A MECHANICAL THEORY FOR CRYSTALLIZATION OF A RIGID SOLID IN A LIQUID MELT; MELTING-FREEZING WAVES

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Dedicated to Bernard Coleman on his sixtieth birthday

1. Introduction.

Crystals of solid helium in a liquid melt exhibit a phenomenon generally not found in other materials: oscillations of the solid-liquid interface in which atoms of the solid move only when they melt and enter the liquid. Such *melting-freezing waves* were predicted by Andreev and Parshin [AP] in 1978 and exhibited experimentally[1] by Keshishev, Parshin, and Babkin [KPB] in 1979.

Motivated by this classic paper of Andreev and Parshin, I develop a continuum theory of crystallization using, as a basis, a framework developed in [G1][2]. I restrict attention to a purely mechanical[3] theory, and, to avoid geometric complications that accompany evolving surfaces, confine the derivation to a two-dimensional theory in which the interface evolves as a plane curve.

One of the chief differences between theories involving phase transitions and the more classical theories of continuum mechanics is the *creation and deletion of material points* as the phase interface moves relative to the underlying material. To describe this process I introduce an *interactive energy-balance* in which the energy and power transferred from the bulk material to the phase interaction is related to the *interactive dissipation*, which is the energy associated with the

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[1] Keshishev, Parshin, and Babkin observed frequencies of 3 kHz; since then frequencies up to 10^{10} KHz have been reported (cf. Castaing, Balibar, and Laroche [CBL] and the references cited by Maris and Andreev [MA]).

[2] See also [G2,G3,AG,GS]. Gurtin and Podio Guidugli [GPG] develop a (possibly oversimplified) theory of melting-freezing waves in which the melt is considered only as a source of atoms for the crystallization process and the inertia - which in the current theory arises from the motion of the melt - is presumed to be an effective inertia endowed to the interface. The results of this simplified model show fair qualitative agreement with the current theory, a major deficiency being a dispersion relation of the form $\omega^2 \sim \lambda^2$ rather than $\omega^2 \sim \lambda^3$ (cf. (1.18)). The chief advantage of the model of [GPG] is a hyperbolic evolution equation for the interface; for an isotropic crystal this equation has the simple form $\rho V^{\circ} + \beta V = \psi K + F$ $(\rho, \beta, \psi = \text{constants} > 0,\ F = \text{constant})$.

[3] As noted by Maris and Andreev [MA], for superconductors such as solid helium solidification is "essentially a mechanical process, rather than a thermal process as it is for ordinary materials".

exchange of atoms between phases. This energy balance and balance of mass and linear momentum are the basic balance laws of the theory.

I suppose that the crystal is rigid, incapable of deformation, and model the melt as an incompressible,[4] inviscid fluid. The interface is characterized by constitutive equations which allow the interfacial energy, the interfacial force, and the interactive dissipation to depend on the orientation and normal velocity of the interface; and a mechanical version of the second law is used to deduce suitable constitutive restrictions.

The theory leads to a free-boundary problem for the evolution of the interface; this problem consists in solving

$$\rho \mathbf{v}^{\cdot} = -\mathrm{grad}\, p, \qquad \mathrm{div}\, \mathbf{v} = 0 \tag{1.1}$$[5]

in the melt and

$$\begin{aligned} &[\psi(\theta) + \psi''(\theta)]K = \beta(\theta)V + F - \tfrac{1}{2}\rho_c \mathbf{v}^2 + (1-\zeta)p, \\ &\mathbf{v}\cdot\mathbf{m} = (1-\zeta)V \end{aligned} \tag{1.2}$$

on the interface, subject to suitable initial and far-field conditions. Here K and V are the curvature and normal velocity of the interface, $\psi(\theta)$ is the interfacial energy[6] as a function of the angle θ to the interface-normal $\mathbf{m}$, $\beta(\theta)$ is the kinetic coefficient of the interface, $\mathbf{v}$ and p are the velocity and pressure of the melt,

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[4] Andreev and Parshin [AP] note that the phase velocity of melting-freezing waves is generally well below the sound velocity.

[5] grad, div, and Δ are the *spatial gradient, spatial divergence,* and *spatial laplacian.* For $\Phi(\mathbf{x},t)$ defined in the melt: Φ_t is the *spatial time-derivative,* $\Phi^{\cdot}$ the *material time-derivative;* thus $\Phi^{\cdot} = \Phi_t + \mathbf{v}\cdot\mathrm{grad}\,\Phi$ for Φ scalar-valued, etc. (cf., e.g., [G4], §6).

[6] I use the term *energy* (for $\psi(\theta)$, Ψ, and Ψ_c) in a generic sense; as to what thermodynamic potentials (free energy, internal energy, etc.) these quantities actually represent depends on what thermodynamic theory this *purely mechanical theory* is meant to "approximate"; the current theory is, of course, independent of such considerations.

$\zeta = \rho_c/\rho$ with ρ_c and ρ the constant crystal and melt densities, and $F = \Psi_c - \zeta\Psi$ with Ψ_c and Ψ the constant crystal and melt energies.

I show, as a consequence of the *crystallization equations* (1.1) and (1.2), that if the far-field does not supply melt, then

$$\begin{aligned} &(d/dt)\mathrm{area}(\mathcal{C}) = 0, \\ &(d/dt)\Big\{\int_{\partial\mathcal{C}} \psi(\theta)ds + \int_{\mathcal{M}} \tfrac{1}{2}\rho v^2 da\Big\} = -\int_{\partial\mathcal{C}} \beta(\theta)V^2 ds \le 0, \end{aligned} \tag{1.3}$$

where $\mathcal{C} = \mathcal{C}(t)$ and $\mathcal{M} = \mathcal{M}(t)$ denote the regions occupied by the crystal and melt. These relations furnish Lyapunov functions for the crystallization problem.

When the melt is irrotational, $\mathbf{v}(\mathbf{x},t)$ is proportional to the gradient of a potential $u(\mathbf{x},t)$; if, in addition, the melt velocity is sufficiently small that the term involving $\mathbf{v}^2$ in (1.2) is negligible, then the crystallization equations reduce to

$$\Delta u = 0 \tag{1.4}$$

in the melt and

$$\begin{aligned} &[\psi(\theta) + \psi''(\theta)]K = \beta(\theta)V - u_t, \\ &\partial u/\partial m = \alpha V \end{aligned} \tag{1.5}$$

on the interface, with $\alpha = (\rho_c - \rho)^2/\rho$.

The system (1.4) and (1.5) with $\beta(\theta) = 0$, *linearized about a flat interface at equilibrium*, reduces to a system proposed by Andreev and Parshin [AP]:

$$\begin{aligned} &u_{xx} + u_{yy} = 0 && (-\infty < x < \infty,\ y > 0,\ t > 0), \\ &(\psi + \psi'')_0 h_{xx} = -u_t, \quad u_y = \alpha h_t && (-\infty < x < \infty,\ y = 0,\ t > 0), \end{aligned} \tag{1.6}$$

where $y = h(x,t)$ defines the interface, the subscript zero indicates evaluation at equilibrium, and the subscripts x and y denote partial differentiation with respect to the corresponding variable. As noted by Andreev and Parshin [AP], this system has an oscillatory solution of the form

$$h(x,t) = e^{i\lambda x} e^{i\omega t} \tag{1.7}$$

with

$$\omega^2 = \frac{\rho(\psi + \psi'')_0 \lambda^3}{(\rho_c - \rho)^2}, \tag{1.8}$$

yielding a proportionality of ω^2 to λ^3 found experimentally by Keshishev, Parshin, and Babkin [KPB].

Global growth relations, similar to (1.3), are established for the linearized equations (1.6) and used to establish uniqueness for the associated initial-value problem.

I discuss the form the basic equations take when the theory is three-dimensional, and, within that context, solve the problem of spherically symmetric crystallization in an infinite melt whose far-field pressure P is finite. The behavior of the crystal is governed by the sign of the constant

$$C = \Psi_c + P - \zeta(\Psi + P):$$

(i) for $C \geq 0$, crystals melt in finite time; (ii) for $C < 0$ and the melt initially at rest, crystals melt in finite time if initially small, but grow unboundedly if initially large.

2. Crystals.

We consider an infinite *crystal lattice* modelled as a two-dimensional continuum, in fact as $\mathbb{R}^2$ (Figure 1). A **crystal** C is then a compact subset of the lattice with boundary, ∂C, a smooth, simple closed curve. ∂C represents the **interface** between the crystal and its **melt**; we write $\mathbf{m}(\mathbf{x})$ for the outward unit normal to ∂C and define a unit tangent $\boldsymbol{\ell}(\mathbf{x})$ (the direction of increasing arc length) so that $\{\boldsymbol{\ell}(\mathbf{x}),\mathbf{m}(\mathbf{x})\}$ is a positively oriented basis of $\mathbb{R}^2$. We write f_s for the derivative, sometimes partial, of f with respect to arc length on ∂C. We then have the Frenet formulas

$$\mathbf{m}_s = -K\boldsymbol{\ell}, \qquad \boldsymbol{\ell}_s = K\mathbf{m}, \tag{2.1}$$

with $K(\mathbf{x})$ the **curvature** of ∂C. We define the **angle** $\theta(\mathbf{x})$, as a smooth function of $\mathbf{x}$, through

$$\mathbf{m} = (\cos\theta,\sin\theta), \qquad \boldsymbol{\ell} = (\sin\theta,-\cos\theta); \tag{2.2}$$

then

$$K = \theta_s. \tag{2.3}$$

Since our goal is to model crystallization, we consider crystals $C(t)$ that evolve with time t, under the assumption that $\partial C(t)$ is a smooth evolving curve (in the sense of [AG]).

We write $V(\mathbf{x},t)$ for the **normal velocity** of $\partial C(t)$ in the direction $\mathbf{m}(\mathbf{x},t)$. Let $\mathbf{V}(\mathbf{x},t) = V(\mathbf{x},t)\mathbf{m}(\mathbf{x},t)$. Fix t and $\mathbf{x}\in\partial C(t)$ and (for β sufficiently close to t) let $\mathbf{y}(\beta)$ denote the curve that passes through $\mathbf{x}$ at time t and has

$$d\mathbf{y}(\beta)/d\beta = \mathbf{V}(\mathbf{y}(\beta),\beta). \tag{2.4}$$

Then the **normal time-derivative** $\Phi^\circ(\mathbf{x},t)$ (following $\partial C(t)$) of a scalar or vector function $\Phi(\mathbf{x},t)$ is defined by

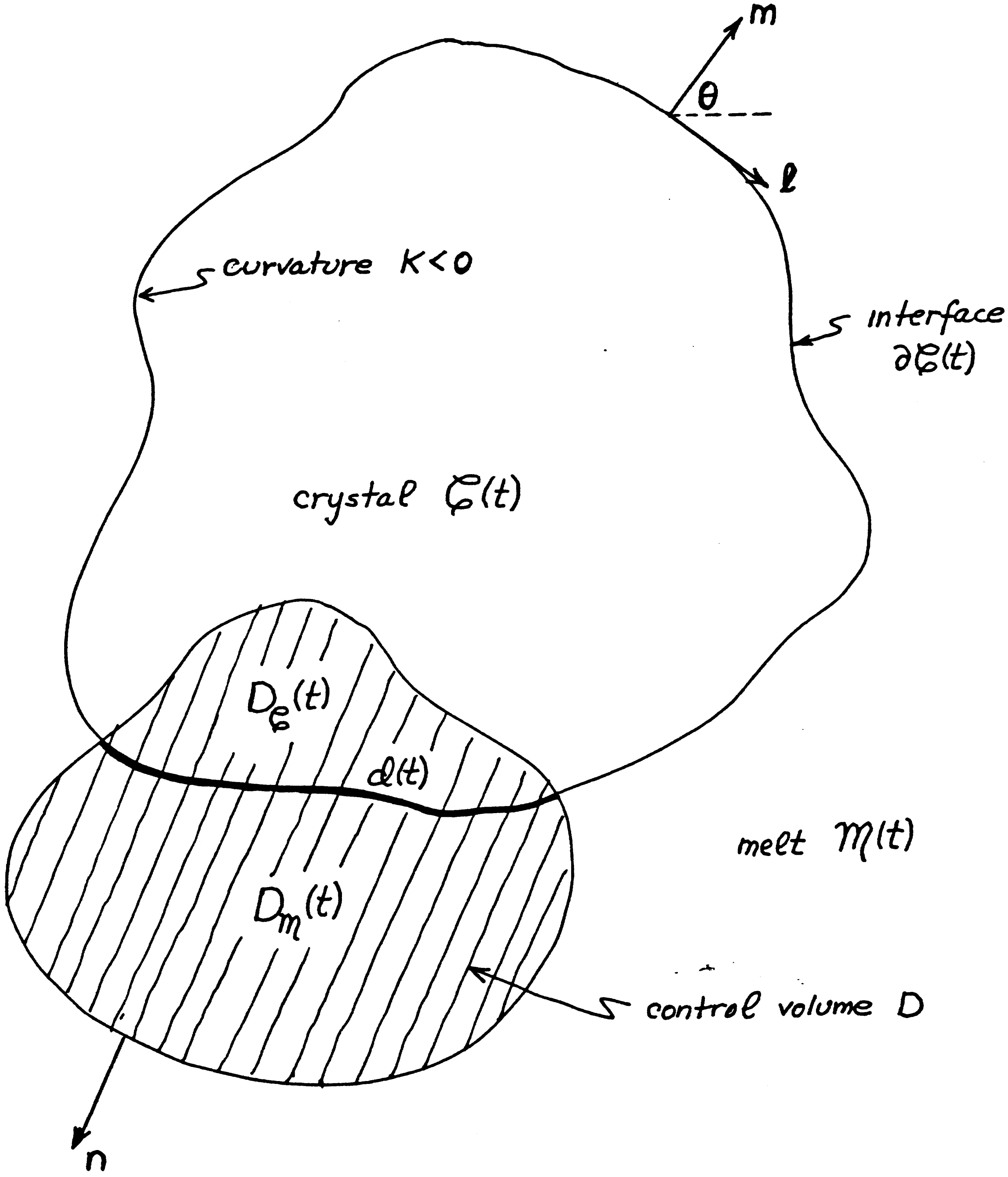

Figure 1. Crystal, melt, and control volume.

$$\Phi^\circ(\mathbf{x},t) = (d/d\beta)\Phi(\mathbf{y}(\beta),\beta)\big|_{\beta=t}. \tag{2.5}$$

The identities

$$\begin{aligned} \theta^\circ &= \boldsymbol{\ell}^\circ\cdot\mathbf{m} = -\mathbf{m}^\circ\cdot\boldsymbol{\ell} = V_s, \\ (V\mathbf{m})_s &= \mathbf{m}\theta^\circ - KV\boldsymbol{\ell}, \\ (V\mathbf{m})^\circ &= V^\circ\mathbf{m} - \theta^\circ V\boldsymbol{\ell}. \end{aligned} \tag{2.6}$$

are standard.[7]

By an **interfacial chunk** we mean a smoothly evolving curve $\mathfrak{c}(t)$ with $\mathfrak{c}(t)\subset\partial\mathcal{C}(t)$ at each time t. We write $(\mathbf{v}_{\partial\mathfrak{c}})_1(t)$ and $(\mathbf{v}_{\partial\mathfrak{c}})_2(t)$ for the **endpoint velocities** of $\mathfrak{c}(t)$:

$$(\mathbf{v}_{\partial\mathfrak{c}})_1(t) = d\mathbf{x}_1(t)/dt, \qquad (\mathbf{v}_{\partial\mathfrak{c}})_2(t) = d\mathbf{x}_2(t)/dt, \tag{2.7}$$

with $\mathbf{x}_1(t)$ and $\mathbf{x}_2(t)$ the initial and terminal points of $\mathfrak{c}(t)$. Then

$$\mathbf{m}(\mathbf{x}_i(t),t))\cdot(\mathbf{v}_{\partial\mathfrak{c}})_i(t) = V(\mathbf{x}_i(t),t)) \qquad (i=1,2). \tag{2.8}$$

Given a smooth function $\Phi(\mathbf{x},t)$ and a smooth vector function $\boldsymbol{\Phi}(\mathbf{x},t)$, we write

$$\begin{aligned} \int_{\partial\mathfrak{c}(t)}\Phi &= \Phi(\mathbf{x}_2(t),t) - \Phi(\mathbf{x}_1(t),t), \\ \int_{\partial\mathfrak{c}(t)}\boldsymbol{\Phi}\cdot\mathbf{v}_{\partial\mathfrak{c}} &= \boldsymbol{\Phi}(\mathbf{x}_2(t),t))\cdot(\mathbf{v}_{\partial\mathfrak{c}})_2(t) - \boldsymbol{\Phi}(\mathbf{x}_1(t),t))\cdot(\mathbf{v}_{\partial\mathfrak{c}})_1(t), \end{aligned} \tag{2.9}$$

so that

$$\int_{\partial\mathfrak{c}(t)}\Phi = \int_{\mathfrak{c}(t)}\Phi_s\,ds. \tag{2.10}$$

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[7] Cf., e.g., [AG], eqts. (2.4), (2.18).

Less trivial is the **transport identity**[8]

$$(d/dt)\int_{\mathcal{S}(t)}\Phi\, ds \;=\; \int_{\mathcal{S}(t)}(\Phi^{\circ}-\Phi K V)\, ds \;+\; \int_{\partial\mathcal{S}(t)}\Phi\boldsymbol{\ell}\cdot\mathbf{v}_{\partial\mathcal{S}}. \qquad (2.11)$$

In what follows, we will generally omit the argument t when writing such integrals.

We write

$$\mathcal{M}(t) = \text{closure of } \mathbb{R}^2\backslash\mathcal{C}(t)$$

for the region occupied by the **melt**. By a **control volume** we mean a *bounded* region $D\subset\mathbb{R}^2$ with D fixed in time;

$$D_{\mathcal{C}}(t) = \mathcal{C}(t)\cap D, \qquad D_{\mathcal{M}}(t) = \mathcal{M}(t)\cap D, \qquad \mathcal{I}(t) = \partial\mathcal{C}(t)\cap D \qquad (2.12)$$

are then the portions of D contained in the crystal, in the melt, and on the interface; we will generally denote by $\mathbf{n}$ the outward unit normal to ∂D (Figure 1).

Let $\varphi(\mathbf{x},t)$ and $\Phi(\mathbf{x},t)$ be smooth functions defined for $\mathbf{x}\in\mathcal{C}(t)$ and $\mathbf{x}\in\mathcal{M}(t)$, respectively. We will repeatedly use the identities

$$\begin{aligned}(d/dt)\int_{D_{\mathcal{C}}}\varphi\, da &= \int_{D_{\mathcal{C}}}\varphi_t\, da + \int_{\mathcal{I}}\varphi V\, ds,\\ (d/dt)\int_{D_{\mathcal{M}}}\Phi\, da &= \int_{D_{\mathcal{M}}}\Phi_t\, da - \int_{\mathcal{I}}\Phi V\, ds,\end{aligned} \qquad (2.13)$$

as well as the special case

$$(d/dt)\text{area}(D_{\mathcal{C}}) = -(d/dt)\text{area}(D_{\mathcal{M}}) = \int_{\mathcal{I}}V\, ds. \qquad (2.14)$$

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[8] Cf., e.g., [AG], eqts. (2.20), (2.34).

3. Capillary force. Balance laws. Dissipation inequality.

3.1. Basic quantities.

The crystals we consider are rigid, incapable of deformation, with corresponding melt an incompressible, inviscid fluid. Let $C(t)$ be an evolving crystal. The mechanics of $C(t)$ is described by five functions,

$\mathbb{C}(x,t)$	**interfacial force**, defined for $x \in \partial C(t)$,
$\psi(x,t)$	**interfacial energy**, defined for $x \in \partial C(t)$,
$T_c(x,t)$	**crystal stress**, defined for $x \in C(t)$,
$p(x,t)$	**melt pressure**, defined for $x \in \mathcal{M}(t)$,
$v(x,t)$	**melt velocity**, defined for $x \in \mathcal{M}(t)$,

and four constants,

ρ_c	**crystal density**,
ρ	**melt density**,
Ψ_c	**crystal energy**,
Ψ	**melt energy**.

$\mathbb{C}(x,t)$ represents the force *within the interface* exerted across x at time t; if we let $\mathscr{S}^-$ and $\mathscr{S}^+$, respectively, denote left and right neighborhoods of x in $\partial C(t)$, then $\mathbb{C}(x,t)$ is the force exerted *on* $\mathscr{S}^-$ *by* $\mathscr{S}^+$. We decompose this force into normal and tangential components:

$$\mathbb{C} = \sigma \boldsymbol{\ell} + \xi m; \tag{3.1}$$

$\sigma(x,t)$ is then the **surface tension**, $\xi(x,t)$ the **surface shear**.

The remaining quantities are standard; because the crystal is **rigid**, the stress T_c is indeterminate. Similarly, the **incompressibility** of the melt leads to the constraint

$$\mathrm{div}\,\mathbf{v} = 0 \tag{3.2}$$

and to the indeterminancy of the melt pressure p.

3.2. Balance of mass.

We *neglect interfacial mass.* Then, as the crystal interior is immobile, **balance of mass** requires that

$$(d/dt)\Big\{\int_{D_c}\rho_c\, da + \int_{D_m}\rho\, da\Big\} + \int_{(\partial D)_m}\rho\mathbf{v}\cdot\mathbf{n}\, ds = 0 \tag{3.3}$$

for every control volume D. Since the densities are constant, if we apply (2.14) and then shrink D to the interface, we are led to the **interfacial mass balance**

$$\rho(\mathbf{v}\cdot\mathbf{m} - V) = -\rho_c V, \tag{3.4}$$

or alternatively,

$$\mathbf{v}\cdot\mathbf{m} = (1-\zeta)V, \tag{3.5}$$

where

$$\zeta = \rho_c/\rho \tag{3.6}$$

is the **mass ratio**. We assume throughout that the crystal and melt densities are unequal:

$$\zeta \neq 1. \tag{3.7}$$

3.3. Balance of momentum.

Balance of momentum is the assertion that, given any control volume D,

$$(d/dt)\int_{D_{\mathfrak{m}}}\rho\mathbf{v}\,da + \int_{(\partial D)_{\mathfrak{m}}}\rho\mathbf{v}(\mathbf{v}\cdot\mathbf{n})\,ds = \int_{\partial\mathcal{A}}\mathbb{C} + \int_{(\partial D)_{c}}\mathbf{T}_c\mathbf{n}\,ds - \int_{(\partial D)_{\mathfrak{m}}}p\mathbf{n}\,ds. \qquad (3.8)$$

Since D is arbitrary, this leads (in the standard manner) to the local balance laws

$$\operatorname{div}\mathbf{T}_c = \mathbf{0}, \qquad \rho\mathbf{v}^{\cdot} = -\operatorname{grad}p \qquad (3.9)$$

in the crystal and in the melt, respectively, and, using (2.13), to

$$\mathbb{C}_s = \mathbf{T}_c\mathbf{m} + p\mathbf{m} + \rho\mathbf{v}(\mathbf{v}\cdot\mathbf{m} - V)$$

on the interface. By (3.4), this last relation reduces to the **interfacial balance law**

$$\mathbb{C}_s = \mathbf{T}_c\mathbf{m} + p\mathbf{m} - \rho_c V\mathbf{v}, \qquad (3.10)$$

or, more succinctly,

$$\mathbb{C}_s + \mathbf{b} = \mathbf{0}, \qquad (3.11)$$

with

$$\mathbf{b} = -\mathbf{T}_c\mathbf{m} - p\mathbf{m} + \rho_c V\mathbf{v} \qquad (3.12)$$

the total force (including inertia) exerted by the crystal and the melt *on* the interface.

Next, (2.1), (2.6), and (3.1) yield

$$(\mathbb{C}\cdot V\mathbf{m})_s = \xi\theta^{\circ} - \sigma KV + V\mathbb{C}_s\cdot\mathbf{m}; \qquad (3.13)$$

thus, by (2.8), (2.11), (3.1), and (3.11), we have the **power identity**[9]

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[9] Cf. [G1], eqt. (3.4).

$$\int_{\partial \mathscr{s}} \mathbb{C}\cdot \mathbf{v}_{\partial \mathscr{s}} + \int_{\mathscr{s}} \mathbf{b}\cdot(V\mathbf{m})\,ds = \int_{\mathscr{s}}(\xi\theta^\circ - \sigma K V)\,ds + \int_{\partial \mathscr{s}} \sigma \boldsymbol{\ell}\cdot \mathbf{v}_{\partial \mathscr{s}} \tag{3.14}$$

for any interfacial chunk $\mathscr{s}(t)$. This identity makes plausible the assumption, made in the next section, that the interfacial force expends power on an interfacial chunk over the velocities of its endpoints. The term $-\sigma KV$ represents power expended in creating new interface; $\xi\theta^\circ$ represents power expended in changing the orientation of the interface; the term involving $\sigma\boldsymbol{\ell}\cdot\mathbf{v}_{\partial\mathscr{s}}$ compensates for the tangential motion of the endpoints of $\partial\mathscr{s}$.

The scalar field

$$p_c = -\mathbf{m}\cdot\mathbf{T}_c\mathbf{m} \tag{3.15}$$

describes the normal interaction between the interface and the crystal. Using (3.5), (3.12), and (3.15), we can write the power identity in the form

$$\int_{\partial \mathscr{s}} \mathbb{C}\cdot \mathbf{v}_{\partial \mathscr{s}} + \int_{\mathscr{s}} \{p_c - p + (1-\zeta)\rho_c V^2\} V\,ds = \int_{\mathscr{s}}(\xi\theta^\circ - \sigma K V)\,ds + \int_{\partial \mathscr{s}} \sigma \boldsymbol{\ell}\cdot \mathbf{v}_{\partial \mathscr{s}}. \tag{3.16}$$

The term involving $(1-\zeta)\rho_c V^2$ represents a supply of kinetic energy induced by the difference in crystal and melt densities.

3.4. Dissipation inequality.

The version of the *second law* that we shall use is the assertion that, for any control volume D, the rate of energy increase plus the energy outflow cannot be greater than the power supplied. The terms

$$\int_{D_c} \Psi_c\,da + \int_{D_{\mathfrak{m}}} (\Psi + \tfrac{1}{2}\rho v^2)\,da + \int_{\mathscr{d}} \psi\,ds \tag{3.17}$$

comprise the total energy of D, while

$$\int_{(\partial D)_{\mathfrak{m}}} (\Psi + \tfrac{1}{2}\rho v^2)(v \cdot n)\,ds \tag{3.18}$$

represents the loss in energy due to the flow of melt across $(\partial D)_{\mathfrak{m}}$. A basic postulate of the theory is that the interfacial force expend power over the velocity[10] of the endpoints of $\mathcal{S}$; the total power expended on D is therefore given by

$$\int_{\partial\mathcal{S}} \mathbb{C} \cdot v_{\partial\mathcal{S}} - \int_{(\partial D)_{\mathfrak{m}}} \rho v \cdot n\,ds. \tag{3.19}$$

In view of this discussion, we assume that the **dissipation inequality**[11]

$$(d/dt)\Big\{\int_{D_c} \Psi_c\,da + \int_{D_{\mathfrak{m}}} (\Psi + \tfrac{1}{2}\rho v^2)\,da + \int_{\mathcal{S}} \psi\,ds\Big\} + \int_{(\partial D)_{\mathfrak{m}}} (\Psi + \tfrac{1}{2}\rho v^2)(v \cdot n)\,ds \le \int_{\partial\mathcal{S}} \mathbb{C} \cdot v_{\partial\mathcal{S}} - \int_{(\partial D)_{\mathfrak{m}}} \rho v \cdot n\,ds \tag{3.20}$$

holds for every control volume D.

This relation is satisfied trivially when D lies solely in the crystal, and, by $(3.9)_2$, also when D lies solely in the melt. On the other hand, if we apply (3.20) to a control volume D which contains the interface, appeal to (2.11), (2.13), (3.4), (3.6), and (3.16), and shrink D to the interface, we see that

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[10] The formulation in [AG] (eqt. (3.7); cf. [G1], eqt. (1.3)) is based on the assumption that the capillary force expend power over the *normal* interfacial velocity $V\mathbf{m}$, while the dissipation inequality in [AG] contains a term to account for an outflow of energy across $\partial\mathcal{S}$, a term which I do not include here. These two views are consistent, since both theories yield the identity $\sigma = \psi$. I believe the current formulation to be conceptually preferrable.

[11] Cf. [G1], §3; [G2] §5; [AG], eqt. (3.7).

$$\int_{\mathcal{A}}\{\psi^\circ - \xi\theta^\circ + (\sigma-\psi)KV + V\{\Psi_c + p_c - \zeta(\Psi + p) - \tfrac{1}{2}\rho_c v^2 + \rho_c(1-\zeta)V^2\}ds \; + \int_{\partial\mathcal{A}}\{(\psi-\sigma)\boldsymbol{\ell}\cdot v_{\partial\mathcal{A}}\} \le 0. \tag{3.21}$$

This inequality must hold for every control volume D. Given a time t_0 and a subcurve $\mathcal{A}_0$ of $\mathcal{S}(t_0)$, we can always find a control volume D such that $\mathcal{A}(t_0) = \mathcal{A}_0$, but the tangential velocities of the endpoints of $\mathcal{A}$ are arbitrary at t_0. Thus, as a consequence of (3.21), we have the well known **identification of surface tension with energy**:

$$\sigma = \psi. \tag{3.22}$$

Finally, it is clear from (3.22) that (3.21) can hold for all control volumes only if

$$\psi^\circ - \xi\theta^\circ + V\{\Psi_c + p_c - \zeta(\Psi + p) - \tfrac{1}{2}\rho_c v^2 + \rho_c(1-\zeta)V^2\} \le 0. \tag{3.23}$$

3.5. Interactive energy-balance.

One of the chief differences between theories involving phase transitions and the more classical theories of continuum mechanics is the *creation and deletion of material points* as the phase interface moves relative to the underlying material. This is essentially a *bulk* interaction between phases, which we now isolate by restricting attention to the bulk material arbitrarily close to the interface. We represent the action of the interface on the bulk material immediately adjacent to it by two functions of $x \in \partial C(t)$ and t:

$\delta(x,t)$	**interactive dissipation,**
$g(x,t)$	**interactive force.**

$\delta(x,t)$ represents the net *outflow* of energy from the bulk material at the interface, per unit length; this is energy associated with the kinetics of attachment in the exchange of atoms between the crystal and the melt. $\mathbf{g}(\mathbf{x},t)$ is the net force, per unit length, exerted by the interface on the bulk material; this force is assumed to expend power over the normal velocity $V\mathbf{m}$.

The interactive fields enter our theory through the **interactive energy-balance**

$$(d/dt)\Big\{\int_{D_c}\Psi_c\,da + \int_{D_{\mathcal{M}}}(\Psi + \tfrac{1}{2}\rho v^2)da\Big\} + \int_{(\partial D)_{\mathcal{M}}}(\Psi + \tfrac{1}{2}\rho v^2)(\mathbf{v}\cdot\mathbf{n})ds + \int_{\mathcal{S}}\delta ds = -\int_{(\partial D)_{\mathcal{M}}}p\mathbf{v}\cdot\mathbf{n}ds + \int_{\mathcal{S}}\mathbf{g}\cdot(V\mathbf{m})ds, \qquad (3.24)$$

which we assume to hold in every control volume D (cf. Figure 2). Using steps analogous to those used to derive (3.21), we find that (3.24) is equivalent to

$$\int_{\mathcal{S}}\big\{(\Psi + \tfrac{1}{2}\rho v^2)(\mathbf{v}\cdot\mathbf{m} - V) + \Psi_c V + p\mathbf{v}\cdot\mathbf{m} - \mathbf{g}\cdot(V\mathbf{m})\big\}ds = -\int_{\mathcal{S}}\delta ds. \qquad (3.25)$$

We now determine the specific form of the force $\mathbf{g}$ using the invariance of (3.25) under **Galilean changes in observer**. Under such a change the velocities transform according to[12]

$$\mathbf{v} \longrightarrow \mathbf{v} + \mathbf{a}, \qquad V\mathbf{m} \longrightarrow V\mathbf{m} + \mathbf{a}, \qquad (3.26)$$

with $\mathbf{a}$ the (constant) relative velocity of the observers. Under (3.26) the term $\Psi_c V$ is invariant, since V there represents a velocity *relative to the crystal.* However, since the crystal is now not at rest, but instead has velocity $\mathbf{a}$, the term

$$\int_{\mathcal{S}}\{(\tfrac{1}{2}\rho_c \mathbf{a}^2)V + \mathbf{T}_c\mathbf{m}\cdot\mathbf{a}\}ds,$$

should be added to the left side of (3.25). Granted this, and assuming that δ is invariant under (3.26), we find, since $\mathbf{a}$ and $\mathcal{S}$ are

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[12] General transformations of observer during crystallization are studied by Gurtin and Struthers [GS].

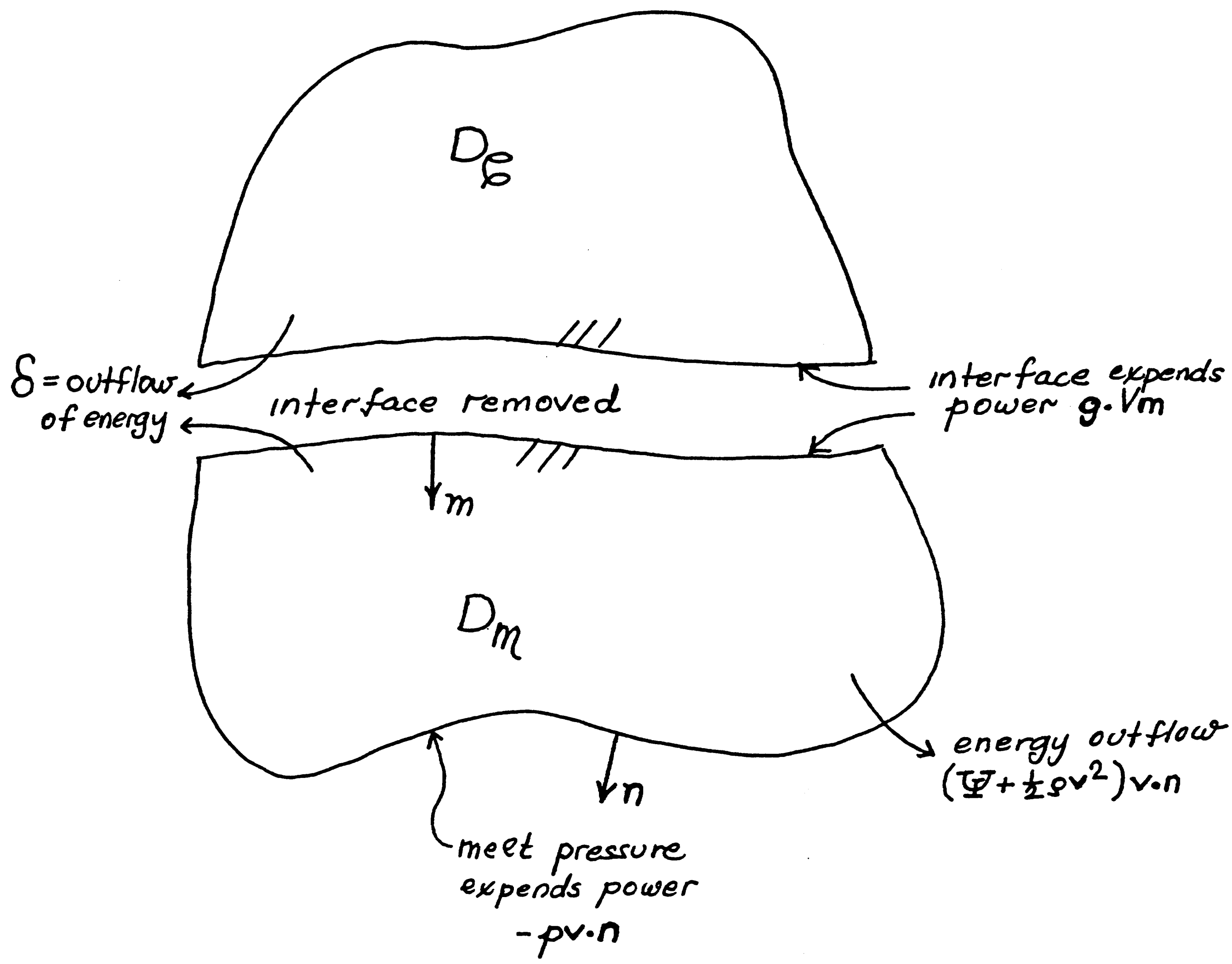

Figure 2. Free-body diagram used to write the interactive energy balance.

arbitrary, that[13]

$$\mathbf{g} = -\mathbf{b}.$$

(The transformed energy-balance contains terms linear and quadratic in $\mathbf{a}$; the linear terms, set equal to zero, yield $\mathbf{g}=-\mathbf{b}$; the quadratic terms yield balance of mass (3.4).) Thus, appealing to (3.5), (3.15), and (3.22), we are led to the (local) **interactive energy-balance**:

$$V\{\Psi_c + p_c - \zeta(\Psi + p) - \tfrac{1}{2}\rho_c v^2 + \rho_c(1-\zeta)V^2\} = -\delta. \qquad (3.27)$$

The interactive dissipation δ is a basic physical quantity of the theory, to be specified by a constitutive equation, and (3.27) is a fundamental balance law to be satisfied in all crystallization processes.

An important feature of (3.27) is that it allows us to rewrite (3.23) as the **dissipation inequality**

$$\psi^\circ - \xi\theta^\circ \le \delta. \qquad (3.28)$$

---

[13] In view of (3.11), we might have taken $\mathbf{g}=-\mathbf{b}$ from the outset. Because of the presence of inertial terms and because of the nonstandard nature of the power expended by an interface, I find it more compelling to derive $\mathbf{g}=-\mathbf{b}$ as a consequence of a standard requirement of invariance.

4. Constitutive equations for the interface.

As **constitutive equations** we allow the interfacial energy, the interfacial force, and the interactive dissipation to depend on the orientation of the interface through the angle θ and on the kinetics of the interface through the normal velocity V:

$$\psi = \psi(\theta,V), \quad \mathbb{C} = \mathbb{C}(\theta,V), \quad \delta = \delta(\theta,V). \tag{4.1}$$

We assume that the relations $(4.1)_{1,2}$ are consistent with (3.22), and, in view of (3.27), we suppose that

$$\delta(\theta,0) = 0. \tag{4.2}$$

Given an evolving crystal $C(t)$, the constitutive equations (4.1) may be used to compute a corresponding **constitutive process**. A basic hypothesis[14] of our theory is the **dissipation axiom**:

> *all constitutive processes must be consistent*
> *with the local dissipation inequality (3.28),*

an axiom which yields the following important constitutive restrictions:[15]

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[14] I rationalize this postulate as follows: Generalize the theory to include body forces f_c and f_m in the crystal and melt, respectively, so that (3.9) are replaced by $\operatorname{div}T_c + f_c = 0$, $\rho v^\cdot = -\operatorname{grad}p + f_m$ (*). Assume that a constitutive process is given. Construct a velocity field v in the melt that is consistent with balance of mass (3.5) and incompressibility (3.2); use (3.10) and (3.27) (supplemented by (3.7)) to compute p and $T_c m$ on the interface; extend p and T_c into the melt and into the crystal; compute f_c and f_m through (*). The corresponding set of fields is consistent with the balance laws of mass and momentum, as well as with the interactive energy-balance, and all that remains is the dissipation inequality (3.28).

[15] These restrictions are obvious modifications of results given in [G1,AG] (Compatibity Theorem), and I refer to [G1,AG] for their proof. The use of the second law to find restrictions on constitutive equations traces back to Coleman and Noll [CN], who used this

(i) *the energy* ψ *and interfacial force* $\mathbb{C}$ *are independent of the normal velocity* V, *and* $\psi(\theta)$ *generates* $\mathbb{C}(\theta)$ *through*[16]

$$\mathbb{C}(\theta) = \psi(\theta)\boldsymbol{\ell}(\theta) + \psi'(\theta)\mathbf{m}(\theta); \tag{4.3}$$

(ii) *the interactive dissipation is given by a relation of the form*

$$\delta(\theta,V) = \beta(\theta,V)V^2, \qquad \beta(\theta,V) \geq 0. \tag{4.4}$$

(Conditions (i) and (ii) are also sufficient that (3.28) hold in all constitutive processes.)

We assume that the **kinetic coefficient** $\beta(\theta,V)$ depends only on θ, and that

$$\psi(\theta), \beta(\theta) > 0. \tag{4.5}$$

Remarks.

1° By (4.3), $\sigma = \sigma(\theta)$ and $\xi = \xi(\theta)$ with

$$\sigma(\theta) = \psi(\theta), \qquad \xi(\theta) = \psi'(\theta). \tag{4.6}$$

2° In view of (3.27) and (4.3), the left side of (3.23) is equal to $-\delta$, which identifies $\delta = \beta(\theta)V^2$ as the *sole rate of energy dissipation;* indeed, tracing backwards the argument leading to (3.28), we find that

$$-\int_{\mathfrak{d}} \beta(\theta)V^2 ds$$

represents the left side of (3.20) minus the right.

3° (2.1), (2.6), and (4.3) yield the identity

$$\mathbb{C} \cdot (V\mathbf{m})_s = \psi^\circ - \psi K V. \tag{4.7}$$

---

proceedure for single-phase thermoelastic materials.

[16] $f'(\theta) = df(\theta)/d\theta$.

4° (3.27) and (4.4) furnish us with a formula for the "crystal pressure":

$$p_c = -\beta(\theta)V + \zeta p - F + \tfrac{1}{2}\rho_c\mathbf{v}^2 - \rho_c(1-\zeta)V^2, \qquad (4.8)$$

with F the *constant*

$$F = \Psi_c - \zeta\Psi. \qquad (4.9)$$

5° It might seem reasonable to allow the constitutive equations (4.1) to depend on the tangential velocity $\upsilon = \mathbf{v}\cdot\boldsymbol{\ell}$ of the melt at the interface. This generalization results in no essential change: the dissipation inequality rules out the dependence of ψ and $\mathbb{C}$ on υ, so that (4.3) remains valid, and (4.5) is replaced by

$$\delta(\theta,V,\upsilon) = \beta(\theta,V,\upsilon)V^2, \qquad \beta(\theta,V,\upsilon) \geq 0. \qquad (4.10)$$

5. Partial differential equations. Free-boundary conditions.

The thermodynamic restrictions (4.3) have important consequences when applied to the interfacial balance law (3.10). Indeed, (2.1), (2.3), and (4.3) imply that

$$\mathbb{C}_s = [\psi(\theta) + \psi''(\theta)]K\mathbf{m}, \tag{5.1}$$

while (3.5), (3.15), (3.10), and (4.8) yield

$$\begin{aligned} \mathbf{m}\cdot\mathbb{C}_s &= p - p_c - \rho_c(1-\zeta)V^2 = \beta(\theta)V + F - \tfrac{1}{2}\rho_c \mathbf{v}^2 - (\zeta - 1)p, \\ \boldsymbol{\ell}\cdot\mathbb{C}_s &= \boldsymbol{\ell}\cdot\mathrm{T}_c\mathbf{m} - \rho_c V\mathbf{v}\cdot\boldsymbol{\ell} \end{aligned} \tag{5.2}$$

The interfacial balance law therefore has the *normal component*

$$[\psi(\theta) + \psi''(\theta)]K = \beta(\theta)V + F - \tfrac{1}{2}\rho_c \mathbf{v}^2 + (1-\zeta)p, \tag{5.3}$$

a crucial relation as it and (3.5) comprise the free-boundary conditions of the theory.

The tangential component of the interfacial balance law,

$$\boldsymbol{\ell}\cdot\mathrm{T}_c\mathbf{m} = \rho_c V\mathbf{v}\cdot\boldsymbol{\ell}, \tag{5.4}$$

gives the tangential component of the crystal traction at the interface;[17] since the crystal stress is indeterminate, (5.4) is of little importance.

Summarizing, the basic system of equations consists of (3.2), (3.5), $(3.9)_2$, and (5.3):

---

[17] In addition, the interfacial shear induces a couple per unit length along the interface which must be balanced by torques in the crystal (cf. [G1], Remark 3.2).

$$\rho \mathbf{v}^{\cdot} = -\mathrm{grad}\, p, \qquad \mathrm{div}\, \mathbf{v} = 0, \quad \text{(melt)} \tag{5.5}$$

$$\left.\begin{aligned} [\psi(\theta) + \psi''(\theta)]K &= \beta(\theta)V + F - \tfrac{1}{2}\rho_c \mathbf{v}^2 + (1-\zeta)p, \\ \mathbf{v}\cdot\mathbf{m} &= (1-\zeta)V. \end{aligned}\right\} \text{(interface)} \tag{5.6}$$

We will refer to (5.5) and (5.6) as the **crystallization equations**; the melt equations (5.5) are to hold in $\mathfrak{M}(t)$ for $t>0$, the interface conditions (5.6) on $\partial\mathcal{C}(t)$ for $t>0$.

There should be cases of interest in which the melt velocity (and its gradient) are small. Granted this, it would appear reasonable to neglect the term $\frac{1}{2}\rho_c \mathbf{v}^2$ in (5.6) and to replace the material time-derivative $\mathbf{v}^{\cdot}$ in (5.5) with the spatial time-derivative $\mathbf{v}_t$; we will refer to this proceedure as the **weak-inertia approximation**.

The crystallization equations can be simplified when the flow is **irrotational**: we write $\mathbf{v}(\mathbf{x},t)$ as the gradient of a *potential* $\varphi(\mathbf{x},t)$,

$$\mathbf{v} = \mathrm{grad}\,\varphi, \tag{5.7}$$

and replace (5.5) by the Bernoulli equation[18]

$$p = -\rho\varphi_t - \tfrac{1}{2}\rho \mathbf{v}^2 \tag{5.8}$$

and the requirement that φ be harmonic. It is actually more convenient to use the potential

$$u(\mathbf{x},t) = \rho(1-\zeta)\varphi(\mathbf{x},t) - Ft; \tag{5.9}$$

then

$$\rho(\zeta - 1)\mathbf{v} = -\mathrm{grad}\, u \tag{5.10}$$

---

[18] Cf.,e.g., [G4], p. 120.

and the crystallization equations take the form:

$$\Delta u = 0, \quad \text{(melt)} \tag{5.11}$$

$$\left.\begin{aligned} [\psi(\theta)+\psi''(\theta)]K &= \beta(\theta)V - u_t - \tfrac{1}{2}\alpha^{-1}(\operatorname{grad}u)^2, \\ \partial u/\partial m &= \alpha V, \end{aligned}\right\} \text{(interface)} \tag{5.12}$$

where $\partial u/\partial m = \mathbf{m}\cdot\operatorname{grad}u$, while

$$\alpha = \rho(1-\zeta)^2. \tag{5.13}$$

Under the *weak-inertia approximation* the term $(\operatorname{grad}u)^2$ in $(5.12)_1$ is dropped, so that $(5.12)_1$ becomes

$$[\psi(\theta)+\psi''(\theta)]K = \beta(\theta)V - u_t, \tag{5.14}$$

but (5.11) and $(5.12)_2$ remain unchanged. Consistent with this approximation, we neglect the term involving $\mathbf{v}^2$ in (5.8), so that, by (5.9),

$$(\zeta-1)p = u_t + F. \tag{5.15}$$

Remark. For an isotropic crystal both ψ and β are constants; for ψ constant and $\beta=0$, and under the weak inertia approximation, we have the equations

$$\Delta u = 0, \qquad \text{(melt)} \tag{5.16}$$

$$u_t = -\psi K, \quad \partial u/\partial m = \alpha V. \qquad \text{(interface)} \tag{5.17}$$

It is interesting to compare the simplified equations (5.16) and (5.17) to those of the (quasi-static) theory of Mullins and Sekerka for thermally-driven solidification when one of the two phases does not conduct heat.[19] There the temperature u of the conducting phase satisfies (5.16) and $(5.17)_2$, but the condition $(5.17)_1$ is replaced by $u = \psi K$.

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[19] Cf., e.g., [G2], eqt. (11.9). (The curvature in [G2] has sign opposite to that here.)

6. The crystallization problem. Global balance relations.

Initial conditions appropriate to the crystallization equations would appear to be a prescription of the region occupied by the crystal (and hence also that occupied by the melt) together with a prescription of the velocity $\mathbf{v}$:

$$\mathcal{C}(0) \ \textit{and} \ \mathbf{v}(\mathbf{x},0) \ \textit{prescribed.} \tag{6.1}$$

Since the melt is infinite, restrictions should be imposed on its behavior at infinity. We here consider the **far-field conditions**:[20]

$$\mathbf{v}(\mathbf{x},t) = o(|\mathbf{x}|^{-1}), \quad p(\mathbf{x},t) = O(1) \quad \text{as} \quad |\mathbf{x}| \to \infty, \tag{6.2}$$

for each t. Note that, by (6.2),

$$\int_{\mathcal{S}_r} \mathbf{v}\cdot\mathbf{n}\, ds \to 0 \quad \text{as} \quad r \to \infty, \tag{6.3}$$

where $\mathcal{S}_r$ is a circle of radius r and $\mathbf{n}$ is the outward unit normal on $\mathcal{S}_r$. Thus the *net flow of melt vanishes at infinity.*

We will use the term **crystallization problem** to designate the free-boundary problem defined by the crystallization equations (5.5) and (5.6), the initial conditions (6.1), and the far-field conditions (6.2). A solution of this problem will be termed **regular** if

$$(d/dt)\int_{\mathcal{M}_r(t)} \mathbf{v}^2\, da \ \to \ (d/dt)\int_{\mathcal{M}(t)} \mathbf{v}^2\, da \quad \text{as} \quad r \to \infty, \tag{6.4}$$

where $\mathcal{M}_r(t)$ is the portion of $\mathcal{M}(t)$ interior to the circle $\mathcal{S}_r$.

The next result yields Lyapunov functions for the crystallization problem.

Global balance relations. *Regular solutions of the crystallization problem satisfy*

---

[20] Another possibility will be considered in Section 11.

$$\begin{aligned}&(d/dt)\,\mathrm{area}(\mathcal{C}) = 0,\\ &(d/dt)\Big\{\int_{\partial\mathcal{C}}\psi(\theta)\,ds + \int_{\mathfrak{M}}\tfrac{1}{2}\rho v^2\,da\Big\} = -\int_{\partial\mathcal{C}}\beta(\theta)V^2\,ds \le 0.\end{aligned} \tag{6.5}$$

Proof. By the divergence theorem, (2.14), (3.5), $(5.5)_2$, and (6.3), for r sufficiently large,

$$0 = \int_{\mathcal{S}_r}\mathbf{v}\cdot\mathbf{n}\,ds - \int_{\partial\mathcal{C}}\mathbf{v}\cdot\mathbf{m}\,ds = (\zeta-1)\int_{\partial\mathcal{C}}V\,ds = (\zeta-1)(d/dt)\,\mathrm{area}(\mathcal{C}), \tag{6.6}$$

which, by virtue of (3.7), implies $(6.5)_1$.

The verification of $(6.5)_2$ is more complicated. First of all, (2.11), (4.7), and an integration by parts yield

$$(d/dt)\int_{\partial\mathcal{C}}\psi\,ds = -\int_{\partial\mathcal{C}}V\,\mathbb{C}_s\cdot\mathbf{m}\,ds. \tag{6.7}$$

Less trivial is the identity

$$\begin{aligned}&(d/dt)\int_{\mathfrak{M}}\mathfrak{k}\,da = \int_{\partial\mathcal{C}}[(1-\zeta)p - \tfrac{1}{2}\rho_c v^2\,]V\,ds,\\ &\qquad\quad \mathfrak{k} = \tfrac{1}{2}\rho v^2,\end{aligned} \tag{6.8}$$

which we now prove. By $(2.13)_2$,

$$(d/dt)\int_{\mathfrak{M}_r}\mathfrak{k}\,da = \int_{\mathfrak{M}_r}\mathfrak{k}_t\,da - \int_{\partial\mathcal{C}}V\mathfrak{k}\,ds. \tag{6.9}$$

Also, we may use (6.2) to conclude that, as $r\to\infty$,

$$\int_{\mathcal{S}_r}\mathfrak{k}\,\mathbf{v}\cdot\mathbf{n}\,ds = o(1), \qquad \int_{\mathcal{S}_r}p\,\mathbf{v}\cdot\mathbf{n}\,ds = o(1). \tag{6.10}$$

Therefore, by (3.4), (3.5), (5.5), and (6.4), as $r\to\infty$,

$$
\begin{aligned}
-\int_{\partial\mathcal{C}}\tfrac{1}{2}\rho_c v^2 V\,ds = \int_{\partial\mathcal{C}}\mathscr{k}(\mathbf{v}\cdot\mathbf{m}-V)\,ds &= -\int_{\mathfrak{M}_r}[\mathscr{k}_t+\mathrm{div}(\mathscr{k}\mathbf{v})]\,da + (d/dt)\int_{\mathfrak{M}_r}\mathscr{k}\,da + o(1)\\
&= -\int_{\mathfrak{M}_r}\mathscr{k}^{\cdot}\,da + (d/dt)\int_{\mathfrak{M}_r}\mathscr{k}\,da + o(1)\\
&= \int_{\mathfrak{M}_r}\mathbf{v}\cdot\mathrm{grad}p\,da + (d/dt)\int_{\mathfrak{M}}\mathscr{k}\,da + o(1)\\
&= -\int_{\partial\mathcal{C}}p\mathbf{v}\cdot\mathbf{m}\,ds + (d/dt)\int_{\mathfrak{M}}\mathscr{k}\,da + o(1)\\
&= -\int_{\partial\mathcal{C}}(1-\zeta)pV\,ds + (d/dt)\int_{\mathfrak{M}}\mathscr{k}\,da + o(1), \qquad (6.11)
\end{aligned}
$$

and, letting $r\to\infty$, (6.8) follows.

In view of (5.1), $\mathbb{C}_s\cdot\mathbf{m}$ is equal to the right side of $(5.6)_1$. Thus we may conclude from (6.7) and (6.8) that the left side of $(6.5)_2$ is equal to

$$
-\int_{\partial\mathcal{C}}V[\beta(\theta)V+F]\,ds, \qquad (6.12)
$$

which yields $(6.5)_2$, since (6.6) implies that the integral of FV over $\partial\mathcal{C}$ vanishes. ■

Remark. The global balance relation $(6.5)_2$ actually follows from the global dissipation inequality (3.20) in conjunction with $(6.5)_1$ and Remark 2° of Section 4. Indeed, let D in (3.20) be the interior of the circle $\mathscr{S}_r$ (with r large enough that D contains the crystal); note that, by $(6.5)_1$, $(d/dt)\,\mathrm{area}(D_{\mathcal{C}}) = (d/dt)\,\mathrm{area}(D_{\mathfrak{M}}) = 0$; using (6.3), (6.4), and (6.10), let $r\to\infty$ in (3.20) (strengthened by Remark 2° of Section 4).

7. Small motions about a flat interface.

7.1. Basic equations.

A flat interface furnishes an *equilibrium* of the crystallization equations (5.5), (5.6) provided

$$F + (1-\zeta)p = 0, \tag{7.1}$$

and this relation, (4.8), and (4.9) yield

$$\Psi_c + p_c = \zeta(\Psi + p), \qquad p_c = p. \tag{7.2}$$

We now consider solutions which are close to an equilibrium of this form. We choose x and y as coordinates in $\mathbb{R}^2$ and, without loss in generality, stipulate that the x-axis represent the equilibrium position of the interface, oriented so that arc length increases with x. We assume that:

(i) the interface is represented as a graph $y=h(x,t)$ (Figure 3) with *interfacial height* h "small";

(ii) the melt velocity $\mathbf{v}$ is irrotational and "small";

and we *formally linearize* the crystallization equations with respect to h and $\mathbf{v}$.

We begin with the system (5.11), (5.12). Considering V, K, and θ as functions of (x,t),

$$V = h_t \sin\theta, \qquad K = h_{xx}\sin^3\theta, \tag{7.3}$$

where subscripts denote partial differentiation with respect to the corresponding variable. Noting that the interface has angle $\theta=\pi/2$ at equilibrium, we define

$$A = (\psi + \psi'')_0, \qquad B = \beta_0, \tag{7.4}$$

where the subscript zero denotes evaluation at $\theta=\pi/2$. Then the

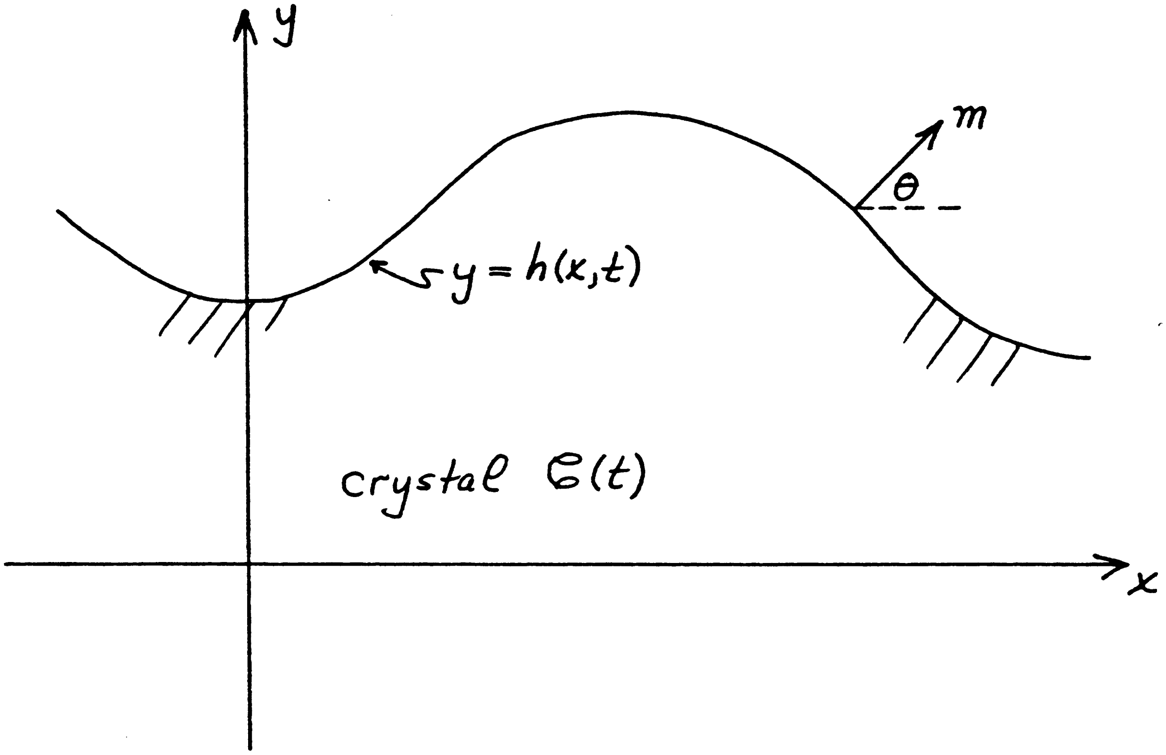

Figure 3. Sign conventions when the interface is a graph $y = h(x,t)$.

interface condition $(5.12)_1$, linearized formally with respect to h and v, is given by

$$Ah_{xx} = Bh_t - u_t. \tag{7.5}$$

Consistent with the approximations leading to (7.5) is the assumption that the melt equation (5.11) hold in the halfspace $y>0$, and that (7.5) and the interface condition $(5.12)_2$ be satisfied on the x-axis with $\partial u/\partial m$ replaced by u_y. Thus the crystallization equations, *linearized about equilibrium*, take the form:[21]

$$\begin{aligned} &u_{xx} + u_{yy} = 0 && (-\infty < x < \infty,\ y>0,\ t>0), \\ &Ah_{xx} = Bh_t - u_t, \quad u_y = \alpha h_t && (-\infty < x < \infty,\ y=0,\ t>0). \end{aligned} \tag{7.6}$$

7.2. Melting-freezing waves.

Andreev and Parshin [AP] note that (7.6) has the solution

$$\begin{aligned} h(x,t) &= C_1 e^{i\lambda x} e^{-(i\omega + \gamma)t}, \\ u(x,y,t) &= C_2 e^{-\lambda y} e^{i\lambda x} e^{-(i\omega + \gamma)t} \end{aligned} \tag{7.7}$$

with

$$\omega^2 = \frac{A\lambda^3}{\alpha} - \frac{B^2\lambda^2}{4\alpha^2}, \qquad \gamma = \frac{B\lambda}{2\alpha}, \tag{7.8}$$

a solution which represents *damped oscillations of the interface.* For $B=0$ (and hence approximately for B small), ω^2 is proportional to λ^3.

---

[21] These equations, for $F=0$, are due to Andreev and Parshin [AP]. F manifests itself when boundary conditions (or conditions at infinity) are expressed in terms of the pressure $p=-(1-\zeta)^{-1}[u_t + F]$ (cf. Section 11).

$$\omega^2 = \frac{\rho(\psi + \psi'')_0 \lambda^3}{(\rho_c - \rho)^2}, \tag{7.9}$$

a proportionality found in the experiments of Keshishev, Parshin, and Babkin [KPB].

Remark. The relation (7.8) corresponds to oscillations on a flat interface at angle θ only if

$$\psi(\theta) + \psi''(\theta) > 0. \tag{7.10}$$

This inequality is essentially a condition of static stability for the interface: it follows from the requirement that straight line-segments locally minimize interfacial energy. There is no compelling physical reason to suppose that (7.10) is satisfied; in fact, material scientists often consider energies which violate (7.10) for particular ranges of θ (cf. Gjostein [G], Cahn and Hoffman [CH]).

7.3. The linearized crystallization problem. Uniqueness.

Initial conditions for the linearized crystalization equations are

$$\begin{aligned} &\mathrm{grad}\,u(x,y,0) \quad (-\infty < x < \infty,\ y > 0) \quad \textit{and} \\ &h(x,0) \quad (-\infty < x < \infty) \quad \textit{prescribed,} \end{aligned} \tag{7.11}$$

while possible **far-field conditions** are the following counterpart of (6.2) (cf. (5.10), (5.15)):

$$\mathrm{grad}\,u(\mathbf{x},t) = o(|\mathbf{x}|^{-1}), \quad u_t(\mathbf{x},t) = O(1) \quad \text{as} \quad |\mathbf{x}| \to \infty. \tag{7.12}$$

Further, since the interface is not a closed curve, but begins and ends at infinity, an **interfacial far-field condition** is needed; one possibility is:

$$h_x(\pm\infty,t) \quad \textit{or} \quad h(\pm\infty,t) \quad \textit{prescribed.} \tag{7.13}$$

We will refer to the problem defined by (7.6) and (7.11)-(7.13) as the **linearized crystallization problem.**[22]

The next result, an analog of the global balance relation $(6.5)_2$, yields uniqueness for the linearized problem. To state this result precisely, let

$$\begin{aligned} \mathcal{M}_\infty &= \{(x,y): \ -\infty < x < \infty, \ \ y > 0\ \}, \\ \mathcal{L}_\infty &= \{(x,y): \ -\infty < x < \infty, \ \ y = 0\ \}; \end{aligned} \tag{7.14}$$

let $\mathcal{M}_r$ denote the portion of $\mathcal{M}_\infty$ interior to a circle of radius r; let $\mathbf{n}$ denote the outward unit normal on $\partial\mathcal{M}_r$; let $\mathcal{S}_r$ denote the *circular portion* of $\partial\mathcal{M}_r$; let $\mathcal{L}_r$ denote the *flat portion* of $\partial\mathcal{M}_r$. We will refer to a solution of the linearized problem as **regular** if

$$\begin{aligned} (d/dt)\int_{\mathcal{M}_r}|\operatorname{grad}u|^2 da &\rightarrow (d/dt)\int_{\mathcal{M}_\infty}|\operatorname{grad}u|^2 da, \\ (d/dt)\int_{\mathcal{L}_r}(h_x)^2 ds &\rightarrow (d/dt)\int_{\mathcal{L}_\infty}(h_x)^2 ds \end{aligned} \tag{7.15}$$

as $r \rightarrow \infty$.

Global balance relation. *Consider a regular solution of the linearized crystallization problem with*

---

[22] An existence theorem for this problem has been established by Rogers [R], who shows that: (i) for sufficiently smooth data the solution goes asymptotically to a steady state; (ii) solutions propagate with finite speed. Rogers analyzes the crystallization equations in the alternative form $h_{tt} = (\alpha\pi)^{-1}\mathcal{I}[Ah_{xxx} - Bh_{xt}]$, where $\mathcal{I}$ is the integral operator consisting of spatial convolution on $(-\infty,\infty)$ with respect to x^{-1}. This integral equation was derived independently by MacCamy (private communication).

$$(h_t h_x)(\pm\infty, t) = 0 \tag{7.16}$$

for all $t > 0$. *Then*

$$(d/dt)\left\{\int_{\mathcal{M}_\infty} |\mathrm{grad}\,u|^2 da + \alpha A \int_{\mathcal{S}_\infty} (h_x)^2 ds\right\} = -2\alpha B \int_{\mathcal{S}_\infty} (h_t)^2 ds \le 0. \tag{7.17}$$

Proof. Since $(\partial u/\partial n) = -u_y$ on $\mathcal{S}_r$, if we apply the divergence theorem to the integral of $u_t(\partial u/\partial n)$ over $\partial\mathcal{M}_r$, we conclude, with the aid of $(7.6)_1$ and (7.12), that

$$\int_{\mathcal{S}_r} u_t u_y ds = -\tfrac{1}{2}(d/dt)\int_{\mathcal{M}_r} |\mathrm{grad}\,u|^2 da + o(1)$$

as $r \to \infty$. On the other hand, $(7.6)_2$ and (7.16) imply that

$$\int_{\mathcal{S}_r} u_t u_y ds = \alpha \int_{\mathcal{S}_r} u_t h_t ds = \alpha \int_{\mathcal{S}_r} h_t (B h_t - A h_{xx}) ds,$$

$$= \alpha B \int_{\mathcal{S}_r} (h_t)^2 ds + \tfrac{1}{2}\alpha A (d/dt) \int_{\mathcal{S}_r} (h_x)^2 ds + o(1).$$

If we equate the last two relations and let $r \to \infty$ using (7.15), we are led to (7.17). ■

The global balance relation yields a certain degree of *stability* for the linear crystallization problem, since for $\alpha, A, B > 0$ it implies decay with time of spatial L^2 norms of $|\mathrm{grad}\,u|$ and h_x, as well as the boundedness of the integral of $(h_t)^2$ over $\mathcal{M}_\infty \times (0,t)$.

An immediate corollary of (7.17) is the following result, in which the assumptions $\alpha > 0$, $A > 0$, $B > 0$ should be kept in mind. (Cf. (3.7), (4.5), (5.13), (7.4), and (7.10); actually, $B \ge 0$ rather than $B > 0$ is used.)

Uniqueness theorem. *The linearized crystallization problem* *(with given data) has at most one regular solution (modulo an additive constant for* u).

Proof. Let h and u denote the interfacial height and potential corresponding to the difference between two solutions. Since the problem is linear, h and u furnish a regular solution of the crystallization problem with *null data,* so that, in particular, (7.16) is satisfied and $\operatorname{grad} u(x,y,0) \equiv 0$, $h(x,0) \equiv 0$. We may therefore use (7.17) to conclude that $u = u(t)$, $h = h(t)$, so that, by (7.6), h and u are constant. But $h(0) = 0$; thus $h \equiv 0$. ■

8. The crystallization problem in a bounded container.

If the crystallization process takes place in a *bounded* **container** Ω, then Ω is the union of the crystal $\mathcal{C}(t)$ and the melt $\mathcal{M}(t)$, and the **interface** between $\mathcal{C}(t)$ and $\mathcal{M}(t)$ is generally not $\partial\mathcal{C}(t)$, but rather

$$\mathcal{S}(t) = \partial\mathcal{C}(t) \cap \partial\mathcal{M}(t) \qquad (8.1)$$

(Figure 4). In this case we need boundary conditions on

$$(\partial\Omega)_{\mathcal{M}}(t) = \partial\Omega(t) \cap \partial\mathcal{M}(t), \qquad (8.2)$$

the portion of the container that bounds the melt, as well as a contact condition on $\partial\mathcal{S}(t)$, the portion of the interface that meets the container. Let $\mathbf{n}$ denote the outward unit normal to $\partial\Omega$. We shall restrict attention to the **boundary condition**

$$\mathbf{v} \cdot \mathbf{n} = 0 \quad \text{on} \quad (\partial\Omega)_{\mathcal{M}} \qquad (8.3)$$

in conjunction with the **contact condition**[23]

$$\mathbb{C}(\theta) \ \text{parallel to} \ \mathbf{n} \ \text{at points of} \ \partial\mathcal{S}. \qquad (8.4)$$

The free-boundary problem defined by the crystallization equations (5.5) and (5.6)[24], the boundary condition (8.3), and the contact condition (8.4) will be referred to as the **crystallization problem in a bounded container**.

Global balance relations. *Solutions of the crystallization problem in a bounded container satisfy*

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[23] I neglect contact energy between the container and the melt and between the container and the crystal.

[24] (5.7) are here required to hold on $\mathcal{S}(t)$.

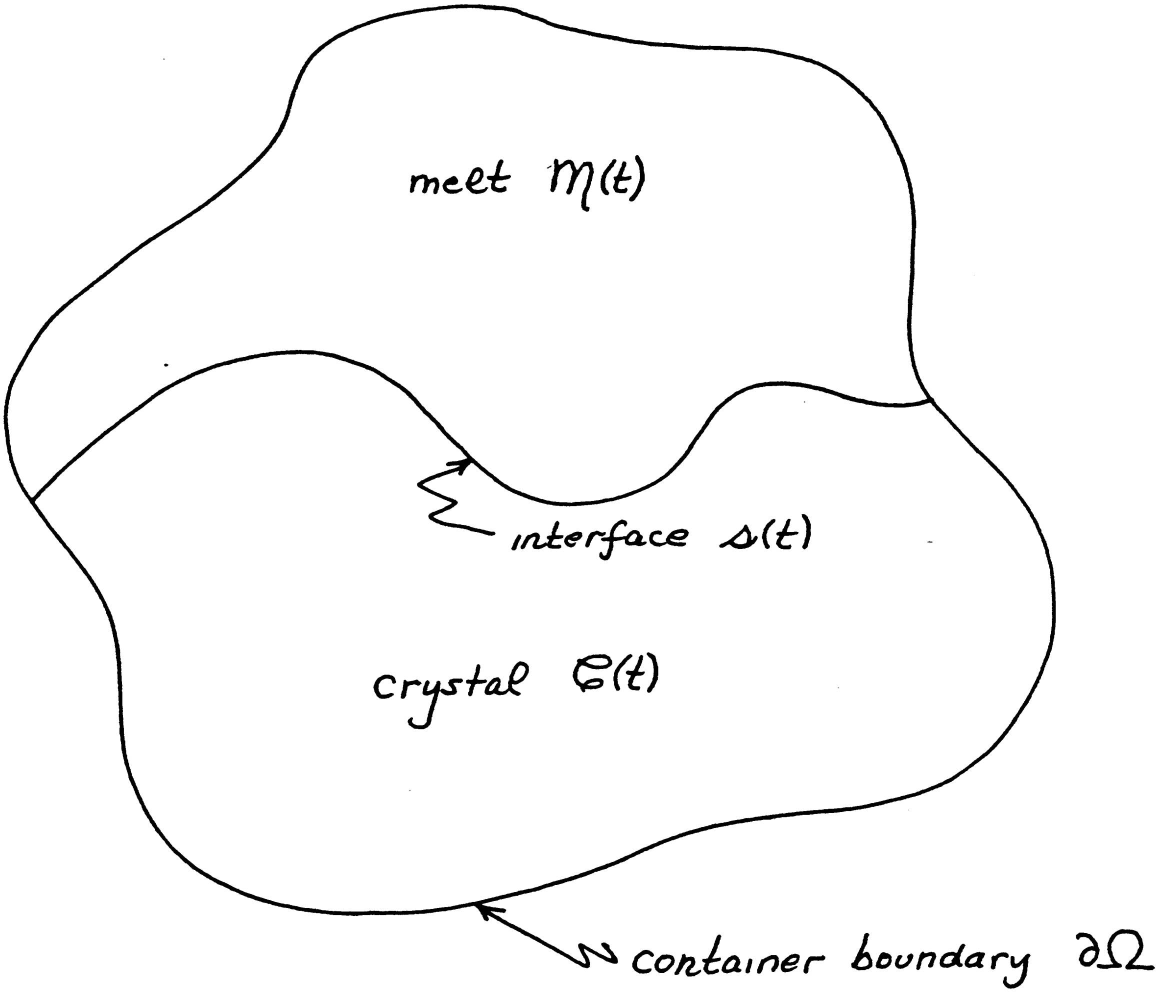

Figure 4. Crystallization in a bounded container Ω.

$$\begin{aligned}&(d/dt)\,\mathrm{area}(C) = 0,\\ &(d/dt)\Big\{\int_{\mathfrak{s}}\psi(\theta)\,ds + \int_{\mathfrak{M}}\tfrac{1}{2}\rho v^2\,da\Big\} = -\int_{\mathfrak{s}}\beta(\theta)V^2\,ds \le 0.\end{aligned}\tag{8.5}$$

Proof. The first of (8.5) follows using (8.3) and the argument shown in (6.6) with ∂C replaced by $\mathfrak{s}$ and $\mathcal{S}_r$ by $(\partial\Omega)_{\mathfrak{M}}$.

The verification of $(8.5)_2$ is based on the identities:

$$\begin{aligned}&(d/dt)\int_{\mathfrak{s}}\psi\,ds = -\int_{\mathfrak{s}}V\,\mathbb{C}_s\cdot\mathbf{m}\,ds,\\ &(d/dt)\int_{\mathfrak{M}}\mathbb{k}\,da = \int_{\mathfrak{s}}[(1-\zeta)p - \tfrac{1}{2}\rho_c v^2\,]V\,ds\end{aligned}\tag{8.6}$$

with $\mathbb{k} = \frac{1}{2}\rho v^2$, and follows as in the paragraph containing (6.12).

Thus we have only to establish (8.6). By (2.7) and (8.4),

$$\int_{\partial\mathfrak{s}}\mathbb{C}\cdot\mathbf{v}_{\partial\mathfrak{s}} = 0,$$

and this relation, (2.8), (2.11), (3.22), and (4.7), yield $(8.6)_1$. The result $(8.6)_2$ follows from (3.4), (3.5), (5.5), and (8.3) using the steps outlined in (6.9) and (6.11) with the o(1) symbol not present, and with ∂C replaced by $\mathfrak{s}$, $\mathfrak{M}_r$ by $\mathfrak{M}$. ■

9. Viscous melt.

We could also allow the melt to be an incompressible, viscous fluid. In this case the melt *stress* is given by the constitutive relation

$$T = -p1 + \mu(\mathrm{grad}v + \mathrm{grad}v^T), \tag{9.1}$$

with $\mu > 0$ the (constant) melt *viscosity*, and the melt equations take the form

$$\rho\dot{v} = -\mathrm{grad}p + 2\mu\Delta v, \qquad \mathrm{div}v = 0. \tag{9.2}$$

In accord with the presence of viscosity is the assumption that *the melt adhere to the crystal*, so that the tangential component of v vanishes at the interface; by (3.5), this is equivalent to the requirement that

$$v = (1-\zeta)Vm. \tag{9.3}$$

Balance of momentum now leads to an obvious counterpart of (3.10):

$$\mathbb{C}_s = T_c m - Tm - \rho_c V v. \tag{9.4}$$

Regarding the dissipation inequality (3.20) and the interactive energy-balance (3.24), we replace $-pv \cdot n$ by $v \cdot Tn$, but the end results are still (3.27) and (3.28). Here we use the fact that, because of $(9.2)_2$ and (9.3),

$$m \cdot (\mathrm{grad}v)m = 0, \tag{9.5}$$

so that, by (9.1),

$$\mathbf{m}\cdot\mathbf{T}\mathbf{m} = -p. \tag{9.6}$$

We continue to postulate constitutive equations of the form (4.1); the resulting thermodynamic restrictions (4.3) and (4.4) remain valid.

Summarizing, the basic equations for an **incompressible, viscous melt** are:

$$\left.\begin{aligned} \rho[\mathbf{v}_t + (\operatorname{grad}\mathbf{v})\mathbf{v}] &= -\operatorname{grad}p + 2\mu\Delta\mathbf{v}, \\ \operatorname{div}\mathbf{v} &= 0, \end{aligned}\right\} \text{(melt)} \tag{9.7}$$

$$\left.\begin{aligned} [\psi(\theta) + \psi''(\theta)]K &= \beta(\theta)V + F - \tfrac{1}{2}\rho_c\mathbf{v}^2 + (1-\zeta)p, \\ \mathbf{v} &= (1-\zeta)V\mathbf{m}, \end{aligned}\right\} \text{(interface)} \tag{9.8}$$

with the terms $(\operatorname{grad}\mathbf{v})\mathbf{v}$ and $\frac{1}{2}\rho_c\mathbf{v}^2$ dropped in the weak inertia approximation.

For a bounded container we replace the boundary condition (8.3) by

$$\mathbf{v} = \mathbf{0} \quad \text{on} \quad (\partial\Omega)_{\mathfrak{M}}. \tag{9.9}$$

Granted these changes, *the global balance relations* (6.5) and (8.5) *remain valid* provided we account for the additional (dissipative) term

$$-\tfrac{1}{2}\mu\int_{\mathfrak{M}} |\operatorname{grad}\mathbf{v} + \operatorname{grad}\mathbf{v}^{T}|^2\,da \tag{9.10}$$

on the right sides of $(6.5)_2$ and $(8.5)_2$.

10. Three-dimensional theory.

When the crystallization process takes place in $\mathbb{R}^3$, the interface evolves as a *surface*, rather than as a curve, but apart from notation the theory is identical. Following the notation and terminology of [G1], we write ∇_{surf} for the *surface gradient*, $\mathbf{L} = -\nabla_{\text{surf}}\mathbf{m}$ for the *curvature tensor*, and $H = \operatorname{tr}\mathbf{L}$ for twice the *mean curvature.* Then the only essential changes regarding the equations presented in Sections 5 and 9 are the replacement of $\psi(\theta)$ by $\psi(\mathbf{m})$, $\beta(\theta)$ by $\beta(\mathbf{m})$, and

$$[\psi(\theta) + \psi''(\theta)]K \quad \text{by} \quad \psi(\mathbf{m})H + \psi_{\mathbf{mm}}(\mathbf{m}) \cdot \mathbf{L}, \tag{10.1}$$

where $\psi_{\mathbf{mm}}(\mathbf{m})$ is the second gradient of $\psi(\mathbf{m})$ on the surface of the unit ball.

In the three-dimensional theory the interfacial force is replaced by an **interfacial stress**[25] $\mathbb{C}$, with $\mathbb{C}(\mathbf{x},t)$ a linear transformation from the tangent space to $\partial\mathcal{C}(t)$ at $\mathbf{x}$ into $\mathbb{R}^3$. For crystallization in a bounded container, as discussed in Section 8, the contact condition takes the form

$$\mathbb{C}(\mathbf{x},t)\boldsymbol{\nu}(\mathbf{x}) \quad \text{parallel to} \quad \mathbf{n}(\mathbf{x}) \quad \text{at points} \quad \mathbf{x} \in \partial\mathcal{A}(t), \tag{10.2}$$

where $\boldsymbol{\nu}(\mathbf{x})$, a vector tangent to $\mathcal{A}(t)$ at $\mathbf{x}$, is the outward unit normal to the boundary curve $\partial\mathcal{A}(t)$. The global balance relations (6.5) and (8.5) then hold with the obvious replacements (area → vol, ds → da, da → dv) provided we require, for (6.5), that

$$v(\mathbf{x},t) = o(|\mathbf{x}|^{-2}), \quad p(\mathbf{x},t) = O(1) \quad \text{as} \quad |\mathbf{x}| \to \infty, \tag{10.3}$$

estimates which imply (6.3).

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[25] Cf. [G1]. The thermodynamic restrictions concerning $\mathbb{C}(\mathbf{m})$ are as given in [G1], eqt. $(4.5)_{2,3}$ and are strictly analogous to (4.3).

11. Radial solutions for an isotropic crystal.

Consider an isotropic crystal, in the shape of a sphere, undergoing spherically symmetric crystalization. For convenience, we use the weak-inertia approximation, so that the underlying equations are (5.11), $(5.12)_2$, and (5.14), as modified by (10.1). *We do not require that the far-field conditions* (10.3) *hold,* as the only spherically symmetric solution consistent with (10.3) has the melt and interface stationary. (This is as expected: because of the incompressibility of the melt, a net flow of melt at infinity is required for a nontrivial spherically symmetric solution.)

The general radial solution $u(r,t)$ of (5.11), exterior to a sphere, is

$$u(r,t) = A(t) + B(t)/r, \tag{11.1}$$

and, if the *melt pressure is constant at infinity,* with value P, then, in view of (4.9) and (5.15),

$$\begin{aligned} A(t) &= -Ct, \\ C &= \Psi_c + P - \zeta(\Psi + P). \end{aligned} \tag{11.2}$$

By (5.3), $C = 0$ for a flat interface at equilibrium; in fact, the sign of C is related to the statical stability of the crystal and melt: the **melt is stable or unstable relative to the crystal** according as $C \geq 0$ or $C < 0$.[26]

The function $B(t)$ determines the melt velocity: by (5.10), the melt velocity is radial with radial component v given by

$$\rho(\zeta - 1)v(r,t) = B(t)/r^2. \tag{11.3}$$

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[26] I take this as a *formal definition* justified by the growth theorem. The energies Ψ_c and Ψ are measured per unit volume; the definition may be more transparent in terms of energies per unit mass; that is, in terms of $\rho_c^{-1}C = \rho_c^{-1}(\Psi_c + P) - \rho^{-1}(\Psi + P)$.

We assume, as is natural, that the crystal density is larger than the melt density. Then

$$\zeta > 1, \tag{11.4}$$

and the velocity field is (initially) **directed outward, directed inward**, or **null** according as $B(0)>0$, $B(0)<0$, or $B(0)=0$.

Since the crystal is isotropic, ψ and β are constant. Further, if $r=R(t)$ designates the interface, then the mean curvature is $-R(t)^{-1}$, while the normal velocity is $dR(t)/dt$. Thus, defining constants

$$\varphi = 2\psi\alpha > 0, \qquad \gamma = C\alpha, \tag{11.5}$$

and writing

$$\tau = t/\alpha, \qquad R^{\cdot} = dR/d\tau, \qquad B^{\cdot} = dB/d\tau, \tag{11.6}$$

the free-boundary conditions $(5.12)_2$ and (5.14), with the change indicated by (10.1), reduce to a pair of ordinary differential equations:

$$\begin{aligned} B^{\cdot} &= \varphi + \gamma R - \beta B R^{-1}, \\ R^{\cdot} &= -BR^{-2}. \end{aligned} \tag{11.7}$$

The phase portrait for this system yields the following

Growth theorem. *Let the melt be stable relative to the crystal. Then (irrespective of the initial conditions) the crystal melts in finite time.*

Let the melt be unstable relative to the crystal.

(i) *If the melt velocity is initially null, then crystals of radius*

$$R(0) > R_{crit} = \varphi/|\gamma| = 2\psi/[\zeta(\Psi + P) - (\Psi_c + P)]$$

grow unboundedly as $t \to \infty$, *crystals of radius* $R(0) < R_{crit}$ *melt completely in finite time.*

(ii) *For any initial radius, but for a melt velocity of sufficiently large magnitude: if the melt velocity is directed outward, then the crystal melts in finite time; if the melt velocity is directed inward, then the crystal grows unboundedly as* $t \to \infty$.

Assume that the melt is *unstable* relative to the crystal, and suppose that the initial data are such that the crystal grows unboundedly as $t \to \infty$. The *large-time approximation* of (11.7) is then obtained formally by setting $\varphi = 0$ in (11.7):

$$\begin{aligned} \dot{B} &= \gamma R - \beta B R^{-1}, \\ \dot{R} &= -B R^{-2}. \end{aligned} \tag{11.8}$$

This equation has a simple solution which, when expressed in terms of t rather than τ (cf. (11.6), has the form

$$R(t) = V_0 t, \qquad B(t) = -\alpha V_0^3 t^2, \tag{11.9}$$

with

$$V_0 = \frac{-\beta + (\beta^2 - 8\gamma)^{\frac{1}{2}}}{4\alpha}. \tag{11.10}$$

Thus, at least formally, the normal velocity of the interface has the limiting value V_0 as $t \to \infty$. This limiting velocity has a more transparent form when $\beta = 0$; namely,

$$V_0 = \frac{\left\{\frac{1}{2}\rho[\zeta(\Psi + P) - (\Psi_c + P)]\right\}^{\frac{1}{2}}}{\rho_c - \rho}. \tag{11.11}$$

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