Sharp interface limits of a thermodynamically consistent solutal phase field model *

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Abstract

Thermal phase-field models were originally introduced to describe the solidification process of pure metals, highly dependent on temperature fluctuations. They are characterized by the introduction of an order parameter for solidification : the phase-field, describing a continuous "thick-interface" between solid and liquid regions. It was then shown that on an asymptotic "sharp-interface" limit, such models become a Stefan problem for the temperature. Later, solutal phase-field models were built to describe the solidification process of binary alloys. In the latter models, concentration plays a key role, while the effect of temperature fluctuations can be neglected. Stefan-like sharp-interface models were derived as asymptotic limits for some simple solutal models. In this paper, we investigate formal asymptotic limits for a more complex, thermodynamically consistent model, based on Warren and Boettinger's model. Four different sharp-interface limits are obtained, two of which remain valid when some of the constraints for thermodynamic consistency are removed from the original model.

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1 Introduction

Phase-field models have become of standard use to describe the solidification of both pure metals [1, 2, 10, 5] and, more recently, alloys [16, 17]. One of their main goals is to obtain a regularized description of the phenomena of dendritic growth, which was earlier described by sharp-interface Stefan-like problems [11, 14]. This is done by introducing an order parameter for solidification : the phase-field ϕ.

Most past works deal with thermal dendritic growth of pure metals, while we are interested in the description of solutal dendritic growth of alloys (neglecting thermal effects). Purely solutal phase-field models deal with the evolution of the concentration c and the phase-field ϕ of a binary alloy, at a fixed temperature T.

It is important to see what limit models can be obtained by taking appropriate asymptotic limits of the phase-field model, in order to reobtain a sharp-interface Stefan-like problem. Extensive studies on asymptotic limits of phase-field equations have been made for thermal phase-field models, and for relatively simple solutal models with separate low-degree

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polynomial non-linear source terms [2, 3, 5, 6, 17]. Our goal is to use similar techniques in order to obtain sharp-interface limits for a more thermodynamically realistic solutal model, based on the Warren and Boettinger isotropic model [7, 16]. We also want to know if it is possible to relax the thermodynamic constraints and still get the proper sharp-interface limit models.

Warren and Boettinger assumed on their paper [16] that the sharp-interface limit of their model when the interface thickness δ becomes small could be taken in the same way as Wheeler, Boettinger and McFadden did for their more simple solutal phase-field model [17]. We found that a simple asymptotic limit where $\delta \to 0$ while all other model parameters remain fixed does not lead to a simple Stefan-like sharp-interface model as expected. However, by imposing various conditions to other model parameters while the limit is taken, we find four different physically-significant sharp-interface limit models, presented on sections 3.1-3.4 and summarized on section 3.5.

Before presenting the formal asymptotic analysis, we recall the model construction and present it in a convenient adimensional formulation on section 2. We point out the constraints implied on the Warren-Boettinger model by thermodynamic consistency, which made the originality of this model. We have found that two of the four asymptotic limit models are actually independent of some of these constraints. This is analogous to a numerical result from Kim *et al.* for thermal phase-field models in [9], where they have found that certain changes on the source term of their evolution equations have small effect on the numerical solution when near the sharp-interface limit.

2 Model

We consider a mixture of two pure elements A and B, present both in liquid and solid states inside a domain Ω. The system can be characterized by a relative concentration $c = c(x,t)$ of element B with respect to the mixture. The relative concentration of element A will then be $1 - c$, and the variable c will take values in the interval $[0, 1]$. We further characterize the system with an order parameter for solidification, the phase field $\phi = \phi(x,t)$, which also takes values in the interval $[0, 1]$. A value of $\phi = 0$ corresponds to a pure solid region, and a value of $\phi = 1$ to a pure liquid region. Since we do not want to account for thermal effects, we assume the temperature $T(t)$ to be homogenous, and we consider it as an external parameter.

To have a thermodynamical description of the evolution of the variables c and ϕ, we introduce a Ginzburg-Landau free energy functional (see [4, 12, 15])

$$F(T,c,\phi) := \int_\Omega \left[f(T,c,\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] dx, \tag{2.1}$$

where f is a free energy density and ε a small parameter (which is linked, as we shall see, to the solid-liquid interface thickness).

The evolution of the quantities c and ϕ in the domain Ω can then be described by the following equations :

$$\left\{ \begin{array}{lll} \dfrac{\partial \phi}{\partial t} & = & -\eta \dfrac{\delta F}{\delta \phi} = \eta \left(\varepsilon^2 \triangle \phi - f_\phi \right), \\ \dfrac{\partial c}{\partial t} & = & \operatorname{div} \left(\mu \nabla \dfrac{\delta F}{\delta c} \right) = \operatorname{div} \left(\mu \left(f_{cc} \nabla c + f_{c\phi} \nabla \phi \right) \right), \end{array} \right. \tag{2.2}$$

where $f_\phi = \frac{\partial f}{\partial \phi}$, $f_{cc} = \frac{\partial^2 f}{\partial c^2}$ and $f_{c\phi} = \frac{\partial^2 f}{\partial c \, \partial \phi}$.

Under the assumption that the coefficients η and μ be positive functions of T, c and ϕ, the previous equations guarantee a locally decreasing free energy (second principle of thermodynamics) as well as the conservation of matter (see [16, 17]). These evolution equations can be coupled to Neumann boundary conditions for c and ϕ, ensuring that both matter and non-thermal free energy are confined in the domain Ω.

The general form (2.2) of solutal phase-field evolution equations is used both by Wheeler, Boettinger and McFadden [17] and Warren and Boettinger [16]. To ensure that we have a thermodynamically consistent model, we shall choose a free energy density $f(T, c, \phi)$ alike to that used by WB [16].

2.1 Free energy density

Warren and Boettinger's thermodynamically consistent free energy density [16] is given by

$$f(T, c, \phi) := (1-c) f^A(T, \phi) + c f^B(T, \phi) + \frac{RT}{v_m}\left[(1-c)\ln(1-c) + c\ln(c)\right], \tag{2.3}$$

where R is Boltzman's constant, v_m the molar volume, and

$$f^\xi(T, \phi) := L^\xi \frac{T_m^\xi - T}{T_m^\xi} p(\phi) + W^\xi \frac{T}{T_m^\xi} g(\phi) + f^\xi(T, 0), \tag{2.4}$$

where ξ stands for either A or B.

The function $g(\phi)$ is a standard double-well potential

$$g(\phi) := \phi^2(1-\phi)^2. \tag{2.5}$$

The constants L^ξ and T_m^ξ are respectively the latent heat and melting temperature for pure element ξ, while W^ξ is a model parameter for the potential barrier height at melting temperature (which we shall see is linked to both interface thickness and surface tension).

The function $p(\phi)$ is introduced in [16] as a regularization of the solid-liquid discontinuity, and must at least follow the constraints

$$\begin{cases} p(0) = 0, \\ p(1) = 1, \\ p'(\phi) > 0, \quad \forall \phi \in]0, 1[. \end{cases} \tag{2.6}$$

In order to have a thermodynamically consistent model, we want the solid and liquid states to always be the only stable states with respect to the order parameter for solidification. In order for the values $\phi = 0$ and $\phi = 1$ to be the two and only minima of $f(T, c, \phi)$ on the interval $\phi \in [0, 1]$, for all values of $T > 0$ and $c \in [0, 1]$, we need these extra constraints on the function p (assuming it is of class C^2) :

$$\begin{cases} p'(0) = p'(1) = 0, \\ p''(0) = p''(1) = 0. \end{cases} \tag{2.7}$$

Warren and Boettinger [16] have chosen the polynomial of smallest degree satisfying constraints (2.6-2.7), which is

$$p(\phi) = 6\phi^5 - 15\phi^4 + 10\phi^3. \tag{2.8}$$

We will only need the constraints, and not a specific choice of p, in order to derive the asymptotic limits of the model. Actually, we are also interested in knowing whether the extra contraints (2.7) that ensure thermodynamic consistency are necessary for the model to have meaningful sharp-interface limits or not. We are motivated in this by [9], who have numerical reasons to believe that (another class of) phase field models yield the same asymptotic limits whether they are thermodynamically consistent or not.

2.2 Determination of parameters W^A, W^B and ε

The stationary one-dimensional pure element ($c \equiv 0$) equation for ϕ at melting temperature $T = T_m^A$ is

$$\varepsilon^2 \frac{\partial^2 \hat{\phi}}{\partial x^2} - W^A g'(\hat{\phi}) = 0. \tag{2.9}$$

It has an explicit solution $\hat{\phi}$ for limit conditions $\hat{\phi}(-\infty) = 1$, $\hat{\phi}(+\infty) = 0$, and fixing $\hat{\phi}(0) = \frac{1}{2}$:

$$\hat{\phi}(x) = \frac{1}{1 + e^{\frac{x}{\delta}}}, \tag{2.10}$$

where $\delta = \varepsilon/\sqrt{2W^A}$ can easily be interpreted as the interface thickness, and should be given numerical values of the order of atomic distances (see [17]), such as $\delta = 5.10^{-8}\ cm$.

Besides, we can compute the total free energy (2.1) for the specific solution $c \equiv 0$, $\phi = \hat{\phi}$. If we give the 1D solution the interpretation of a planar 3D solution, then the total free energy of the 1D solution can be given the interpretation of a surface energy

$$\sigma^A = F(T_m^A, 0, \hat{\phi}) = \frac{\varepsilon\sqrt{2W^A}}{6}. \tag{2.11}$$

Such surface tensions for stationary planar solutions at melting temperature are experimantally known and can be used to fit the model. For a pure metal A, we can therefore link the model parameters W^A and ε to physically known quantities as

$$W^A = 3\frac{\sigma^A}{\delta} \quad \text{and} \quad \varepsilon^2 = 6\sigma^A\delta \qquad \text{when} \quad c = 0. \tag{2.12}$$

Analogous parameter adjustements also hold for pure element B when $c = 1$.

For the alloy, we will keep the adjusted values for the potential barrier heights

$$W^A := 3\frac{\sigma^A}{\delta} \quad \text{and} \quad W^B := 3\frac{\sigma^B}{\delta}. \tag{2.13}$$

We want however to keep ε^2 a constant, so we will choose it as the average of the pure element values :

$$\varepsilon^2 := 3(\sigma^A + \sigma^B)\delta. \tag{2.14}$$

This approximation is valid under the assumption that c remains bounded on a small interval. Note that we make a similar assumption for the molar volume v_m.

2.3 Diffusion

We want to ensure that the evolution equation for c on a pure solid ($\phi \equiv 0$) or a pure liquid ($\phi \equiv 1$) is a classical diffusion equation of the form

$$\begin{cases} \dfrac{\partial c}{\partial t} = D_s \triangle c & \text{if} \quad \phi \equiv 0, \\ \dfrac{\partial c}{\partial t} = D_l \triangle c & \text{if} \quad \phi \equiv 1, \end{cases} \tag{2.15}$$

where D_s and D_l are the solid and liquid diffusion coefficients (assumed to be independent of c).

Generalizing these particular cases, we want the equation for c to be of the form

$$\frac{\partial c}{\partial t} = D(\phi) \triangle c, \tag{2.16}$$

whenever ϕ is homogeneous in space, where

$$D(\phi) = D_s + q(\phi)(D_l - D_s) \tag{2.17}$$

is a variable diffusion coefficient, such that q is a monotonous increasing function of $\phi \in [0,1]$ with values $q(0) = 0$ and $q(1) = 1$. For instance, Warren and Boettinger choose $q(\phi) = p(\phi)$, since these two functions play analogous roles on the regularization of the solid-liquid transition. We will see that the particular choices for p and q don't play any role on the asymptotic limits, which depend only on some of the properties that were imposed to these functions upon construction.

This determines the positive coefficient μ as

$$\mu(T, c, \phi) := \frac{D(\phi)}{f_{cc}(T, c, \phi)}, \tag{2.18}$$

We will also assume that the positive phase-field diffusion coefficient

$$M := \eta \varepsilon^2 \tag{2.19}$$

is a constant.

2.4 Adimensional problem

Recollecting all the steps of the model construction, we obtain evolution equations for c and ϕ, which can be adimensionalized by changing space coordinates to $\tilde{x} = \frac{x}{l}$, where l is a characteristic length of the domain Ω, and time coordinates to $\tilde{t} = \frac{D_l t}{l^2}$, where $\frac{l^2}{D_l}$ is a characteristic liquid diffusion time. Furthermore, we won't explicitly write the temperature T anymore, since it plays the role of a parameter. The evolution equations then become, for $\tilde{\phi}(\tilde{x}, \tilde{t}) = \phi(x, t)$,

$$\begin{cases} \dfrac{\partial \tilde{\phi}}{\partial \tilde{t}} &= \widetilde{M} \left(\tilde{\triangle} \tilde{\phi} - \dfrac{1}{\tilde{\delta}} \tilde{f}_{\tilde{\phi}}(\tilde{c}, \tilde{\phi}) \right), \\ \dfrac{\partial \tilde{c}}{\partial \tilde{t}} &= \widetilde{\operatorname{div}} \left[\tilde{\mu}(\tilde{c}, \tilde{\phi}) \left(\tilde{f}_{\tilde{c}\tilde{c}}(\tilde{c}, \tilde{\phi}) \widetilde{\nabla} \tilde{c} + \tilde{f}_{\tilde{c}\tilde{\phi}}(\tilde{c}, \tilde{\phi}) \widetilde{\nabla} \tilde{\phi} \right) \right], \end{cases} \tag{2.20}$$

where $\widetilde{M} = \frac{M}{D_l}$, $\tilde{\delta} = \frac{\delta}{l}$,

$$
\begin{aligned}
\tilde{f}(\tilde{c}, \tilde{\phi}) &:= \frac{\delta l}{\varepsilon^2} f(\tilde{c}, \tilde{\phi}) \\
&= \frac{\alpha(\tilde{c})}{\tilde{\delta}} g(\tilde{\phi}) + \beta(\tilde{c}) p(\tilde{\phi}) + \frac{1}{\gamma} \left[(1-\tilde{c}) \ln(1-\tilde{c}) + \tilde{c} \ln \tilde{c}\right] + \tilde{f}_0(\tilde{c})
\end{aligned}
\tag{2.21}
$$

and

$$
\tilde{\mu}(\tilde{c}, \tilde{\phi}) := \frac{\varepsilon^2}{D_l \delta l} \mu(\tilde{c}, \tilde{\phi}) = \gamma \tilde{c}(1-\tilde{c}) \widetilde{D}(\tilde{\phi}) \tag{2.22}
$$

where

$$
\widetilde{D}(\tilde{\phi}) = \tilde{D}_s + q(\tilde{\phi}) \left(\tilde{D}_l - \tilde{D}_s\right),
$$

with $\tilde{D}_l = 1$ and $\tilde{D}_s = \frac{D_s}{D_l}$, $\tilde{f}_0(c)$ is an unimportant affine function,

$$
\gamma := 3 \frac{v_m}{RT} \frac{\sigma^A + \sigma^B}{l} \tag{2.23}
$$

and

$$
\begin{cases}
\alpha(\tilde{c}) := (1-\tilde{c}) \alpha^A + \tilde{c} \alpha^B \\
\beta(\tilde{c}) := (1-\tilde{c}) \beta^A + \tilde{c} \beta^B
\end{cases}
\tag{2.24}
$$

where

$$
\begin{cases}
\alpha^\xi := \dfrac{\sigma^\xi}{\sigma^A + \sigma^B} \dfrac{T}{T_m^\xi} \\
\beta^\xi := \dfrac{l}{3} \dfrac{L_\xi}{\sigma^A + \sigma^B} \dfrac{T_m^\xi - T}{T_m^\xi}
\end{cases}
, \quad \xi = A \text{ or } B. \tag{2.25}
$$

We will omit the tildes from now on in all quantities except $\tilde{f}$ and $\tilde{\mu}$. Note that the phase field diffusion coefficient M is the only model parameter yet to be linked to physical quantities. Let us remark that the well-posedness of problem (2.20) coupled with Neumann boundary conditions and appropriate initial conditions has been proved in [13].

3 Sharp-interface limits

Our goal in this section is to establish formal asymptotic limits of equations (2.20) when $\delta \to 0$, using assumptions (2.6-2.7) on function p. We assume the boundedness of ϕ and c in the following way :

$$
\begin{cases}
0 \le \phi(x,t) \le 1, \quad x \in \Omega, t \ge 0, \\
0 < c_{\min} \le c(x,t) \le c_{\max} < 1, \quad x \in \Omega, \quad t \ge 0.
\end{cases}
\tag{3.1}
$$

We also assume that

$$
D_s > 0, \tag{3.2}
$$

which means that a pure solid inhomogenous in c is not a stationary solution of (2.20). We shall only consider the case of bidimensional space domains.

Besides, we define liquid and solid free energy densities by

$$
\begin{cases}
f^{\mathrm{liq}}(c) := f(c,1), \\
f^{\mathrm{sol}}(c) := f(c,0).
\end{cases}
\tag{3.3}
$$

3.1 Small surface tension limit : classical Stefan-like problem

We consider the limit where δ, σ^A and σ^B tend to zero with δ/σ^A, δ/σ^B, and M kept fixed. Let us define a modified adimensional free energy density that will be independent of δ on this particular limit (except for the uninteresting last term that doesn't contribute to the derivatives of f appearing in (2.20)):

$$\begin{aligned} \hat{f}(c,\phi) &= \delta \tilde{f}(c,\phi) \\ &= \alpha(c)g(\phi) + \hat{\beta}(c)p(\phi) + \frac{1}{\hat{\gamma}}\left[(1-c)\ln(1-c) + c\ln c\right] + \delta \tilde{f}_0(c), \end{aligned} \tag{3.4}$$

where $\hat{\beta}(c) := \delta\beta(c)$ and $\hat{\gamma} := \gamma/\delta$.

Since δ/σ^A and δ/σ^B are kept fixed, $\alpha(c)$, $\hat{\beta}(c)$ and $\hat{\gamma}$ are independent of δ (see definitions (2.23-2.25)). We also define

$$\hat{\mu}(c,\phi) = \frac{\tilde{\mu}(c,\phi)}{\delta} = \hat{\gamma}c(1-c)D(\phi). \tag{3.5}$$

The equations (2.20) can then be written :

$$\left\{ \begin{aligned} \frac{\delta^2}{M}\frac{\partial \phi}{\partial t} &= \delta^2 \triangle \phi - \hat{f}_\phi(c,\phi), \\ \frac{\partial c}{\partial t} &= \operatorname{div}\left[\hat{\mu}(c,\phi)\left(\hat{f}_{cc}(c,\phi)\nabla c + \hat{f}_{c\phi}(c,\phi)\nabla\phi\right)\right], \end{aligned} \right. \tag{3.6}$$

Outer solution

We now consider the previous equations when δ tends to zero at macroscopic scale : the first equation becomes

$$\hat{f}_\phi(c,\phi) = 0. \tag{3.7}$$

If we assume the constraints (2.7) on function p, pure liquid $\phi \equiv 1$ and solid $\phi \equiv 0$ are possible solutions independently of the behaviour of c. These solutions can be proved to be stable with respect to small perturbations for positive temperatures. Putting them on the second equation, we get (using definition (2.18)) respectively

$$\left\{ \begin{aligned} \frac{\partial c}{\partial t} &= D_l \triangle c \quad \text{on regions where } \phi \equiv 1, \\ \frac{\partial c}{\partial t} &= D_s \triangle c \quad \text{on regions where } \phi \equiv 0. \end{aligned} \right. \tag{3.8}$$

Let us now consider the case when both a liquid region Ω_l and a solid region Ω_s are present, delimited by an interface Γ. Such a configuration might locally look like figure 1.

We expect to be able to study the transition between the pure phase regions at a space scale of order δ on the direction normal to the interface. To be able to do this, we assume that the interface (formally defined as the level set $\phi = 0.5$) can be described by a C^2 parametrisation $\Gamma(s,t)$, and that a normal velocity $v_n(s,t)$ and a mean curvature $\kappa(s,t)$ can be defined at the macroscopic scale. Under these assumptions, we may define a time dependent local invertible space coordinates change $(x,y) \leftrightarrow (r,s)$, where r denotes the

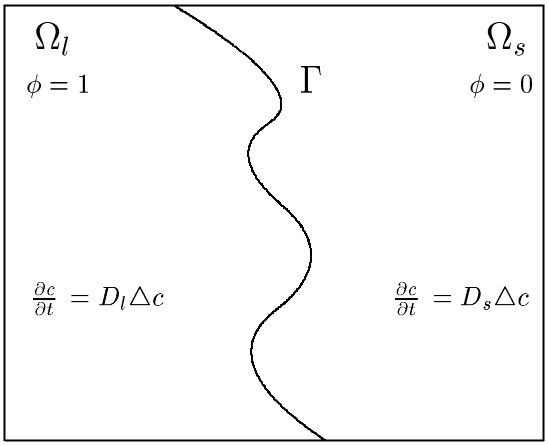

Figure 1: macroscopic domains

normal distance to the interface and s is a curvilinear coordinate of the interface. Using Frenet formulae we can then establish the properties :

$$\begin{cases} \dfrac{\partial r}{\partial t} = -v_n, \\ |\nabla r|^2 = 1, \\ \nabla r . \nabla s = 0, \\ \triangle r = \dfrac{\kappa}{1+\kappa r}. \end{cases} \tag{3.9}$$

Let us assume that the system is liquid at the left and solid at the right of the interface. We call $c_l(s,t)$ and $c_s(s,t)$ the left and right limits of the "outer" function c when r tends to zero, and $\left(\frac{\partial c}{\partial r}\right)_l(s,t)$ and $\left(\frac{\partial c}{\partial r}\right)_s(s,t)$ the corresponding limits of $\frac{\partial c}{\partial r}$. These values provide limit conditions for the diffusion equations (3.8).

inner solution

To link the quantities across the interface, we will formally examine the problem (3.6) near the interface by re-scaling the r coordinate as

$$r = \delta \rho. \tag{3.10}$$

Let us now consider the "inner" functions $\bar{\phi}$ and $\bar{c}$ inside the interface region as functions of the new set of space-time coordinates (ρ, s, t), and formally develop them with respect to the small parameter δ as :

$$\begin{cases} \bar{\phi}(\rho,s,t) &= \phi_0(\rho,s,t) + \delta\phi_1(\rho,s,t) + \dots \\ \bar{c}(\rho,s,t) &= c_0(\rho,s,t) + \delta c_1(\rho,s,t) + \dots \end{cases} \tag{3.11}$$

As $\rho \to \pm\infty$, we take limit conditions for the inner functions that are C^1-compatible with the outer functions :

$$
\left\{
\begin{array}{l}
\lim_{\rho \to -\infty} \phi_0(\rho, s, t) = 1, \\
\lim_{\rho \to +\infty} \phi_0(\rho, s, t) = \lim_{\rho \to \pm\infty} \dfrac{\partial \phi_0}{\partial \rho}(\rho, s, t) = 0, \\
\lim_{\rho \to \pm\infty} \phi_1(\rho, s, t) = \lim_{\rho \to \pm\infty} \dfrac{\partial \phi_1}{\partial \rho}(\rho, s, t) = 0, \\
\lim_{\rho \to -\infty} c_0(\rho, s, t) = c_l, \quad \lim_{\rho \to +\infty} c_0(\rho, s, t) = c_s, \\
\lim_{\rho \to -\infty} \dfrac{\partial c_1}{\partial \rho}(\rho, s, t) = \left(\dfrac{\partial c}{\partial r} \right)_l (s, t), \quad \lim_{\rho \to +\infty} \dfrac{\partial c_1}{\partial \rho}(\rho, s, t) = \left(\dfrac{\partial c}{\partial r} \right)_s (s, t), \\
\lim_{\rho \to \pm\infty} c_1(\rho, s, t) = \lim_{\rho \to \pm\infty} \dfrac{\partial c_0}{\partial \rho}(\rho, s, t) = 0.
\end{array}
\right.
\tag{3.12}
$$

Inside the re-scaled domain, we can use the interface properties (3.9) combined to the rescaling (3.10) and the asymptotic series (3.11) in (3.6) to establish

$$
\left\{
\begin{array}{l}
\delta \dfrac{\partial \bar{\phi}}{\partial t} = -v_n \dfrac{\partial \phi_0}{\partial \rho} + \dots, \\
\delta^2 \triangle \bar{\phi} = \dfrac{\partial^2 \phi_0}{\partial \rho^2} + \delta \left(\dfrac{\partial^2 \phi_1}{\partial \rho^2} + \kappa \dfrac{\partial \phi_0}{\partial \rho} \right) + \dots,
\end{array}
\right.
\tag{3.13}
$$

as well as analogous formal series for $\frac{\partial \bar{c}}{\partial t}$ and $\triangle \bar{c}$, and also

$$
\nabla \bar{c}.\nabla \bar{\phi} = \frac{\partial c_0}{\partial \rho} \frac{\partial \phi_0}{\partial \rho} + \delta^2(\dots) + \dots . \tag{3.14}
$$

order 0 in δ

The equations (3.6) therefore become at lowest order on δ :

$$
\left\{
\begin{array}{l}
\dfrac{\partial^2 \phi_0}{\partial \rho^2} - \hat{f}_\phi(c_0, \phi_0) = 0, \\
\dfrac{\partial}{\partial \rho} \left[\hat{\mu}(c_0, \phi_0) \left(\hat{f}_{cc}(c_0, \phi_0) \dfrac{\partial c_0}{\partial \rho} + \hat{f}_{c\phi}(c_0, \phi_0) \dfrac{\partial \phi_0}{\partial \rho} \right) \right] = 0
\end{array}
\right.
\tag{3.15}
$$

Let us first look at the second equation. Under assumptions (3.1-3.2), the function $\hat{\mu}(c_0, \phi_0)$ remains strictly positive in all the domain. We know however by (3.12) that $\frac{\partial c_0}{\partial \rho}$ and $\frac{\partial \phi_0}{\partial \rho}$ both become zero on the limits when ρ tends to plus or minus infinity. We may therefore conclude that

$$
\hat{f}_{cc}(c_0, \phi_0) \frac{\partial c_0}{\partial \rho} + \hat{f}_{c\phi}(c_0, \phi_0) \frac{\partial \phi_0}{\partial \rho} = 0 \tag{3.16}
$$

inside all the rescaled interface.

This can be rewritten as

$$
\frac{\partial}{\partial \rho} \hat{f}_c(c_0, \phi_0) = 0. \tag{3.17}
$$

In particular, this gives us a first interface condition, using definitions (3.3) :

$$\boxed{\hat{f}_c^{\mathrm{liq}}(c_l) = \hat{f}_c^{\mathrm{sol}}(c_s).} \tag{3.18}$$

Actually $\hat{f}_c(c_0, \phi_0) \equiv \hat{C}$ is a constant for all values of ρ (at s and t fixed), and this gives us an algebraic relationship between c_0 and ϕ_0. It happens that this relationship can be described with an univoquous function $c_0 = h(\phi_0)$, that we do not need to write explicitly for our purposes. Therefore,

$$\frac{\partial}{\partial \phi}\left[\hat{f}\left(h(\phi), \phi\right) - \hat{C}h(\phi)\right]\Big|_{\phi=\phi_0} = \hat{f}_\phi\left(h(\phi_0), \phi_0\right), \tag{3.19}$$

and the first equation of (3.15) can be rewritten as

$$\frac{\partial^2 \phi_0}{\partial \rho^2} = \frac{\partial}{\partial \phi}\left[\hat{f}\left(h(\phi), \phi\right) - \hat{C}h(\phi)\right]\Big|_{\phi=\phi_0}. \tag{3.20}$$

By multiplying this equation by $\frac{\partial \phi_0}{\partial \rho}$ and integrating on ρ we then obtain

$$\frac{1}{2}\left|\frac{\partial \phi_0}{\partial \rho}\right|^2\Bigg|_{-\infty}^{+\infty} = \left[\hat{f}\left(h(\phi), \phi\right) - \hat{C}h(\phi)\right]\Big|_{-\infty}^{+\infty}, \tag{3.21}$$

which, by using the limit conditions (3.12) and the definition of $h(\phi_0)$, gives us a second interface condition :

$$\boxed{\hat{f}^{\mathrm{liq}}(c_l) - \hat{f}_c^{\mathrm{liq}}(c_l)c_l = \hat{f}^{\mathrm{sol}}(c_s) - \hat{f}_c^{\mathrm{sol}}(c_s)c_s.} \tag{3.22}$$

The two conditions (3.18) and (3.22) mean that there is a common tangent to the graphs of functions $f^{\mathrm{liq}}(c)$ and $f^{\mathrm{sol}}(c)$, tangent to the graphs at respectively concentrations $c = c_l$ and $c = c_s$. Actually, if the temperature T of the system is inside the interval delimited by the melting temperatures of the two pure elements A and B, then there is a single set of concentrations (c_s, c_l) allowing for such a geometric construction, and these concentrations, as functions of T, provide the (T,c) equilibrium "lens-type" phase diagram for the alloy.

order 1 in δ

Using properties (3.13) and (3.14), we can write the equation for c in (3.6) at order 1 on δ, greatly simplified by relationship (3.17) :

$$-v_n \frac{\partial c_0}{\partial \rho} = \frac{\partial}{\partial \rho}\left\{\hat{\mu}(c_0, \phi_0)\frac{\partial}{\partial \rho}\left[\hat{f}_c(c_0, \phi_0)c_1 + \hat{f}_\phi(c_0, \phi_0)\phi_1\right]\right\}. \tag{3.23}$$

We may simply integrate on ρ from $-\infty$ to $+\infty$ to obtain a third interface condition. Assuming that the normal velocity v_n, a macroscopic quantity, is uniform in ρ, we obtain, using (2.17-2.18) and limit conditions (3.12) :

$$\boxed{-v_n(c_s - c_l) = D_s\frac{\partial c_s}{\partial n} - D_l\frac{\partial c_l}{\partial n}.} \tag{3.24}$$

This corresponds to the conservation of matter through the interface.

Note that on all steps used to derive interface conditions (3.18), (3.22) and (3.24), we implicitly used constraints (2.6) on function p, but never needed the extra constraints (2.7).

Stefan-like problem

Regrouping results (3.8, 3.18, 3.22, 3.24,) and recalling the definitions of $\hat{f}$ and $\tilde{f}$, we can write the sharp-interface small surface tension asymptotic limit when $\delta, \sigma^A$and σ^B tend to zero with δ/σ^A, δ/σ^B, and M kept fixed as the following Stefan problem :

$$\left\{\begin{array}{ll} \dfrac{\partial c}{\partial t} = D_l \triangle c, & \text{in} \quad \Omega_l, \\ \dfrac{\partial c}{\partial t} = D_s \triangle c, & \text{in} \quad \Omega_s, \\ \left\{\begin{array}{l} -v_n \left[c\right]_l^s = \left[D\, \dfrac{\partial c}{\partial n}\right]_l^s, \\ \left[f_c\right]_l^s = 0, \\ \left[f - f_c c\right]_l^s = 0, \end{array}\right. & \text{on} \quad \Gamma, \end{array}\right. \tag{3.25}$$

where $[.]_l^s$ denotes the jump of a quantity across the liquid-solid interface. This limit can be easily interpreted : on liquid and solid regions there is a classical diffusion of matter, while through the interface there is on the one hand, conservation of matter as the interface moves, and on the other hand, concentration takes liquid ans solid equilibrium values on respective sides of the interface.

3.2 Small surface tension and low phase-field diffusivity limit : kinetic effects

We now consider the limit when $\delta, \sigma^A, \sigma^B$ and M tend to zero with δ/σ^A, δ/σ^B, and δ/M kept fixed. We use the same modified free energy density $\hat{f}$ defined by (3.4) on the last section. We define a new quantity independent of δ :

$$\hat{M} = \frac{M}{\delta}, \tag{3.26}$$

and the evolution equations (3.6) can then be written

$$\left\{\begin{array}{rcl} \dfrac{\delta}{\hat{M}} \dfrac{\partial \phi}{\partial t} & = & \delta^2 \Delta\phi - \hat{f}_\phi(c,\phi), \\ \dfrac{\partial c}{\partial t} & = & \operatorname{div}\left[\hat{\mu}(c,\phi)\left(\hat{f}_{cc}(c,\phi)\nabla c + \hat{f}_{c\phi}(c,\phi)\nabla\phi\right)\right], \end{array}\right. \tag{3.27}$$

The outer solutions will be the same as (3.8), and the macroscopic behaviour still corresponds to figure 1. All the steps to obtain interface conditions (3.18) and (3.24) depend only on the second equation in (3.27), and are therefore unmodified; equation (3.17) also still holds. However, the first equation in (3.15) now becomes

$$-\frac{v_n}{\hat{M}} \frac{\partial \phi_0}{\partial \rho} = \frac{\partial^2 \phi_0}{\partial \rho^2} - \hat{f}_\phi(c_0, \phi_0), \tag{3.28}$$

from which we can derive an analogous of (3.20) :

$$\frac{\partial^2 \phi_0}{\partial \rho^2} + \frac{v_n}{\hat{M}} \frac{\partial \phi_0}{\partial \rho} = \frac{\partial}{\partial \phi} \left[\hat{f}\left(h(\phi), \phi\right) - \hat{C} h(\phi)\right]\Big|_{\phi=\phi_0}, \tag{3.29}$$

and finally, multiplying by $\frac{\partial \phi_0}{\partial \rho}$ and integrating on ρ :

$$\boxed{\left[\hat{f} - \hat{f}_c c\right]_l^s = \frac{\Gamma}{\hat{M}} v_n,} \tag{3.30}$$

where

$$\Gamma := \int_{-\infty}^{+\infty} \left| \frac{\partial \phi_0}{\partial \rho} \right|^2 d\rho. \tag{3.31}$$

The limit where $\delta, \sigma^A, \sigma^B$ and M tend to zero therefore corresponds to a modified Stefan problem, equivalent to (3.25) where the last interface condition is to be replaced by (3.30). There is still classical diffusion on pure phase regions, separed by δ-width interfaces, through which the concentration and its normal derivative jump in such a way that matter is conserved. However, the values of concentration on both sides of the interface are no longer equilibrium values, but are obtained through a "parallel tangent construction" dependent upon the local interface velocity. On regions where the interface is static, we find again the equilibrium values of c_l and c_s corresponding to the phase diagram.

3.3 Similar elements limit : kinetic and curvature effects

We now want to consider a sharp-interface limit with finite surface tension. However, taking the limit when δ tends to zero with all other quantities fixed does not yield valid interface conditions using Caginalp [2, 3] methods as we did in preceding subsections. We therefore choose to have an extra constraint : we want the coefficient $\alpha(c)$ defined in (2.24) to be a constant at lowest order in δ :

$$\alpha(c) = \bar{\alpha} + \delta \Delta\alpha c. \tag{3.32}$$

This is equivalent to assume that the quantity

$$\alpha^B - \alpha^A = \frac{T}{\sigma^A + \sigma^B} \left(\frac{\sigma^B}{T_m^B} - \frac{\sigma^A}{T_m^A} \right) = \delta \Delta\alpha \tag{3.33}$$

is of order δ, i.e. that the two components of the alloy are similar enough in the sense of (3.33). Another interpretation of this assumption can be given using the potential barrier heights W^A and W^B defined in (2.13) : as δ tends to zero, both potential barriers become infinite, but their difference (ponderated by respective melting temperatures) is kept fixed.

We introduce yet another modified free energy density :

$$\begin{aligned} \check{f}(c,\phi) &:= \tilde{f}(c,\phi) - \frac{\bar{\alpha}}{\delta} g(\phi) \\ &= \Delta\alpha c g(\phi) + \beta(c) p(\phi) + \frac{1}{\gamma} \left[(1-c)\ln(1-c) + c \ln c \right] + \tilde{f}_0(c) \end{aligned} \tag{3.34}$$

The equations (2.20) can then be written as

$$\left\{ \begin{aligned} \frac{\delta^2}{M} \frac{\partial \phi}{\partial t} &= \delta^2 \Delta \phi - \bar{\alpha} g'(\phi) - \delta \check{f}_\phi(c,\phi), \\ \frac{\partial c}{\partial t} &= \operatorname{div} \left[\tilde{\mu}(c,\phi) \left(\check{f}_{cc}(c,\phi) \nabla c + \check{f}_{c\phi}(c,\phi) \nabla \phi \right) \right], \end{aligned} \right. \tag{3.35}$$

On the asymptotic limit where δ tends to zero, for the outer solution, equation (3.7) is now replaced by

$$g'(\phi) = 0. \tag{3.36}$$

This still gives the same behaviour as (3.8) outside the interface, but we no longer need to assume that the constraints (2.7) on function p are satisfied.

As for the inner solution, the second equation in (3.35) is analogous to the second equation in (3.6), and will therefore yield interface conditions analogous to (3.18) and (3.24). Noting that

$$\check{f}_c = \tilde{f}_c = \frac{\hat{f}_c}{\delta}, \tag{3.37}$$

we conclude that the two interface conditions on c obtained in this case are actually strictly equivalent to (3.18) and (3.24).

We must now look at the evolution equation for ϕ in (3.35). At lowest order in δ it becomes simply

$$\frac{\partial^2 \phi_0}{\partial \rho^2} = \hat{\alpha} g'(\phi_0). \tag{3.38}$$

With the limit conditions (3.12), and fixing $\phi_0 = \frac{1}{2}$, this equation has a unique solution :

$$\phi_0(\rho) = \frac{1}{1 + e^{\sqrt{2\bar{\alpha}}\rho}}. \tag{3.39}$$

This doesn't give us an interface condition yet, so we must look at the next order in δ of the first equation in (3.35) :

$$-\frac{v_n}{M}\frac{\partial \phi_0}{\partial \rho} = \frac{\partial^2 \phi_1}{\partial \rho^2} + \kappa \frac{\partial \phi_0}{\partial \rho} - \bar{\alpha} g''(\phi_0)\phi_1 - \check{f}_\phi\left(h(\phi_0), \phi_0\right). \tag{3.40}$$

Let's call $\mathcal{L}$ the operator

$$\mathcal{L} = \bar{\alpha} g''(\phi_0) - \frac{\partial^2}{\partial \rho^2}. \tag{3.41}$$

We can then rewrite (3.40) as

$$\mathcal{L}\frac{\partial \phi_1}{\partial \rho} = \left(\kappa + \frac{v_n}{M}\right)\frac{\partial \phi_0}{\partial \rho} - \check{f}_\phi\left(h(\phi_0), \phi_0\right), \tag{3.42}$$

and by deriving (3.38) with respect to ρ we find that

$$\mathcal{L}\frac{\partial \phi_0}{\partial \rho} = 0. \tag{3.43}$$

In fact, $\mathcal{L}$ is a self-adjoint operator on functions satisfying limit conditions (3.12), for the L^2 scalar product on variable ρ. Therefore, we have an orthogonality condition for (3.42) to be solvable when (3.43) is true :

$$\left(\kappa + \frac{v_n}{M}\right)\int_{-\infty}^{+\infty}\left|\frac{\partial \phi_0}{\partial \rho}\right|^2 d\rho - \int_{-\infty}^{+\infty}\check{f}_\phi\left(h(\phi_0), \phi_0\right)\frac{\partial \phi_0}{\partial \rho}\, d\rho = 0. \tag{3.44}$$

Using limit conditions (3.12) and equation (3.19), we then find the following interface condition :

$$\boxed{\left[\check{f} - \check{f}_c c\right]_l^s = \check{\Gamma}\left(\kappa + \frac{v_n}{M}\right),} \tag{3.45}$$

where the explicit form of constant $\check{\Gamma}$ can be obtained using (3.39) :

$$\check{\Gamma} = \frac{1}{\int_{-\infty}^{+\infty}\left|\frac{\partial\phi_0}{\partial\rho}\right|^2 d\rho} = \sqrt{\frac{2}{\bar{\alpha}}}. \tag{3.46}$$

The limit where δ tends to zero with $\Delta\alpha$ fixed therefore also corresponds to a modified Stefan problem, similar to (3.25) where the last interface condition is to be replaced by (3.45). There is also still classical diffusion on pure phase regions, separed by δ-width interfaces, through which the normal derivative of concentration jumps in such a way that matter is conserved. However, the values of concentration on both sides of the interface are now obtained through a "parallel tangent construction" dependent upon both local interface velocity and local curvature. On regions where the interface is both planar and static, we find again the equilibrium values of c_l and c_s corresponding to the phase diagram.

Note that the solvability condition technique implemented through the operator $\mathcal{L}$ can also be used to obtain an interesting limit in the case of a pure element ($c \equiv 0$ or $c \equiv 1$). We then have only the equation for the evolution of ϕ in (3.35). The outer solutions will still be chosen as liquid ($\phi \equiv 1$) on the left and solid ($\phi \equiv 0$) on the right of the interface. The inner development will however now yield only one interface condition, which in the case of pure element A would be :

$$\kappa + \frac{v_n}{M} = \frac{[\check{f}]}{\check{\Gamma}} = \frac{L^A}{l\sigma^A}\frac{T - T_m^A}{T_m^A}. \tag{3.47}$$

This describes an interface moving by mean curvature. The preceeding equation can also be compared, when $\kappa = 0$, to phenomenological laws, in order to adjust M with a known kinetic coefficient, and have a numerical value to use on the original phase-field model.

3.4 Similar elements limit with large phase-field diffusivity : curvature effects only

We consider the same conditions as in the last subsection, except that now the quantity

$$\check{M} = M\delta \tag{3.48}$$

is supposed to be fixed.

With analogous steps, we find a similar limit problem as in the last paragraph. It is also a modified version of problem (3.25), where the last equation is replaced by

$$\boxed{\left[\check{f} - \check{f}_c c\right]_l^s = \check{\Gamma}\kappa.} \tag{3.49}$$

The "parallel tangent construction" is now dependent upon local curvature only, and the equilibrium values of c_l and c_s corresponding to the phase diagram can now be found on all regions where the interface is plane, even if it moves.

3.5 Summary of the results

The limit problems for the evolution equations (2.20) when the interface thickness δ vanishes, as seen in sections 3.1-3.4, are all of the generic form

$$\begin{cases} \dfrac{\partial c}{\partial t} = D_l \triangle c, & \text{in} \quad \Omega_l, & (A) \\ \dfrac{\partial c}{\partial t} = D_s \triangle c, & \text{in} \quad \Omega_s, & (B) \\ -v_n \, [c]_l^s = \left[D \, \dfrac{\partial c}{\partial n} \right]_l^s, & \text{on} \quad \Gamma & (C) \\ [f_c]_l^s = 0, & \text{on} \quad \Gamma & (D) \\ [f - f_c c]_l^s = \mathcal{F}(v_n, \kappa), & \text{on} \quad \Gamma & (E) \end{cases} \tag{3.50}$$

In all of these limits, pure liquid (A) and pure solid (B) regions with classical diffusion coexist, separed by sharp interfaces that evolve ensuring the conservation of matter (C). Besides, the values of concentration at the interface can be obtained through a "parallel tangent construction" ((D) and (E)), using solid and liquid free energy densities, and dependent either on the local interface velocity, the local interface curvature, both or none, through the generic linear function $\mathcal{F}(v_n, \kappa)$. This function is dependent on the type of limit :

section	σ_A, σ_B	$\frac{\sigma_A}{T_m^A} - \frac{\sigma_B}{T_m^B}$	M	$\mathcal{F}$
3.1	$O(\delta)$	$O(\delta)$	$O(1)$	0
3.2	$O(\delta)$	$O(\delta)$	$O(\delta)$	$\propto \quad v_n$
3.3	$O(1)$	$O(\delta)$	$O(1)$	$\propto \quad \kappa + \frac{v_n}{M}$
3.4	$O(1)$	$O(\delta)$	$O(\frac{1}{\delta})$	$\propto \quad \kappa$

(3.51)

For the asymptotic limits presented on sections 3.3 and 3.4, all the steps of the asymptotic analysis and all the results depend of the choice of a function p only through its regularity (it should be at least C^1) and through its values at $\phi = 0$ and $\phi = 1$. The constraints (2.6) are therefore sufficient to get the proper limits. The extra constraints (2.7), while necessary to have a thermodynamically consistent mesoscopic model, are not necessary to get these limits. Therefore, instead of the function (2.8), we could simply define p as

$$p(\phi) = \phi \tag{3.52}$$

and still get the same limits.

However, to get the low interface thickness at low surface tensions asymptotic limits presented on sections 3.1 and 3.2, the extra constraints (2.7) on function p are also required.

4 Conclusion

We have obtained four different formal asymptotic limits for a thermodynamically consistent phase-field model based on Warren and Boettinger. The knowledge of these limits can guide us to adjust the less intuitive model parameters in order to reproduce one of four particular physical situations, where the limit concentrations at the solid-liquid interface either take equilibrium values, or are dependent on either the local interface velocity, the local interface curvature, or both. Also, the formal asymptotic limits let us compare two drastically different kinds of models that describe the same physical phenomena : phase-field and Stefan-like models, in the case of the purely solutal binary alloy solidification process.

We are currently working on the numerical analysis [8] and simulation of both kinds of models. We expect to be able to compare numerical results in the future, in order to establish which of the models is better adapted to the numerical simulation of a given physical situation.

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