

# SOLIDIFICATION FRONTS AND SOLUTE TRAPPING IN A BINARY ALLOY

CHAIM CHARACH,

Center for Energy and Environmental Physics,  
J. Blaustein Institute of Desert Research,  
Ben-Gurion University, Sde Boqer Campus 84990, Israel  
and

PAUL C. FIFE \*, Mathematics Department,  
University of Utah, Salt Lake City, Utah 84112, USA

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## Abstract

A phase field model with order parameter, concentration, and temperature as field variables is used to study the properties of solidification fronts in a binary alloy. As in previous papers, the model includes dependence of the free energy density not only on these field variables, but also on the gradients of the order parameter and concentration. Terms with these gradients represent surface free energy associated with the phase interface and with the jump in concentration. We treat them as conceptually and physically different; in particular, the thicknesses of the two interfaces will generally be different. Based on the smallness of the coefficients of these gradient terms and the largeness of the ratio of solute diffusivity in the liquid to that of the solid, asymptotic analyses in various parameter regimes are performed which reveal information on such things as the dependence of the discontinuity of concentration at the front on its velocity and on the above mentioned parameters. More broadly, we investigate the spatial structure of the concentration jump interface in various parameter ranges. Formulations are given to the problem of directional solidification and to free boundary problems for the free motion of a solidification front. Corrections due to curvature of the interface are found.

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# 1 Introduction

During the process of solidification of molten binary alloys, the composition of the mixture is generally discontinuous at the solidification front. For slow processes, the composition on the liquid and solid sides of the interface can be predicted using the equilibrium phase diagram for the alloy. Departure from local thermodynamic equilibrium at the interface increases with the solidification rate and the out-of-equilibrium effects are reflected in the kinetic phase diagram. In this kinetic diagram, the liquidus and solidus curves are velocity-dependent, and account for kinetic undercooling and for the variation of the concentration gap at the front with the solidification rate. A firmly based physical theory predicting these kinetics is lacking.

In the present paper we consider alloys for which the equilibrium solute concentration in the solid is smaller than that in the liquid, i.e. the equilibrium partition coefficient (the ratio of these two) is smaller than unity. For such alloys, this coefficient increases with velocity of the interface and tends to unity when the solidification rate tends to infinity. This phenomenon is known as solute trapping. Indeed, from simple heuristic arguments it is clear that at sufficiently high rates the diffusion time, defined with respect to the interface thickness, exceeds the time required for the front to advance by a distance of the order of that thickness.

The analysis of the thermodynamic issues associated with solute trapping in solidification of binary alloys was pioneered by Baker and Cahn [4]. Models of interfacial kinetics with solute trapping were developed and studied in [15, 1, 6, 3, 2]. Tractable problems related to directional solidification were addressed in [19, 18] and for isothermal growth in [12]. These models are based on experimentally verified assumptions that for metallic alloys the typical velocity scale for trapping effects is of the order of meters per second, whereas the kinetic undercooling velocity scale is of the order of the velocity of sound. (The former velocity scale is typically estimated as the ratio of the mass diffusion coefficient in the melt to the interface thickness.)

It was pointed out by Wheeler, Boettinger and McFadden [25] that at typical trapping velocity scales, for sharp interface models the thickness of the diffusion boundary layer in the melt is comparable to the phase interface thickness, so that these models face serious conceptual difficulties just in the regime where we need an adequate description of the physics of the process. They therefore constructed a solute trapping theory in [25] within the phase field context and recovered, for directional solidification, the qualitative results of one of the versions of the sharp interface model suggested by Aziz

and Kaplan [3].

At these velocities we are dealing with nonequilibrium phenomena, for which no good continuum theory exists which is firmly based in physics. Phase field models provide good candidates for theories in these circumstances. They consist of evolution PDE's which relax a free energy or entropy functional, so that the latter is a Lyapunov functional for the evolution governed by the PDE's. Alternatively (see [21], [11]), the PDE's follow in a natural way from the first and second laws of thermodynamics when one posits that the free energy, entropy, and internal energy densities depend on an order parameter or phase variable, the spatial gradient of the order parameter, and whatever other field variables are important for modeling the phenomenon being investigated.

In [25], a 1D isothermal model of this type was proposed and studied. It uses a Helmholtz free energy functional of a solute concentration  $c$ , the temperature, and an order parameter  $\phi$ . In addition to its dependence on the gradient of  $\phi$ , the free energy density in that paper depends on the gradient of  $c$ , and it is this dependence which gives rise to solute trapping in their model. In later work, some of these authors reported that a model without gradients of  $c$  can exhibit solution trapping as well [7], and in fact the results can be correlated to the model in [3]. Finally, in [14] a numerical study was given of high-speed solidification, again using a phase field model without gradients in  $c$ .

In these phase field models, the terms involving gradients in  $\phi$  and  $c$  are in fact representations of assumed surface free energies (1) at the solid-liquid phase interface, and (2) due to the sudden change in concentration at the solidification front. This latter change creates an interface which generally does not coincide in width with the phase interface, although we consider the possibility of parameter ranges for which it does. We feel that gradients of  $c$  should be included along with gradients of  $\phi$ , for a physically consistent theory. In this paper, we make a careful study of a phase field model, as in [25], which accounts for both kinds of surface free energy. It should be noted that in [25] the authors relate the gradient term in  $c$  with the explicitly obtained fact that the surface tension in some alloys increases by about 10% with addition of a solute.

We build on [25] in the following ways:

- We account for thermal effects, including release of latent heat and its diffusive transport. The model is therefore based on the principle that the local entropy production must be nonnegative.

- We present a detailed asymptotic analysis of the concentration and temperature profiles at the solidification front. This analysis is based in part on the smallness of two parameters  $\epsilon$  and  $\delta$ , which are measures, respectively, of the two kinds of surface free energies mentioned above. Other relevant parameters are a characteristic velocity (or rate of solidification)  $\rho$ , the large ratio  $\lambda$  of material diffusivity in the liquid to that in the solid, and the small Lewis number  $\mathcal{L}$  (ratio of material to thermal diffusivity). All of these parameters typically have orders of magnitude different from unity. What results is therefore a complicated multi-scale analysis. The structure of the concentration profile at the front, and in particular solute trapping or lack of it, is investigated within six characteristic regions in parameter space. Within one of them, we conclude that the jump in concentration decreases like  $(\mathcal{L}/\rho\delta\lambda)^{1/3}$  as the latter quantity approaches zero (in particular, as the velocity  $\rho$  gets large enough).

Two peculiarities are exhibited in our asymptotic layer analysis: (a) one layer (the  $\epsilon$ -layer representing the phase interface) is usually embedded within a thicker layer, which could have one of several possible widths, representing the concentration interface. Also (b) in some cases the larger layer is asymmetric, in that it involves a different stretching parameter on the liquid and solid sides of the embedded phase interface. This asymmetry is due to the largeness of  $\lambda$ , typically  $O(10^4)$ .

It is natural to expect curvature dependences analogous to the Gibbs-Thompson effect in each case, and in fact those effects are studied in the context of one of our parameter regimes in sec. 10.

- We derive free boundary problems in higher space dimensions with prescribed conditions at the free boundary deduced from our asymptotic analysis. Directional solidification problems, in which the position and velocity of the solidification front are controlled by a temperature field, are also included in our treatment. Stability considerations will be reserved for a later paper. Depending on the boundary conditions, some variants of the free boundary problem here may be ill posed unless they are regularized by the inclusion, in the appropriate interface condition, of higher order terms (sec. 10) involving the curvature of the interface.
- The class of phase field models we study is quite general, and includes

the one used in [25] as well as one (not applicable to solute trapping) given in [10]. For example, the dependence of the bulk free energy on the temperature, concentration, and order parameter are general, subject only certain required qualitative properties. These qualitative requirements are simply that it be a double well function of the order parameter, a strictly convex function of the concentration, and that the latent heat and heat capacity functions be positive.

The basic evolution PDE's for temperature, concentration, and order parameter are described in secs. 2 and 3. Our dimensionless parameters are introduced there as well. The equations are rewritten in terms of various scaled coordinates in sec. 4. A multiparameter analysis within the concentration interface is developed in secs. 5 and 6. The layer analyses provide interface conditions for an associated free boundary problem valid in the outer region; this is formulated in secs. 7 and 8. There are digressions in secs. 9 and 10. In the former section, we formulate two illustrative examples, one involving the free motion of a solidification front, and the other involving directional solidification. In sec. 10, curvature corrections to the concentration gap are studied. A discussion is given in sec. 11.

## 2 The thermodynamic functions.

Our most basic field variables are a phase order parameter  $\phi(x, t)$ , a concentration variable  $c(x, t)$  representing the mole fraction of one of the components (the solute species) of the alloy, and the temperature  $T(x, t)$ . We assume that the density is constant and that the material is isotropic. The function  $\phi$  takes on values in the interval  $-1 \leq \phi \leq 1$ ; the liquid (disordered) phase is characterized by values of  $\phi$  near -1, the solid by values near +1. Being a mole fraction,  $c$  ranges between 0 and 1.

In terms of these three, we suppose that other smooth bulk thermodynamic functions have also been defined, for uniform systems:

- the Helmholtz free energy density  $f(\phi, c, T)$
- the internal energy density  $e(\phi, c, T) = \frac{\partial(f/T)}{\partial(1/T)}$

A prototypical form for the free energy is

$$f(\phi, c, T) = (1 - c)f_a(\phi, T) + cf_b(\phi, T) + \frac{RT}{v_m}[(1 - c) \ln(1 - c) + c \ln c], \quad (1)$$

where  $f_a$  and  $f_b$  are the free energies of the pure materials corresponding to  $c = 0$  and  $c = 1$ , respectively [24, 25],  $v_m$  is an alloy molar volume, and  $R$  is the gas constant. We shall refer to this example occasionally in the following.

For nonuniform systems (which will be our concern), we allow that these functions also depend on gradients, as follows:

$$f'(\phi, c, T, \nabla\phi, \nabla c) = f(\phi, c, T) + \epsilon_f^2 |\nabla\phi|^2 + \delta_f^2 |\nabla c|^2, \quad (2)$$

$$e'(\phi, c, T, \nabla\phi, \nabla c) = e(\phi, c, T) + \epsilon_e^2 |\nabla\phi|^2 + \delta_e^2 |\nabla c|^2, \quad (3)$$

although the gradient dependence in  $e'$  will be curtailed (see (13) below).

**I.** Our most basic assumption on  $f$  is its double well nature, as a function of  $\phi$ . We assume, for each pair  $(c, T)$ , that  $f(\phi, c, T)$  has local minima when  $\phi = \pm 1$ , where it has positive second  $\phi$ -derivative, and a single local maximum at only one other value of  $\phi$  between  $\pm 1$ . Moreover, there is a smooth curve  $M$ , which we shall call the *equi-free energy curve*, in the  $(c, T)$  plane such that

$$f(1, c, T) = f(-1, c, T) \quad \text{if and only if} \quad (c, T) \in M. \quad (4)$$

In the literature this is commonly called the “ $T_0$ -line”.

**II.** Our next assumption on  $f$  is that for each  $(\phi, T)$ ,

$$f(\phi, c, T) \text{ is a strictly convex function of } c. \quad (5)$$

**III.** We define the latent heat  $L(c, T)$  at a given concentration and temperature as

$$L(c, T) = e(-1, c, T) - e(1, c, T), \quad (6)$$

and make a third assumption:

$$L(c, T) > 0. \quad (7)$$

**IV.** Finally, we define the heat capacity by

$$c_p(\phi, c, T) = \frac{\partial e}{\partial T} = -T f_{TT} \quad (8)$$

and assume

$$c_p > 0. \quad (9)$$

It will be convenient also to denote by  $F$  and  $g$  the following functions defined in terms of  $f$ :

$$F(\phi, c, T) = \frac{1}{T} \frac{\partial f}{\partial \phi}, \quad g(\phi, c, T) = \frac{1}{T} \frac{\partial f}{\partial c}. \quad (10)$$

(The function  $g$  is a modified chemical potential.) Then assumption (4) takes the form

$$\int_{-1}^1 F(\phi, c, T) d\phi = 0 \quad \text{if and only if} \quad (c, T) \in M, \quad (11)$$

and (5) becomes, since  $f$  is smooth,

$$\partial g / \partial c > 0. \quad (12)$$

### 3 The evolution equations

Model equations can be obtained, as in [11], by using the Gibbs formula, the first law, (2) and (3) to obtain an expression for the time derivative of the entropy, as a function of the energy flux, the basic field variables, their gradients, and their time derivatives. From this, one identifies the local entropy production. The simplest way to guarantee that it is nonnegative, while mass is conserved, is by requiring that the time derivatives of  $\phi$  and  $c$  and the energy flux satisfy certain equations. General positive kinetic functions appear in these equations; we call them  $M_\phi$ ,  $\hat{K}$ , and  $L_{cc}$  below in (14)–(16).

We shall use the equations derived this way under the simplifying assumptions (see (2), (3)) that

$$\epsilon_e = \delta_e = 0, \quad \epsilon_f^2 / T = \text{const}, \quad \delta_f^2 / T = \text{const}. \quad (13)$$

In particular, this implies that we disregard the differences in the surface tensions of solute and solvent, these parameters being some average value in the temperature range considered.

Little is actually known from physics about the magnitude of the effects due to the parameters  $\epsilon_e$  and  $\delta_e$  being different from zero, or about the temperature variation of  $\delta_f$  and  $\epsilon_f$ , although the analysis in [11] for a pure material suggests that such effects are of minor importance in the present context. The latter is tied to the temperature dependence of the surface tension at the solid-liquid interface for alloys. In this paper, one of our main aims is to demonstrate the influence that the velocity of the front, the parameter  $\delta_f$ , the ratio  $\lambda$  of diffusivities, and the Lewis number have

on solute trapping. These appear to be the dominant factors contributing to this effect, so in order not to further complicate the paper we make the assumptions (13), while recognizing that a more accurate model may well include nonzero  $\epsilon_e$  and  $\delta_e$ . These coefficients have been mentioned in previous papers, such as [21, 26, 11].

### 3.1 Dimensional version

We thus obtain our basic dimensional system

$$\frac{\partial \phi}{\partial t} = -M_\phi T \left[ \frac{f_\phi}{T} - \frac{\epsilon_f^2}{T} \nabla^2 \phi \right], \quad (14)$$

$$\frac{\partial e}{\partial t} = \nabla \cdot \hat{K} \nabla T, \quad (15)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left\{ L_{cc} \nabla \left[ \frac{f_c}{T} - \frac{\delta_f^2}{T} \nabla^2 c \right] \right\}. \quad (16)$$

Here  $\hat{K}$  is the dimensional thermal conductivity. For definiteness we take  $L_{cc}$  in accordance with (1) to be of the form  $\frac{v_m}{R} \hat{\mathcal{D}}_c(\phi) c(1-c)$ . In this expression  $\hat{\mathcal{D}}_c(\phi)$  is identified as the mass diffusion coefficient. The value of  $\hat{\mathcal{D}}_c$  varies dramatically from liquid ( $\ell$ ) to solid ( $s$ ). Setting  $\hat{\mathcal{D}}_{c\ell} = \hat{\mathcal{D}}_c(-1)$ , etc., we have the typical value

$$\lambda \equiv \hat{\mathcal{D}}_{c\ell} / \hat{\mathcal{D}}_{cs} \sim 10^4. \quad (17)$$

The parameters  $\lambda$  and  $\mathcal{L}$  below will figure prominently in our asymptotics.

Write

$$\hat{\mathcal{D}}_c(\phi) = \hat{\mathcal{D}}_{c\ell} u(\phi), \quad (18)$$

where  $u$  is a monotone function with

$$u(-1) = 1, \quad u(1) = \lambda^{-1}. \quad (19)$$

We introduce the thermal diffusivity

$$\hat{\mathcal{D}}_T = \frac{\hat{K}}{c_p}. \quad (20)$$

For our asymptotic analysis, it will be convenient but not necessary to assume that  $\hat{K}$  and  $c_p$  are independent of  $\phi$ ,  $c$  and  $T$ . We make that assumption.

### 3.2 Dimensionless version

We now nondimensionalize. Symbols with bars will denote nondimensional quantities,  $L^*$  is a typical value of latent heat,  $X$  is a macroscopic length, and  $T^* = L^*/c_p$ . We set

$$f = \bar{f}L^*, \quad e = \bar{e}L^*, \quad \theta = T/T^*, \quad \bar{x} = x/X, \quad \bar{t} = \hat{K}t/c_pX^2.$$

We define the Lewis number

$$\mathcal{L} = \frac{\hat{\mathcal{D}}_{cl}}{\hat{\mathcal{D}}_T}, \quad (21)$$

and dimensionless diffusivities  $\mathcal{D}$  and  $\tilde{\mathcal{D}}$  by

$$\mathcal{D}(\phi, c, \theta) = \frac{L_{cc}c_p}{\hat{\mathcal{D}}_T} = \frac{\hat{\mathcal{D}}_c(\phi)}{\hat{\mathcal{D}}_T} \frac{c_p v_m}{R} c(1-c) \equiv \frac{\hat{\mathcal{D}}_{cl}}{\hat{\mathcal{D}}_T} u(\phi) \frac{c_p v_m}{R} c(1-c) \equiv \mathcal{L}\tilde{\mathcal{D}}(\phi, c, \theta). \quad (22)$$

New dimensionless parameters are as follows:

$$\epsilon^2 = \frac{(\epsilon_f)^2}{L^*X^2\theta}, \quad \delta^2 = \frac{(\delta_f)^2}{L^*X^2\theta}, \quad \alpha = \frac{\hat{K}}{M_\phi(\epsilon_f)^2c_p}, \quad v_0 = \frac{\hat{K}}{Xc_p}.$$

In accordance with (13), we assume them to be constant.

Also, (see (10))

$$\bar{F}(\phi, c, \theta) = \frac{T^*}{L^*}F(\phi, c, T^*\theta), \quad \bar{g}(\phi, c, \theta) = \frac{T^*}{L^*}g(\phi, c, T^*\theta) \quad (23)$$

In this way, we obtain the following dimensionless equations, where now the symbol  $\nabla$  denotes the gradient with respect to the dimensionless space variable  $\bar{x}$ :

$$\alpha\epsilon^2\frac{\partial\phi}{\partial\bar{t}} = \epsilon^2\nabla^2\phi - \bar{F}(\phi, c, \theta), \quad (24)$$

$$\frac{\partial}{\partial\bar{t}}\bar{e}(\phi, c, \theta) = \nabla^2\theta. \quad (25)$$

$$\frac{\partial c}{\partial\bar{t}} = \nabla \cdot \mathcal{D}\nabla(\bar{g}(\phi, c, \theta) - \delta^2\nabla^2c). \quad (26)$$

The velocity  $V$  of the solidification front may in some cases be used as a control parameter, and in any case its order of magnitude will be important in our asymptotics. We nondimensionalize it by setting  $V = v_0\bar{V}$  and further separate out the order of magnitude of  $\bar{V}$  by setting  $\bar{V} = \rho v$  so that  $v$  is

an  $O(1)$  dimensionless velocity. At the same time we rescale dimensionless time with this same factor. In all,

$$V = v_0 v \rho, \quad \tilde{t} = \bar{t} \rho, \quad v = O(1). \quad (27)$$

Thus  $\rho$  is a dimensionless parameter measuring the rapidity of the solidification process. We now obtain, omitting the tildes on the symbol  $\tilde{t}$  and bars from  $\bar{F}$ ,  $\bar{g}$ ,  $\bar{e}$ , and  $\bar{K}$ ,

$$\alpha \epsilon^2 \rho \frac{\partial \phi}{\partial t} = \epsilon^2 \nabla^2 \phi - F(\phi, c, \theta), \quad (28)$$

$$\rho \frac{\partial}{\partial t} e(\phi, c, \theta) = \nabla^2 \theta. \quad (29)$$

$$\rho \frac{\partial c}{\partial t} = \nabla \cdot \mathcal{D} \nabla (g(\phi, c, \theta) - \delta^2 \nabla^2 c). \quad (30)$$

It should be brought out that the form in which  $\epsilon$  appears in (28) is like that used in [9], [17] and [5], rather than that in [25, 22] and other papers. In the latter,  $\epsilon$  is considered to be independent of the surface tension, but is tied to the free energy density. In our approach,  $\epsilon$  has meaning as a nondimensional surface tension, and is unrelated to the bulk free energy density. A careful comparison of the two approaches can be found in [5].

### 3.3 Typical parameter values

Before proceeding, we provide some estimates for physical parameters here in the case of the alloy Ni–Cu, taken from data in [23, 25, 14]:

**a.**  $X \sim 10^{-2}$ cm,  $\hat{D}_T \sim .155$ cm<sup>2</sup>/s,  $v_0 \sim 15.5$ cm/sec. The length scale  $X$  is of course not a universal quantity.

**b. Mass diffusion:**

$$\mathcal{L} \sim 10^{-4}, \quad \lambda \sim 10^4, \quad \frac{c_p v_m}{R} \sim O(1), \quad \frac{c_p v_m}{R} c(1-c) \leq 0.25, \quad \mathcal{D} \leq 0.25 \mathcal{L} u(\phi).$$

**c.  $\epsilon$ ,  $\delta$  parameters**

$$\epsilon \sim 0.7 \cdot 10^{-6}, \quad \delta \sim 0.4 \cdot 10^{-5} - 0.4 \cdot 10^{-3}.$$

Little is known about the value of  $\delta$ ; the values given here are based on the range of values assumed in [25]. In our analysis we shall not always assume that  $\delta$  is in this range, or in fact that  $\delta > \epsilon$ .

This provides characteristic length scales  $\ell_\epsilon$  and  $\ell_\delta$  associated with  $\epsilon$  and  $\delta$ :

$$\ell_\epsilon = X\epsilon \sim 0.7 \cdot 10^{-8} \text{cm}, \quad \ell_\delta = X\delta. \quad (31)$$

(The actual interphase thickness is known to be of the order  $O(5 \cdot 10^{-8})$ cm.)

The ratio  $(\frac{\epsilon}{\delta})^2$  then turns out to be in the range  $3 \cdot 10^{-6}$  to  $3 \cdot 10^{-2}$ . If we assume it is  $O(10^{-4})$ , then this is comparable to both  $\mathcal{L}$  and  $\lambda^{-1}$ . However, in some of the following we will allow that this ratio may be  $\geq O(1)$ . Throughout, we assume

$$\epsilon \ll 1, \quad \delta \ll 1, \quad \lambda \gg 1, \quad \mathcal{L} \ll 1. \quad (32)$$

**d. Parameter  $\alpha$ .** For both materials (Ni and Cu),  $\alpha \sim 35$ , as taken from data in the references above and the expression

$$\alpha = \frac{\hat{\mathcal{D}}_T L^*}{\mu' T^* \sigma^*},$$

the constant  $\mu'$  in turn taken from the kinetic undercooling relation  $\mu'(T^* - T) = V$ ,  $\sigma^*$  being the surface tension.

### 3.4 Velocity regimes

We now designate several velocity regimes, i.e. ranges of the parameter  $\rho$ , which will be useful in our analysis.

We shall later identify a characteristic value  $c^0$  of  $c$  in the interface.

The thickness of the temperature boundary layer is of the order  $\hat{\mathcal{D}}_T/V \sim \hat{\mathcal{D}}_T/v_0\rho \equiv \ell_T$  and that of the diffusional layer in the liquid is  $\hat{\mathcal{D}}_{cl}c^0(1 - c^0)/v_0\rho \equiv \ell_{cl}$ . Since  $\mathcal{L} \sim 10^{-4}$ , the smaller of the two thicknesses is that of mass diffusion, and that will be the relevant one in the following. For the liquid,

$$\ell_{cl} = \frac{\hat{\mathcal{D}}_{cl}c^0(1 - c^0)}{v_0\rho} = \frac{\hat{\mathcal{D}}_T\mathcal{L}c^0(1 - c^0)}{v_0\rho} = \frac{\mathcal{L}c^0(1 - c^0)X}{\rho}, \quad (33)$$

and for the solid

$$\ell_{cs} = \frac{\hat{\mathcal{D}}_{cs}c^0(1 - c^0)}{v_0\rho} = \frac{\mathcal{L}c^0(1 - c^0)X}{\lambda\rho}. \quad (34)$$

We shall use define the following critical values of the velocity  $\rho$  to delineate the main cases dictating particular asymptotic procedures :

$$\rho_1 = \frac{c^0(1-c^0)\mathcal{L}}{\lambda\delta}; \quad \rho_2 = \frac{c^0(1-c^0)\mathcal{L}}{\lambda\epsilon}; \quad \rho_3 = \frac{c^0(1-c^0)\mathcal{L}}{\delta}; \quad \rho_4 = \frac{c^0(1-c^0)\mathcal{L}}{\epsilon}. \quad (35)$$

The thicknesses  $\ell_{cl}$  and  $\ell_{cs}$  should be compared to  $\ell_\epsilon$  and  $\ell_\delta$  (31). The four corresponding ratios will be proportional to  $\rho_1/\rho$  through  $\rho_4/\rho$ , so that

$$\rho_1 = \rho \frac{\ell_{cs}}{\ell_\delta}; \quad \rho_2 = \rho \frac{\ell_{cs}}{\ell_\epsilon}; \quad \rho_3 = \rho \frac{\ell_{cl}}{\ell_\delta}; \quad \rho_4 = \rho \frac{\ell_{cl}}{\ell_\epsilon}. \quad (36)$$

When  $\epsilon < \delta$  and  $\delta < \lambda\epsilon$  we have the ordering

$$\rho_1 < \rho_2 < \rho_3 < \rho_4. \quad (37)$$

## 4 Multiscale formulation

We shall construct solutions of (28 - 30) for which the phase function  $\phi(x, t)$  has a layer structure, i.e. there is a moving surface  $\Gamma(t)$ , called a phase interface, in an  $\epsilon$ -neighborhood of which  $\phi$  undergoes a transition from values near  $\phi \approx -1$  (on one side) to  $\phi \approx 1$  on the other. In regions of space away from  $\Gamma$ ,  $\phi$  will remain near  $\pm 1$ . Thus  $\Gamma$  serves to separate the material into a liquid region  $\Omega_-$  (the former case) and a solid region  $\Omega_+$  (the latter).

We proceed by formal internal layer asymptotics based on the smallness of  $\epsilon$ . This will later be supplemented by analyses based on assumed magnitudes of certain other combinations of the parameters  $\epsilon$ ,  $\delta$ ,  $\rho$ ,  $\lambda$ , and  $\mathcal{L}$ .

In regions away from  $\Gamma$ , the solution triple  $(\phi, c, \theta)$ , expressed in the independent variables  $(x, t)$ , is assumed to depend in a regular fashion on  $\epsilon$  for small values of  $\epsilon$ . The typical procedure would be to expand the solution in powers of  $\epsilon$ , producing the “ $\epsilon$ -outer expansion”.

Near  $\Gamma$ , on the other hand, the solution triple is assumed to depend in such a regular way when it is expressed as a function of stretched local coordinates, as is shown below and in many other places (see [9] and [16], for example). This generates the inner expansion, whose terms would be matched in a standard way to those of the outer expansion. In the present problem, it will suffice to consider only the 0-th order terms (i.e. the basic approximation) in the inner and outer regions. On the other hand, there will be a great deal of complication when we move to consider the other relevant parameters.

## 4.1 Outer problem

For the outer expansion of the order parameter, we use the approximation, to all orders in  $\epsilon$ ,

$$\phi(x, t) = 1 \text{ on the solid side of } \Gamma, \quad (38)$$

$$\phi(x, t) = -1 \text{ on the liquid side of } \Gamma. \quad (39)$$

These constants are indeed solutions of (28) for all values of  $c$ ,  $\epsilon$  and  $\theta$ , because  $F(\pm 1, c, \theta) = 0$ . This follows from (10) and our basic assumption (I) of the double well nature of  $f$ .

Substituting these values of  $\phi$  into (30) and (29), we find that the lowest order outer solutions  $c^0(x, t)$ ,  $\theta^0(x, t)$  must satisfy, on the two sides ( $\Omega_{\pm}$ ) of  $\Gamma$ ,

$$\frac{\rho}{\mathcal{L}} \frac{\partial c^0}{\partial t} = \nabla \cdot \tilde{\mathcal{D}}^{\pm}(c^0, \theta^0) \nabla (g^{\pm}(c^0, \theta^0) - \delta^2 \nabla^2 c^0), \quad (40)$$

$$\rho \frac{\partial e^{\pm, 0}}{\partial t} = \nabla^2 \theta^0, \quad (41)$$

where  $\tilde{\mathcal{D}}^{\pm}(c, \theta) = \tilde{\mathcal{D}}(\pm 1, c, \theta)$ , and similarly for  $g^{\pm}$  and  $e^{\pm}$ .

## 4.2 Inner problem

We now turn to the inner expressions. Let  $r(x, t; \epsilon)$  denote the distance from  $x$  to  $\Gamma(t; \epsilon)$  (we are now recognizing that  $\Gamma(t; \epsilon)$  will depend on  $\epsilon$ ; this dependence was suppressed before). We make our definition of  $\Omega_{\pm}$  more precise: near  $\Gamma$ , points with  $r > 0$  will be in  $\Omega_+$ , those with  $r < 0$  in  $\Omega_-$ .

We may rewrite the evolution equations (28) - (30) in terms of a local spatial orthogonal coordinate system  $(r, s)$  near  $\Gamma$ , in which  $s$ , the tangential coordinates, represents position on the surface  $\Gamma$ . Since  $r$  is a function also of  $t$ , terms involving the derivative  $\partial r / \partial t$  come from the time derivatives on the left of (28) - (30). We shall not display the rewritten equations explicitly, because we only need the inner expansion carried out to a low order; and the only relevant terms will then be those in which no tangential derivatives appear. With those terms omitted, we obtain PDE's in the two variables  $t$  and  $r$  only (here subscripts denote partial derivatives):

$$\rho \alpha \epsilon^2 (\phi_t - v \phi_r) = \epsilon^2 (\phi_{rr} + \kappa(s, t) \phi_r) - F(\phi, c, \theta) + \dots, \quad (42)$$

where  $\kappa$  is the sum of the two principal curvatures of  $\Gamma(t)$  at the point  $s$ , and (as in (27))  $v = -r_t$  is the rescaled dimensionless normal velocity of  $\Gamma$ ;

$$\frac{\rho}{\mathcal{L}}(c_t - vc_r) = (\partial_r \cdot \tilde{\mathcal{D}}\partial_r + \tilde{\mathcal{D}}\kappa\partial_r) \left[ g(\phi, c, \theta) - \delta^2(c_{rr} + \kappa c_r) \right] + \dots; \quad (43)$$

$$\rho(\partial_t - v\partial_r)e(\phi, c, \theta) = \theta_{rr} + \kappa\theta_r \dots \quad (44)$$

Next, we define the stretched variable  $z = r/\epsilon$ , at the same time using the following notation for our dependent functions, when written in terms of the stretched local coordinates:  $\phi(x, t) = \Phi(z, s, t)$ ,  $c(x, t) = C(z, s, t)$ ,  $\theta(x, t) = \Theta(z, s, t)$ ,  $E(z, s, t) = e(\Phi(z, s, t), C(z, s, t), \Theta(z, s, t))$ . The equations (42) - (44) now become

$$\rho\alpha(\epsilon^2\Phi_t - v\epsilon\Phi_z) = \Phi_{zz} + \epsilon\kappa(s, t)\Phi_z - F(\Phi, C, \Theta) + \dots, \quad (45)$$

$$\begin{aligned} \frac{\rho}{\mathcal{L}} \left( \frac{\epsilon^4}{\delta^2} C_t - v \frac{\epsilon^3}{\delta^2} C_z \right) &= \\ &= (\partial_z \tilde{\mathcal{D}}\partial_z + \epsilon \tilde{\mathcal{D}}\kappa\partial_z) \left[ \frac{\epsilon^2}{\delta^2} g - (C_{zz} + \epsilon\kappa C_z) \right] + \dots, \end{aligned} \quad (46)$$

$$\rho(\epsilon^2 E_t - v\epsilon E_z) = \Theta_{zz} + \epsilon\kappa\Theta_z \dots \quad (47)$$

## 5 Inner multiscale analysis: scale of $C$ larger than that of $\Phi$

Our analysis will take into consideration the orders of magnitude of our basic parameters  $\epsilon$ ,  $\delta$ ,  $\rho$ ,  $\lambda$ , and  $\mathcal{L}$  (those of  $\delta$  and  $\rho$  may not be known). Due to the immense complication, we do not pursue a systematic expansion scheme, but will rather be content with “lowest order” approximations based on the smallness of various combinations of parameters.

We define two important combinations

$$\sigma = \frac{\rho\epsilon^3}{\mathcal{L}c^0(1-c^0)\delta^2}, \quad \beta = \frac{\epsilon^2}{\delta^2} \quad (48)$$

and in this section, except for sec. 5.3.4, assume

$$(\lambda\sigma)^{1/3}, \beta^{1/2} \ll 1. \quad (49)$$

The latter means that  $\epsilon \ll \delta$ . In terms of the characteristic lengths defined before, (49) means

$$\ell_\epsilon \ll \left[ \ell_\delta^2 \ell_{cs} \right]^{1/3}, \quad \ell_\epsilon \ll \ell_\delta.$$

Since  $\sigma$  is proportional to  $\rho$ , the first of (49) gives an upper bound for the velocity  $\rho$ . In the case of Ni–Cu, the upper bound would correspond to a velocity  $V \sim 1$  m/sec when  $c^0 \sim 10\%$ .

It is easy to see from (46) that to lowest order,  $C_{zz} = 0$ , and since  $C$  is bounded to lowest order (in order to match with the outer solution),  $C(z) \sim \text{const.}$  on the scale of the variable  $z$ . This will characterize all the solutions found in this section. Thus  $C$  will vary on a longer space scale than that of the phase interface, which will be embedded in the concentration profile.

We set  $C(z) = C^0$  in (45) and (47) to obtain the lowest order approximations to  $\Phi$  and  $\Theta$ . In addition to (49), we assume that

$$\rho\epsilon \ll 1, \quad \text{i.e. } \mathcal{L}\ell_\epsilon c^0(1 - c^0) \ll \ell_{cl}. \quad (50)$$

Our lowest order approximation is obtained as follows.

### 5.1 Temperature $\Theta^0$

By (50), we may neglect the left hand side of (47). Therefore we obtain the lowest order relation

$$\Theta_z^0 = \text{constant in } z. \quad (51)$$

Matching to the outer solution requires that  $\Theta^0(z)$  be bounded, hence

$$\Theta^0 = \text{constant in } z, \quad (52)$$

although it may depend on  $s$  and  $t$ . Again by matching, the constant pair

$$(C^0, \Theta^0) = (c^0, \theta^0)|_\Gamma, \quad (53)$$

the latter being the values of the outer functions  $c^0$  and  $\theta^0$  at the interface. In the following, we denote them simply by  $c^0$  and  $\theta^0$ .

In subsection 5.3 below, we shall discover that whereas  $C$  is constant in the frame of the variable  $z$ , it may vary significantly on a scale which is larger than that of  $z$ , but smaller than that of the original space variable  $x$  or  $r$ . We briefly indicate here that this is not true of  $\Theta$ . When a change of variable in (47) is made according to one of the prescriptions in sec. 5.3),

either the last term on the left or the first on the right (or both) will be the dominant term in (47). We only give the details when just one of these terms is dominant. In the latter case,  $\Theta \sim \text{const}$  and our claim is justified. We therefore need only consider the former case, in which  $E(\Phi, C, \Theta) \sim \text{const}$ . This holds away from the phase interface (in fact on the shorter scale of  $z$ ,  $E$  does make a transition, representing the latent heat). We may therefore set  $\Phi = \pm 1$ . Then the equation  $E(\pm 1, C, \Theta) = \text{const}$  can be solved for  $\Theta = \Theta^\pm(C)$ , say. An examination of the various cases in sec. 5.3 shows, however, that whenever the scaling results in the equation  $E(\Phi, C, \Theta) \sim \text{const}$ , the concentration  $C$  is almost constant, hence  $\Theta$  is as well, on that scale.

## 5.2 Phase function $\Phi^0$

By (50) again and (45), together with the matching conditions between  $\Phi^0$  and the outer solution  $\phi^0 = \pm 1$ , we have

$$\Phi_{zz}^0 - F(\Phi^0, C^0, \Theta^0) = 0, \quad \Phi^0(\pm\infty, s, t) = \pm 1. \quad (54)$$

In this equation, the quantities  $C^0$  and  $\Theta^0$  occurring as arguments of the function  $F$  are unknown constants, by (52). For a solution to exist, clearly  $F$  must vanish at the two limits  $z = \pm\infty$ , hence when its first argument equals  $\pm 1$ . But this was already guaranteed by our assumption (I) that  $f(\phi, c, \theta)$  is of double well type independently of  $(c, \theta)$  i.e.  $F$  is bistable.

Furthermore, the same assumption on the bistable nature of  $F$  implies that (54) has a solution if and only if  $\int_{-1}^1 F(\phi, C^0, \Theta^0) d\phi = 0$ , i.e. (by (11)) if and only if  $(C^0, \Theta^0) \in M$ . By (53), we now have that the lowest order outer functions  $\theta^0$  and  $c^0$  are continuous across  $\Gamma$ , and

$$(c^0, \theta^0) \in M \text{ at all points on } \Gamma \quad (55)$$

if  $C^0(z) = \text{const}$ .

Given that (55) holds, there is a well-known solution

$$\Phi^0(z) = \psi(z) \quad (56)$$

of (54) which is made unique by requiring that  $\psi(0) = 0$ . This solution also depends on the values of  $c^0$  and  $\theta^0$ , which in turn depend on  $s$  and  $t$ .

The function  $\Phi$  will be well approximated by  $\pm 1$  on all scales larger than  $z$ .

### 5.3 The concentration interface

Continuing with the inner analysis, we now investigate conditions under which  $C$  varies on a longer space scale than  $z$ , but shorter than the original scale of  $x$ . Our analysis begins with (46).

In view of (46), (49), we have

$$\partial_z \tilde{\mathcal{D}} \partial_z (C_{zz} - \beta g) = \sigma c^0 (1 - c^0) v C_z + \tilde{\mathcal{D}} O(\epsilon) + O(\epsilon \sigma).$$

We integrate once, divide by  $\tilde{\mathcal{D}}$ , and use the fact, from (22), that  $\tilde{\mathcal{D}} \geq O(\lambda^{-1})$ . We thus obtain from this, (56), and (49)

$$\partial_z (C_{zz} - \beta g(\psi(z), C, \theta^0)) = \frac{\sigma c^0 (1 - c^0) v}{\tilde{\mathcal{D}}} (C + B') + O(\epsilon), \quad (57)$$

where  $B'$  is an integration constant. We look for solutions for which  $C$  and  $C_{zz}$  are  $O(1)$ , so take  $B' = O(1)$ .

We shall shortly make approximations under which  $g$  and  $\tilde{\mathcal{D}}$  are discontinuous. The solutions  $C$  of the resulting equations must, however, satisfy

$$C_{zz} - \beta g, \quad C_z, \quad C \text{ are continuous.} \quad (58)$$

The reasons are (a) (57) provides an a priori estimate for the derivative of the first of these quantities (so the derivative could not be a delta-function), and (b) its continuity in turn provides an a priori estimate for  $C_{zz}$ , so that  $C_z$ , hence  $C$ , are continuous. Of course  $C_{zz}$  itself will be discontinuous.

For simplicity we ignore the variation of  $c$  about  $c_0$  in the function  $\tilde{\mathcal{D}}$ , and also assume the function  $u$  (18) to make its transition suddenly at  $z = 0$ . Thus

$$\frac{c^0(1-c^0)}{\tilde{\mathcal{D}}} = d_- = O(1), \quad z < 0; \quad \frac{c^0(1-c^0)}{\tilde{\mathcal{D}}} = d_+ \lambda = O(\lambda), \quad z > 0. \quad (59)$$

This approximation will be justified if there is a sufficiently narrow concentration gap (as in Ni-Cu) or if the velocity of the solidification front is large, so that sufficient trapping occurs.

We now rewrite (57), omitting the error terms, in three different ways in terms of rescaled space variables

$$\eta = \sqrt{\beta} z, \quad \zeta = \sigma^{1/3} z, \quad \xi = (\lambda \sigma)^{1/3} z. \quad (60)$$

The function  $C(z)$  is represented this way as a new function of  $\eta$ ,  $\zeta$ , or  $\xi$ . To avoid a surplus of notation, we denote the three new functions by the

same symbol  $C$ ; the contexts will remove any ambiguity. We obtain

For  $z < 0$ :

$$\partial_\eta \left[ C_{\eta\eta} - g\left(\psi\left(\frac{\eta}{\sqrt{\beta}}\right)\right), C \right] = \frac{\sigma d_-}{\beta^{3/2}} v(C + B'); \quad (61)$$

$$\partial_\zeta \left[ C_{\zeta\zeta} - \frac{\beta}{\sigma^{2/3}} g\left(\psi\left(\frac{\zeta}{\sigma^{1/3}}\right)\right), C \right] = v d_-(C + B'). \quad (62)$$

For  $z > 0$ :

$$\partial_\eta \left[ C_{\eta\eta} - g\left(\psi\left(\frac{\eta}{\sqrt{\beta}}\right)\right), C \right] = \frac{\lambda\sigma d_+}{\beta^{3/2}} v(C + B'); \quad (63)$$

$$\partial_\xi \left[ C_{\xi\xi} - \frac{\beta}{(\lambda\sigma)^{2/3}} g\left(\psi\left(\frac{\xi}{(\lambda\sigma)^{1/3}}\right)\right), C \right] = v d_+(C + B'). \quad (64)$$

In these equations, there are parameters which can be identified as ratios of characteristic thicknesses given in (36):

$$\frac{\sigma}{\beta^{3/2}} = \frac{\ell_\delta}{\ell_{cl}}; \quad \frac{\lambda\sigma}{\beta^{3/2}} = \frac{\ell_\delta}{\ell_{cs}}. \quad (65)$$

This suggests a classification based on the relative size of these thicknesses. We shall always assume that  $\lambda \gg 1$ , hence  $\ell_{cs} \ll \ell_{cl}$ . In all cases, we shall seek a solution  $C$  which approaches finite limits  $c_\pm$  (unknown at this point) as  $z \rightarrow \pm \infty$ .

### 5.3.1 Case A: $\rho \ll \rho_1$ , i.e. $\ell_\delta \ll \ell_{cs} \ll \ell_{cl}$ .

In this case we may use the scaled variable  $\eta$  and by (65) neglect the right sides of both (61) and (63) (they are small, by (65) and the assumptions of this case). Moreover, since  $\sqrt{\beta} \ll 1$  by (49), we replace the argument  $\psi\left(\frac{\eta}{\sqrt{\beta}}\right)$  in (61) by  $-1$  (since  $\eta < 0$  and  $\psi(-\infty) = -1$ ) and by  $+1$  in (63) (since  $\eta > 0$ ). Consider first the case of the resulting approximation to (63). We integrate it, denoting by  $B$  the new integration constant. We have

$$C_{\eta\eta} - g(1, C) - B = 0, \quad \eta > 0; \quad C(0) = c^0; \quad C(\infty) = c_+.$$

A similar equation (with the same  $B$ ) and limit condition hold for  $\eta < 0$ , using (61). The limits  $c_\pm$  at  $\pm\infty$  must satisfy

$$g(\pm 1, c_\pm, \theta^0) + B = 0. \quad (66)$$

Therefore we eliminate  $B$  to obtain

$$C_{\eta\eta} - (g(1, C, \theta^0) - g(1, c_+, \theta^0)) = 0, \quad \eta > 0; \quad C(0) = c^0, \quad (67)$$

and similarly for  $\eta < 0$ .

We assume that  $g(1, c, \theta) > g(-1, c, \theta)$  always. Then (12) guarantees that for each choice of  $B$ , there exist unique numbers  $c_{\pm}$ ,  $c_+ < c_-$ , satisfying (66).

If we also require that  $g(\phi, c, \theta) \rightarrow \infty$  as  $c \rightarrow 1$  and  $\rightarrow -\infty$  as  $c \downarrow 0$  (as is true in the case of (1)), then given any value of  $c_+$ , there exists a unique  $B$ , hence a unique  $c_-$  (and similarly if  $c_-$  is given).

This boundary value problem (67) has a unique solution for every given data pair  $c^0 > c_+$ . We show this by the method of sub- and super-solutions, using again the fact that  $g$  is an increasing function of  $c$  (12). Our super-solution is  $\bar{C} = c^0$ . To verify that this constant function is a supersolution, we note that

$$L\bar{C} \equiv \bar{C}_{\eta\eta} - (g(1, \bar{C}, \theta^0) - g(1, c_+, \theta^0)) = -(g(1, c^0, \theta^0) - g(1, c_+, \theta^0)) < 0.$$

Similarly, we may check that the constant  $\underline{C} \equiv c_+$  is a subsolution. Therefore there exists, as claimed, an exact solution between them. Its uniqueness follows from the maximum principle.

In a similar way, we construct a solution of the corresponding boundary value problem for (61) for  $\eta < 0$ .

The combination of these two solutions will be solution of the approximation to (57) in which the right side is set = 0, for all  $z$ , if we can arrange for (58) to hold at  $z = \eta = 0$ . It will represent an inner approximation (for small  $r$ ) to the desired solution of (43), hence (30). The continuity of  $C_{zz} - \beta g$  is automatic from our construction. For the other parts of (58), we first obtain an expression for  $C_z(0\pm)$ .

We multiply (67) by  $C_{\eta}$  and integrate from 0 to  $\infty$ . Using (66) and the dimensionless form of (10), we obtain

$$\frac{1}{2}(C_{\eta}(0+))^2 = \frac{1}{\theta^0} \left[ f(1, c^0, \theta^0) - f(1, c_+, \theta^0) - (C - c_+)f_c(1, c_+, \theta^0) \right], \quad (68)$$

and similarly with 1 replaced by  $-1$  and  $c_+$  by  $c_-$ .

For the continuity of  $C_{\eta}$ , we must have that the two versions (+ and -) of the right side of (68) are equal when  $C = c^0$ . But the condition (55) implies (4), and (66) implies

$$f_c(1, c_+, \theta^0) = f_c(-1, c_-, \theta^0) \equiv P. \quad (69)$$

We thus obtain

$$f(1, c_+, \theta^0) - f(-1, c_-, \theta^0) = P(c_+ - c_-). \quad (70)$$

Given  $(c^0, \theta^0)$  satisfying (55), we see that (69) and (70) serve to determine  $c_+$  and  $c_-$  uniquely, by the double tangent construction, since  $f$  is strictly convex in  $c$ .

To summarize, in Case (A), we have shown that for any given  $(c^0, \theta^0)$  satisfying (55), there are numbers  $c_{\pm}$  and an approximate solution of (46) in the rescaled variable  $\eta$  satisfying the limiting values  $c_{\pm}$  at  $\pm\infty$ .

This solution represents a transition between  $c_-$  and  $c_+$  in a space interval of width  $O(1)$  on the  $\eta$  scale, i.e.  $O(\sqrt{\beta})$  on the  $z$  scale, or  $O(\epsilon\sqrt{\beta}) = O(\frac{\epsilon^2}{\delta})$  on the original space scale. Our basic assumptions (49b), (32) imply that this layer thickness satisfies  $\epsilon^2 \ll \frac{\epsilon^2}{\delta} \ll \epsilon$ . It represents no solute trapping; in fact it is valid for small velocities  $\rho \ll \rho_1$  and the jump in concentration  $c_- - c_+$  is independent of velocity in this case.

### 5.3.2 Case B: $\rho_1 \ll \rho \ll \rho_3$ , i.e. $\ell_{cs} \ll \ell_{\delta} \ll \ell_{cl}$ .

In fact, we shall assume  $(\frac{\ell_{cs}}{\ell_{\delta}})^{2/3} \ll 1$ . This may be the most interesting case, as it shows the variation of the concentration jump with velocity. It is appropriate to use the variable  $\eta$  and (61) for  $z < 0$ , and the variable  $\xi$  and (64) for  $z > 0$ . Again, we approximate these equations by setting a small term equal to 0, integrate once, and replace the integration constant by a term which reflects the boundary condition at  $\pm\infty$ . The solution for  $\eta < 0$  is the same as in Case A. For  $\xi > 0$ , we obtain for (64) the boundary value problem

$$C_{\xi\xi\xi} + d_+v(C - c_+) = 0, \quad C(0) = c^0. \quad (71)$$

The solution may be written down immediately, noting that  $v < 0$ :

$$C(\xi) = c_+ + (c^0 - c_+)e^{(vd_+)^{1/3}\xi}, \quad (72)$$

wherein we take the negative cube root.

Finally, we obtain an approximate solution on the whole line by arranging for (58) to hold.

In view of (68) and (72), we obtain the continuity requirement for  $C_z$  in the form

$$0 = C_z^2(0+) - C_z^2(0-) = (\lambda\sigma)^{2/3}C_{\xi}^2(0+) - \beta C_{\eta}^2(0-)$$

$$\begin{aligned}
&= (\lambda\sigma)^{2/3}(c^0 - c_+)^2(d_+v)^{2/3} - \frac{2\beta}{\theta^0} \left[ f(-1, c^0, \theta^0) - f(-1, c_-, \theta^0) - f_c(-1, c_-, \theta^0)(c^0 - c_-) \right] \\
&= (\lambda\sigma)^{2/3}(c^0 - c_+)^2(d_+v)^{2/3} - 2\beta g_c(-1, c_-, \theta^0)(c^0 - c_-)^2 + O(c^0 - c_-)^3.
\end{aligned}$$

It will turn out that the last (cubic) term is relatively small. We drop it and obtain

$$(c^0 - c_+) = a \left( \frac{\ell_{cs}}{\ell_\delta} \right)^{1/3} |d_+v|^{-1/3} (c_- - c^0), \quad (73)$$

where  $a = \sqrt{2g_c(-1, c_-, \theta^0)} > 0$ .

We now apply the first continuity condition in (58). We have

$$0 = C_{zz}(0+) - \beta g(1, c^0, \theta^0) - (C_{zz}(0-) - \beta g(-1, c^0, \theta^0)),$$

hence

$$(\lambda\sigma)^{2/3} C_{\xi\xi}(0+) - \beta C_{\eta\eta}(0-) = \beta\gamma, \quad (74)$$

where  $\gamma = g(1, c^0, \theta^0) - g(-1, c^0, \theta^0) > 0$ .

Thus from (72) and (67),

$$(\lambda\sigma)^{2/3}(c^0 - c_+)(vd_+)^{2/3} - \beta(g(1, c^0, \theta^0) - g(1, c_+, \theta^0)) = \beta\gamma,$$

or

$$\frac{(\lambda\sigma)^{2/3}}{\beta} a \left( \frac{\ell_{cs}}{\ell_\delta} \right)^{1/3} (c^0 - c_-)(d_+v)^{1/3} = \gamma + g(1, c^0, \theta^0) - g(1, c_+, \theta^0) \sim \gamma + \frac{a^2}{2}(c^0 - c_+). \quad (75)$$

We combine (73) and (75), use (65), and neglect  $(c^0 - c_+)$  relative to  $\lambda$  to obtain the approximate relations

$$c_- - c^0 = \left( \frac{\ell_{cs}}{\ell_\delta} \right)^{1/3} |d_+v|^{-1/3} \frac{\gamma}{a} = \left( \frac{\mathcal{L}}{\lambda\delta d_+ \rho |v|} \right)^{1/3} \frac{\gamma}{a}; \quad c^0 - c_+ = \left( \frac{\ell_{cs}}{\ell_\delta} \right)^{2/3} |d_+v|^{-2/3} \gamma. \quad (76)$$

Thus  $c^0 - c_+$  is smaller than  $c_- - c^0$ , and the concentration jump in this regime decays like (velocity) $^{-1/3}$ .

The partition coefficient  $k = \frac{c_+}{c_-}$  can now be approximated by

$$k \sim \frac{c^0}{c_-} \sim 1 - \left( \frac{\mathcal{L}}{\lambda\delta d_+ \rho |v|} \right)^{1/3} \frac{\gamma}{c^0 a}.$$

We shall return to Case B in sec. 8.

**5.3.3 Case C:**  $\rho \gg \rho_3$ , i.e.  $\ell_{cs} \ll \ell_{cl} \ll \ell_\delta$ .

In this case it is appropriate to use the scaled variable  $\zeta$  for  $z < 0$  and  $\xi$  for  $z > 0$ , and the approximate versions of (62) (neglecting  $\frac{\beta}{\sigma^{2/3}}$ ) and (64). For  $\xi > 0$  we obtain the same solution (72). But for  $\zeta < 0$ , we have the solution

$$C = c_- + (c^0 - c_-) e^{-(d_- v)^{1/3} \zeta / 2} \left[ \cos[\sqrt{3}(d_- v)^{1/3} \zeta / 2] + R \sin[\sqrt{3}(d_- v)^{1/3} \zeta / 2] \right], \quad (77)$$

where  $R$  is a constant unknown at this point.

Then applying (58) in this case again results in very small concentration jumps, namely

$$c_- - c^0 = \lambda^{-1/3} O\left(\frac{\ell_{cs}}{\ell_\delta}\right)^{2/3}, \quad c^0 - c_+ = \lambda^{-2/3} O\left(\frac{\ell_{cs}}{\ell_\delta}\right)^{2/3}.$$

This behavior at high velocities is similar to that of [25] except for the effect of  $\lambda$ , which is taken there to be unity.

So in this high-velocity case, there is complete solute trapping, and effectively no variation in the concentration profile at the solidification front.

**5.3.4 Case D:**  $\rho \gg \rho_1 \left(\frac{\delta}{\epsilon}\right)^3$ ,  $\frac{\epsilon}{\delta} \leq O(1)$ .

This means

$$\lambda\sigma \gg 1, \quad \beta \leq O(1).$$

This case may overlap with Case C. Contrary to the assumption in (49a), this gives a lower bound on the velocity  $\rho$ ; it represents a very high solidification rate.

In this case, when  $z > 0$ , by (59) we neglect all terms of (57) except the first on the right. This implies that  $C(z) = \text{const} = c_+$ ,  $z > 0$ .

For  $z < 0$  (liquid region), the concentration profile is governed by some other equation; but matching with the solution on the right constrains the concentration to be very near  $c_+$  throughout. This is the case when the velocity is high enough. The outcome is similar to Case C above; the trapping is complete.

## 6 Inner multiscale analysis: scale of $C$ comparable to that of $\Phi$

We now consider the possibility of concentration profiles for which the variation of  $C$  in the variable  $z$  is not constant, as was the case in the previous

section and all of our analysis up to this point. This occurs when (49) is violated because of small  $\delta$ .

When (49) is no longer assumed, the error term in (57) becomes  $O(\epsilon(1 + \beta))$ . We assume this is  $\ll 1$ ; thus  $\epsilon^3 \ll \delta^2$ .

### 6.1 Case E: $\rho \ll \rho_1 \left(\frac{\delta}{\epsilon}\right)^3$ , $\frac{\epsilon}{\delta} \geq O(1)$ .

This means

$$\lambda\sigma \ll 1, \quad \beta \geq O(1).$$

We discard the right hand side of (57) to obtain

$$\partial_z(C_{zz} - \beta g(\Phi^0, C, \theta^0)) = 0 \tag{78}$$

Thus

$$C_{zz} - \beta(g(\Phi^0, C, \theta^0) + B) = 0, \tag{79}$$

$B$  an unknown constant.

We have a system of two second order equations for  $\Phi^0(z)$  and  $C(z)$ : (54) and (79), involving also an unknown constant  $B$ . They are to be solved for  $B$  and for bounded functions with limits at  $\pm\infty$ . The limits for  $\Phi^0$  are given by (54); and from (79) and the fact that  $C_{zz} = 0$  at infinity,

$$C(\pm\infty) = c_{\pm}, \tag{80}$$

where  $c_{\pm}$  satisfy (66).

We assume that (54), (79), (80) has a solution, for any choice of  $\beta$ . We expect the solution  $C$  to decrease monotonically from  $c_-$  to  $c_+$  as  $z$  goes from  $-\infty$  to  $\infty$ , and that  $B$ , which may depend on  $\beta$ , is bounded.

We examine the extreme case when  $\beta \gg 1$ , in which we are able to construct an approximate solution. We neglect the first term in (79) to obtain

$$g(\Phi^0(z), C(z), \theta^0) + B = 0, \tag{81}$$

an algebraic relation which, because  $g$  is monotonic in  $c$  (12), may be solved uniquely for

$$C(z) = H(\Phi^0(z), \theta^0, B). \tag{82}$$

This expression may then be substituted into (54) to obtain an equation for the phase and concentration profiles, both of which will have width  $O(\epsilon)$ .

The equation so obtained for  $\Phi^0$  is

$$\Phi_{zz}^0 - F(\Phi^0, H(\Phi^0, \theta^0, B), \theta^0) = 0, \quad \Phi^0(\pm\infty) = \pm 1. \tag{83}$$

There exists a solution if and only if

$$\int_{-1}^1 F(\phi, H(\phi, \theta^0, B)) d\phi = 0. \quad (84)$$

But (suppressing dependence on  $\theta^0$ ), by (23), (10), (81), we note that

$$\begin{aligned} \frac{d}{d\phi} f(\phi, H(\phi, B)) &= f_\phi(\phi, H(\phi, B)) + H_\phi(\phi, B) f_c(\phi, H(\phi, B)) = \\ &= \frac{T}{T^*} [F(\phi, H(\phi, B)) + H_\phi(\phi, B) g(\phi, H(\phi, B))] = \frac{T}{T^*} [F(\phi, H(\phi, B)) - B H_\phi(\phi, B)] \end{aligned}$$

by (81). For  $B$  we use the expression (81) with  $z = \pm\infty$ . Now (84) becomes

$$\begin{aligned} 0 &= \int_{-1}^1 \left[ \frac{d}{d\phi} f(\phi, H(\phi)) - \frac{T^*}{T} g(\pm 1, c_\pm) H_\phi(\phi, B) \right] d\phi = \\ &= f(1, H(1)) - f(-1, H(-1)) - f_c(\pm 1, c_\pm) (H(1) - H(-1)) = \\ &= f(1, c_+) - f(-1, c_-) - P(c_+ - c_-). \end{aligned}$$

This is the double tangent determination of  $c_+$  and  $c_-$ , already encountered in Case A ((69) and (70)).

In summary, we use the double tangent construction to determine  $c_+$  and  $c_-$ . This gives  $B$  from (81) with  $z = \pm\infty$ , hence  $H(\Phi^0)$  and then  $\Phi^0$  from (83). Finally,  $C(z)$  is found from (82).

## 6.2 Case F: $\delta = 0$ .

This assumption violates the intent of the paper, but we include it for its interest. It was studied in [14] and [7].

We multiply (46) by  $\delta^2$  and then set  $\delta = 0$ . Then integrate the resulting equation to obtain to lowest order

$$-\frac{\rho}{\mathcal{L}} v \epsilon (C + B) = \tilde{\mathcal{D}} g_z. \quad (85)$$

Introduce again  $d_\pm$  as in (59) and define

$$\sigma' = \frac{\rho \epsilon}{\mathcal{L} c^0 (1 - c^0)},$$

so that

$$g_z = \begin{cases} d_- \sigma' v (C + B), & z < 0, \\ \lambda d_+ \sigma' v (C + B), & z > 0. \end{cases}$$

We can consider two limiting cases:

(i)  $\lambda\sigma' \ll 1$ . This brings us back to the equilibrium phase diagram as in Case E.

(ii)  $\sigma' \gg 1$ . In this case,  $C = \text{const}$  to leading order and this constant belongs to the M-curve (4) by the consistency of the phase field equation. Thus complete trapping is expected for  $\sigma' \gg 1$ . This is due to the fact that the mass flux in the outer regions vanishes.

The dimensional growth rate for complete trapping is now bounded from below as

$$V \gg c^0(1 - c^0) \frac{\hat{D}_{cl}}{\ell_\epsilon}$$

For Ni-Cu at  $c^0 \sim 10\%$  this yields  $V \gg c^0(1 - c^0) \cdot 1000 \text{ cm/sec}$ , consistent with observations.

## 7 Other concentration interface conditions

The last three sections were concerned with determining, to lowest order, the variation of  $\Phi, C$ , and  $\Theta$  on the scale of the variable  $z$ ,  $\eta$ ,  $\xi$ , or  $\zeta$ . All of them are shorter-range space scales than  $x$  or  $r$ , and the solutions constitute our inner approximation. These inner functions have limits  $(\Phi, C, \Theta) \rightarrow (1, c_+, \theta^0)$  as  $z \rightarrow \infty$ , and limits  $(-1, c_-, \theta^0)$  at  $-\infty$ . These limiting values must match the values assumed on the appropriate side of  $\Gamma$  by the solution of the outer problem, a function of the original variables  $x$  and  $t$ .

In addition to the prescription of these interfacial values, the outer problem requires other conditions on  $\Gamma$ , namely Stefan conditions which express the conservation of energy and mass. We give the details only for the mass conservation relation.

We proceed from (43), which we approximate by setting  $\delta = 0$ . Integrate that equation from  $r = -a$  to  $r = a$ , where  $a$  is a small quantity independent of the other small parameters of the problem. Thus

$$\frac{\rho}{\mathcal{L}} \int_{-a}^a c_t dr - \frac{\rho}{\mathcal{L}} v [c]_{-a}^a = [\tilde{D} \partial_r g^*]_{-a}^a + \kappa \int_{-a}^a \tilde{D} \partial_r g^* dr + \int_{-a}^a R dr, \quad (86)$$

where  $g^* = g - \delta^2(c_{rr} + \kappa c_r)$  and  $R$  represents the error terms, all of which involve tangential derivatives.

We assume the points  $r = \pm a$  are in the outer region, but that  $a$  is small enough that the values of the functions indicated at  $r = \pm a$  are well

approximated by the limit of the outer solution as  $\Gamma$  is approached from the solid or liquid side. Thus e.g.  $c = c_+$  at  $r = a$ .

Assume, in the moving frame, that  $c_t$  is bounded and all tangential derivatives as well, relative to the normal derivatives  $c_r, c_{rr}$ . Thus we disregard the first and last terms in (86), since  $a$  is small.

For the last remaining integral on the right, we take (59), so that

$$\begin{aligned} \int_{-a}^a \tilde{\mathcal{D}} \partial_r g^* dr &= c^0(1 - c^0) \left[ d_-^{-1} \int_{-a}^0 \partial_r g^* dr + d_+^{-1} \lambda^{-1} \int_0^a \partial_r g^* dr \right] \\ &= c^0(1 - c^0) \left[ d_-^{-1} [g^*]_{-a}^0 + d_+^{-1} \lambda^{-1} [g^*]_0^a \right]. \end{aligned}$$

This integral is therefore negligible, provided that we can show that  $[g^*]_{-a}^0$  and  $[g^*]_0^a$  are. This will follow, since it can be shown that the variation of  $g^*$  through the inner region is small.

For example, consider Case A in subsec. 5.3. In terms of the coordinate  $\eta$ , we have  $g^* = g - C_{\eta\eta}$ , which we showed to be approximately constant in  $\eta$ . The claim is therefore verified in this case. The same argument holds in Case E. The claim can also be verified in the other cases; we shall not give the details.

We therefore have the relation

$$[\tilde{\mathcal{D}} \partial_r g] = -\frac{\rho}{\mathcal{L}} v [c]. \quad (87)$$

Similarly, the energy Stefan condition is derived from (44) and takes the form

$$[\partial_r \theta] = \rho v [e]. \quad (88)$$

## 8 Free boundary problem

We are now ready to formulate the outer problem for  $c$  and  $\theta$ . In the two domains  $\Omega_{\pm}$  separated by  $\Gamma(t)$ , field equations (40) and (41) are to be solved with the approximation  $\delta = 0, \phi = \pm 1$ :

$$\frac{\rho}{\mathcal{L}} \frac{\partial c}{\partial t} = \nabla \cdot \tilde{\mathcal{D}}^{\pm}(c, \theta) \nabla g^{\pm}(c, \theta), \quad (89)$$

$$\rho \frac{\partial}{\partial t} e^{\pm}(c, \theta) = \nabla^2 \theta. \quad (90)$$

On the common boundary  $\Gamma$ , the following conditions, relating the limiting values  $(c_+, \theta_+)$  and the limits of the derivatives as  $\Gamma$  is approached from the solid side to the corresponding limits from the liquid side, are to hold:

$$\theta_- = \theta_+ = \theta^0, \quad (91)$$

(55), (87), and (88). In addition,  $c_+$  and  $c_-$  are related to  $c^0$  according to the case (A through F). In cases A and E,  $c_{\pm}$  are determined by the double tangent construction (69) and (70). In Cases C, D, and F, we have found that approximately  $c_+ = c_- = c^0$ . Finally in Case B, we have (76), the second part of which provides the approximation  $c_+ \sim c^0$ .

The various cases will generally change when the velocity  $\rho$  changes. This may happen during the course of the solution's evolution in time, so that one approximation scheme with its concomitant interface conditions may hold at one time, then another later. The change can be detected in a free solidification problem when the evolving scaled velocity  $v$  ceases to be  $O(1)$ .

These are simply the interface conditions. In addition, there may be initial conditions to be satisfied, and boundary conditions for  $c$  and  $\theta$  on the boundary of  $\Omega_{\pm}$  other than  $\Gamma$ , or at infinity.

A natural one-phase problem arises by setting  $c = \text{const} = c_+$  in  $\Omega_+$ .

The system (89), (90) is a quasilinear evolution system of parabolic type, as we shall show, for the pair of functions  $(c, \theta)$ . It has "cross terms", as can be seen by writing  $\nabla g$  as  $g_c \nabla c + g_{\theta} \nabla \theta$  and  $e_t$  as  $e_c c_t + e_{\theta} \theta_t$ . The terms  $\nabla \cdot \tilde{D} g_{\theta} \nabla \theta$  and  $e_c c_t$  are the cross terms, analogous to cross diffusion terms in other contexts. The parabolicity of the system is crucial to its well posedness. To test the parabolic nature, we disregard all but the highest order spatial derivatives, writing the system as

$$A \frac{\partial Y}{\partial t} = B \nabla^2 Y + \dots,$$

where

$$Y = \begin{bmatrix} c \\ \theta \end{bmatrix}, \quad A = \frac{\rho}{\mathcal{L}} \begin{bmatrix} 1 & 0 \\ \mathcal{L} e_c & \mathcal{L} e_{\theta} \end{bmatrix}, \quad B = \begin{bmatrix} \tilde{D} g_c & \tilde{D} g_{\theta} \\ 0 & 1 \end{bmatrix}$$

It is parabolic if, for each  $(c, \theta)$ , the eigenvalues  $\lambda_1, \lambda_2$  of the matrix  $A^{-1}B$  both have positive real parts. This is true if the determinant and trace of  $A^{-1}B$  are both positive. We calculate

$$\det(A^{-1}B) = g_c \tilde{D} / e_{\theta} > 0$$

by (9), (12); and

$$\text{tr}(A^{-1}B) = (e_\theta)^{-1}(\tilde{\mathcal{D}}(g_c e_\theta - g_\theta e_c) + 1).$$

For the latter to be positive, it suffices for  $g_c e_\theta - g_\theta e_c > 0$ . But this quantity is

$$-f_{cc}f_{\theta\theta} + \theta^{-2}(f_c - \theta f_{c\theta})^2 \geq -f_{cc}f_{\theta\theta} = \theta^{-1}e_\theta g_c > 0,$$

again by (8), (9) and (12).

The existence and stability of solutions of this free boundary problem, and the ones given below, undoubtedly depend on the boundary and possibly initial conditions. As in the case of the analogous problems for a pure material (so  $c = \text{const}$ ), when those conditions reflect the free solidification of an undercooled melt, they may be ill posed, but can be regularized by the inclusion of terms involving the curvature of  $\Gamma$  in the interface conditions. Those terms will be examined in sec. 10.

## 9 Two one-dimensional examples.

### 9.1 Free motion

First, consider the free motion of a solidification front in 1D, so space is the real line. We formulate the problem for Case B, showing below how to verify this is the proper case. We take the linear approximation that the derivatives of  $e^\pm$  and  $g^\pm$  with respect to  $c$  and  $\theta$  are constants. Moreover, since it is often the case that the ‘‘cross terms’’ involving  $g_\theta$  and  $e_c$  in (89) and (90) are relatively small, we neglect them. Our nondimensionalization in sec. 3.2 implies that the dimensionless heat capacity and latent heat  $e_\theta = L = 1$ . Finally, we assume (59) to hold.

We denote the position of  $\Gamma$  by  $x = \bar{X}(t)$ ,  $\bar{X}(0) = 0$ , with solid on the right. Thus  $v = \bar{X}'(t) < 0$ . We assume  $c$  and  $\theta$  are constant in the solid:

$$\theta \equiv \theta^0, \quad c \equiv c^0, \quad x > \bar{X}(t), \tag{92}$$

so that our problem is a one-phase problem.

We prescribe initial data for  $c$  and  $\theta$ :

$$c(x, 0) = c_0(x), \quad \theta(x, 0) = \theta_0(x), \quad x \leq 0, \quad \theta_0(0) = \theta^0, \quad c_0(0^-) > c^0,$$

subject to the following compatibility conditions from (4) and Case B:

$$(1) \quad (\theta^0, c^0) \in M$$

(2) There exists a  $\rho > 0$  with

$$c_0(0^-) - c^0 = K_1 \rho^{-1/3}, \quad c_{0x}(0^-) = K_2 \rho^{2/3},$$

where  $K_1, K_2$  are constants which can be found from (87) and (76).

This determines the parameter  $\rho$ . With  $\rho$  known, we can check whether Case B holds. If it does, we proceed with the solution of the free boundary problem given below. If not, then we do the analogous procedure for another case.

With the given initial data, the equations to be solved are the following, for the determination of  $\theta(x, t)$ ,  $c(x, t)$ , and  $\bar{X}(t)$ :

$$\rho \theta_t = \theta_{xx}, \quad x < \bar{X}(t), \quad (93)$$

$$\theta(\bar{X}(t)^-, t) = \theta^0, \quad (94)$$

$$\theta_x(\bar{X}(t)^+, t) = \rho v, \quad (95)$$

$$\rho c_t = \frac{\mathcal{L}c^0(1-c^0)}{d_-} g_c^- c_{xx}, \quad x < \bar{X}(t), \quad (96)$$

$$c(\bar{X}(t)^-, t) = c^0 + K_1(\rho v)^{-1/3} \quad (97)$$

$$c_x(\bar{X}(t)^-, t) = K_2(\rho v)^{2/3}, \quad (98)$$

and initial conditions. Here of course the function  $v(t) = \bar{X}'(t)$  is to be determined. By the choice of  $\rho$ , we have  $v(0) = 1$ .

This is a very nonlinear free boundary problem; we expect existence and uniqueness, but to our knowledge they have not been proved. In the course of the evolution, if it happens that  $v$  ceases to be  $O(1)$ , then different interface conditions should replace (97) and (98).

## 9.2 Directional solidification

As second example, we consider a directional solidification problem, again under the conditions of Case B. In the laboratory frame, the material moves to the right with (in contrast to the previous example) prescribed constant velocity  $\rho$ , and the solidification front is fixed. Relative to the material, the solidification front therefore moves left with that velocity. Let  $x$  be a coordinate moving with the material, and  $y = x + \rho t$  be the laboratory

frame coordinate. We look for traveling wave solutions, so that  $\theta$  and  $c$  are functions only of  $y$ .

The interface is taken to be at  $y = 0$ . The solidification chamber is the interval  $-Y < y < Y$ . In place of boundary conditions at  $x = -\infty$ , we set boundary values on the temperature and concentration at the entrance to the directional solidification chamber at  $y = -Y$ , and also prescribe the temperature at the exit, where  $y = Y$ .

The functions  $\tilde{D}$  and  $g^\pm$  are as in the first example, and  $v = -1$ , since the velocity  $\rho v = -\rho$ . We obtain the following problem for  $c(y)$ ,  $\theta(y)$ ,  $\theta^0$ ,  $c^0$ . Since  $\rho$  is a prescribed velocity of the front, the two temperatures  $\theta_1^*$ ,  $\theta_2^*$  at  $y = \pm Y$  are not independent; only one of them can be prescribed. The other one is then another unknown to be determined.

$$-\rho(\theta') = \theta'', \quad y \neq 0, \quad (99)$$

$$\theta(0+) = \theta(0-) = \theta^0, \quad (100)$$

$$[\theta']_{y=0} = -\rho, \quad (101)$$

$$\rho c' = \frac{\mathcal{L}c^0(1-c^0)}{d_-} g_c^- c'', \quad y < 0, \quad (102)$$

$$\lambda \rho c' = \frac{\mathcal{L}c^0(1-c^0)}{d_-} g_c^+ c'', \quad y > 0, \quad (103)$$

$$c(0+) = c^0, \quad (104)$$

$$c(0-) = c^0 - K_1 \rho^{-1/3}, \quad (105)$$

$$c'(0-) = K_2 \rho^{2/3}, \quad (106)$$

$$(\theta^0, c^0) \in M, \quad (107)$$

$$c(-Y) = c^*, \quad \theta(-Y) = \theta_1^*, \quad \theta(Y) = \theta_2^*. \quad (108)$$

Thus neither  $c^0$  nor  $\theta^0$  is prescribed at the interface  $y = 0$ , but rather a single relation between them (that the pair lies on  $M$ ).

## 10 Corrections due to curvature

The various interfacial relations giving the jump in concentration were derived from the inner equations to lowest order. Since they depend on the velocity, they incorporate kinetic, i.e. solute trapping, effects. The next order terms in the appropriate equations contain contributions relating to the curvature of  $\Gamma$ , as well as further kinetic corrections.

We shall explore the effects of curvature in Case A, so write the inner equations in terms of the variable  $\eta$ . We thus reconsider (46) to obtain equations analogous to (61) and (63). Case A is the small velocity case with  $\rho \ll \rho_1$ , so that velocity effects are negligible. We in fact assume  $\rho$  is so small that the left side of (46) can be neglected, even to first order in the small parameter  $\delta$ . We therefore have

$$\partial_\eta \tilde{\mathcal{D}} \partial_\eta (C_{\eta\eta} - g) = \delta \left\{ \tilde{\mathcal{D}} \kappa \partial_\eta (g - C_{\eta\eta}) - \kappa \partial_\eta \tilde{\mathcal{D}} C_{\eta\eta} \right\}. \quad (109)$$

Thus  $\delta$  is our perturbation parameter. Sec. 5.3.1 concerned the lowest order approximation, for which (67)  $C_{\eta\eta} - g = \text{const.}$  As a result, the first term in braces on the right is higher order and can be dropped. We therefore obtain

$$\partial_\eta \tilde{\mathcal{D}} \partial_\eta (C_{\eta\eta} + \delta \kappa C_\eta - g) = 0,$$

and by the same boundedness argument as before, the following generalization of (67) holds:

$$C_{\eta\eta} + \delta \kappa C_\eta - (g(1, C, \theta^0) - (g(1, c_+, \theta^0))) = 0, \quad \eta > 0, \quad (110)$$

with the analogous equation ( $1 \rightarrow -1$ ,  $c_+ \rightarrow c_-$ ) for  $\eta < 0$ .

The new limits  $c_\pm$ , which differ from the old by  $O(\delta)$  amounts, still satisfy (66). Hence (69) holds with a new  $P$ .

As before, we apply the continuity condition that  $C_\eta(0+) = C_\eta(0-)$ . In place of (68), we have

$$\frac{1}{2}(C_\eta(0+))^2 = \frac{1}{\theta^0} \left[ f(1, c^0, \theta^0) - f(1, c_+, \theta^0) - (C - c_+) f_c(1, c_+, \theta^0) \right] + \delta \kappa \int_0^\infty C_\eta^2 d\eta, \quad (111)$$

and in place of (70).

$$f(1, c_+, \theta^0) - f(-1, c_-, \theta^0) = P(c_+ - c_-) + \delta \kappa \theta^0 \int_{-\infty}^\infty C_\eta^2 d\eta. \quad (112)$$

In evaluating the integral in the correction term, the lowest order solution  $C(\eta)$  found in sec. 5.3.1 may be used.

This gives a small curvature-dependent deviation from the double tangent construction. It is easy to show that our assumption (12) ensures that the new limiting values  $c_+$  and  $c_-$  of  $c$  are determined uniquely as  $O(\delta)$  deviations from the old ones.

This is not a Gibbs–Thompson effect, but rather the effect of curvature on the concentration gap and hence on the partition coefficient  $k$ .

## 11 Discussion

Our main purpose has been to study the structure of the concentration profile at a solidification front in the context of a phase field model which accounts for surface free energies of phase transitions and concentration jumps. The model yields a solute trapping effect, a basically nonequilibrium phenomenon.

Rough multiparameter asymptotics was seen to be very useful in deriving information about the solutions of our model equations, which are a generalization of previous phase field models. In particular, a picture of how solute trapping depends on velocity and other parameters emerged in the form of Cases A–F in secs. 5 and 6. Roughly speaking, the cases were arranged according to how the velocity compares with certain critical velocities, and the results of each case gave either no (or very little) trapping, partial trapping, or complete trapping (in which case the partition coefficient  $k$  is approximately unity). We give below the cases and their outcomes in dimensional form. All cases given are extreme ones, between which interpolations are no doubt possible. The critical velocities are

$$V_1 = c^0(1 - c^0)\frac{\hat{D}_{cl}}{\lambda\delta X}, \quad V_2 = c^0(1 - c^0)\frac{\hat{D}_{cl}}{\delta X}.$$

A	$\frac{\epsilon}{\delta} \ll 1, V \ll V_1$	No trapping
B	$\frac{\epsilon}{\delta} \ll 1, V \ll V_1 \left(\frac{\delta}{\epsilon}\right)^3, V_1 \ll V \ll V_2$	Partial trapping
C	$\frac{\epsilon}{\delta} \ll 1, V \ll V_1 \left(\frac{\delta}{\epsilon}\right)^3, V \gg V_2$	Complete trapping
D	$\frac{\epsilon}{\delta} \leq O(1), V \gg V_1 \left(\frac{\delta}{\epsilon}\right)^3,$	Complete trapping
E	$\frac{\epsilon}{\delta} \geq O(1), V \ll V_1 \left(\frac{\delta}{\epsilon}\right)^3,$	No trapping

In the case B of partial trapping, the concentration gap  $\Delta c$ , as a function of velocity, behaves like

$$\Delta c \sim \left(\frac{V_1}{V}\right)^{1/3}.$$

A sixth case was when  $\delta = 0$ . Then conditions were given under which no trapping or complete trapping holds.

The above arrangement of velocity regimes relies heavily on the great difference in mass diffusivity between liquid and solid, the ratio being  $\lambda = \frac{V_2}{V_1} \sim 10^4$  (typical value). This feature was not seen in previous treatments of the phenomenon. Another new feature which comes out of our analysis is the asymmetry in the internal diffusion layers. For example in Case B, our choice of scaled variables  $\eta$  and  $\xi$  shows that the ratio of thicknesses of this layer on the two sides is  $\left(\frac{\lambda \rho \delta}{\mathcal{L} c^0 (1-c^0)}\right)^{1/3}$ . And we obtain partial trapping in this case.

Solute trapping effects were seen when  $\delta \gg \epsilon$ ,  $\delta = O(\epsilon)$ , and even when  $\delta = 0$ . On the basis of these results one may conjecture that trapping would manifest itself at certain velocities for any ratio of  $\epsilon$  to  $\delta$ . Definitely the typical trapping velocity is model dependent, affected by the relative magnitudes of the various parameters.

The thermal diffusion takes place on much larger scales than that of mass diffusion. The main effect of the temperature field is to position the temperature at the interface and to fix this way the concentration  $c^0$  at the phase interface via the equi-free energy curve.

To summarize, the model produces, in lowest order, the kinetic phase diagrams for various regimes of crystal growth and accounts for the ratio of the thicknesses of the phase and concentration interfaces.

As is usual in such approaches, limiting free boundary problems can be obtained, to be solved for the position of the solidification interface and the temperature and concentration field away from it. In one important case, the interface conditions are highly nonlinear and lack a rigorous theory. Directional solidification problems can also be formulated. One-dimensional examples of each were given.

The curvature of the solidification front affects the above results in two ways: it modifies the concentration jump, and it modifies the condition that  $(c^0, \theta^0)$  must lie on the  $T_0$ -curve (55) (the Gibbs–Thompson effect in this context). This first effect was derived for Case A in sec. 10; the other is not calculated in this paper. Obviously, this calculation is a preliminary one and disregards the modification of the equi-free energy curve due to capillarity undercooling. The combined trapping and capillarity effects are now under investigation.

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