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**ON THE MOTION OF A PHASE INTERFACE  
BY SURFACE DIFFUSION**

by

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## On the motion of a phase interface by surface diffusion

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### 1. Introduction.

Mullins, in a series of papers concerned with thermal grooving [M2,M3], thermal etching [M5], and general surface morphologies [M6] developed a surface dynamics for phase interfaces whose evolution is controlled by mass diffusion *within* the interface.<sup>1</sup> It is our purpose here to embed Mullins's theory within a general framework of the type proposed in [G1].<sup>2</sup>

The theory we propose—appropriate to an interface between bulk phases—is based on balance laws for mass and capillary forces in conjunction with a version of the second law, appropriate to a purely mechanical theory, which asserts that the rate at which the free energy increases cannot be greater than the energy inflow plus the power supplied. The balance laws have local forms

<sup>1</sup>Mullins also includes evaporation-condensation and, in [M4,M5], bulk diffusion. Here, for the most part, we limit our discussion to interfacial diffusion. For other studies concerning interfacial diffusion see Nichols and Mullins [NM] and the references cited therein, and Burton, Cabrera, and Frank [BCF].

<sup>2</sup>The chief purpose of this study (and [G1]) is the logical development of the theory; we find it gratifying that the general laws we propose lead—via appropriate constitutive assumptions—to evolution equations deduced earlier by Mullins.

$$\begin{aligned}\delta^\circ + (\rho - \delta\kappa)v &= -\text{div}h, \\ \sigma\kappa + \text{div}c + \pi &= 0,\end{aligned}\tag{1.1}$$

where  $\sigma$  is the surface tension,  $c$  is the surface shear,  $\pi$  is a normal force which represents the interaction between the interface and the bulk material,  $\delta$  is the interfacial mass,  $h$  is the interfacial mass flux,  $\rho$  is the jump in bulk density across the interface,  $\kappa$  is the total curvature (twice the mean curvature),  $v$  is the normal velocity, the symbol " $\circ$ " indicates differentiation with respect to time following the interface, and  $\text{div}$  is the surface divergence. To this list of variables we add the interfacial free-energy  $\psi$ , the jump  $\Psi$  in bulk free-energy, and the chemical potential  $\mu$ , and we define bulk and interfacial Gibbs-functions

$$G = \Psi - \mu\rho, \quad g = \psi - \mu\delta.\tag{1.2}$$

As constitutive equations we allow  $g$ ,  $\delta$ ,  $\sigma$ ,  $c$ ,  $\pi$ , and  $h$  to depend on  $\mu$ , its surface gradient  $\nabla\mu$ , and the unit normal  $n$  to the interface,

$$\begin{aligned}g &= g(\mu, \nabla\mu, n), & \delta &= \delta(\mu, \nabla\mu, n), \\ \sigma &= \sigma(\mu, \nabla\mu, n), & c &= c(\mu, \nabla\mu, n), \\ h &= h(\mu, \nabla\mu, n), & \pi &= \pi(\mu, \nabla\mu, n),\end{aligned}\tag{1.3}$$

and to these we adjoin the standard bulk relations

$$\Psi = \Psi(\mu), \quad \rho = \rho(\mu) = -G'(\mu).\tag{1.4}$$

We show, as a consequence of the second law: that  $g$ ,  $\psi$ ,  $\delta$ ,  $\sigma$ , and  $c$  are independent of  $\nabla\mu$ ; that

$$\sigma = g(\mu, n), \quad \delta = -\partial_\mu g(\mu, n), \quad c = -\partial_n g(\mu, n);\tag{1.5}^3$$

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<sup>3</sup> $\partial_a f(a, b, c, \dots)$  denotes the partial derivative of  $f(a, b, c, \dots)$  with respect to  $a$ .

that  $\pi$  is independent of  $\nabla\mu$  and  $n$ , with

$$\pi = -G(\mu); \quad (1.6)$$

and that  $h$  satisfies the inequality

$$h(\mu, \nabla\mu, n) \cdot \nabla\mu \leq 0. \quad (1.7)$$

The evolution equations for the interface consist of the balance laws (1.1) supplemented by the thermodynamically-restricted constitutive relations. These equations are complicated, and for that reason we develop a *formal* approximation based on the assumption that the mass and energy of the interface are small. For an isotropic interface this leads to the evolution equation<sup>4</sup>

$$v = -C\Delta\kappa, \quad (1.8)$$

where  $\Delta$  is the surface laplacian, while  $C > 0$  is a constant. Further, within this approximation the chemical potential is close to the transition potential  $\mu_0$ , where  $G(\mu_0) = 0$ , and the potential difference  $u = \mu - \mu_0$  and the mass flux (rendered dimensionless) have approximate forms:<sup>5</sup>

$$u = -C\kappa, \quad h = C\nabla\kappa. \quad (1.9)$$

A consequence of (1.8) is that, for the interface the boundary of a region  $\Omega(t)$ , *the area of the interface decreases, the enclosed volume remains constant:*

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<sup>4</sup>This equation was first proposed by Mullins [M2].

<sup>5</sup>(1.9) were first proposed by Herring [He]; an independent derivation of (1.9)<sub>2</sub> was given by Mullins [M2].

$$d/dt\{\text{area}(\partial\Omega)\} \leq 0, \quad d/dt\{\text{vol}(\Omega)\} = 0. \quad (1.10)$$

For an anisotropic interface (1.8) is replaced by<sup>6</sup>

$$v = -\text{div}\{D(n)\nabla[g_0(n)\kappa + \partial_n\partial_n g_0(n) \cdot L]\}, \quad (1.12)$$

with  $g_0(n) = g(\mu_0, n)$ , and the counterparts of (1.9) are<sup>7</sup>

$$\begin{aligned} u &= -g_0(n)\kappa - \partial_n\partial_n g_0(n) \cdot L, \\ h &= D(n)\nabla[g_0(n)\kappa + \partial_n\partial_n g_0(n) \cdot L], \end{aligned} \quad (1.13)$$

so that diffusion is controlled by the entire curvature tensor  $L$ . The evolution equation (1.12) implies a result of the form (1.10) with  $\text{area}(\partial\Omega)$  replaced by the free-energy of  $\partial\Omega$  at  $\mu_0$ .

We show the form the theory takes when the interface evolves as a curve in  $\mathbb{R}^2$ , rather than as a surface in  $\mathbb{R}^3$ , and within this framework establish the existence of a steadily-evolving interface.<sup>8</sup>

We also discuss the form the evolution equations take when mass transport by evaporation-condensation accompanies surface diffusion. For an isotropic interface the analogs of (1.8) and (1.9) are<sup>9</sup>

$$\begin{aligned} v &= -C\Delta\kappa + A\kappa + F, \\ u &= -C\kappa, \quad h = C\nabla\kappa, \quad r = A\kappa + F, \end{aligned} \quad (1.14)$$

where  $A$  is a constant associated with the evaporation-condensation

<sup>6</sup>(1.12) is implicit in the work of Mullins [M6], who derives the corresponding approximate equation appropriate to an almost-flat interface.

<sup>7</sup>These equations were proposed by Herring [He].

<sup>8</sup>Mullins [M1] developed a steady solution for the curve-shortening equation  $v = \kappa$ , a solution rediscovered by differential geometers and referred to by them as the "grim reaper".

<sup>9</sup>Cf. Mullins [M2].

process, while  $F$  measures the extent of supersaturation.

As our final topic, we discuss interfacial heat conduction. We show that this mode of transport can be discussed in a manner completely parallel to our treatment of interfacial mass diffusion; in fact, for small interfacial entropy and energy the resulting approximate evolution equations have the form (1.8) or (1.12) (granted an appropriate interpretation of the underlying constitutive quantities).



## 2. Basic equations.

### 2.1. Basic concepts.

We consider two phases separated by an *interface*  $\Delta(t)$  which evolves smoothly<sup>10</sup> with time  $t$ . We assume that one of the phases has bulk density strictly larger than the other, and we *orient*  $\Delta(t)$  by a smooth unit normal field  $n(x,t)$  directed outward from the denser phase. We write  $\nabla$  and  $\text{div}$  for the *surface gradient* and *surface divergence* on  $\Delta(t)$  ( $t$  fixed),  $v(x,t)$  for the *normal velocity* of  $\Delta(t)$  in the direction  $n(x,t)$ ,  $L(x,t)$  for the *curvature tensor* on  $\Delta(t)$ , and  $\kappa = \text{trace } L$  for the *total curvature* (twice the mean curvature). Then

$$L = -\nabla n, \quad n^\circ = -\nabla v, \quad (2.1)$$

where the superscript " $\circ$ " denotes the *normal time-derivative*, the time derivative following the interface.

The physics of the interface is described by eight functions of  $x \in \Delta(t)$  and  $t$ :

- (1)  $\mu(x,t)$ , the *chemical potential*;
- (2)  $\Psi(x,t)$  and  $\rho(x,t)$ , the *jumps in bulk free energy and bulk density* across the interface (dense phase minus the other phase);
- (3)  $\psi(x,t)$  and  $\delta(x,t)$ , the *interfacial free-energy and density* (per unit area);
- (4)  $h(x,t)$ , a *tangential vector field*, the *diffusive mass-flux within the interface* (per unit length);
- (5)  $C(x,t)$ , a linear transformation that maps vectors  $v$  tangent to  $\Delta(t)$  at  $x$  to vectors  $C(x,t)v$  in  $\mathbb{R}^3$ , the *stress within the interface* (per unit length);
- (6)  $\pi(x,t)$ , a vector in  $\mathbb{R}^3$ , the *net force* exerted on the interface (per unit area) by the bulk material.

The basic laws for the interface consist of balance of forces,

<sup>10</sup>Precisely, we assume that  $\Delta(t)$  is a smoothly propagating surface in  $\mathbb{R}^3$  in the sense of the Appendix of [G1], where the notation and many of the results used here may be found.

balance of mass, and a version of the second law, appropriate to a mechanical theory, which asserts that the rate at which the free energy increases cannot be greater than the energy inflow plus the power supplied. When writing these laws it is useful to visualize smoothly propagating subsurfaces  $c(t)$  of  $\Delta(t)$  as *infinitesimally thin regions* consisting of points of the interface together with points of the solid and the environment immediately adjacent to the interface. When this interpretation is meant we will refer to  $c(t)$  as an *evolving control volume*. Let  $c(t)$  be an evolving control volume, with  $\nu(x,t)$ , a vector field tangential to  $\Delta(t)$ , the outward unit normal to  $\partial c(t)$ . Then  $c(t)$  *evolves normally* if, given any local time-dependent parametrization  $r(\lambda,t)$  of the boundary curve  $\partial c(t)$ ,  $\nu(r(\lambda,t),t) \cdot (\partial/\partial t)r(\lambda,t) = 0$ .

Let  $c(t)$  be an evolving control volume. By the surface divergence theorem,<sup>11</sup>

$$\int_{\partial c} h \cdot \nu ds = \int_c \text{div} h da, \quad \int_{\partial c} C \nu ds = \int_c \text{div} C da, \quad (2.2)$$

while a standard transport theorem<sup>12</sup> implies that, for  $c(t)$  normally evolving and for  $f(x,t)$  defined and smooth for all  $x \in \Delta(t)$  and all  $t$ ,

$$(d/dt) \left\{ \int_c f da \right\} = \int_c (f^\circ - f k \nu) da. \quad (2.3)$$

## 2.2. Balance of forces.<sup>13</sup>

We assume that  $C(x,t)$  consists of a surface tension<sup>14</sup> within the interface and a surface shear normal to the interface; more

<sup>11</sup>Cf. (A15) and (A16) of [G1].

<sup>12</sup>Cf. [GSW] and (B3)<sub>2</sub> of [G1].

<sup>13</sup>Cf. Sect. 3.1 of [G1].

<sup>14</sup>Replacing the surface tension  $\sigma$  by a linear transformation  $\Sigma$  from tangent vectors to tangent vectors would not change the final results: the skew part of  $\Sigma$  would then be irrelevant, and the dissipation inequality would reduce the symmetric part to a surface tension (cf. Remark 3.3 and (4.5)<sub>3</sub> of [G1]).

precisely, we assume there are a scalar  $\sigma(x,t)$  and a *tangent* vector  $c(x,t)$  such that

$$\mathbf{C}(x,t)\nu = \sigma(x,t)\nu + [c(x,t) \cdot \nu]n(x,t) \quad (2.4)$$

for every vector  $\nu$  tangent to  $\Delta(t)$  at  $x$ . The scalar  $\sigma(x,t)$  is the *surface tension*; the vector  $c(x,t)$  represents the *surface shear*.

We will refer to

$$\pi = \pi \cdot n \quad (2.5)$$

as the *normal interaction*; we leave as *indeterminate*<sup>15</sup> the tangential component of the force  $\pi$ .

Balance of forces for an evolving control volume  $c(t)$  is the assertion that<sup>16</sup>

$$\int_{\partial c} \mathbf{C}\nu ds + \int_c \pi da = 0; \quad (2.6)$$

since this relation is to hold for all such  $c(t)$ , we may use (2.2) to conclude that

$$\text{div } \mathbf{C} + \pi = 0. \quad (2.7)$$

For an interfacial tensor field  $\mathbf{C}$  of the form (2.4),<sup>17</sup>

$$n \cdot \text{div } \mathbf{C} = \sigma \kappa + \text{div } c, \quad (2.8)$$

and the normal component of (2.7) becomes

$$\sigma \kappa + \text{div } c + \pi = 0. \quad (2.9)$$

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<sup>15</sup>Cf. Remark 3.3 of [G1].

<sup>16</sup>We neglect inertia. Cf. [GPG], where inertial effects are included.

<sup>17</sup>Cf. (A14) of [G1].

(We need not consider the tangential component of (2.7), since the tangential component of  $\pi$  is indeterminate.)

### 2.3. Balance of mass.<sup>18</sup> Decrease of free energy.

Let  $c(t)$  be a normally evolving control volume.<sup>19</sup> Then

$$\frac{(d/dt)\{\int_{c} \delta da\}}{c}, \quad \frac{(d/dt)\{\int_{c} \psi da\}}{c} \quad (2.10)$$

represent the rate at which the interfacial mass and interfacial energy of  $c(t)$  are increasing;

$$\int_{c} \rho v da, \quad \int_{c} \Psi v da \quad (2.11)$$

represent the rate at which  $c(t)$  loses bulk mass and bulk energy due to its motion;

$$-\int_{\partial c} h \cdot v ds, \quad -\int_{\partial c} \mu h \cdot v ds \quad (2.12)$$

represent mass and energy flow into  $c(t)$  across  $\partial c(t)$  by diffusion within the interface;

$$\int_{\partial c} (\mathbf{C}v) \cdot (vn) ds = \int_{\partial c} vc \cdot v ds \quad (2.13)$$

represents power expended on  $c(t)$  by the interfacial stress.<sup>20</sup> A basic assumption of our theory is that *there be no mass flux to the interface from the bulk material.*

The laws of balance of mass and decrease of free energy for  $c(t)$  have the form

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<sup>18</sup>Cf. [G3].

<sup>19</sup>Cf. [G1,GS], where the control volumes are not assumed to evolve normally; in fact, the structure used in [GS], when applied to our theory, gives  $\sigma = g$  as a consequence of the basic laws, without appeal to constitutive assumptions.

<sup>20</sup>Cf. Section 3.1 of [G1].

$$\left(\frac{d}{dt}\right)\left\{\int_c \delta da\right\} + \int_c \rho v da = -\int \mathbf{h} \cdot \mathbf{v} ds, \quad (2.14)$$

$$\left(\frac{d}{dt}\right)\left\{\int_c \psi da\right\} + \int_c \Psi v da \leq -\int \mu \mathbf{h} \cdot \mathbf{v} ds + \int \mathbf{v} c \cdot \mathbf{v} ds,$$

and, appealing to (2.2), (2.3), and the requirement that  $c(t)$  be arbitrary, we arrive at the local forms of these laws:

$$\delta^\circ + (\rho - \delta \kappa) v = -\text{div} \mathbf{h}, \quad (2.15)$$

$$\psi^\circ + (\Psi - \psi \kappa) v \leq -\text{div}(\mu \mathbf{h}) + \text{div}(\mathbf{v} c).$$

The function

$$\gamma = -\text{div}(\mu \mathbf{h}) + \text{div}(\mathbf{v} c) - \psi^\circ - (\Psi - \psi \kappa) v \geq 0 \quad (2.16)$$

represents the *interfacial energy dissipation*, per unit area, since

$$\left(\frac{d}{dt}\right)\left\{\int_c \psi da\right\} + \int_c \Psi v da + \int_c \mu \mathbf{h} \cdot \mathbf{v} ds - \int_c \mathbf{v} c \cdot \mathbf{v} ds = -\int_c \gamma da \leq 0. \quad (2.17)$$

We define bulk and interfacial *Gibbs-functions*  $G(x,t)$  and  $g(x,t)$  through

$$G = \Psi - \mu \rho, \quad g = \psi - \mu \delta; \quad (2.18)$$

then (2.1), (2.9), and (2.15) may be combined to give the *local dissipation-inequality*

$$g^\circ + \delta \mu^\circ + c \cdot \mathbf{n}^\circ + (\sigma - g) \kappa v + (G + \pi) v + \mathbf{h} \cdot \mathbf{p} = -\gamma \leq 0, \quad (2.19)$$

with  $\mathbf{p}$  the potential gradient

$$\mathbf{p} = \nabla \mu. \quad (2.20)$$

#### 2.4. Global growth relations for $\mathcal{A} = \partial \Omega$ .

It is possible to derive global growth relations for the special case in which the denser phase occupies a region  $\Omega(t)$  with the interface  $\Delta(t)$  the complete boundary  $\partial\Omega(t)$ . In this case  $\partial\Delta = \emptyset$ , and taking  $c = \Delta = \partial\Omega$  in (2.14) and (2.19), we conclude that:

$$\frac{d}{dt} \left\{ \int_{\partial\Omega} \delta da \right\} + \int_{\partial\Omega} \rho v da = 0, \quad (2.21)$$

$$\frac{d}{dt} \left\{ \int_{\partial\Omega} \psi da \right\} + \int_{\partial\Omega} \Psi v da = - \int_{\partial\Omega} \gamma da \leq 0,$$

so that the *total mass is constant but the free energy decreases*. For the special case in which  $\rho$  and  $\Psi$  are constant, we may use the standard identity

$$\frac{d}{dt} \{ \text{vol}(\Omega) \} = \int_{\partial\Omega} v da \quad (2.22)$$

with

$$\text{vol}(\Omega(t)) = \text{volume}\Omega(t) \quad (2.23)$$

to conclude that

$$\frac{d}{dt} \left\{ \int_{\partial\Omega} \delta da + \rho \text{vol}(\Omega) \right\} = 0, \quad (2.24)$$

$$\frac{d}{dt} \left\{ \int_{\partial\Omega} \psi da + \Psi \text{vol}(\Omega) \right\} = - \int_{\partial\Omega} \gamma da \leq 0.$$

### 3. Constitutive theory.

#### 3.1. Bulk constitutive relations.

We consider bulk constitutive relations of the form

$$\Psi = \Psi(\mu), \quad \rho = \rho(\mu) = -G'(\mu); \quad (3.1)$$

these follow from corresponding relations for the individual phases in conjunction with the tacit assumption that the interfacial chemical potential  $\mu$  represent the limit of the bulk chemical potential from either phase. We assume there is a *unique* chemical potential  $\mu_0 (>0)$ , called the *transition potential*, at which the jump in the bulk Gibbs function vanishes:

$$G(\mu_0) = 0. \quad (3.2)$$

Then, letting

$$\rho_0 = \rho(\mu_0), \quad \Psi_0 = \Psi(\mu_0), \quad (3.3)$$

(2.18), (3.1), and (3.2) yield

$$\rho_0 = \Psi_0/\mu_0 = -G'(\mu_0). \quad (3.4)$$

We are interested in behavior near the transition potential and therefore introduce the *potential difference*

$$u = \mu - \mu_0; \quad (3.5)$$

for  $u$  small,

$$G(\mu) = -\rho_0 u + O(u^2), \quad \Psi(\mu) = \mu_0 \rho_0 + O(u), \quad \rho(\mu) = \rho_0 + O(u). \quad (3.6)$$

#### 3.2. Interfacial constitutive relations.

We allow the density  $\delta$ , the free energy  $\psi$ , the surface tension  $\sigma$ , the surface shear  $c$ , the normal interaction  $\pi$ , and the mass flux  $h$  to depend on the chemical potential  $\mu$  and its gradient  $p$ , and—to have a theory of sufficient generality to model crystals—also on the orientation  $n$ :

$$\begin{aligned} \delta &= \delta(\mu, p, n), & \psi &= \psi(\mu, p, n), \\ \sigma &= \sigma(\mu, p, n), & c &= c(\mu, p, n), \\ h &= h(\mu, p, n), & \pi &= \pi(\mu, p, n). \end{aligned} \quad (3.7)$$

By (2.18), these constitutive equations induce an auxiliary relation for the interfacial Gibbs-function:

$$g = g(\mu, p, n). \quad (3.8)$$

### 3.3. Consequences of the dissipation inequality.

The local dissipation-inequality (2.19) severely limits the constitutive equations (3.7). If we substitute (3.7) into (2.19), we find that

$$\begin{aligned} (\partial_\mu g + \delta)\mu^\circ + (\partial_p g) \cdot p^\circ + (\partial_n g + c) \cdot n^\circ + \\ (\sigma - g)\kappa v + (\pi + G)v + h \cdot p = -\gamma \leq 0, \end{aligned} \quad (3.9)$$

and, arguing as in the proof of the compatibility theorem of [G1], we see that (3.9)—adjoined by (2.18), (3.1), and (3.7)—holds for all smoothly propagating surfaces  $\Delta(t)$  and all choices of the chemical potential field  $\mu(x, t)$  if and only if the constitutive equations are consistent with the following restrictions:

(T1)  $g$ ,  $\psi$ ,  $\delta$ ,  $\sigma$ , and  $c$  are independent of  $p$ , and

$$\begin{aligned} \sigma &= g(\mu, n), & \psi &= g(\mu, n) - \mu \partial_\mu g(\mu, n), \\ \delta &= -\partial_\mu g(\mu, n), & c &= -\partial_n g(\mu, n); \end{aligned} \quad (3.10)$$



(T2) the normal interaction  $\pi$  depends only on  $\mu$  and is given by

$$\pi = -G(\mu); \quad (3.11)$$

(T3) the energy dissipation  $\gamma$  is determined by  $h$  through the inequality

$$h(\mu, p, n) \cdot p = -\gamma \leq 0. \quad (3.12)$$

We shall henceforth assume that the constitutive equations are consistent with the restrictions (T1)-(T3), and that

$$\rho_0, \mu_0, g_0(n), \delta_0(n) > 0, \quad (3.13)$$

where here and in what follows a subscript zero designates evaluation at the transition potential  $\mu_0$ ; i.e., for  $F = F(\mu)$ ,  $f = f(\mu, n)$ ,

$$F_0 = F(\mu_0) \quad f_0(n) = f(\mu_0, n). \quad (3.14)$$

#### 3.4. Asymptotic relations for the mass flux.

By (3.12), the dissipation

$$\gamma = \gamma(\mu, p, n) \quad (3.15)$$

has a minimum at  $p = 0$  for any choice of  $\mu$  and  $n$ . Thus the first derivative of  $\gamma(\mu, p, n)$  with respect to  $p$  vanishes at  $p = 0$ , while the second derivative is positive semi-definite:

$$h(\mu, 0, n) = 0, \quad a \cdot [\partial_p h(\mu, 0, n)] a \leq 0 \quad (3.16)$$

for all vectors  $a$ .

For a stationary, flat interface at equilibrium (uniform chemical potential), (3.16)<sub>1,2</sub> imply that  $h = 0$ , while the constitutive relations imply that all of the relevant fields are constant. Thus balance of

mass (2.15)<sub>1</sub>, is satisfied automatically, but, in view of (3.9), the force balance (2.9) is satisfied only if the bulk Gibbs function  $G(\mu)$  vanishes, so that, by the assumption containing (3.2),  $\mu = \mu_0$ . Thus a stationary, flat interface at equilibrium necessarily has chemical potential equal to the transition potential.

By (3.16)<sub>2</sub>, the diffusivity tensor

$$\mathbf{D}(n) = -\partial_p h(\mu_0, 0, n) \quad (3.17)$$

is a positive semi-definite linear transformation from tangent vectors to tangent vectors; we shall strengthen this slightly by assuming

$$\mathbf{D}(n) \text{ is positive definite.} \quad (3.18)$$

Consider now situations with chemical potential close to the transition potential in the sense that

$$U = |u| + |\nabla u| \quad (3.19)$$

is small, where  $u$  is the potential difference (3.5). Then, appealing to (3.16)<sub>1</sub> and (3.17), we have the asymptotic relation

$$h = -\mathbf{D}(n)\nabla u + O(U^2), \quad (3.20)$$

so that, by (3.12),

$$\gamma = \nabla u \cdot \mathbf{D}(n)\nabla u + O(U^3). \quad (3.21)$$

The relations (3.16)<sub>1</sub> and (3.17) also lead to the formal identity

$$\operatorname{div} h = -\operatorname{div}\{\mathbf{D}(n)\nabla u\} + O(U^2), \quad (3.22)$$

with  $U$  here given by

$$U = |u| + |\nabla u| + |\nabla \nabla u|. \quad (3.23)$$

### 3.5. Isotropy.

For an isotropic interface the orientation  $n$  is not present in the constitutive equations; thus, by (3.10),

$$\sigma = g(\mu), \quad \delta = -g'(\mu), \quad c = 0, \quad h = h(\mu, \nabla \mu), \quad (3.24)$$

and (3.18) reduces to

$$D(n) = D_0 I(n), \quad (3.25)$$

with  $I(n)$  the identity on the plane perpendicular to  $n$ . The scalar constant  $D_0 > 0$  is called the *diffusivity*; by (3.20) and (3.21) reduce to

$$h = -D_0 \nabla u + O(U^2), \quad \gamma = D_0 |\nabla u|^2 + O(U^3). \quad (3.26)$$

#### 4. Isotropic interfaces with small mass and energy.

##### 4.1. Approximate equations.

The system of equations describing the evolution of an isotropic interface consists of

$$\begin{aligned} g\kappa &= G, & \delta^\circ + [\rho - \delta\kappa]v &= -\operatorname{div}h, \\ \rho &= -G'(\mu), & \delta &= -g'(\mu), & h &= h(\mu, \nabla\mu). \end{aligned} \quad (4.1)$$

These equations are complicated. We now discuss a *formal* approximation based on the assumption of small interfacial mass and energy. Precisely, letting  $\ell$  denote the length scale of interest, we assume that the dimensionless parameter

$$\varepsilon = \delta_0/\rho_0\ell \quad (4.2)$$

is small, and that  $g_0/\rho_0\mu_0\ell$  is  $O(\varepsilon)$  (cf. (3.14)). We let  $\tau$  denote a time scale—to be specified—relative to which diffusion is important, and write  $x^* = x/\ell$ ,  $t^* = t/\tau$ , so that the normal velocity and curvature have the dimensionless forms

$$v^* = v\tau/\ell, \quad \kappa^* = \kappa\ell. \quad (4.3)$$

Then, in terms of the dimensionless quantities

$$\begin{aligned} u^* &= u/\mu_0 = (\mu - \mu_0)/\mu_0, & \delta^* &= \delta/\delta_0, & g^* &= g/\delta_0\mu_0, \\ (\partial_\mu\delta)^* &= (\partial_\mu\delta)\mu_0/\delta_0, & \rho^* &= \rho/\rho_0, \\ G^* &= G/\rho_0\mu_0, & h^* &= h\tau/\rho_0\ell^2, \end{aligned} \quad (4.4)$$

the balance laws have the form

$$\begin{aligned} \epsilon g^* \kappa^* &= G^*, \\ \epsilon (\partial_\mu \delta)^* (u^*)^\circ + [\rho^* - \epsilon \delta^* \kappa^*] v^* &= -\text{div} h^*, \end{aligned} \quad (4.5)$$

where the divergence and normal time-derivative are relative to the new time and length scales. We will use the expansions (3.6), (3.21) (with (3.25)), and (3.26), which we now write in the dimensionless form

$$\begin{aligned} h^* &= -D_0^* \nabla u^* + O(U^{*2}), & \text{div} h^* &= -D_0^* \Delta u^* + O(U^{*2}), \\ G^* &= -u^* + O(U^{*2}), & U^* &= |u^*| + |\nabla u^*| + |\nabla \nabla u^*|, \end{aligned} \quad (4.6)$$

where  $\nabla$  is with respect to  $x^*$ ,  $\Delta = \text{div} \nabla$  is the *surface laplacian*, and

$$D_0^* = D_0 \mu_0 \tau / \rho_0 \ell^3. \quad (4.7)$$

We want the time scale to be one for which diffusive effects are important; therefore, guided by (4.7), we take

$$\tau = \rho_0 \ell^3 / D_0 \mu_0, \quad D_0^* = 1. \quad (4.8)$$

Consider the formal expansions

$$\begin{aligned} u^* &= u_0 + \epsilon u_1 + O(\epsilon^2), & v^* &= v_0 + \epsilon v_1 + O(\epsilon^2), \\ \kappa^* &= \kappa_0 + \epsilon \kappa_1 + O(\epsilon^2). \end{aligned}$$

Because of (4.5) and (4.6), a "zeroth-order solution" is furnished by

$$u_0 = v_0 = 0,$$

and corresponds to a stationary state with chemical potential equal to the transition potential. Continuing in this manner, we see that, since  $\rho_0^* = 1$ ,

$$g_0^* \kappa_0 = -u_1, \quad v_1 = \Delta u_1.$$

Further, to within terms of  $O(\epsilon^2)$  the mass flux is given by  $\epsilon h_1$  with

$$h_1 = -\nabla u_1.$$

The remainder of this section will be devoted to these equations, which we henceforth write without subscripts on  $u$ ,  $v$ ,  $\kappa$ , and  $h$ .

Writing

$$C = g_0^* = g_0 / \delta_0 \mu_0 > 0, \quad (4.9)$$

we are led to the evolution equation<sup>21</sup>

$$v = -C \Delta \kappa. \quad (4.10)$$

This equation is to be supplemented by a purely *kinematical* relation between  $v$  and  $\kappa$  which may be derived as a consequence of (2.1). In conjunction with (4.10), we have the relations

$$u = -C\kappa, \quad h = C \nabla \kappa \quad (4.11)$$

giving the chemical potential as a linear function of the curvature, the mass flux as a linear function of the curvature gradient. In writing (4.11) it is to be understood that

$$\begin{aligned} \mu + \epsilon \mu_0 u + O(\epsilon^2), \quad \ell^{-1} \kappa + O(\epsilon), \quad \epsilon (\rho_0 \ell^2 / D_0 \mu_0) v + O(\epsilon^2), \\ \epsilon (D_0 \mu_0 / \ell) h + O(\epsilon^2), \end{aligned} \quad (4.12)$$

respectively, represent the original non-dimensionalized chemical potential, curvature, normal velocity, and mass flux.

<sup>21</sup>(4.10) should be compared to the curve-shortening equation  $v = \kappa$ ; evolution according to (4.10) might be termed *motion by laplacian of curvature*.

In situations for which  $\delta(\mu)$  depends strongly on  $\mu$  in the sense that  $(\partial_\mu \delta)_0^* = \lambda/\epsilon$  with  $\lambda = O(1)$ , (4.10) is replaced by

$$\lambda u^\circ + v = -C\Delta\kappa,$$

but (4.11) remain unchanged.

#### 4.2. Global growth relations.

The evolution equation (4.10) was derived as an approximation of the general isotropic relations (4.1), but, interestingly, (4.10) also follows as an *exact equation* based on constitutive relations which, before being rendered dimensionless, have the form

$$\begin{aligned} \rho &= \text{constant} = \rho_0, & \Psi &= \mu_0 \rho_0, & G(\mu) &= -\rho_0 u, \\ \sigma &= \psi = g = \text{constant} = \psi_0, & \delta &= 0, & c &= 0, \\ h &= -D_0 \nabla u, & D_0 &\geq 0. \end{aligned} \quad (4.13)$$

This observation is nontrivial: the constitutive relations (4.13) are consistent with the thermodynamic relations (3.1) and (3.10)-(3.12) with

$$\gamma = D_0 |\nabla u|^2, \quad (4.14)$$

and hence the global growth relations (2.24) are valid within this simplified framework. Thus, when the solid phase occupies a region  $\Omega(t)$  with  $\phi(t) = \partial\Omega(t)$ ,

$$\begin{aligned} d/dt\{\text{area}(\partial\Omega)\} &= -\psi_0^{-1} \int_{\partial\Omega} D_0 |\nabla u|^2 da \leq 0, \\ d/dt\{\text{vol}(\Omega)\} &= 0, \end{aligned} \quad (4.15)$$

so that *the area of the interface decreases, the enclosed volume remains constant.*

### 4.3. Almost flat interfaces.

To discuss small deviations from a flat interface, we represent the interface as the graph of a function  $x_3 = z(x_1, x_2, t)$ . Then, writing  $\nabla$  and  $\Delta$  for the gradient and laplacian in  $\mathbb{R}^2$ , we have, to within higher-order terms in  $|\nabla z|$ , the approximations

$$v = z_t, \quad \kappa = \Delta z, \quad \varphi^\circ = \varphi_t \quad (4.16)$$

(the subscript  $t$  denotes  $\partial/\partial t$ ), and (4.10) reduces to the classical fourth-order parabolic equation

$$z_t = -C\Delta^2 z. \quad (4.17)$$



## 5. Anisotropic interfaces with small mass and energy.

### 5.1. Evolution equations.

The system of equations describing the evolution of an anisotropic interface consists of

$$\begin{aligned} g\kappa + \operatorname{div} c &= G, & \delta^\circ + (\rho - \delta\kappa)v &= -\operatorname{div} h, \\ \rho &= -G'(\mu), & \delta &= -\partial_\mu g(\mu, n), & c &= -\partial_n g(\mu, n), \\ & & h &= h(\mu, \nabla\mu, n). \end{aligned} \quad (5.1)$$

We now deduce an approximate system appropriate to situations in which the interfacial mass and energy are small in the sense described in Section 4.1. The analysis parallels that of the isotropic theory. We let  $\ell$  denote the length scale of interest and consider the time scale

$$\tau = \rho_0 \ell^3 / D_0 \mu_0, \quad (5.2)$$

where  $D_0 > 0$  is some measure of the diffusivity tensor (for example, the average of  $\mathbf{D}(n)$  over the surface of the unit ball). Then, in terms of the dimensionless variables  $\mathbf{x}^* = \mathbf{x}/\ell$ ,  $t^* = t/\tau$ , the normal velocity and curvature have the forms

$$v^* = v\tau/\ell, \quad L^* = L\ell, \quad \kappa^* = \kappa\ell.$$

We define dimensionless quantities  $u^*$ ,  $\delta^*$ ,  $g^*$ ,  $\rho^*$ ,  $G^*$ , and  $h^*$  through (4.4), and, in addition, let

$$\begin{aligned} \mathbf{D}^*(n) &= \mathbf{D}(n)/D_0, & (\partial_\mu \delta)^* &= (\partial_\mu \delta)\mu_0/\delta_0, & (\partial_n \delta)^* &= (\partial_n \delta)/\delta_0, \\ (\partial_\mu c)^* &= (\partial_\mu c)/\ell\rho_0, & (\partial_n c)^* &= (\partial_n c)/\ell\rho_0\mu_0. \end{aligned}$$

Then (2.1) and (5.1) yield the equations

$$\begin{aligned} \epsilon[g^*\kappa^* + (\partial_\mu c)^* \cdot \nabla\mu - (\partial_n c)^* \cdot L^*] &= G^*, \\ \epsilon[(\partial_\mu \delta)^*(u^*)^\circ - (\partial_n \delta)^* \cdot \nabla v^*] + [\rho^* - \epsilon\delta^*\kappa^*]v^* &= -\text{div}h^*, \end{aligned} \quad (5.3)$$

where the divergence and normal time-derivative are relative to the new time and length scales. Arguing as in the isotropic theory, we consider the formal expansions

$$\begin{aligned} u^* &= u_0 + \epsilon u_1 + O(\epsilon^2), & v^* &= v_0 + \epsilon v_1 + O(\epsilon^2), \\ L^* &= L_0 + \epsilon L_1 + O(\epsilon^2). \end{aligned}$$

A "zeroth-order solution" is then furnished by  $u_0 = v_0 = 0$ , while to the next order in  $\epsilon$ ,

$$g_0^*(n)\kappa_0 + \partial_n \partial_n g_0^*(n) \cdot L_0 = -u_1, \quad v_1 = \text{div}[D^*(n)\nabla u_1] \quad (5.4)$$

(cf. (3.22)). Further, to within an error of  $O(\epsilon^2)$ , the mass flux is given by  $\epsilon h_1$  with

$$h_1 = -D^*(n)\nabla u_1. \quad (5.5)$$

We shall henceforth write these equations without the asterisks and without the subscripts on  $u$ ,  $v$ ,  $\kappa$ , and  $h$ .

Defining a linear transformation  $\Phi(n)$  (from tangent vectors to tangent vectors) by

$$\Phi(n) \cdot L = g_0(n)\kappa + \partial_n \partial_n g_0(n) \cdot L, \quad (5.6)$$

we are led to the evolution equation

$$v = -\text{div}[D(n)\nabla(\Phi(n) \cdot L)], \quad (5.7)$$

supplemented by

$$u = -\Phi(n) \cdot L, \quad h = -D(n) \nabla u, \quad (5.8)$$

so that here the chemical potential is a linear function of the curvature *tensor*.

## 5.2. Global growth relations for uniform interfaces.

The equation (5.7) was derived as an approximation, but, as in the isotropic theory, (5.7) follows as an *exact equation* based on the constitutive relations

$$\begin{aligned} \rho &= \text{constant} = \rho_0, & \Psi &= \mu_0 \rho_0, & G(\mu) &= -\rho_0 u, \\ \psi &= g(n), & \delta &= 0, & c &= c(n) = -\partial_n \psi(n), \\ & & h &= -D(n) \nabla u. \end{aligned} \quad (5.9)$$

These constitutive relations are consistent with the thermodynamic relations (3.1) and (3.10)-(3.12) with

$$\gamma = \nabla u \cdot D(n) \nabla u, \quad (5.10)$$

and hence the global growth relations (2.24) are valid within this simplified framework. Thus, when the solid phase occupies a region  $\Omega(t)$  with  $\partial(t) = \partial\Omega(t)$ ,

$$\frac{d}{dt} \left\{ \int_{\partial\Omega} \psi(n) da \right\} = - \int_{\partial\Omega} \nabla u \cdot D(n) \nabla u da \leq 0, \quad (5.11)$$

$$d/dt \{ \text{vol}(\Omega) \} = 0,$$

so that the interfacial free-energy decreases, the enclosed volume remains constant.

## 6. Two-dimensional theory.

### 6.1. Geometric considerations.

We now consider a two-dimensional theory in which the interface is a curve  $\Delta(t)$ . We continue to suppose that  $n$  is directed outward from the dense phase, but now define the unit tangent  $\ell(x,t)$ , the direction of increasing arc length  $s$ , and the angle  $\theta(x,t)$  so that  $\{\ell(x,t), n(x,t)\}$  is a positively oriented basis of  $\mathbb{R}^2$  and  $n = (\cos\theta, \sin\theta)$ ,  $\ell = (\sin\theta, -\cos\theta)$ . We then have the identities<sup>22</sup>

$$\begin{aligned} \kappa &= \theta_s, & \theta^\circ &= v_s, \\ \kappa^\circ &= v_{ss} + \kappa^2 v, & (\phi^\circ)_s &= (\phi_s)^\circ - \kappa v \phi_s. \end{aligned} \tag{6.1}$$

For connected sections of the interface on which  $\kappa$  does not vanish (convex sections) we may use  $(\theta, t)$  as independent variables: writing  $\kappa = \kappa(\theta, t)$  and  $v = v(\theta, t)$ , we have the identity<sup>23</sup>

$$\kappa_t = \kappa^2 (v_{\theta\theta} + v). \tag{6.2}$$

### 6.2. Physical considerations.

The surface stress may now be considered a vector

$$C = \sigma \ell + \xi n,$$

with  $\sigma(x,t)$  the *surface tension* and  $\xi(x,t)$  the (scalar) *surface shear*, and the interfacial mass-flux can be identified with a scalar  $h$ , where

$$h = h \ell.$$

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<sup>22</sup>Cf. (2.5), (2.17), and (2.18) of [AG]. Here and in what follows the subscripts  $s$  and  $\theta$  indicate partial differentiation with respect to arc length  $s$  and angle  $\theta$ . We will use a prime to denote differentiation when  $\theta$  is the only independent variable.

<sup>23</sup>Cf. (2.23), of [AG].

The equations (2.9) and (2.15), expressing force and mass balance now have the forms

$$\begin{aligned}\xi_s + \sigma\kappa + \pi &= 0, \\ \delta^\circ + (\rho - \delta\kappa)v &= -h_s,\end{aligned}\tag{6.3}$$

while the local dissipation-inequality (2.19) becomes

$$g^\circ + \delta\mu^\circ - \xi\theta^\circ + (\sigma - g)\kappa v + (\pi + G)v + h\mu_s = -\gamma \leq 0.$$

As is natural, we replace  $n$  in the constitutive equations (3.7) by  $\theta$ ; the counterparts of the restrictions (3.10)-(3.12) are then

$$\begin{aligned}\sigma &= g(\mu, \theta), & \psi &= g(\mu, \theta) - \mu\partial_\mu g(\mu, \theta), \\ \delta &= -\partial_\mu g(\mu, \theta), & \xi &= \partial_\theta g(\mu, \theta), \\ \pi &= -G(\mu), & h(\mu, \mu_s, \theta)\mu_s &= -\gamma \leq 0,\end{aligned}\tag{6.4}$$

while the asymptotic relations (3.20) and (3.21) here have the form

$$\begin{aligned}h &= -D(\theta)u_s + O(U^2), \\ \gamma &= D(\theta)u_s^2 + O(U^3).\end{aligned}\tag{6.5}$$

with  $U$  the obvious analog of (3.19).

The approximate equation (4.10) for an *isotropic interface with small mass and energy* here has the form

$$v = -C\kappa_s s.\tag{6.6}$$

This equation relates the normal velocity  $v$  to the curvature  $\kappa$ ; a second such equation is given by the kinematical equation (6.1)<sub>3</sub>. We can use (6.1)<sub>1,2</sub> to write (6.6) as a partial differential equation for  $\theta$ :

$$\theta^\circ = -C\theta_{ssss}. \quad (6.7)$$

On convex sections we can consider  $\kappa$  and  $v$  as functions of  $(\theta, t)$ ; then, by (6.1), we can express (6.6) in the form

$$v = -C[\kappa^2\kappa_{\theta\theta} + \kappa\kappa_{\theta}^2]; \quad (6.8)$$

a second equation relating  $v$  and  $\kappa$  is furnished by (6.2).

Similarly, the approximate equation (5.5) for an *anisotropic interface* here becomes

$$u = -\Phi(\theta)\kappa, \quad v = [D(\theta)u_s]_s, \quad (6.9)$$

with

$$\Phi(\theta) = g_0(\theta) + g_0''(\theta), \quad (6.10)$$

and these combine to give

$$v = -\{D(\theta)[\Phi(\theta)\kappa]_s\}_s, \quad (6.11)$$

or equivalently, by (6.1),

$$\theta^\circ = \{D(\theta)[\Phi(\theta)\theta_s]_s\}_{ss}. \quad (6.12)$$

### 6.3. Stationary interfaces.

We now discuss stationary solutions of the general equations (6.3), (6.4), assuming only that the constitutive functions obey

$$\begin{aligned} h(\mu, \mu_s, \theta)\mu_s &< 0 \quad \text{for } \mu_s \neq 0, \\ g(\mu, \theta) + g''(\mu, \theta) &> 0. \end{aligned} \quad (6.13)$$

We let  $\Omega$  denote the (fixed) region in  $\mathbb{R}^2$  occupied by the solid phase, and therefore seek a solution in which (6.3) and (6.4) represent the boundary curve  $\partial\Omega$ . Since  $v$  and the normal time derivatives in these equations must vanish, (6.3)<sub>2</sub> yields  $h_s = 0$ , so that  $h$  is a constant. Thus, by (6.13)<sub>1</sub>,  $\mu_s$  vanishes identically or never vanishes. But  $\mu_s$  cannot be of one sign, since  $\partial\Omega$  is a closed curve; thus  $\mu$  is constant. We may therefore conclude from (3.9), (6.3)<sub>1</sub>, and (6.4) that

$$[g(\mu, \theta) + g''(\mu, \theta)]\kappa = G(\mu),$$

and, granted (6.13)<sub>2</sub> and  $G(\mu) \neq 0$ , this equation defines a closed, convex curve with position vector<sup>24</sup>

$$r(\theta) = G(\mu)^{-1}[g'(\mu, \theta)\xi(\theta) - g(\mu, \theta)n(\theta)].$$

For  $G(\mu) < 0$ ,  $\Omega$  is the bounded region interior to the curve; for  $G(\mu) > 0$ ,  $\Omega$  is the unbounded region exterior to the curve (cf. Figure 1).

We therefore have a stationary solution for every (constant) value of the chemical potential  $\mu \neq \mu_0$ .

#### 6.4. Steady interfacial motions.

We seek solutions in which the interface appears stationary to an observer moving with uniform translational velocity. Precisely, we assume that  $q$ , the (scalar) translational velocity, acts in the direction defined by  $\theta = 0$ , so that the normal velocity of the interface is given by

$$v = q \cos \theta. \tag{6.14}$$

We consider an *isotropic interface* as characterized by the approximate equation (6.6), and seek solutions in which the interface is unbounded and convex. Then, by (6.1)<sub>1</sub> and (6.14), we can write (6.6)

<sup>24</sup>This is essentially Wulff's solution (cf. [AG], Sect. 6.1).

as an ordinary differential equation for  $\kappa = \kappa(\theta)$ :

$$\kappa^2 \kappa'' + \kappa(\kappa')^2 + (q/C) \cos \theta = 0. \quad (6.15)$$

We assume that

$$C > 0, \quad q > 0;$$

the second of these involves no loss in generality.

Since the interface is to be unbounded, the curvature must tend to zero as the arc length tends to  $\pm\infty$ ; thus we seek a solution  $\kappa(\theta)$  on a finite angle-interval  $[\theta_1, \theta_2]$  such that  $\kappa(\theta_1) = \kappa(\theta_2) = 0$ ; as is clear from (6.15), this is possible only if the interval is  $[-\pi/2, \pi/2]$ .

The desired solutions have  $v(\theta)\kappa(\theta)$  nonzero on  $(-\pi/2, \pi/2)$  and therefore represent<sup>25</sup> "steadily evolving bumps"; which, because of our convention regarding the choice of normal and the definition of curvature, are *advancing* or *receding* according as  $\kappa(\theta) < 0$  for all  $\theta$  or  $\kappa(\theta) > 0$  for all  $\theta$ .

Next, ~~writing  $\kappa$  for the sign of  $\kappa$~~ , the substitution

$$y(\theta) = (C/2q)^{\frac{1}{2}} \kappa^2(\theta) \quad (6.16)$$

yields the reduced equation

$$-y''(\theta) = \underset{(\text{sgn } \kappa)}{s} y(\theta)^{-\frac{1}{2}} \cos \theta. \quad (6.17)$$

By (6.16) and (6.17),  $y > 0$  on  $(-\pi/2, \pi/2)$ , while  $y''$  cannot change sign; thus, since  $y$  vanishes at the endpoints,  $y'' < 0$  and we may conclude from (6.17) that  $\kappa > 0$  on  $(-\pi/2, \pi/2)$ . Thus *the only possible steadily evolving bumps are receding*.

We are therefore led to the boundary-value problem:

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<sup>25</sup>In the sense of [AG], Sect. 2.2.



$$-y''(\theta) = y(\theta)^{-\frac{1}{2}} \cos \theta \quad \text{on } (-\pi/2, \pi/2), \quad y(-\pi/2) = y(\pi/2) = 0. \quad (6.18)$$

The remainder of the section will be devoted to establishing<sup>26</sup> existence and uniqueness for this problem and hence for steadily evolving receding bumps.

We first prove uniqueness. Let

$$\Theta = [-\pi/2, \pi/2].$$

Let  $y_1 \neq y_2$  be two solutions, let  $z = y_1 - y_2$ , and assume, without loss in generality, that  $z > 0$  somewhere on  $(-\pi/2, \pi/2)$ . Then there is an interval  $(\theta_1, \theta_2) \subset \Theta$  such that

$$z > 0 \quad \text{on } (\theta_1, \theta_2), \quad z(\theta_1) = z(\theta_2) = 0. \quad (6.19)$$

On the other hand, since  $y_1$  and  $y_2$  satisfy (6.18),  $z'' > 0$  on  $(\theta_1, \theta_2)$ , which contradicts (6.19). Thus (6.18) has at most one solution.

Consider, for the moment, the general problem

$$-y''(\theta) = f(y(\theta), \theta) \quad \text{on } (a, b), \quad y(a) = y(b) = 0. \quad (6.20)$$

A continuous function  $y_{\text{sub}}$  on  $[a, b]$  that satisfies

$$-y_{\text{sub}}''(\theta) \leq f(y_{\text{sub}}(\theta), \theta) \quad \text{on } (a, b), \quad y_{\text{sub}}(a) = y_{\text{sub}}(b) = 0$$

is called a *subsolution* of (6.20), and a *supersolution*  $y_{\text{sup}}$  is defined analogously with " $\leq$ " replaced by " $\geq$ ". By definition,  $y - y_{\text{sub}}$  and  $y_{\text{sup}} - y$  each have second derivative  $\leq 0$  on  $(a, b)$ , and each vanish at  $a$  and  $b$ , so that

$$y_{\text{sub}}(\theta) \leq y(\theta) \leq y_{\text{sup}}(\theta) \quad \text{on } [a, b].$$

Let  $C_0(\Theta)$  denote the subspace of  $C(\Theta)$  consisting of those

<sup>26</sup>The main ideas were furnished by Giorgio Vergara-Caffarelli (private communication).

functions in  $C(\Theta)$  that vanish at the endpoints of  $\Theta$ , and let  $\zeta: C_0(\Theta) \rightarrow C_0(\Theta)$  denote the operator defined by

$$(\zeta y)(\theta) = \int_{-\pi/2}^{\pi/2} G(\theta, \varphi) y(\varphi)^{-\frac{1}{2}} \cos \varphi d\varphi \quad \text{for all } \theta \in \Theta, \quad (6.21)$$

where  $G: \Theta \times \Theta \rightarrow \mathbb{R}$  is the Green's function for  $-d^2/d\theta^2$  and the boundary conditions in (6.18). Finding a solution  $y$  of (6.18) then reduces to finding a  $y \in C_0(\Theta)$  such that

$$\zeta y = y.$$

With this in mind, we will find a *convex* subset  $\mathcal{K}$  of  $C_0(\Theta)$  such that  $\zeta(\mathcal{K})$  is a *compact* subset of  $C_0(\Theta)$  and  $\zeta(\mathcal{K}) \subset \mathcal{K}$ . Once this is done, Schauder's fixed-point theorem will guarantee the existence of a  $y \in \mathcal{K}$  such that  $\zeta y = y$ .

Let  $y_{\text{sub}}, y_{\text{sup}} \in C_0(\Theta)$  be defined by

$$y_{\text{sub}}(\theta) = \lambda \cos \theta, \quad y_{\text{sup}}(\theta) = \omega \cos^{\frac{2}{3}} \theta. \quad (6.22)$$

A calculation then shows that  $y_{\text{sub}}$  and  $y_{\text{sup}}$  are a *subsolution* and *supersolution* of (6.18) provided

$$\lambda \leq 1, \quad \omega \geq (3/2)^{4/3}. \quad (6.23)$$

Let  $\mathcal{K}$  denote the *convex* set

$$\mathcal{K} = \{y \in C_0(\Theta) \mid \lambda \cos \theta \leq y(\theta) \leq \omega \cos^{\frac{2}{3}} \theta, \theta \in \Theta\}. \quad (6.24)$$

The Green's function  $G$  is continuous and piecewise  $C^1$  on  $\Theta \times \Theta$ ; we may therefore conclude from (6.21) and (6.24) that  $|(d/d\theta)(\zeta y)(\theta)|$  is bounded uniformly in  $\theta \in \Theta$  and  $y \in \mathcal{K}$ ; thus, by the Ascoli-Arzelà theorem,  $\zeta(\mathcal{K})$  is a *compact* subset of  $C_0(\Theta)$ .

Next, it is clear from (6.24) that

$$\omega^{-\frac{1}{2}} \cos^{-\frac{1}{2}} \theta \leq y(\theta)^{-\frac{1}{2}} \leq \lambda^{-\frac{1}{2}} \cos^{-\frac{1}{2}} \theta$$

for  $y \in \mathcal{K}$ , so that

$$\mathcal{G}[\omega^{-\frac{1}{2}} \cos^{\frac{1}{2}}(\cdot)] \leq \mathcal{G}y \leq \mathcal{G}[\lambda^{-\frac{1}{2}} \cos^{\frac{1}{2}}(\cdot)].$$

Let  $z(\theta)$  and  $Z(\theta)$ , respectively, denote the extreme left and right sides of this inequality. Then

$$\begin{aligned} -z''(\theta) &= \omega^{-\frac{1}{2}} \cos^{\frac{1}{2}} \theta \quad \text{on } (-\pi/2, \pi/2), & z(-\pi/2) &= z(\pi/2) = 0, \\ -Z''(\theta) &= \lambda^{-\frac{1}{2}} \cos^{\frac{1}{2}} \theta \quad \text{on } (-\pi/2, \pi/2), & Z(-\pi/2) &= Z(\pi/2) = 0, \end{aligned} \quad (6.25)$$

and a calculation shows that if

$$\omega^{\frac{1}{2}} \lambda \leq 1, \quad \omega \lambda^{\frac{1}{2}} \geq 9/2, \quad (6.26)$$

then  $y_{\text{sub}}(\theta)$  is a subsolution of (6.25)<sub>1</sub>, while  $y_{\text{sup}}(\theta)$  is a supersolution of (6.25)<sub>2</sub>. Thus, granted (6.23) and (6.26),  $\mathcal{G}(\mathcal{K}) \subset \mathcal{K}$ . Thus to complete the proof of existence, we have only to show that the inequalities (6.23) and (6.26) have a solution. One such solution is furnished by  $\lambda = (2/9)^{2/3}$ ,  $\omega = (9/2)^{4/3}$ .

## 7. Mass transport by evaporation-condensation.

### 7.1. Extension of the general theory.

Thus far the only form of mass transport considered is interfacial diffusion. For an interface that separates a solid phase from an associated vapor phase, mass transport by evaporation-condensation may also be important. We now modify the theory to include this mode of transport.

We let  $\mu(x,t)$ ,  $p(x,t)$ , and  $\Psi(x,t)$  represent the chemical potential, the bulk density, and the free energy of the solid at the interface, and we assume that  $\mu(x,t)$  also represents the chemical potential of the interface. The vapor at the interface is assumed to have constant chemical potential  $\mu_v$ , in general different from  $\mu$ . The flow of mass, per unit area, to the interface from the vapor is characterized by the *evaporative supply*  $r(x,t)$ , and this mass flow induces a corresponding flow of energy of amount  $\mu_v r(x,t)$ .

Balance of forces is unchanged, but the laws expressing balance of mass and decrease of free energy have the forms

$$\left(\frac{d}{dt}\right)\left\{\int_c \delta da\right\} + \int_c p v da = -\int_c h \cdot v ds + \int_c r da, \quad (7.1)$$

$$\left(\frac{d}{dt}\right)\left\{\int_c \psi da\right\} + \int_c \Psi v da \leq -\int_c \mu h \cdot v ds + \int_c \mu_v r da + \int_c v c \cdot v ds$$

for all evolving control volumes  $c(t)$ , and are equivalent to

$$\delta^\circ + (p - \delta\kappa)v = -\text{div}h + r, \quad (7.2)$$

$$\gamma = -\text{div}(\mu h) + \mu_v r + \text{div}(vc) - \psi^\circ - (\Psi - \psi\kappa)v \geq 0,$$

where  $\gamma$ , the *interfacial energy-dissipation*, has integral over  $c$  equal to the right side of (7.1)<sub>2</sub> minus the left. When the interface is the complete boundary of the region  $\Omega(t)$  occupied by the solid, (7.1) with  $c = \partial\Omega$  and the fact that  $\mu_v$  is constant yield the global growth relation

$$\frac{(d/dt)\{\int(\psi - \mu_v \delta) da\}}{\partial \Omega} + \frac{\int(\Psi - \mu_v \rho) v da}{\partial \Omega} = -\frac{\int \gamma da}{\partial \Omega} \leq 0. \quad (7.3)$$

We define the *Gibbs functions*  $G(x,t)$  and  $g(x,t)$  through (2.18), but  $G$  now represents the bulk Gibbs function for the solid phase, the corresponding quantity for the vapor being irrelevant. The relations (7.2) then yield the *local dissipation-inequality*

$$g^\circ + \delta\mu^\circ + c \cdot n^\circ + (\sigma - g)k\nu + (G + \pi)v + h \cdot p + r(\mu - \mu_v) = -\gamma \leq 0, \quad (7.4)$$

with  $p$  the potential gradient (2.20) and  $n$  the unit normal to the interface directed outward from the solid phase.

We again consider constitutive equations of the form<sup>27</sup> (3.1) (for the solid phase) and (3.7), which we supplement with a relation for the evaporative supply  $r$ :

$$r = r(\mu, p, n).$$

The thermodynamic restrictions (T1) and (T2) then remain unchanged, but (T3) is replaced by (T3') the energy dissipation  $\gamma$  is determined by  $h$  and  $r$  through the inequality

$$h(\mu, p, n) \cdot p + r(\mu, p, n)(\mu - \mu_v) = -\gamma \leq 0. \quad (7.5)$$

Let

$$u = \mu - \mu_0, \quad w = \mu_v - \mu_0; \quad (7.6)$$

$w$ , the *supersaturation potential*, measures the extent to which the vapor is supersaturated. When

<sup>27</sup>The constant vapor potential  $\mu_v$  is assumed prescribed and hence not a constitutive variable, but we could, with only minor changes, allow  $\mu_v$  to be an arbitrary function of  $(x,t)$  and to enter the constitutive equations.

$$U = |u| + |\nabla u| + |w| \quad (7.7)$$

is small, so that *both*  $\mu$  and  $\mu_v$  are close to the transition potential  $\mu_0$ . (7.5) leads to the asymptotic relations

$$\begin{aligned} h &= -D(n)\nabla u - d(n)(u-w) + O(U^2), \\ r &= -a(n)\cdot\nabla u - \alpha(n)(u-w) + O(U^2). \end{aligned} \quad (7.8)$$

Thus diffusion due to a potential difference and evaporation due to a potential gradient are not ruled out, even for small departures from the "transition state". Here  $D(n)$  and  $a(n)$  are the derivatives of  $h(\mu,p,n)$  and  $r(\mu,p,n)$  with respect to  $p$  at  $(\mu_0,0,n)$ ,  $d(n)$  and  $\alpha(n)$  are the derivatives of  $h(\mu,p,n)$  and  $r(\mu,p,n)$  with respect to  $\mu$  at  $(\mu_0,0,n)$ , and the linear transformation defined in the natural manner by  $D(n)$ ,  $d(n)$ ,  $a(n)$ , and  $\alpha(n)$  is positive semi-definite.

When the interface is isotropic the relations (7.8) have the simple form

$$\begin{aligned} h &= -D_0\nabla u + O(U^2), \\ r &= -\alpha_0(u-w) + O(U^2), \end{aligned} \quad (7.9)$$

so that to first order surface diffusion is driven by potential gradients, evaporation-condensation by potential differences between solid and vapor. We will refer to  $\alpha_0$  as the *evaporation modulus*.

## 7.2. Isotropic interfaces with small mass and energy.

The basic equations for an isotropic interface are

$$\begin{aligned} \rho\kappa &= G, & \delta^\circ + [\rho - \delta\kappa]v &= -\operatorname{div}h + r, \\ \rho &= -G'(\mu), & \delta &= -g'(\mu), & h &= h(\mu, \nabla\mu), & r &= r(\mu, \nabla\mu). \end{aligned} \quad (7.10)$$

We now discuss these equations assuming that

$$\rho_0, \mu_0, g_0, \delta_0, D_0, \alpha_0 > 0,$$

and that the mass and energy are small in the sense of Section 4.1. Let  $\ell$  denote the length scale of interest, and let  $\tau$  and  $\epsilon$  be given by (4.2) and (4.6). We assume that the *supersaturation is small*, in fact that  $w/\mu_0 = O(\epsilon)$ , and we adjoin to the list of dimensionless quantities specified in (4.4) the dimensionless evaporation modulus  $\alpha_0^*$  and the dimensionless supersaturation potential  $w^*$  defined by

$$\alpha_0^* = \alpha_0 \mu_0 \tau / \rho_0 \ell, \quad w^* = w / \epsilon \mu_0. \quad (7.11)$$

Then the argument given in Section 4.1 yields, as an approximate evolution equation,

$$v = -C\Delta k + Ak + F, \quad (7.12)$$

supplemented by

$$u = -Ck, \quad h = C\nabla k, \quad r = Ak + F, \quad (7.13)$$

where

$$\begin{aligned} C = g_0^* &= g_0 / \delta_0 \ell, & A = \alpha_0^* C &= \alpha_0 g_0 \ell^2 / D_0 \delta_0 \mu_0, \\ F &= \alpha_0^* w^* &= \alpha_0 \ell^2 (\mu_v - \mu_0) / D_0 \mu_0. \end{aligned} \quad (7.14)$$

(These relations should be interpreted as in the sentence containing (4.12) with analogous expressions added for  $r$  and  $w$ .) The relations (7.12) and (7.13) are counterparts of (4.10) and (4.11); (7.13) give the chemical potential as a linear function of the curvature, the diffusive mass flux as a linear function of the curvature gradient, and the evaporative supply as a constant proportional to the supersaturation plus a linear function of the curvature. Our convention for curvature endows a spherical solid with negative mean curvature. For  $F=0$  the

relation (7.13), implies that negative mean curvature induces evaporation, positive mean curvature induces condensation.

The evolution equation (7.12) also follows as an *exact equation* based on constitutive relations which have the (dimensional) form

$$\begin{aligned} \rho &= \text{constant} = \rho_0, & \Psi &= \mu_0 \rho_0, & G(\mu) &= -\rho_0 u, \\ \sigma &= \psi = g = \text{constant} = \psi_0, & \delta &= 0, & c &= 0, \\ h &= -D_0 \nabla u, & r &= -\alpha_0 (\mu - \mu_v), & D_0, \alpha_0 &\geq 0. \end{aligned} \quad (7.15)$$

These relations are consistent with the thermodynamic restrictions (T1), (T2), and (T3') with

$$\gamma = D_0 |\nabla u|^2 + \alpha_0 (\mu - \mu_v)^2, \quad (7.16)$$

and therefore (7.4) yields the global growth relation

$$\begin{aligned} d/dt \{ \psi_0 \text{area}(\partial\Omega) + \rho_0 (\mu_0 - \mu_v) \text{vol}(\Omega) \} = \\ - \int_{\partial\Omega} \{ D_0 |\nabla u|^2 + \alpha_0 (\mu - \mu_v)^2 \} da \leq 0. \end{aligned} \quad (7.17)$$

A tacit assumption underlying the derivation of (7.12) and (7.13) is that the coefficients  $\alpha_0$  and  $D_0$  are  $O(1)$ . For situations in which the *evaporation is small* in the sense that  $\alpha_0 \ell^2 / D_0 = O(\epsilon)$ , the analysis yields (4.10) and (4.11) rather than (7.12) and (7.13).

For *small diffusion* the choice of time scale should be based on evaporation. Precisely, for  $D_0 / \alpha_0 \ell^2 = O(\epsilon)$  we let

$$\tau = \rho_0 \ell / \alpha_0 \mu_0, \quad (7.18)$$

so that  $\alpha_0^* = 1$ ,  $D_0^* = D_0 / \alpha_0 \ell^2$ . The corresponding asymptotic analysis then yields, in place of (7.12) and (7.13),

$$v = Ck + F, \quad (7.19)$$



supplemented by

$$u = -Ck, \quad r = Ck + F, \quad (7.20)$$

with

$$C = g_0^* = g_0/\delta_0 l, \quad F = w^* = (\mu_v - \mu_0)/\mu_0. \quad (7.21)$$

Thus in the absence of supersaturation ( $F=0$ ) the motion of the interface has velocity proportional to curvature.<sup>28</sup>

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<sup>28</sup>The evolution equation  $v=Ck$ , apparently due to Mullins [M1], has a large literature (cf., e.g., Brakke [Br], Allen and Cahn [AC], Sethien [Se], Gage and Hamilton [GH], Grayson [Gr], Osher and Sethien [OS], Angenent and Gurtin [AG], Evans and Spruck [ES], Chen, Giga, and Goto [CGG]).

## 8. Interfacial heat conduction.

### 8.1. Basic concepts.

The theory developed thus far applies almost without change when the basic transport mechanism is interfacial heat conduction. We consider two phases, one labeled as *reference*, separated by an *interface*  $\Delta(t)$ , with unit normal  $n(x,t)$  directed outward from the reference phase. The basic physical quantities are:

- (1)  $T(x,t)$ , the *absolute temperature*;
- (2)  $E(x,t)$  and  $S(x,t)$ , the *jumps in bulk internal-energy and bulk entropy* across the interface (reference phase minus the other phase);
- (3)  $\epsilon(x,t)$  and  $\eta(x,t)$ , the *interfacial internal-energy and entropy* (per unit area);
- (4)  $q(x,t)$ , a *tangential* vector field, the *diffusive mass-flux* within the interface (per unit length);
- (5)  $C(x,t)$ , the *interfacial stress* (defined as before);
- (6)  $\pi(x,t)$ , the *net force* (defined as before).

The basic physical laws are balance of forces (as described in Section 2.2), and balance of energy and growth of entropy, which, for a normally evolving control volume  $c(t)$ , are given by<sup>29</sup>

$$\begin{aligned} (d/dt)\left\{\int_c \epsilon da\right\} + \int_c E v da &= -\int_{\partial c} q \cdot v ds + \int_{\partial c} v c \cdot v ds, \\ (d/dt)\left\{\int_c \eta da\right\} + \int_c S v da &\geq -\int_{\partial c} (q/T) \cdot v ds, \end{aligned} \quad (8.1)$$

or equivalently,

$$\begin{aligned} \epsilon^\circ + (E - \epsilon\kappa)v &= -\operatorname{div} q + \operatorname{div}(vc), \\ \gamma &= \eta^\circ + (S - \eta\kappa)v + \operatorname{div}(q/T) \geq 0, \end{aligned} \quad (8.2)$$

where  $\gamma$ , the *interfacial entropy-production*, has integral over  $c$

<sup>29</sup>These laws were proposed (within a more general context) in Remark 3.4 of [61] and in [63].

equal to the right side of (B.1)<sub>2</sub> minus the left.

We define the bulk and interfacial *free-energies*  $\Psi(x,t)$  and  $\psi(x,t)$  through

$$\Psi = E - TS, \quad \psi = \varepsilon - T\eta; \quad (B.3)$$

then (2.1), (2.9), and (B.2) may be combined to give the *local dissipation-inequality*

$$\psi^\circ + \eta T^\circ + c \cdot n^\circ + (\sigma - \psi) \kappa \nu + (\Psi + \pi) \nu + T^{-1} \mathbf{q} \cdot \mathbf{g} = -T\gamma \leq 0, \quad (B.4)$$

with  $\mathbf{g}$  the temperature gradient

$$\mathbf{g} = \nabla T.$$

## B.2. Constitutive theory.

We consider bulk constitutive relations of the form

$$E = E(T), \quad S = S(T) = -\Psi'(T). \quad (B.5)$$

We assume there is a unique *transition temperature*  $T_0$  at which the jump in bulk free energy vanishes:<sup>30</sup>

$$\Psi(T_0) = 0. \quad (B.6)$$

The jump

$$E_0 = E(T_0) \quad (B.7)$$

in energy between phases at the transition temperature is the *latent heat*, which we assume to be nonzero. By (B.3) and (B.6),

$$S_0 = S(T_0) = E_0/T_0; \quad (B.8)$$

<sup>30</sup> Cf., e. g., [G2], Sect. 2.1.

thus, for

$$u = T - T_0 \quad (8.9)$$

small,

$$\Psi(T) = -S_0 u + O(u^2), \quad E(T) = S_0 T_0 + O(u), \quad S(T) = S_0 + O(u). \quad (8.10)$$

We consider *interfacial constitutive-equations* of the form:

$$\begin{aligned} \varepsilon &= \varepsilon(T, g, n), & \eta &= \eta(T, g, n), \\ \sigma &= \sigma(T, g, n), & c &= c(T, g, n), \\ q &= q(T, g, n), & \pi &= \pi(T, g, n), \end{aligned} \quad (8.11)$$

so that

$$\psi = \psi(T, g, n). \quad (8.12)$$

The local dissipation-inequality (8.4) then yields the following restrictions:

(R1)  $\psi$ ,  $\varepsilon$ ,  $\sigma$ , and  $c$  are independent of  $g$ , and

$$\begin{aligned} \sigma &= \psi(T, n), & \varepsilon &= \psi(T, n) - T \partial_T \psi(T, n), \\ \eta &= -\partial_T \psi(T, n), & c &= -\partial_n \psi(T, n); \end{aligned} \quad (8.13)$$

(R2) the normal interaction depends only on  $T$  and is given by

$$\pi = -\Psi(T); \quad (8.14)$$

(R3) the entropy production  $\gamma$  is determined by  $q$  through the *inequality*

$$\mathbf{q}(T, \mathbf{g}, n) \cdot \mathbf{g} = -T^2 \gamma \leq 0. \quad (8.15)$$

The steps leading to (3.16)-(3.21) here yield

$$\mathbf{q}(T, \mathbf{0}, n) = \mathbf{0} \quad (8.16)$$

and the asymptotic relations

$$\begin{aligned} \mathbf{q} &= -\mathbf{K}(n) \nabla u + O(U^2), \\ T_0^2 \gamma &= \nabla u \cdot \mathbf{K}(n) \nabla u + O(U^3), \end{aligned} \quad (8.17)$$

with  $u$  given by (8.9) and  $U$  by (3.19), and with

$$\mathbf{K}(n) = -\partial_{\mathbf{g}} \mathbf{q}(T_0, \mathbf{0}, n), \quad (8.18)$$

the *conductivity tensor*, a positive semi-definite linear transformation from tangent vectors to tangent vectors.

Next, by (8.2) and (3.7),

$$\eta^\circ + (S - \eta \kappa) v = -T^{-1} \operatorname{div} \mathbf{q}. \quad (8.19)$$

This relation expresses *balance of entropy*; granted the constitutive restrictions (R1) and the force balance (2.9), (8.19) is equivalent to the energy balance (8.2)<sub>1</sub>. Further, a simple calculation based on (8.16) leads to the following asymptotic form for the right side of (8.19):

$$-T^{-1} \operatorname{div} \mathbf{q} = \operatorname{div} \{ T_0^{-1} \mathbf{K}(n) \nabla u \} + O(U^2), \quad (8.20)$$

with  $U$  given by (3.23).

For an isotropic interface

$$\sigma = \psi(T), \quad \eta = -\psi'(T), \quad \mathbf{c} = \mathbf{0}, \quad \mathbf{q} = \mathbf{q}(T, \nabla T), \quad (8.21)$$

and the asymptotic relations (8.17) reduce to

$$\mathbf{q} = -K_0 \nabla u + O(U^2), \quad \gamma = K_0 |\nabla u|^2 + O(U^3), \quad (8.22)$$

with  $K_0$  the conductivity.

### 8.3. Basic equations. Similarity of mass diffusion and thermal diffusion.

Summarizing, the basic equations are

$$\begin{aligned} \psi \kappa + \operatorname{div} \mathbf{c} &= \Psi, & \eta^\circ + (S - \eta \kappa) v &= -T^{-1} \operatorname{div} \mathbf{q}, \\ S &= -\Psi'(\mu), & \eta &= -\partial_T \psi(T, n), & \mathbf{c} &= -\partial_n \psi(T, n), & (8.23) \\ \mathbf{q} &= \mathbf{q}(T, \nabla T, n). \end{aligned}$$

If we compare these equations to the equations (5.1) describing interfacial mass-diffusion we see that the identifications:

mass diffusion	thermal diffusion
$\mu$	$T$
$\psi$	$\epsilon$
$g$	$\psi$
$\delta$	$\eta$
$G$	$\Psi$
$\rho$	$S$
$\psi$	$E$
$\sigma$	$\sigma$
$\mathbf{c}$	$\mathbf{c}$
$h$	$T_0^{-1} \mathbf{q}$
$D$	$T_0^{-1} K$

render the two theories almost identical, the only difference being the term  $\operatorname{div} h$  in (5.1)<sub>2</sub> as compared with  $T^{-1} \operatorname{div} \mathbf{q}$  (rather than  $T_0^{-1} \operatorname{div} \mathbf{q}$ ) in (8.23)<sub>2</sub>. However, a comparison of the asymptotic relations (3.22) and (8.20) shows that this difference does not effect

the approximate theory which corresponds to small mass and energy in the original theory and to small interfacial entropy and internal energy in the present theory. In particular, the approximate evolution equations and global growth relations<sup>31</sup> derived in Sections 4-6 are valid without change in the present theory provided the underlying quantities are properly identified.

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<sup>31</sup>The analog of (5.9) obeys (R1)-(R3).

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**Abstract.**

Mullins, in a series of papers, developed a surface dynamics for phase interfaces whose evolution is controlled by mass diffusion *within* the interface. It is our purpose here to embed Mullins's theory within a general framework based on balance laws for mass and capillary forces in conjunction with a version of the second law, appropriate to a purely mechanical theory, which asserts that the rate at which the free energy increases cannot be greater than the energy inflow plus the power supplied. We develop an appropriate constitutive theory, and deduce general and approximate equations for the evolution of the interface.

**Abstract (Italian).**

Mullins, in una serie di articoli inerenti la morfologia delle superfici di interfaccia tra fasi, ha sviluppato una dinamica delle superfici la cui evoluzione e' governata dal fenomeno di diffusione di massa all'interno dell'interfaccia. Scopo di questo articolo e' inserire la teoria di Mullins in uno schema piu' generale basato su leggi di bilancio della massa e delle azioni capillari nonche' su una formulazione puramente meccanica del secondo principio della termodinamica, asserente che l'incremento di energia libera non possa essere superiore al flusso di energia ed alla potenza fornite all'interfaccia. Viene successivamente sviluppata una appropriata teoria costitutiva, e vengono dedotte le equazioni di evoluzione sia in forma generale che approssimata.

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