.5), we arrive at (6.14), and solving this for T yields (6.15). $\square$

Remarks.

(i) If $e=s=0$, which is the assumption underlying the classical theory of melting, or if $k=0$, then, as a direct consequence of (6.15),

$$T = [E]/[S] \tag{6.16}$$

and

$$[F] = 0. \tag{6.17}$$

Thus, granted the assumption that the free energies $F_i(T)$ coincide at exactly one temperature, we find, as a consequence of the laws of thermodynamics, that in the absence of interfacial structure the

free-boundary condition (6.15) must necessarily reduce to the classical condition

$$T = T_M \text{ on } I.$$

(ii) Even though the notion of force does not enter our theory, we can define pressure by noting that, since $F_i(T)$ is the free-energy per unit volume, $VF_i(T)$ is the free-energy a region of volume V would have if occupied solely by phase i ; differentiating this expression with respect to volume yields the negative of the *pressure*:

$$p_i = -F_i(T).$$

A similar argument identifies $f(T)$ with *surface tension* σ . With these definitions (6.14) is the Gibbs-Thompson relation¹

$$p_1 - p_2 = k\sigma.$$

It must be emphasized that our derivation of (6.14) makes no use whatsoever of the notion of equilibrium.

(iii) It is not difficult to show that

$$P(B) = \sum_{B_i} k_i \int T^{-2} |\text{grad} T|^2,$$

so that, as would be expected, the entire production of entropy is due to heat conduction.

We close this section by listing what might be considered a complete system of field equations and free-boundary conditions for the general nonlinear theory: namely, (6.2), (6.4), (6.6), and (6.15). We do not need (6.5), since, granted (6.4), the conditions (6.15) and (6.5) are equivalent. The system is, then,

$$C_i(T) T^* = -\text{div} \mathbf{q}, \quad \mathbf{q} = -k_i(T) \text{grad} T, \quad \text{in } B_i, \quad (6.18)$$

$$T = ([E] - k_e)/([S] - k_s), \quad [\mathbf{q}] \cdot \mathbf{m} = v[E] - v k_e - e^A \quad \text{on } I, \quad (6.19)$$

$$v \mathbf{m} \cdot \mathbf{n} = 0 \quad \text{on } \partial I, \quad (6.20)$$

with E , S , e , and s given by the constitutive equations (2.1), (2.2), (2.12), and (2.13).

¹Gibbs [1878], Eq. (500).

7. Boundary conditions. A bound on interfacial area.

Throughout this paper we will be concerned with the following boundary conditions:¹

(i) isolated boundary:

$$\mathbf{q} \cdot \mathbf{n} = 0 \text{ on } \partial B; \quad (7.1)$$

(ii) isothermal boundary:

$$T = T_0 \text{ on } \partial B \quad (T_0 \text{ constant}). \quad (7.2)$$

These boundary conditions, when combined with (5.2), (5.4), and (6.6), yield the

Global growth conditions. *If the boundary is isolated,*

$$\begin{aligned} \left(\int_B E + \int_I e \right)' &= 0, \\ \left(\int_B S + \int_I s \right)' &= P(B) \geq 0. \end{aligned} \quad (7.3)$$

If the boundary is isothermal or isolated,

$$\left\{ \int_B (E - T_0 S) + \int_I (e - T_0 s) \right\}' \leq -T_0 P(B) \leq 0, \quad (7.4)$$

with the constant $T_0 \geq 0$ arbitrary when ∂B is isolated.

Remark. Note that the variational characterizations (3.3) and (3.10) can be deduced from the above theorem under the assumption that each process consistent with boundary conditions (7.1) or (7.2) approach a stable equilibrium as $t \rightarrow \infty$.

If we integrate (7.4) from the initial time $t=0$ to an arbitrary time, we conclude, with the aid of (2.19), that

$$F_1(T_0) \text{vol}(B_1) + F_2(T_0) \text{vol}(B_2) + f(T_0) \text{area}(I(t)) \leq F(0),$$

$$F(0) = \text{the initial-value of } \int_B (E - T_0 S) + \int_I (e - T_0 s).$$

¹We do not mean to imply that these are the only boundary conditions of interest. In fact, here and in subsequent sections, all results for an isothermal boundary are valid without change for the boundary condition: $T = T_0$ on A_1 , $\mathbf{q} \cdot \mathbf{n} = 0$ on A_2 , with A_1 complementary (nontrivial) subsets of ∂B .

Thus, letting

$$F_{\min}(T_0) = \min\{F_1(T_0), F_2(T_0)\}, \quad V = \text{vol}(B),$$

we are led to the following

Bound on interfacial area. *Assume that the boundary is isolated or isothermal. Then for all time t ,*

$$\text{area}(I(t)) \leq f(T_0)^{-1}\{F(0) - VF_{\min}(T_0)\}, \quad (7.5)$$

with T_0 arbitrary when ∂B is isolated.

Note that, in addition to (8.5), we have the estimate

$$VF_{\min}(T_0) \leq \int_B (E - T_0 S) \leq F(0).$$

Intuitively, one type of dendrite might be a "set" with vanishingly small volume, but nonzero surface area. The following definition¹ makes this idea precise.

We say that phase I approaches a **dendrite with null volume** if:

$$\lim_{t \rightarrow \infty} \text{vol}(B_I(t)) = 0, \quad \liminf_{t \rightarrow \infty} \text{area}(I(t)) > 0. \quad (7.6)$$

Remark. The inequality (7.5) asserts that $\text{area}(I(t))$ is bounded uniformly in t by a constant which depends only on: (i) the bulk and interfacial free-energies at T_0 ; (ii) the initial data. At first glance it might seem that this bound on interfacial area precludes the formation of an interface which is too wild. But this is not so. Indeed, dendrites with null volume are completely consistent with (7.5). Moreover, as we shall see, the theory discussed here will predict such instabilities, but only on a very small length scale.

¹A more general definition would use the limit $t \rightarrow t^*$ with t^* finite or infinite.

8. Quasi-static theory.

8.1. Basic equations. Growth conditions.

In this section we attempt to model situations in which the interface moves slowly compared with the time scale for heat conduction.¹ The constitutive hypothesis underlying our model is that - in each of the phases - both the bulk energy and the bulk entropy are constant. Since the two phases coexist at the interface, the constant values of energy and entropy should be the values in the real material at the transition temperature. Thus, by (2.5) and (2.8), and since there is no loss of generality in allowing the energy and entropy to vanish in phase 1, we base our model on the constitutive assumptions:

$$\begin{aligned} E_1 &= 0, & E_2 &= L, \\ S_1 &= 0, & S_2 &= L/T_M, \end{aligned} \tag{8.1}$$

with $L > 0$ the latent heat (2.5). In addition to (8.1), we suppose that²

$$e, s, \text{ and } k_i \text{ are strictly-positive constants; } f(T_M) > 0. \tag{8.2}$$

Remark. By (8.1), the bulk and interfacial specific-heats are identically zero. Note also that, because of (8.2), the resulting interfacial free-energy has the form $f(T) = e - Ts$ and is negative for large values of T . It is therefore tacit that - for this model - we are dropping assumptions (A3) and (A6).

For convenience, we shall generally refer to

$$u = T - T_M \tag{8.3}$$

as the *temperature*. This definition and (8.1) allow us to write the interface condition (6.19)₁ in the form:

$$u = -h\kappa/(1-a\kappa), \tag{8.4}$$

where h and a are capillarity lengths defined by

$$h = T_M f(T_M)/L, \quad a = T_M s/L. \tag{8.5}$$

¹This assumption is discussed by Mullins and Sekerka [1963].

²Although we make these assumptions for convenience only, we may infer from remarks of Adam [1930], p. 20 that for many liquids the assumptions concerning e and s are reasonable over a wide range of temperatures.

Thus, by (6.18)-(6.20), we base our model on the equations:

$$\Delta u = 0, \quad q = -k_1 \text{grad} u \quad \text{in } B_1, \quad (8.6)$$

$$u = -h\epsilon/(1-\alpha\epsilon), \quad [q] \cdot m = (L - \epsilon e)v \quad \text{on } I, \quad (8.7)$$

$$vm \cdot n = 0 \quad \text{on } \partial I. \quad (8.8)$$

Remarks.

(i) By (8.2), (8.3) and (8.5), T computed using (8.7), has the unfortunate property:

$$T \leq 0 \quad \text{for } L/e \leq \epsilon \leq L/(T_M s);$$

hence *this range of curvatures lies outside the range of validity of our model*. Mullins and Sekerka [1963] estimate that $f(T_M)/L$ has 10^{-7} cm. as order-of-magnitude. If we take this value as an estimate for e/L , we see that this range of curvatures corresponds to radii of curvature $< 10^{-7}$ cm.
(ii) It is not difficult to verify (by simply reversing the steps of the arguments given in Section 5) that solutions of the system (8.6)-(8.8) are consistent with the first two laws as presented in Section 5.

In view of the preceding remark, under appropriate boundary conditions solutions of (8.6)-(8.8) satisfy the growth relations (7.3) and (7.4) as well as the area estimate (7.5). We can, however, deduce more interesting estimates. We begin by writing the *isothermal boundary-condition* (7.2) in the form

$$u = u_0 \quad \text{on } \partial B \quad (u_0 = T_0 - T_M). \quad (8.9)$$

Next,

$$\text{vol}(B_1)^* = -\text{vol}(B_2)^*, \quad (8.10)$$

and, by (8.1) and (8.3), for $g = e$ or s ,

$$\left(\int_B E \right)^* = L \text{vol}(B_2)^* = T_M \left(\int_B S \right)^*, \quad \left(\int_I g \right)^* = g \text{area}(I)^*$$

Therefore, if we write

$$\mu = T_M f(T_0)/L, \quad \beta = e/L$$

(so that $\beta > 0$), and assume that $\mu > 0$ in the case of an isothermal boundary, then (7.3) and (7.4), with $T_0 = T_M$ in the case of an isolated boundary, yield the following

Growth conditions.

(i) *For an isolated boundary,*

$$\text{vol}(B_2)^* + \beta \text{area}(I)^* = 0, \quad \text{area}(I)^* \leq 0. \quad (8.11)$$

(ii) *For an isothermal boundary,*

$$u_0 \text{vol}(B_1)^* + \mu \text{area}(I)^* \leq 0. \quad (8.12)$$

Appropriate initial conditions for the system (8.6)–(8.8) are:

$$B_i(0) = B_{0i}, \quad (8.13)$$

with (B_{01}, B_{02}) the initial distribution of phases. We shall designate by **Problem QS** the initial-value problem defined by (8.6)–(8.8), (7.1) or (8.9), and (8.13).

Questions.

1. What is an appropriate weak formulation of Problem QS?
2. Is Problem QS well posed?

The growth conditions for QS yield a uniform bound on interfacial area, and hence imply that the interface cannot become too wild. However, as we have remarked in Section 5, estimates of this nature do not, a-priori, rule out dendrites with null volume. To discuss this possibility, let

$$E_0 = \text{vol}(B_2(0)) + \beta \text{area}(I(0)), \quad (8.14)$$

so that E_0 is essentially the **initial energy**. Then we have the following mathematically trivial, but physically interesting, consequence of the growth conditions.

Corollary. *For an isolated boundary, if the initial energy is small enough ($E_0 < V$), then dendrites with null volume cannot form.*

Proof. In view of (8.10) and (8.11),

$$\text{vol}(B_2)^* \geq 0,$$

so that for a dendrite with null volume to form, $\text{vol}(B_2) \rightarrow V$. But by (8.11) and (8.14),

$$\text{vol}(B_2(t)) \leq E_0, \quad (8.15)$$

and the desired conclusion follows. $\square$

Remark. By (8.14), for $B_1(0)$ a sphere of radius r , the condition $E_0 > V$ is equivalent to $r < 3\beta$. Using the Mullins and Sekerka [1963] estimate of 10^{-7}cm. as an order-of-magnitude for $\beta = e/L$, we see that for the formation of dendrites as discussed above we must have $r < 10^{-7}\text{cm.}$

8.2. Equilibrium in the quasi-static theory.

We now turn to a discussion, mostly formal, of the equilibrium behavior of solutions to Problem QS. Consider, then, a solution of Problem QS and suppose that

$$\text{as } t \rightarrow \infty, \text{ an equilibrium state } (u_\infty, B_{1\infty}, B_{2\infty}) \text{ exists.} \quad (8.15)$$

Let I_∞ denote the interface corresponding to $(B_{1\infty}, B_{2\infty})$. For convenience, we consider separately the two types of boundary conditions.

A. Isolated boundary.

Let $E_0 \geq 0$ be the initial energy (8.14). Then by (8.10) and (8.11) it seems reasonable to expect that $(B_{1\infty}, B_{2\infty})$ is a solution, or at least a local minimizer, of the variational problem: *minimize*

$$\text{area}(I_\infty)$$

subject to the constraint

$$\text{vol}(B_{2\infty}) + \beta \text{area}(I_\infty) = E_0.$$

The solution of this variational problem, *if* say, is given in Theorem 2 of the Appendix; the results are:

- (i) If $E_0 \leq V$, then *if* has a solution. Moreover, every solution will have minimal interface, and hence will have an interface of constant mean curvature which meets ∂B orthogonally.
- (ii) If $E_0 > V$, then *if* has no solution in the standard sense. Minimizing sequences (B_{1n}, B_{2n}, I_n) will have

$$\text{vol}(B_{1n}) \rightarrow 0, \quad \text{area}(I_n) \rightarrow (E_0 - V)/\beta > 0. \quad (8.17)$$

Remark. By our convention (Section 2), phase 1 is the solid phase. Thus if the initial "energy" is large enough, then, for each minimizing sequence, the region occupied by the solid phase approaches a "set" which has zero volume, but non-zero boundary-area, a result which, by (7.6), seems indicative of the formation of dendrites. Note that this phenomenon does not arise in the general theory (cf. the theorem of Section 3.3). In the quasi-static theory the bulk energies are constant, and thus sufficiently large energies can be attained only with the formation of a large interface; this is the reason for the behavior specified in (ii) above.

On the other hand, in the general theory the bulk energies increase to infinity with temperature, and thus large energies are attainable without creating a large interface.

B. Isothermal boundary.

By (8.12) the equilibrium configuration should

$$\text{minimize } u_0 \text{vol}(B_{1\infty}) + \mu \text{area}(I_\infty).$$

This variational problem has an obvious solution. For $u_0 = 0$, $B_{1\infty}$ is either B or $\emptyset$. Further, since

$$\text{vol}(B_{1\infty}) + \text{vol}(B_{2\infty}) = V,$$

for $u_0 \neq 0$, $B_{1\infty}$ is either B or $\emptyset$ according $u_0 < 0$ or $u_0 > 0$. Thus, granted the validity of this variational problem, B is ultimately single phase, the solid phase prevailing if $u_0 < 0$, the liquid phase if $u_0 > 0$. As would be expected, these results are consistent with the Transition Theorem (Section 3.1).

8.3. Quasi-static theory with B unbounded.

We now allow B to be all of space, but assume that

$$\text{one of the regions } B_i(t) \text{ is bounded for all } t \quad (8.18)^1$$

(cf. Section 3.2). Then for B_2 bounded the constitutive equations (8.1) lead to finite values for total energy and entropy. This will be true also for B_1 bounded provided we stipulate that for this case (8.1) be replaced by

$$E_1 = -L, \quad E_2 = 0,$$

$$S_1 = -L/T_M, \quad S_2 = 0.$$

In addition, we write $r=|x|$ and replace the boundary conditions by either of the following conditions:

(i) **body isolated at infinity:**

$$q(x,t) \rightarrow 0 \text{ as } r \rightarrow \infty,$$

(ii) **body isothermal at infinity:**

$$u(x,t) \rightarrow u_0 \text{ as } r \rightarrow \infty.$$

Then, since u is harmonic in a neighborhood of infinity, we have the following estimates as $r \rightarrow \infty$:

$$u(x,t) = g(t) + O(r^{-1}), \quad q(x,t) = O(r^{-2}) \quad \text{if isolated at infinity,}$$

$$u(x,t) = u_0 + O(r^{-1}), \quad q(x,t) = O(r^{-2}) \quad \text{if isothermal at infinity.}$$

These estimates allow us to establish (7.3) and (7.4) under the present hypotheses: we simply replace D in (5.2) and (5.3) by a large ball whose radius is ultimately allowed to tend to infinity. Using the extended versions of (7.3) and (7.4), it is a simple matter to verify the following:

¹Then the analysis of Sections 5 and 6 extend; we need only require that the first two laws hold in every bounded subregion of B . Note that the contact condition (6.6) is here vacuous.

Growth conditions for an unbounded body. *Let B_i be the bounded phase region.*

(i) *If the body is isolated at infinity, then*

$$(-1)^i \text{vol}(B_i)^* + \beta \text{area}(I)^* = 0, \quad \text{area}(I)^* \leq 0. \quad (8.19)$$

(ii) *If the body is isothermal at infinity, then*

$$(-1)^{i+1} u_0 \text{vol}(B_i)^* + \mu \text{area}(I)^* \leq 0. \quad (8.20)$$

8.4. Equilibrium with B unbounded.

We assume that (8.16) is satisfied and, for convenience, consider separately the two conditions at infinity.

A. Body isolated at infinity.

For B_i the bounded region let

$$E_0 = \text{the initial-value of } (-1)^i \text{vol}(B_i) + \beta \text{area}(\partial B_i), \quad (8.21)$$

so that, as before, E_0 is essentially the initial energy. Here we have used the fact that

$$I = \partial B_i.$$

For convenience, write

$$D = B_{i_\infty}$$

for the region occupied by the bounded phase at equilibrium. Then by (8.19) it seems reasonable to expect that D is a solution of the variational problem:

$$\begin{aligned} &\text{minimize} \quad \text{area}(\partial D) \\ &\text{subject to} \quad (-1)^i \text{vol}(D) + \beta \text{area}(\partial D) = E_0. \end{aligned} \quad (8.22)$$

Case 1. Liquid phase bounded ($i = 2$).

The solution is a sphere consistent with the constraint.

Case 2. Solid phase bounded ($i = 1$).

In this case (8.22) has the equivalent formulation

$$\begin{aligned} &\text{minimize} \quad \text{vol}(D) \\ &\text{subject to} \quad -\text{vol}(D) + \beta \text{area}(\partial D) = E_0. \end{aligned} \quad (8.23)$$

For $E_0 = 0$ the solution is $D = \emptyset$. For $E_0 < 0$ the solution is a sphere consistent with the constraint. For $E_0 > 0$ (8.23) has no solution; minimizing sequences $\{D_n\}$ have

$$\text{vol}(D_n) \rightarrow 0, \quad \text{area}(\partial D_n) \rightarrow E_0/\beta.$$

Again we have an indication of a dendrite with null volume. If we consider an initially-spherical solid of radius r , then, by (8.21), for $E_0 > 0$ it is necessary that $r < 3\beta$ (cf. the last remark in Section 8.1).

B. Body isothermal at infinity.

Case 1. Bounded phase superthermal at u_0 .

In view of the definition of the term "superthermal" (cf. Section 2.1), for this case either $i = 1$ and $u_0 > 0$, or $i = 2$ and $u_0 < 0$. For either (8.20) leads to the conclusion that, at equilibrium, the bounded phase should

$$\text{minimize} \quad |u_0| \text{vol}(D) + \mu \text{area}(\partial D);$$

hence $D = \emptyset$. Thus a superthermal bounded phase should ultimately disappear.

Case 2. Unbounded phase superthermal at u_0 .

Here the bounded phase should

$$\text{minimize} \quad -|u_0| \text{vol}(D) + \mu \text{area}(\partial D). \quad (8.24)$$

This problem is no different than (3.7) (provided we identify¹ b with μ/u_0), and our conclusions may be inferred from (i) of the theorem of Section 3.2. In particular, (8.24) has no solution (other than a local minimum at $D = \emptyset$); and $\{D_n\}$ is a minimizing sequence if and only if it is consistent with the area-volume limit and has corresponding volumes which tend to infinity. Examples of minimizing sequences exhibiting dendritic behavior are given in Section 3.2.

¹Note that, by (3.8), the constant b of Section 3.2 is approximately $\mu/|u_0|$; in fact, for bulk free-energies which are linear in T , which is the case here, the relation is exact.

PART III. THEORIES BASED ON THE CAPILLARITY RELATION.

9. Approximations. The capillarity relation.

By assumption (A4), $F_1(T) = F_2(T)$ when, and only when, $T = T_M$; thus, appealing to (6.17) and (2.5): *if interfacial energy and entropy are neglected, or if the interface is flat, then*

$$[E] = L \text{ and } T = T_M \text{ on } I. \quad (9.1)$$

If interfacial energy and entropy are not negligible, then the interfacial temperature T will generally not equal the transition temperature, but instead will depend - through (6.15) - on the jumps in energy and entropy, as well as the curvature, energy, and entropy of the interface.

We now use (6.14) to derive a simple approximation for the interfacial temperature which is valid when the interfacial energies are small. More precisely, we assume that

$$f(T) = \epsilon f_0(T), \quad e(T) = \epsilon e_0(T) \quad (9.2)$$

with ϵ a small parameter. By (6.14),

$$F_2(T) - F_1(T) = \epsilon f(T). \quad (9.3)$$

Clearly, (9.3) has the form $g(T, \epsilon) = 0$ and for $\epsilon = 0$ has the unique solution $T = T_M$. Further, the partial derivative of g with respect to T at $(T_M, 0)$ is $S_1(T_M) - S_2(T_M)$, which, by (2.8), is nonzero. Thus, by the implicit function theorem, (9.3) has a unique solution $T = T(\epsilon)$ near $\epsilon = 0$, and $T = T_M + O(\epsilon)$. We therefore write

$$u = T - T_M$$

and expand (9.3) about $\epsilon = 0$; using (2.7) and the fact that $u = O(\epsilon)$, we are led to the following estimate, valid to within terms of $O(\epsilon^2)$:

$$u \approx -h\epsilon \quad (9.4)^1$$

with $h = O(\epsilon)$ the capillarity length² (8.5)₁. We shall refer to (9.4) as the **capillarity relation**; this relation is central to all of what follows.

¹ Cf. Delves [1974] for a derivation of (9.4) based on equilibrium thermodynamics. In Delves's derivation, as well as in all others of which I am aware, the curvature enters through the classical relation $[p] = \epsilon f$ with $[p]$ the jump in pressure across the interface, a quantity irrelevant to the theory discussed here.

² But here f is arbitrary, not necessarily of the form assumed in Section 8.

Our next step is to derive a corresponding approximation to the interfacial balance-law for energy. Trivially, (2.5) and (9.4) yield, to $O(d)$,

$$[E] \approx L, \quad (9.5)$$

and combining (9.5) with (6.4) leads to the following interface condition for energy:

$$[q] \cdot m \approx Lv, \quad (9.6)^1$$

again valid to $O(d)$.

The remainder of the paper will be concerned with models based on the approximate interface conditions (9.4) and (9.6).

Remarks.

(i) In the foregoing analysis the parameter d always appears in the product dk , and therefore it is tacit in our scaling that dk be small. Thus *equations based on the capillarity relation (9.4) are probably not valid for problems involving large curvatures.*¹

(ii) The approximation (9.6), to terms of $O(d^2)$ rather than $O(d)$, is

$$[q] \cdot m \approx \{L + kh(C_1 - C_2) - ke\}v, \quad (9.7)^2$$

provided e is constant. This relation with the term ke omitted is common in the literature. However, the terms $kh(C_1 - C_2)$ and ke are both $O(d)$, and to neglect one without the other is inconsistent. In any event, since $L=O(1)$, (9.6) seems to be the most rational approximation to use in conjunction with (9.4), except possibly when the temperature away from the interface (for example at the boundary) is not close to T_M .

¹Also, as Rogers [1983] has noted, the interfacial temperature as given by (9.4) can have negative values for sufficiently large curvatures; in fact, for $k > L/(T_M)$. (Cf. (i) of the remark following (8.8).)

²Cf. Wollkind [1979], who derives (9.7) assuming constant specific heats.

10. Quasi-linear theory.

10.1. Basic equations. Growth conditions.

We now consider a model based the interface conditions (6.6), (9.4), and (9.6) in conjunction with assumptions of constant specific heats $C_i > 0$ and constant conductivities $k_i > 0$. Thus, writing

$$u = T - T_M,$$

we are led to the system

$$C_i u^\circ = k_i \Delta u, \quad q = -k_i \text{grad} u \quad \text{in } B_i, \quad (10.1)$$

$$u = -h\kappa, \quad [q] \cdot m = Lv \quad \text{on } I, \quad (10.2)$$

$$vm \cdot n = 0 \quad \text{on } \partial I, \quad (10.3)$$

for all time. As before, we refer to u as the temperature. Also, in view of (2.7) and (8.5), it is natural to suppose that

$$L > 0, \quad h > 0. \quad (10.4)$$

Remark. The system (6.18)–(6.20), or the simpler version (8.6)–(8.8), have the advantage of being consistent with the first two laws. Therefore, for an isolated boundary these systems have a natural conservation law, balance of energy, and a natural Liapunov function, the total entropy; and similarly for an isolated boundary. Because of this we were able to obtain estimates such as the bound (7.5) on interfacial area. On the other hand, because of the approximations involved, the system (10.1)–(10.4) is, in general, not consistent with the second law (5.3). Therefore, results such as the global growth conditions (7.3) and (7.4) and the area bound (7.5) must be established anew.

Our discussion of (10.1)–(10.4) is based on the following pair of identities:

$$-L \text{vol}(B_2)^\circ - \sum_{B_i} C_i u^\circ = \int_{\partial B} q \cdot n, \quad (10.5)$$

$$-h L \text{area}(I)^\circ - \sum_{B_i} u C_i u^\circ = L \| \text{grad} u \|_1^2 + \int_{\partial B} u q \cdot n, \quad (10.6)$$

where $\|\cdot\|_1$ is the norm defined by

$$\|p\|_1^2 = k_1 \int_{B_1} |p|^2 + k_2 \int_{B_2} |p|^2. \quad (10.7)$$

To prove (10.5) and (10.6), note first that (4.3) with g the characteristic function for B_1 , (4.6), and (10.3) yield

$$\text{area}(I)^* = \int_I \kappa v, \quad \text{vol}(B_1)^* = \int_I v = -\text{vol}(B_2)^*. \quad (10.8)$$

Note also that

$$\int_B q \cdot \text{gradu} = -L \|\text{gradu}\|_1^2. \quad (10.9)$$

By (10.1), (10.2), (10.8), (10.9), and (6.11),

$$\begin{aligned} -L \text{vol}(B_2)^* &= \int_I [q] \cdot m = \int_{\partial B} q \cdot n + \sum_{B_i} \int_{B_i} C_i u^*, \\ -h L \text{area}(I)^* &= \int_I [u] q \cdot m = -\int_B q \cdot \text{gradu} + \int_{\partial B} u q \cdot n + \sum_{B_i} \int_{B_i} u C_i u^*, \end{aligned} \quad (10.10)$$

which yield (10.5) and (10.6).

Equations (10.5) and (10.6) simplify when

$$C_1 = C_2. \quad (10.11)$$

Indeed, since u is continuous, (10.5) and (10.6) reduce to

$$[\text{vol}(B_2) + C \int_B u]^* = -L^{-1} \int_{\partial B} q \cdot n, \quad (10.12)$$

$$[h \text{area}(I) + (C/2) \int_B u^2]^* = -L \|\text{gradu}\|_1^2 - L^{-1} \int_{\partial B} u q \cdot n, \quad (10.13)$$

with

$$C = C_i/L. \quad (10.14)$$

These identities and the boundary conditions (7.1) and (7.2), with the latter written in the form (8.9), yield, as a consequence, the relations listed below; there V is the *total volume*, while $u_m = u_m(t)$ is the *mean temperature*:

$$V = \text{vol}(B), \quad u_m = V^{-1} \int_B u. \quad (10.15)$$

Growth conditions. Assume that $C_1 = C_2$.

(i) For an isolated boundary,

$$\{ \text{vol}(B_2) + CVu_m \}^* = 0, \quad (10.16)$$

$$\{ h \text{ area}(I) - u_m \text{vol}(B_2) + (C/2) \int_B (u - u_m)^2 \}^* \leq 0. \quad (10.17)$$

(ii) For an isothermal boundary,

$$\{ h \text{ area}(I) - u_0 \text{vol}(B_2) + (C/2) \int_B (u - u_0)^2 \}^* \leq 0. \quad (10.18)$$

Proof. Consider first an isolated boundary. Then (10.12) and (10.13) reduce to (10.16) and

$$\{ h \text{ area}(I) + (C/2) \int_B u^2 \}^* = - \| \text{grad} u \|_1^2. \quad (10.19)$$

By (10.15),

$$u_m \left(\int_B u \right)^* = \int_B u_m u^* = \int_B (u_m u)^* - u_m \int_B u = (1/2) \int_B [2(u_m u)^* - (u_m^2)^*], \quad (10.20)$$

and if we multiply (10.16) by u_m , subtract the resulting equation from (10.19), and use (10.20) and the fact that $\text{grad } u_m = 0$, we arrive at (10.17).

Consider next an isothermal boundary. Then multiplying (10.12) by u_0 and subtracting the result from (10.13), we conclude, with the aid of (10.14), that (10.18) holds. $\square$

Remark. In (10.17) and (10.18) the ≤ 0 may be replaced by

$$= - \| \text{grad}(u - u_m) \|_1^2 \leq 0. \quad (10.21)$$

Appropriate **initial conditions** for the system (10.1)–(10.3) are:

$$u(x, 0) = g_0(x) \text{ for } x \text{ in } B, \quad B_i(0) = B_{0i}, \quad (10.22)$$

with g_0 the initial temperature-distribution and (B_{01}, B_{02}) the initial distribution of phases. We shall designate by **Problem QL** the initial-value problem defined by the field equations (10.1), the

free-boundary conditions (10.2) and (10.3), the boundary conditions (7.1) or (8.9), and the initial conditions (10.22).

Question.¹ What is an appropriate weak formulation of Problem QL?

Since $0 \leq \text{vol}(B_2) \leq V$, (10.16) yields a bound for $|u_m(t)|$ which is uniform in t , and this, with (10.17), yields bounds for $\text{area}(I(t))$ and for the $L^2(B)$ norm of $u(t) = u(\cdot, t)$; similar bounds follow from (10.18). Thus the growth conditions have the following

Corollary. *Assume that $C_1 = C_2$. Then each solution of Problem QL has (on its interval of existence)*

$$\text{area}(I(t)) \quad \text{and} \quad \|u(t)\|_{L^2(B)}$$

bounded uniformly in t by constants which depend only on the data²

Remark. The bound on $\text{area}(I(t))$ precludes the formation of an interface which is too wild. This stability is a consequence of interfacial free-energy, manifested in the constant h . (As h tends to zero, the bound on $\text{area}(I(t))$ tends to infinity.)

The relations (10.16)–(10.18) can possibly be used as a basis for a study of existence, uniqueness, and stability for Problem QL, as they yield a-priori estimates for u and for the interface. Such a study, however, is beyond the scope of this paper.

¹Cf. Visintin [1984], who – for a closely related problem – gives a weak formulation and establishes global existence.

²i.e., only on B, C, h, u_0 (for an isothermal boundary), and the initial data.

10.2. Equilibrium in the quasi-linear theory.

In this section we discuss the equilibrium behavior of solutions to Problem QL, assuming throughout that

$$C_1 = C_2.$$

Consider, then, a solution of QL and suppose that

as $t \rightarrow \infty$, an equilibrium state $(u_\infty, B_{1\infty}, B_{2\infty})$ exists.

Further, let u_m denote the corresponding mean temperature and I_∞ the corresponding interface, and let

$$E_0 = \text{the initial-value of } \text{vol}(B_2) + CVu_m. \quad (10.23)$$

A. Isolated boundary.

By (10.17) it seems reasonable to expect that

$$u_- = \text{constant} = u_m.$$

and therefore, in view of (10.16) and (10.17), the equilibrium state should be consistent with the variational problem:

$$\text{minimize} \quad hCV \text{area}(I_\infty) + \text{vol}(B_{-2})(\text{vol}(B_{-2}) - E_0). \quad (10.24)$$

(In deriving (10.24), u_m was eliminated using the constraint equation obtained from (10.16).) This problem is nonstandard, but easily solved. Since $hCV > 0$, if (10.24) has a minimizer B_{-2} , then (B_{-1}, B_{-2}) has minimal interface in the sense explained in the Appendix. In fact, solving (10.24) is equivalent to finding a v in $[0, V]$ that minimizes

$$hCV a_{\min}(v) + v(v - E_0). \quad (10.25)$$

In view of the properties of $a_{\min}(v)$ expressed in Theorem 1 of the Appendix, (10.25) has a solution v , and the corresponding solution of M_v (cf. the Appendix) minimizes (10.24). In particular, for $E_0 > 2V$, $B_{-2} = B$; for $E_0 < 0$, $B_{-2} = \emptyset$. Thus, granted the validity of (10.24), the equilibrium configurations will have minimal interface, and hence the interface will

have constant mean curvature and meet ∂B orthogonally. Further, by (10.23), the fluid phase will ultimately disappear if the initial mean-temperature is low enough; the solid phase will disappear if the initial mean-temperature is high enough.

B. Isothermal boundary.

By (10.18), it seems reasonable to expect that $(B_{1\infty}, B_{2\infty})$ will solve the variational problem:

$$\text{minimize} \quad u_0 \text{vol}(B_{1\infty}) + h \text{area}(I_{\infty}).$$

This is the problem discussed under (B) of Section 8.2, and the conclusions are no different.

11. Quasi-static theory.

11.1. Basic equations. Growth conditions.

A standard model for solidification is based on the system (10.1)–(10.3) with

$$C_1 = C_2 = 0,$$

and hence on the equations

$$\Delta u = 0, \quad q = -k_i \text{grad} u \quad \text{in } B_i, \quad (11.1)$$

$$u = -h_i, \quad [q] \cdot m = Lv \quad \text{on } I, \quad (11.2)$$

$$vm \cdot n = 0 \quad \text{on } \partial I. \quad (11.3)$$

These equations, although simple, have several interesting consequences, chief among them being the instability of the interface in certain circumstances.¹

We begin our discussion of this model by first noting the following consequences of (10.16)–(10.18):

Growth conditions.

(i) *For an isolated boundary the interfacial area decreases with time while the phase volumes remain constant:*

$$\text{vol}(B_i)' = 0, \quad \text{area}(I)' \leq 0. \quad (11.4)$$

(ii) *For an isothermal boundary,*

$$u_0 \text{vol}(B_i)' + h \text{area}(I)' \leq 0. \quad (11.5)$$

Appropriate initial conditions for the system (11.1)–(11.3) are:

$$B_i(0) = B_{0i}, \quad (11.6)$$

with (B_{01}, B_{02}) the initial distribution of phases. We shall designate by **Problem MS** the initial-value problem defined by (11.1)–(11.3), (7.1) or (8.9), and (11.6).

Question. What is an appropriate weak formulation of Problem MS?

¹Mullins and Sekerka [1963, 1964]. See also Wagner [1956].

As in Section 8.3, it is not difficult to extend our results for bounded B to situations in which B is all of space with one of the phase regions bounded for all time (cf. (8.18)). In particular, we have the following

Growth conditions for an unbounded body. *Let B_1 be the bounded phase region.*

(i) *For the body isolated at infinity,*

$$\text{vol}(B_1)^* = 0, \quad \text{area}(I)^* \leq 0. \quad (11.7)$$

(ii) *For the body isothermal at infinity,*

$$(-1)^{i+1} u_0 \text{vol}(B_1)^* + h \text{area}(I)^* \leq 0. \quad (11.8)$$

Remark. In (11.4) and (11.5), respectively, the ≤ 0 may be replaced by

$$= -h^{-1} \|\text{grad} u\|_1^2 \leq 0 \quad \text{and} \quad = -\|\text{grad} u\|_1^2 \leq 0;$$

an analogous assertion applies to (11.7) and (11.8).

11.2. Equilibrium in the quasi-static theory.

Consider a solution of Problem MS and suppose that

as $t \rightarrow \infty$, an equilibrium state $(u_\infty, B_\infty, B_\infty)$ exists.

A. Isolated boundary.

1. B bounded.

In view of (11.4), we expect that the equilibrium configuration should have minimal interfacial-area (as defined in the Appendix), and hence the equilibrium interface should have constant mean curvature and meet ∂B orthogonally.

2. B unbounded.

Here, because of (11.7), the bounded phase region, at equilibrium, should have minimal surface-area when compared to other regions of equal volume. Granted this: *the bounded phase region is spherical at equilibrium.*

B. Isothermal boundary.

Since (11.5) and (11.8) are the same as (8.12) and (8.20), the variational problems describing equilibrium states in the current theory are exactly the same as those discussed in (B) of Section 8.2 and (B) of Section 8.4, and the conclusions are the same. In particular, the assertions in (B) of Section (8.4) concerning interfacial instabilities - such as those exhibited by the prickly ball - are here fortified by the work of Mullins and Sekerka [1963], who established interfacial instabilities for unbounded B when the bounded phase is an infinitesimal perturbation of a sphere.

11.3. Quasi-static theory when one phase does not conduct heat.

Suppose that one of the two phases, phase 2 say, is a poor conductor of heat. If we model this by setting $k_2 = 0$; then, as is clear from the derivation of (11.1) - (11.3), the temperature in phase 2 is indeterminate, while the temperature in phase 1 obeys the relations¹

$$\begin{aligned} \Delta u &= 0 && \text{in } B_1, \\ u &= -h\kappa, \quad \partial u / \partial n = L_1 v && \text{on } \partial B_1, \end{aligned} \tag{11.9}$$

where, for convenience, we have assumed that the region $B_1(t)$ occupied by phase 1 is bounded, but that B itself is all of space. Here $L_1 = L/k_1$, while $\partial u / \partial n$ is the outward normal derivative on ∂B_1 .

Using steps analogous to those used to derive (10.5) and (10.6), it is not difficult to verify that (11.9) yield the growth conditions:

$$\text{vol}(B_1)^* = 0, \quad \text{area}(\partial B_1)^* \leq 0. \tag{11.10}$$

Because of (11.10), one might expect solutions of (11.9) to stabilize at large time with $B_1(t)$ ultimately spherical.

An appropriate initial condition for the system (11.9) is

$$B_1(0) = B_{01}, \tag{11.11}$$

with B_{01} the region occupied by phase 1 at $t = 0$.

Remark. In this model only one phase enters the system (11.9), and the notions of supercooling and superheating are extraneous; for that reason the instabilities discussed previously should not be encountered. This conjecture is reinforced by (11.10) and, even more so, by work of Duchon and Robert [1984], who establish local existence and uniqueness for the problem (11.9), (11.11) in $\mathbb{R}^2$ with B_{01} unbounded.²

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¹Cr. Mullins [1960], who uses this system (with u concentration) to model corrosion.

²See also Caroli, Caroli, Roulet, and Langer [1985], who study the existence of needle crystals using the system (11.9) (in a moving frame of reference).

Appendix. Some variational problems involving interfaces.

Let R be a sufficiently nice subset of B , and let Γ_R denote the corresponding interface; that is, is the portion of ∂R contained in the interior of B . Let

$$V = \text{vol}(B),$$

and, for each $v \in [0, V]$, consider the problem

$$\mathcal{M}_v: \text{minimize } \text{area}(\Gamma_R) \text{ subject to } \text{vol}(R) = v.$$

Let $a_{\min}(v)$ denote the corresponding minimal area:

$$a_{\min}(v) = \inf \{ \text{area}(\Gamma_R) : \text{vol}(R) = v \}. \quad (1)$$

Theorem 1.¹ *For each $v \in [0, V]$, $\mathcal{M}_v$ has a solution, and for each solution the corresponding interface has constant mean curvature and meets ∂B orthogonally. Moreover, $a_{\min}(v)$ is continuous on $[0, V]$, strictly positive on $(0, V)$, and zero at $v = 0, V$.*

For convenience, we say that a partition $(R, B \setminus R)$ has **minimal interface** provided R solves $\mathcal{M}_v$ for $v = \text{vol}(R)$.

Let $\beta > 0$ and $q \geq 0$ be given. Consider the problem

$$\mathcal{W}_q: \text{minimize } \text{area}(\Gamma_R) \text{ subject to } \text{vol}(R) + \beta \text{area}(\Gamma_R) = q.$$

Theorem 2.²

- (i) *For $q \leq V$, $\mathcal{W}_q$ has a solution, and each solution R solves $\mathcal{M}_v$ for some $v \in [0, V]$.*
- (ii) *For $q > V$, $\mathcal{W}_q$ does not have a solution in the standard sense. If $\{R_n\}$ is a minimizing sequence with $\{\Gamma_n\}$ the corresponding sequence of interfaces, then*

$$\text{vol}(R_n) \rightarrow V, \quad \beta \text{area}(\Gamma_n) \rightarrow q - V > 0,$$

so that $B \setminus R_n$ approaches a set with zero volume, but nonzero surface area.

¹Cf., Massari and Pepe [1974]; Giusti [1981]; Gonzalez, Massari, and Tamanini [1983]; Gurtin [1985].

²This solution of Problem $\mathcal{W}_q$ is due to F. Almgren (private communication).

Proof. We can clearly write $\mathcal{W}_q$ in the form

$$\text{maximize } \text{vol}(R) \text{ subject to } \text{vol}(R) + \text{Barea}(\mathcal{L}_R) = q.$$

Thus, since

$$a_{\min}(\text{vol}(R)) \leq \text{area}(\mathcal{L}_R),$$

this motivates the problem

$$\text{maximize } v \text{ subject to } v + a_{\min}(v) \leq q, \quad 0 \leq v \leq V. \quad (2)$$

This problem clearly has a solution. For $q \leq V$, the solution v has $v + a_{\min}(v) = q$, and it is not difficult to verify that any solution R of $\mathcal{M}_v$ solves $\mathcal{W}_q$. This yields assertion (i) of the theorem. For $q > V$, the solution is $v = V$, and this yields assertion (ii). $\square$

Appendix. Scaling the quasi-linear theory. Discussion.

Insight into the approximations underlying the theories developed in Sections 10 and 11 can be obtained with the aid of appropriate scalings. Consider the length and time scales defined by

$$L = f(T_M)/L, \quad t = L^2 L / k_1 T_M,$$

and replace the coordinates x and t by the dimensionless coordinates

$$x^* = x/L, \quad t^* = t/t.$$

Then, using the dimensionless temperature, curvature and velocity

$$u^* = (T - T_M)/T_M, \quad k^* = kL, \quad v^* = vt/L,$$

and the dimensionless parameters

$$d^* = T_M C_1 / L, \quad k^* = k_2 / k_1, \quad c^* = C_2 / C_1,$$

we can render (10.1)–(10.3) dimensionless; the result, with the superscript $*$ omitted, is

$$du = \Delta u \quad \text{in } B_1, \quad dcu = k \Delta u \quad \text{in } B_2, \quad (1)$$

$$u = -k, \quad (\text{gradu}_1 - k \text{gradu}_2) \cdot m = v \quad \text{on } I, \quad (2)$$

$$vm \cdot n = 0 \quad \text{on } \partial I. \quad (3)$$

Here time derivatives are with respect to t^* , spatial derivatives with respect to x^* ; B_i and I are appropriately scaled; and gradu_i denotes the limit of gradu as I is approached from B_i .

Remarks.

(i) The quasi-static theory studied in Section 11 follows, as a formal approximation to (1)–(3), under the assumptions:

$$d \ll 1, \quad cd/k \ll 1, \quad k = O(1).$$

Thus the assumptions underlying the quasi-static theory are that the specific heats C_i be small compared to the ratio L/T_M , and that the order-of-magnitude of the conductivities k_1 and k_2 be equal.

(ii) The theory of Section 11.3 (for phase 2 a nonconductor of heat) follows formally from (1)-(2) under the assumptions:

$$d \ll 1, \quad k \ll 1.$$

(By (2), the second assumption renders the temperature in phase 2 irrelevant to the determination of the temperature in phase 1.) Thus this theory is based on two assumptions: that the conductivity in phase 2 be small compared to the conductivity in phase 1; that the specific heats C_i be small compared to the ratio L/T_M .

(iii) The assumptions

$$d = O(1), \quad k \ll 1$$

yield the following quasi-linear generalization of (11.9):

$$du = \Delta u \quad \text{in } B_1,$$

$$u = -k, \quad m \cdot \text{grad} u_1 = v \quad \text{on } \partial B_1.$$

(iv) Generally, the length scale L will be very small. Thus the treatment with Ω finite probably has physical relevance only when the maximum diameter of Ω (before rescaling) is small, of a size comparable to the length scale L .

(v) It might be that problems with Ω infinite - but not all of $\mathbb{R}^3$ - are important. Although we have not considered this case, it is clear that the basic results deduced in Section 6, as well as much of what we have established in other sections, remain valid for such Ω .

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