



Multiscale Problems in
Solidification Processes

Christof Eck, Harald Garcke and Björn Stinner

Preprint Nr. 08/2006

Multiscale Problems in Solidification Processes

Christof Eck¹, Harald Garcke², and Björn Stinner²

¹ Institute for Applied Mathematics, University Erlangen-Nürnberg, Martensstr. 3,
91058 Erlangen

`eck@am.uni-erlangen.de`

² NWF I - Mathematik, University of Regensburg, 93040 Regensburg

`harald.garcke@mathematik.uni-regensburg.de`,

`bjorn.stinner@mathematik.uni-regensburg.de`

Summary. Our objective is to describe solidification phenomena in alloy systems. In the classical approach, balance equations in the phases are coupled to conditions on the phase boundaries which are modelled as moving hypersurfaces. The Gibbs-Thomson condition ensures that the evolution is consistent with thermodynamics. We present a derivation of that condition by defining the motion via a localized gradient flow of the entropy. Another general framework for modelling solidification of alloys with multiple phases and components is based on the phase field approach. The phase boundary motion is then given by a system of Allen-Cahn type equations for order parameters. In the sharp interface limit, i.e., if the smallest length scale δ related to the thickness of the diffuse phase boundaries converges to zero, a model with moving boundaries is recovered. In the case of two phases it can even be shown that the approximation of the sharp interface model by the phase field model is of second order in δ . Nowadays it is not possible to simulate the microstructure evolution in a whole workpiece. We present a two-scale model derived by homogenization methods including a mathematical justification by an estimate of the model error.

1 Introduction

Solidification of alloys based on iron, aluminum, copper, zinc, nickel, and other materials which are of importance in industrial applications involves the occurrence of structures on an intermediate length scale of some μm between the atomic scale of the crystal lattice and the typical size of the workpiece. This so-called microstructure consists of regions (in the following labelled phases) differing in the crystalline structure, in the composition or only in the orientation of the crystal lattice, and it is responsible for a broad range of material properties and, hence, for the quality and durability of the material.

Being a result of the solidification process the microstructure is not in thermodynamic equilibrium. Its formation is classically modelled using moving hypersurfaces for the phase boundaries. The Gibbs-Thomson condition couples the form and the motion of the interface to its surface energy and to the local thermodynamic potentials of the adjacent phases. In addition, balance equations for the internal energy and the concentrations of the components have to be taken into account. This leads to diffusion equations in the phases and jump conditions on the moving phase boundaries.

In the last years, the phase field approach has emerged as a powerful tool to simulate microstructure formation. Phase field variables are introduced standing for the presence of related phases. Instead of jumping across the phase boundaries, the phase field variables and all the thermodynamic quantities change smoothly but rapidly within a narrow transition layer. It scales with a new length scale δ smaller

than the typical scale of the microstructure to be described. This leads to the notion of a diffuse interface in contrast to the sharp interface model with the moving phase boundaries. The Gibbs-Thomson condition is replaced by a diffuse version which can be viewed as a gradient flow of an appropriate Ginzburg-Landau energy. The balance equations for the conserved quantities are reformulated in terms of the new variables where the jump conditions enter in a natural way. As a main advantage, numerically simulating microstructure formation is restricted to solving a system of parabolic differential equations, and explicit tracking of the phase boundaries in the sharp interface model is avoided.

The limit of vanishing diffuse interface thickness, i.e., the limit as $\delta \searrow 0$, is of particular interest. The first question is whether a related sharp interface model is obtained in the following sense: given solutions to the diffuse interface model for every δ , is there a limit of the solutions, and which equations do the limiting fields fulfill? This question is related to the calibrations problem when quantitatively investigating a certain alloy. Usually, material parameters such as latent heats, surface tensions, and several mobility and diffusion coefficients entering the sharp interface model are measured in experiments, and the question is how they should enter the diffuse interface model.

Problems involving multiple length scales not only result from the modelling approach but are also inherent in the physical problems itself. Diffusion of the temperature is much faster than mass diffusion. Because of the boundary conditions – solidifying workpieces are usually cooled from outside – and the release of latent heat the temperature field is expected to suffer changes over a scale proportional to the size of the the workpiece. On the other hand, the concentrations of the components should exhibit strong gradients only near the solidification front. The available numerical techniques and computational power only allow for the simulation of small domains in acceptable computation time, the direct computation of the microstructure of a whole workpiece is not feasible. For the latter purpose, macroscopic models involving heuristic assumptions on the distribution of the solidified parts and the released latent heat have been in use. Newer mathematical methods are based on a two-scale approach and allow for effective, homogenized equations for the temperature distribution but also for taking the microstructure evolution into account.

The structure of the present article is as follows. The first section is dedicated to models for alloy solidification. First, the governing equations from the classical approach for modelling alloy solidification are presented. In particular, the Gibbs-Thomson condition is derived by locally varying the entropy. After, the phase field approach is presented. In the second section, the relation between the sharp and the diffuse approaches is elucidated. Comments on the calibration problem are given including appropriate potentials for the phase field model with good calibration properties. Exemplary, a model for a binary alloy is derived. In the third section, a mathematically rigorous approach to the derivation of homogenized models for phase transitions with equiaxed dendritic microstructure is given. Asymptotic expansions are used to derive a macroscopic heat equation coupled to microscopic cell problems for the dendritic growth. A mathematical justification is carried out, i.e., an estimate is established comparing the solution to the two-scale model with that to the original model.

Acknowledgments. This work has been supported by the German Research Foundation (DFG) through the Priority Program 1095 “Analysis, Modeling and Simulation of Multiscale Problems”. We thank Britta Nestler and Frank Wendler for the inspiring discussions, mainly emerging from numerical simulations based on the presented phase field model.

2 Models for alloy solidification

The production of certain microstructural morphologies is often achieved by imposing appropriate conditions before and during the solidification process. In order to get a deeper understanding of the process, the scientific challenge is to describe the microstructure formation with a mathematical model where the imposed conditions enter the equations governing the evolution as initial and boundary values or as additional forces and parameters.

A framework for continuum modelling of alloy solidification can be derived from thermodynamic principles for irreversible processes (cf. [Mu01]). Balancing the conserved quantities energy and mass respectively concentrations of the components yields diffusion equations in the bulk phases as well as continuity and jump conditions on the moving phase boundaries. A coupling of the phase boundary motion to the thermodynamic quantities of the adjacent phases, the Gibbs-Thomson condition, is derived by localizing an appropriate gradient flow of the entropy. The balance equations and the Gibbs-Thomson condition, together with certain angle conditions in junctions where several phases meet and which are due to local force balance, enable to show that the local entropy production is non-negative and to prove an entropy inequality.

An entropy functional involving bulk and surface contributions plays a central role also in non-equilibrium thermodynamics. In the phase field approach, the interfacial entropy (or energy) is modelled with the help of a Ginzburg-Landau type functional. Evolution equations for the phase fields can then be derived as gradient flows (see [FP90]) or within the theory of rational thermodynamics (see [AP96, Ha06]). A small length scale is involved which is related to the thickness of the interfacial layers.

We proceed as follows. First, the classical approach to model alloy solidification, namely with moving phase boundaries, is presented. In the second subsection, the Gibbs-Thomson condition is derived. After, the phase field variables are defined, and the phase field approach is presented. As an example, a model for non-isothermal solidification of a binary alloy involving two phases is derived. Finally we briefly comment on the solvability of the differential equations of the phase field model.

For general informations on the theory and models of phase transitions we refer to the books [BS96, Vi96]. In this section, partial derivatives sometimes are denoted by subscripts after a comma. For example, $s_{,e}$ is the partial derivative of the function $s = s(e, \hat{c})$ with respect to the variable e .

2.1 Classical approach with moving hypersurfaces

An alloy of $N \in \mathbb{N}$ components occupying an open domain $\Omega \in \mathbb{R}^d$, $d = 1, 2, 3$, during some time interval $I_{\mathcal{T}} = (0, T)$ is considered. Changes in volume or pressure are neglected (cf. [Ha94], Section 5.1). Moreover, the mass density is assumed to be constant (only concentrations will be considered). The only transport mechanism is diffusion, and there are no forces present leading to flows or deformations. Such effects can strongly influence the growing structures (cf. [Da01]). The applicability of the model presented in the following is therefore restricted to cases where such effects can be neglected.

Let $M \in \mathbb{N}$ be the number of possible phases. The domain Ω is decomposed into sub-domains $\Omega_1(t), \dots, \Omega_M(t)$, $t \in I_{\mathcal{T}}$, which are called phases. The phase boundaries $\Gamma_{\alpha\beta}(t) := \overline{\Omega_{\alpha}(t)} \cap \overline{\Omega_{\beta}(t)}$, $1 \leq \alpha \neq \beta \leq M$, are supposed to be piecewise smooth evolving points, curves, or hypersurfaces, depending on the dimension (cf. Def. A.1 in the Appendix). The unit normal on $\Gamma_{\alpha\beta}$ pointing into phase Ω_{β} is denoted by $\nu_{\alpha\beta}$. If $d \geq 2$ the intersections of the curves or hypersurfaces are denoted by $T_{\alpha\beta\delta}(t) := \overline{\Omega_{\alpha}(t)} \cap \overline{\Omega_{\beta}(t)} \cap \overline{\Omega_{\delta}(t)}$ for pairwise different $\alpha, \beta, \delta \in \{1, \dots, M\}$, and

the points where the phase boundaries hits the external boundary by $T_{\alpha\beta,ext}(t) := \overline{\Omega_\alpha(t)} \cap \overline{\Omega_\beta(t)} \cap \partial\Omega$. If $d = 2$ then $T_{\alpha\beta\delta}$ is a set of triple junctions, i.e., piecewise smooth evolving points. If $d = 3$ triple lines can appear which are piecewise smooth evolving curves.

During evolution, it may happen that one of the phases vanishes, namely if the adjoining phase boundaries coalesce. It is also possible that a piece of a phase boundary vanishes so that one of the sets $T_{\alpha\beta\delta}$ includes a quadruple point or line. Typically, the latter configuration is not in mechanical equilibrium and will instantaneously split up forming new phase boundaries (see [GNS99, BGN06]). It is supposed that such singularities only occur at finitely many times $t \in I_{\mathcal{T}}$ during the evolution. This is why only piecewise smooth evolution is assumed. The evolution equations stated in the following are only valid for times at which no such singularity occurs.

Before proceeding let us introduce some notation. For $K \in \mathbb{N}$ define the sets

$$\mathbf{H}\Sigma^K := \left\{ v \in \mathbb{R}^K : \sum_{i=1}^K v_i = 1 \right\}, \quad \Sigma^K := \left\{ v \in \mathbf{H}\Sigma^K : v_i \geq 0 \quad \forall i \right\}. \quad (2.1)$$

The tangent space on $\mathbf{H}\Sigma^K$ can be naturally identified in every point $v \in \mathbf{H}\Sigma^K$ with the subspace

$$\mathbf{T}_v \mathbf{H}\Sigma^K \cong \mathbf{T}\Sigma^K := \left\{ w \in \mathbb{R}^K : \sum_{i=1}^K w_i = 0 \right\}. \quad (2.2)$$

The map $\mathcal{P}^K : \mathbb{R}^K \rightarrow \mathbf{T}\Sigma^K$ is the orthogonal projection given by

$$\mathcal{P}^K w = \left(w_k - \frac{1}{K} \sum_{l=1}^K w_l \right)_{k=1}^K = \left(\text{Id}_K - \frac{1}{K} \mathbf{1}_K \otimes \mathbf{1}_K \right) w$$

where $\mathbf{1}_K = (1, \dots, 1) \in \mathbb{R}^K$ and Id_K is the identity on \mathbb{R}^K .

The following bulk fields are considered in the phases Ω_α , $1 \leq \alpha \leq M$:

- c_i^α : concentration of component i , $1 \leq i \leq N$,
- $c_0^\alpha := e^\alpha$: internal energy density,
- f^α : (Helmholtz) free energy density,
- μ_i^α : chemical potential of component i , $1 \leq i \leq N$,
- T^α : temperature,
- s^α : entropy density,
- $u_0^\alpha := \frac{-1}{T^\alpha}$: inverse negative temperature,
- $u_i^\alpha := \frac{\mu_i^\alpha}{T^\alpha}$: reduced chemical potential difference of component i , $1 \leq i \leq N$.

On the interfaces $\Gamma_{\alpha\beta}$, $1 \leq \alpha \neq \beta \leq M$, there are the following surface fields:

- $\nu_{\alpha\beta}$: unit normal pointing into Ω_β ,
- $\sigma_{\alpha\beta}(\nu_{\alpha\beta})$: surface tension,
- $\gamma_{\alpha\beta}(\nu_{\alpha\beta})$: capillarity coefficient,
- $m_{\alpha\beta}(\nu_{\alpha\beta})$: mobility coefficient,
- $v_{\alpha\beta}$: normal velocity towards $\nu_{\alpha\beta}$,
- $\kappa_{\alpha\beta}$: curvature.

The concentrations fulfill the constraint $\hat{c}^\alpha = (c_1^\alpha, \dots, c_N^\alpha) \in \Sigma^N$. Following [Mu01], Section 11.2, the evolution in the phases is governed by balance equations for the conserved quantities, i.e.,

$$\partial_t c_i^\alpha = -\nabla \cdot J_i^\alpha = \nabla \cdot \left(\sum_{j=0}^N L_{ij}^\alpha \nabla u_j^\alpha \right), \quad 0 \leq i \leq N. \quad (2.3)$$

Let us briefly comment on the fluxes J_i^α . In thermodynamics of irreversible processes the relations between the fields are based on the principle of local thermodynamic equilibrium. In the present situation the entropy density s^α is a function of the conserved quantities. Its derivatives are the inverse temperature and the chemical potential difference reduced by the temperature, i.e.,

$$s^\alpha = s^\alpha(e^\alpha, \hat{c}^\alpha) \quad \text{and} \quad ds^\alpha = \frac{1}{T^\alpha} de^\alpha + \frac{-\bar{\mu}^\alpha}{T^\alpha} \cdot d\hat{c}^\alpha = -u^\alpha \cdot c^\alpha.$$

In the above equation the identity $\bar{\mu}^\alpha = \mathcal{P}^N \mu^\alpha$ was used, where $\mu^\alpha = (\mu_1^\alpha, \dots, \mu_N^\alpha)^T$. The fluxes are postulated to be linear combinations of the thermodynamic forces ∇u_j^α , $0 \leq j \leq N$, with coefficients L_{ij}^α which may depend on the thermodynamic potentials u_j^α or on the conserved quantities c_i^α . This phenomenological theory was already introduced in [On31]. It is assumed that the matrix $L = (L_{ij}^\alpha)_{i,j=0}^N$ is positive semi-definite. To fulfill the constraint $\hat{c}^\alpha \in \Sigma^N$ it is required that $\sum_{i=1}^N L_{ij}^\alpha = 0$, $1 \leq j \leq N$, which also means that $\sum_{i=1}^N J_i^\alpha = 0$.

Onsager's law of reciprocity states the symmetry of L and can be proven and experimentally observed if the fluxes and forces are independent (cf. [KY87], Section 3.8). The above fluxes are not independent. But even in the present case Onsager's law can be shown to hold by a certain choice of the coefficients (see [KY87], Section 4.2, and the reference therein; there the calculation is performed for the isothermal case, but another additional independent force can be taken into account without any problem). We remark that, considering $J_i - J_N$, the definition of the fluxes as above is equivalent to the definition in [Mu01], Section 11.2.

On the phase boundaries $\Gamma_{\alpha\beta}$ the continuity conditions

$$[u_i]_\alpha^\beta = 0, \quad 0 \leq i \leq N, \quad (2.4)$$

have to be satisfied. Mass and energy balance imply furthermore the jump conditions

$$[c_i]_\alpha^\beta v_{\alpha\beta} = [J_i]_\alpha^\beta \cdot \nu_{\alpha\beta}, \quad 0 \leq i \leq N. \quad (2.5)$$

Here, $[\cdot]_\alpha^\beta$ denotes the jump of the quantity in brackets across $\Gamma_{\alpha\beta}$, e.g., $[e]_\alpha^\beta = e^\beta - e^\alpha$.

The matrix of surface tensions $(\sigma_{\alpha\beta}(\nu))_{\alpha,\beta}$ is symmetric for every unit vector ν (the diagonal entries are not of interest and may be set to zero). The relation between surface tension and capillarity coefficient is given by

$$\gamma_{\alpha\beta}(\nu_{\alpha\beta}) = \frac{\sigma_{\alpha\beta}(\nu_{\alpha\beta})}{T_{ref}}$$

with some reference temperature T_{ref} . The surface tensions are one-homogeneous in their argument while the mobility coefficients $m_{\alpha\beta}(\nu_{\alpha\beta})$ are zero-homogeneous in their argument.

The evolution of the phase boundaries is coupled to the thermodynamic fields by the Gibbs-Thomson condition

$$m_{\alpha\beta}(\nu_{\alpha\beta}) v_{\alpha\beta} = -\nabla_\Gamma \cdot D\gamma_{\alpha\beta}(\nu_{\alpha\beta}) + \left[-u_0 f(T, \hat{c}) + \sum_{i=1}^N u_i c_i \right]_\alpha^\beta \quad (2.6)$$

which is derived in the following subsection. By $\nabla_\Gamma \cdot$ the surface divergence is denoted. In the case of an isotropic surface entropy, i.e., $\gamma_{\alpha\beta}(\nu) = \bar{\gamma}_{\alpha\beta}|\nu|$ with some constant $\bar{\gamma}_{\alpha\beta}$ independent of the direction, there is the identity $-\nabla_\Gamma \cdot D\gamma_{\alpha\beta}(\nu) = \bar{\gamma}_{\alpha\beta}\kappa_{\alpha\beta}$ where $\kappa_{\alpha\beta}$ is the mean curvature.

To avoid wetting effects (cf. [Ha94], Section 3.4, for a discussion and references) the surface tensions are assumed to fulfill the constraints

$$\sigma_{\alpha\beta} + \sigma_{\beta\delta} > \sigma_{\alpha\delta}. \quad (2.7)$$

Capillary forces acting on $\Gamma_{\alpha\beta}$ are related to the vectors (cf. [CH74, WM97])

$$\xi_{\alpha\beta}(\nu_{\alpha\beta}) := D\sigma_{\alpha\beta}(\nu_{\alpha\beta}) = \sigma_{\alpha\beta}(\nu_{\alpha\beta})\nu_{\alpha\beta} + D_{S^{d-1}}\sigma_{\alpha\beta}(\nu_{\alpha\beta}) \quad (2.8)$$

where $D_{S^{d-1}}$ is the surface gradient on the sphere S^{d-1} . The identity $D = D_{S^{d-1}} + \nu_{\alpha\beta}(\nu_{\alpha\beta} \cdot D)$ was used as well as the fact that $\sigma_{\alpha\beta}$ is one-homogeneous implying $D\sigma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \nu_{\alpha\beta} = \sigma_{\alpha\beta}(\nu_{\alpha\beta})$.

In points x belonging to $T_{\alpha\beta\delta}$ forces are in equilibrium. In the three-dimensional case $T_{\alpha\beta\delta}$ consists of triple lines that can be oriented with a unit tangent vector $\tau_{\alpha\beta\delta}(x)$. If the whole space is cut with the plane orthogonal to $\tau_{\alpha\beta\delta}(x)$ through x then the picture in Fig. 2.1 is obtained. Due to the surface tension $\Gamma_{\alpha\beta}$ exerts a force on x which is given by $\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \times \tau_{\alpha\beta\delta}(x)$, whence equilibrium of forces means that

$$0 = \sum_{(i,j) \in \mathcal{A}} \xi_{ij}(\nu_{ij}(x)) \times \tau_{\alpha\beta\delta}(x) \quad (2.9)$$

where $\mathcal{A} := \{(\alpha, \beta), (\beta, \delta), (\delta, \alpha)\}$. A short calculation shows that in the situation of Fig. 2.1

$$\xi_{\alpha\beta}(\nu_{\alpha\beta}) \times \tau_{\alpha\beta\delta} = (\nabla\sigma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \tau_{\alpha\beta})(-\nu_{\alpha\beta}) + \sigma_{\alpha\beta}(\nu_{\alpha\beta})\tau_{\alpha\beta}.$$

Similarly, if $x \in T_{\alpha\beta,ext}$ there is a unit tangent vector $\tau_{\alpha\beta,ext}(x)$, and the force acting on x is given by $\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \times \tau_{\alpha\beta,ext}(x)$. Force balance in x implies that this force is not tangential to $\partial\Omega$. Since it is already orthogonal to $\tau_{\alpha\beta,ext}(x)$ by definition this is true if and only if

$$\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \cdot \nu_{ext}(x) = 0. \quad (2.10)$$

In particular, angle conditions in $T_{\alpha\beta\delta}$ and $T_{\alpha\beta,ext}$ are due to the above force balance conditions (2.9) and (2.10).

To obtain a well-posed problem the governing equations (2.3)–(2.6), (2.9), and (2.10) must be provided with initial conditions for the fields and the moving boundaries and boundary conditions. If not otherwise stated, the isolated case

$$J_i^\alpha \cdot \nu_{ext} = 0 \text{ on } \partial\Omega, \quad 0 \leq i \leq N, \quad 1 \leq \alpha \leq M, \quad (2.11)$$

is considered.

The total entropy of the system being given by

$$S(t) = \sum_{\alpha=1}^M \int_{\Omega_\alpha(t)} s^\alpha(c^\alpha) d\mathcal{L}^d - \sum_{\alpha < \beta, \alpha, \beta=1}^M \int_{\Gamma_{\alpha\beta}(t)} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) d\mathcal{H}^{d-1} \quad (2.12)$$

it can be shown that the evolution equations (2.3)–(2.11) imply non-negative entropy production:

Theorem 2.1. *The entropy (2.12) satisfies*

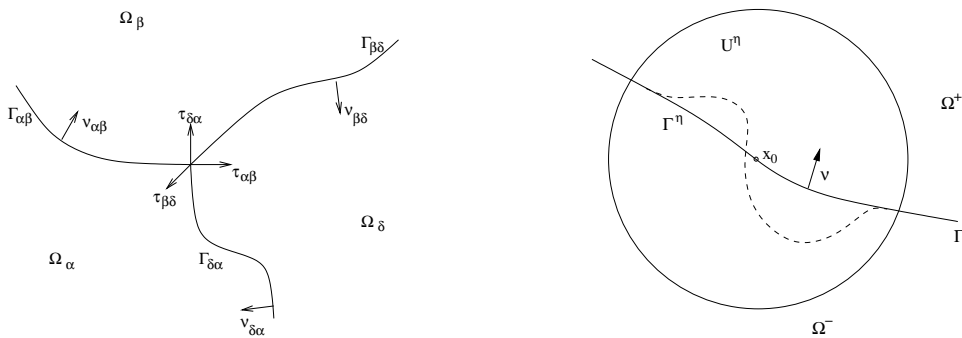


Fig. 2.1. On the left: triple junction x with orientations of the forming curves; such a picture is also obtained in the 3D-case by cutting the space with the plane spanned by $\nu_{\alpha\beta}(x)$, $\tau_{\alpha\beta}(x)$. On the right: local situation around a point x_0 on a phase boundary for the derivation of the Gibbs-Thomson condition; a local deformation is indicated by the dashed line.

$$\begin{aligned} \frac{d}{dt}S(t) &= \sum_{1 \leq \alpha \leq M} \int_{\Omega_\alpha(t)} \sum_{i,j=0}^N \nabla u_i^\alpha \cdot L_{ij}^\alpha \nabla u_j^\alpha d\mathcal{L}^d \\ &+ \sum_{1 \leq \alpha < \beta \leq M} \int_{\Gamma_{\alpha\beta}(t)} m_{\alpha\beta} (v_{\alpha\beta})^2 d\mathcal{H}^{d-1}. \end{aligned}$$

The proof can be found in the Appendix of [GNS04].

2.2 Derivation of the Gibbs-Thomson condition

In this section a physical motivation of the Gibbs-Thomson condition (2.6) based on thermodynamic principles is given. The idea is to define the motion of the phase boundaries as a gradient flow of the entropy. On the set of admissible surfaces the tangent space of a surface is defined by the smooth real valued functions f on the surface supplied with a weighted L^2 -product. A variation of the surface entropy in the direction f is then the rate of change of the entropy when deforming the surface towards its normal with a strength given by f . Such a deformation of a phase boundary usually changes the volumes of the adjacent phases. Thanks to this fact the bulk fields can enter the Gibbs-Thomson condition. But changes in the conserved quantities must be counterbalanced. Since (2.6) is a local motion law, only local deformations of an η -ball around a point x_0 on a phase boundary are considered. Conservation of energy and mass is ensured by taking a non-local Lagrange multiplier into account. In the limit as $\eta \rightarrow 0$ all terms become local after appropriate scaling so that the desired equation is obtained.

For keeping the presentation simple we do not consider the general situation as in the previous subsection but the one depicted in Fig. 2.1. There, Γ is a smooth compactly embedded $d-1$ -dimensional hypersurface separating two phases Ω^+ and Ω^- with unit normal ν pointing into Ω^+ . Such a surface respectively configuration is said to be admissible.

Definition 2.2. Let G be the set of the admissible surfaces. The tangent space is defined by $T_\Gamma G := C^1(\Gamma, \mathbb{R})$. A Riemannian structure on $T_\Gamma G$ is defined by the weighted L^2 product

$$(v, \xi)_\Gamma := \int_\Gamma m(\nu) v \xi d\mathcal{H}^{d-1} \quad \forall v, \xi \in T_\Gamma G$$

where $m(\nu)$ is a non-negative mobility function.

The bulk fields for energy density and concentrations, here denoted by c^0 , are allowed to suffer jump discontinuities across Γ , but the potentials $s, c = -u$ are supposed to be Lipschitz continuous. Within the phases Ω^+ and Ω^- all fields are smooth.

Variations of the entropy are based on local deformations of the domain. Let $x_0 \in \Gamma$ and consider the family of open balls $\{U^\eta\}_{\eta>0}$ centered in x_0 with radius η . Given arbitrary functions $\xi^\eta \in C_0^1(U^\eta)$ it can be shown that there are vector fields

$$\xi^\eta \in C_0^1(U^\eta, \mathbb{R}^d) \text{ with } \xi^\eta = \xi^\eta \nu \text{ on } \Gamma^\eta := \Gamma \cap U^\eta. \quad (2.13)$$

The solution $\theta^\eta : U^\eta \rightarrow U^\eta$ to

$$\theta^\eta(0, y) = y, \quad \theta_{,\delta}^\eta(\delta, y) = \xi^\eta(\theta^\eta(-\delta, y)) \text{ for } \delta \in [-\delta_0^\eta, \delta_0^\eta],$$

yields a local deformation of U^η . The restriction of δ is such that $\Gamma^\eta := U^\eta \cap \Gamma$ remains a smooth surface imbedded into U^η , i.e., the sets

$$\Gamma_\delta^\eta = \{\theta^\eta(\delta, x) : x \in \Gamma^\eta\}, \quad \delta \in [-\delta_0^\eta, \delta_0^\eta],$$

define an evolving $(d-1)$ -dimensional surface in U^η in the sense of Def. A.1.

A short calculation yields the identity

$$\frac{d}{d\delta} \det \theta_{,\delta}^\eta(\delta, x) = \nabla \cdot \xi^\eta(\theta^\eta(\delta, x)) \det \theta_{,\delta}^\eta(\delta, x). \quad (2.14)$$

The functional mapping L^1 -functions on U^η onto their mean value is denoted by \mathcal{M}^η , i.e.,

$$\mathcal{M}^\eta : L^1(U^\eta) \rightarrow \mathbb{R}^m, \quad \mathcal{M}^\eta(f) := \frac{1}{|U^\eta|} \int_{U^\eta} f(x) dx = \int_{U^\eta} f(x) dx$$

where $|U^\eta| = \mathcal{L}^d(U^\eta)$ with the d -dimensional Lebesgue measure \mathcal{L}^d .

Definition 2.3. *Under the local deformation θ^η of U^η the densities of the conserved quantities are*

$$c(\delta, y) := c^0(\theta^\eta(-\delta, y)) - \mathcal{M}^\eta(c^0(\theta^\eta(-\delta, \cdot)) - c^0(\cdot)), \quad y \in U^\eta. \quad (2.15)$$

The local entropy consists of the bulk part

$$S_B^\eta(\delta) := \int_{U^\eta} s(c(\delta, y)) dy \quad (2.16)$$

and the surface part

$$S_S^\eta(\delta) := - \int_{\Gamma_\delta^\eta} \gamma(\nu(\delta)) d\mathcal{H}^{d-1}. \quad (2.17)$$

The Lagrange multiplier $\mathcal{M}^\eta(c^0(\theta^\eta(-\delta, \cdot)) - c^0(\cdot))$ in (2.15) ensures that energy and mass are conserved under the deformation.

Lemma 2.4. *The derivative of the bulk entropy with respect to δ in $\delta = 0$ is*

$$\frac{d}{d\delta} S_B^\eta(0) = \int_{U^\eta} \left(s(c^0) + \mathcal{M}^\eta(u) \cdot c^0 \right) \nabla \cdot \xi^\eta dx.$$

Proof. By definition (2.15), the bulk entropy (2.16) is

$$\begin{aligned} & \int_{U^\eta} s\left(c^0(\theta^\eta(-\delta, y)) - \mathcal{M}^\eta(c^0(\theta^\eta(-\delta, \cdot)) - c^0)\right) dy \\ &= \int_{U^\eta} s\left(c^0(x) - \mathcal{M}^\eta(c^0(\theta^\eta(-\delta, \cdot)) - c^0)\right) \det \theta_{,\delta}^\eta(\delta, x) dx \end{aligned}$$

where the transformation $y = \theta^\eta(\delta, x)$ was used. The equation (2.14) yields together with $\theta^\eta(0, x) = x$ and $\det(\theta_{,x}^\eta(0, x)) = \det \text{Id} = 1$

$$\begin{aligned} \frac{d}{d\delta} \int_{U^\eta} c^0(\theta^\eta(-(\cdot), z)) dz \Big|_{\delta=0} &= \frac{d}{d\delta} \int_{U^\eta} c^0(x) \det \theta_{,x}^\eta(\delta, x) dx \Big|_{\delta=0} \\ &= \int_{U^\eta} c^0(x) \nabla \cdot \boldsymbol{\xi}^\eta(x) dx. \end{aligned}$$

With $s_{,c} = -u$ the desired identity can be shown as follows:

$$\begin{aligned} \frac{d}{d\delta} S_B^\eta(0) &= \int_{U^\eta} s \left(c^0(x) - \mathcal{M}^\eta(c^0(\theta^\eta(0, \cdot)) - c^0) \right) \nabla \cdot \boldsymbol{\xi}^\eta(x) dx \\ &\quad - \int_{U^\eta} s_{,c}(c^0(x)) \cdot \frac{d}{d\delta} \frac{1}{|U^\eta|} \int_{U^\eta} c^0(\theta^\eta(-(\cdot), z)) dz \Big|_{\delta=0} dx \\ &= \int_{U^\eta} s(c^0(x)) \nabla \cdot \boldsymbol{\xi}^\eta(x) dx + \frac{1}{|U^\eta|} \int_{U^\eta} u(x) dx \cdot \int_{U^\eta} c^0(x) \nabla \cdot \boldsymbol{\xi}^\eta(x) dx \\ &= \int_{U^\eta} \left(s(c^0) + \mathcal{M}^\eta(u) \cdot c^0 \right) \nabla \cdot \boldsymbol{\xi}^\eta(x) dx. \end{aligned}$$

Lemma 2.5. *The derivative of the surface entropy with respect to δ in $\delta = 0$ is*

$$\frac{d}{d\delta} S_S^\eta(0) = - \int_{\Gamma^\eta} \nabla_\Gamma \cdot D\gamma(\nu) \xi^\eta d\mathcal{H}^{d-1}.$$

Proof. Interpreting $\{\Gamma_\delta^\eta\}_\delta$ as evolving surface, the scalar normal velocity is ξ^η and the vectorial normal velocity is $\boldsymbol{\xi}^\eta = \xi^\eta \nu$. The scalar curvature is denoted by κ_Γ . Applying Th. A.4 from the Appendix yields (observe that the boundary integrals over $\partial\Gamma^\eta$ vanish since the velocity $\boldsymbol{\xi}^\eta$ has a compact support in U^η)

$$\frac{d}{d\delta} S_S^\eta(0) = - \int_{\Gamma^\eta} (\partial^\circ \gamma(\nu) - \gamma(\nu) \boldsymbol{\xi}^\eta \cdot \boldsymbol{\kappa}_\Gamma) d\mathcal{H}^{d-1}$$

which is using (A.3), (A.2), (A.4), and the one-homogeneity of γ

$$= \int_{\Gamma^\eta} (\nabla \gamma(\nu) \cdot \nabla_\Gamma \xi^\eta + \nabla \gamma(\nu) \cdot \nu \kappa_\Gamma \xi^\eta) d\mathcal{H}^{d-1}.$$

Applying Th. A.3 to $\boldsymbol{\varphi} = \nabla \gamma(\nu) \xi^\eta$ (again the boundary integral vanishes) and again (A.2) on the last term it follows the desired identity:

$$\begin{aligned} \dots &= \int_{\Gamma^\eta} (-\nabla_\Gamma \cdot \nabla \gamma(\nu) \xi^\eta - \boldsymbol{\kappa}_\Gamma \cdot \nabla \gamma(\nu) \xi^\eta + \nabla \gamma(\nu) \cdot \boldsymbol{\kappa}_\Gamma \xi^\eta) d\mathcal{H}^{d-1} \\ &= - \int_{\Gamma^\eta} (\nabla_\Gamma \cdot \nabla \gamma(\nu) \xi^\eta) d\mathcal{H}^{d-1}. \end{aligned}$$

As stated at the beginning of this section, the goal is to define the motion as a localized version of a gradient flow. This is realized in the following definition. Let $|\Gamma^\eta| := \mathcal{H}^{d-1}(\Gamma^\eta)$.

Definition 2.6. *The motion of the phase boundary Γ is defined as follows: In each point $x_0 \in \Gamma$ the identity*

$$\lim_{\eta \rightarrow 0} \frac{1}{|\Gamma^\eta|} (v, \xi^\eta)_\Gamma = \lim_{\eta \rightarrow 0} \frac{1}{|\Gamma^\eta|} \frac{d}{d\delta} (S_B^\eta + S_S^\eta)(0) \quad (2.18)$$

holds for all families of functions $\xi^\eta \in C_0^1(U^\eta)$ where $S_B^\eta(\delta)$ and $S_S^\eta(\delta)$ are defined by (2.16) and (2.17) respectively.

Theorem 2.7. *The localized gradient flow (2.18) yields the Gibbs-Thomson condition (2.6).*

To prove the theorem the following lemma is useful:

Lemma 2.8. *Let $g \in L^\infty(U^\eta)$ with $g \in C^1(\overline{\Omega^+ \cap U^\eta})$ and $g \in C^1(\overline{\Omega^- \cap U^\eta})$, and let $z \in \mathbb{R}$ be given. There is a family of functions $\{\xi^\eta\}_{\eta>0} \subset C^1(U^\eta)$ with $\xi^\eta(x_0) = z$ for all η such that*

$$\begin{aligned} \frac{1}{|\Gamma^\eta|} \int_{U^\eta} g \nabla \cdot \xi^\eta dx &= - \int_{\Gamma^\eta} [g]_-^+ \xi^\eta d\mathcal{H}^{d-1} - \frac{1}{|\Gamma^\eta|} \int_{U^\eta} \nabla g \cdot \xi^\eta dx \\ &\rightarrow -[g(x)]_-^+ z \quad \text{as } \eta \rightarrow 0 \end{aligned}$$

where the functions ξ^η are uniformly bounded and satisfy condition (2.13). By g^+ the limit of g in $x \in \Gamma$ when approximated from the side Ω^+ is denoted. Analogously g^- is defined when approximating $x \in \Gamma$ from Ω^- , and $[g]_-^+ = g^+ - g^-$ is the difference.

Proof. The first identity follows from the divergence theorem applied to the two parts $U^\eta \cap \Omega^+$ and $U^\eta \cap \Omega^-$ of U^η using that ξ^η vanishes on the external boundary ∂U^η . For the limiting behavior consider the functions

$$\tilde{\xi}^\eta := \begin{cases} z & \text{on } U^{\eta-\eta^2}, \\ 0 & \text{on } U^\eta \setminus U^{\eta-\eta^2}. \end{cases}$$

Let ζ be a smooth function with compact support on the unit ball $U^1(0) \subset \mathbb{R}^d$ such that $\int_{\mathbb{R}^d} \zeta = 1$ and define ξ^η by the convolution of $\tilde{\xi}^\eta$ with $\eta^{-3d}\zeta(\cdot/\eta^3)$, i.e.,

$$\xi^\eta(x) := (\eta^{-3d}\zeta(\frac{\cdot}{\eta^3}) * \tilde{\xi}^\eta)(x).$$

Then for η small enough $\xi^\eta = z$ on $\Gamma \cap U^{\eta-2\eta^2} =: \tilde{\Gamma}^\eta$.

Observe that thanks to the smoothness of Γ the \mathcal{H}^{d-1} -measure of $\Gamma^\eta \setminus \tilde{\Gamma}^\eta$ is of order η^d whence $|\Gamma^\eta \setminus \tilde{\Gamma}^\eta|/|\Gamma^\eta| = O(\eta)$ as $\eta \rightarrow 0$. By assumption, the function $f = [g]_-^+$ is Lipschitz continuous on Γ . Thanks to the special choice of ξ^η it can easily be derived that

$$\int_{\Gamma^\eta} f \xi^\eta d\mathcal{H}^{d-1} = \int_{\Gamma^\eta} f z d\mathcal{H}^{d-1} + \int_{\Gamma^\eta} f(\xi^\eta - z) d\mathcal{H}^{d-1} \rightarrow f(x_0)z$$

as $\eta \rightarrow 0$. As moreover the \mathcal{L}^d -measure of U^η is of order η^d but the \mathcal{H}^{d-1} -measure of Γ^η is of order η^{d-1} and since $|\nabla g \cdot \xi^\eta|$ is bounded in U^η the assertion follows.

Proof. (Th. 2.7) First, observe that $\mathcal{M}^\eta(u) \rightarrow u(x_0)$ as $\eta \rightarrow 0$ since u is Lipschitz continuous. Choose some arbitrary $z \in \mathbb{R}$ and a family of functions $\{\xi^\eta\}_{\eta>0}$ as in Lemma 2.8 and let $\{\xi^\eta\}_{\eta>0}$ be the corresponding vector fields. Then

$$\begin{aligned} \frac{1}{|\Gamma^\eta|} \int_{U^\eta} \mathcal{M}^\eta(u) \cdot c^0(x) \nabla \cdot \xi^\eta(x) dx &= \mathcal{M}^\eta(u) \cdot \frac{1}{|\Gamma^\eta|} \int_{U^\eta} c^0(x) \nabla \cdot \xi^\eta(x) dx \\ &\rightarrow u(x_0) \cdot [c^0(x_0)]_-^+ z = [u \cdot c^0]_-^+(x_0)z. \end{aligned}$$

The limit of the right hand side of (2.18) is, using the Lemmata 2.4, 2.5, and 2.8,

$$\begin{aligned} &\frac{1}{|\Gamma^\eta|} \frac{d}{d\delta} (S_B^\eta + S_S^\eta)(0) \\ &= \frac{1}{|\Gamma^\eta|} \int_{U^\eta} (s(c^0) + \mathcal{M}^\eta(u) \cdot c^0) \nabla \cdot \xi^\eta dx - \int_{\Gamma^\eta} \nabla_\Gamma \cdot \nabla \gamma(\nu) d\mathcal{H}^{d-1} \\ &\rightarrow \left(-[s(c^0)]_-^+(x_0) + \left[\frac{e^0}{T}\right]_-^+(x_0) + \left[\frac{-\bar{\mu} \cdot \hat{c}^0}{T}\right]_-^+(x_0) - \nabla_\Gamma \cdot \nabla \gamma(\nu(x_0)) \right) z \\ &= \left(\left[\frac{f(T, \hat{c}^0) - \bar{\mu} \cdot \hat{c}^0}{T}\right]_-^+(x_0) - \nabla_\Gamma \cdot \nabla \gamma(\nu(x_0)) \right) z. \end{aligned}$$

For the last two lines the identities $c^0 = (e^0, \hat{c}^0)$, $u_0 = -\frac{1}{T}$, $(u_1, \dots, u_N)^T = \frac{\bar{\mu}}{T}$, and the thermodynamic relation $e = f + sT$ were applied. The left hand side of (2.18) yields in the limit as $\eta \rightarrow 0$

$$\frac{1}{|\Gamma^\eta|} (v, \xi^\eta)_\Gamma = \int_{\Gamma^\eta} m(\nu) v \xi^\eta d\mathcal{H}^{d-1} \rightarrow m(\nu(x_0)) v(x_0) z.$$

Since $z \in \mathbb{R}$ can be chosen arbitrarily the condition (2.6) follows in x_0 .

2.3 Phase field approach

In phase field models, the individual phases are distinguished by phase field variables. In different phases they attain different values, and interfaces are modelled by a diffuse interface layer, i.e., the phase fields and all other thermodynamic quantities change smoothly on a thin transition layer (the diffuse interface) instead of suffering discontinuous transitions.

Let $\phi = (\phi_\alpha)_{\alpha=1}^M$ where each variable ϕ_α describes the local fraction of a corresponding phase α . The vector of these phase field variables is required to fulfill the constraint $\phi \in \Sigma^M$. The interfacial contribution in (2.12) is replaced by a Ginzburg-Landau type functional (cf. [LG50]) of the form

$$- \int_{\Omega} \left(\delta a(\phi, \nabla \phi) + \frac{1}{\delta} w(\phi) \right) dx. \quad (2.19)$$

The function $a : \Sigma^M \times (\mathbb{T}\Sigma^M)^d \rightarrow \mathbb{R}$ is a gradient energy density which is assumed to be smooth and to satisfy

$$a(\phi, X) \geq 0 \text{ and } a(\phi, \eta X) = \eta^2 a(\phi, X) \quad \forall (\phi, X, \eta) \in \Sigma^M \times (\mathbb{T}\Sigma^M)^d \times \mathbb{R}^+.$$

The function $w : \Sigma^M \rightarrow \mathbb{R}$ is smooth and has exactly M global minima at the points $e_\beta = (\delta_{\alpha\beta})_{\alpha=1}^M$, $1 \leq \beta \leq M$, with $w(e_\beta) = 0$, i.e.,

$$w(\phi) \geq 0, \quad \text{and } w(\phi) = 0 \Leftrightarrow \phi = e_\beta \text{ for some } \beta \in \{1, \dots, M\}.$$

Possible choices for a and w will be given later.

The surface contribution to the entropy is described above. Let us now comment on the bulk entropy contribution and its dependence on the phase field variables. The (Helmholtz) free energy of the system can be defined as an appropriate interpolation of the free energies $\{f^\alpha(T, \hat{c})\}_\alpha$ of the possible phases, i.e.,

$$f(T, \hat{c}, \phi) = \sum_{\alpha=1}^M f^\alpha(T, \hat{c}) h(\phi_\alpha) \quad (2.20)$$

with an interpolation function $h : [0, 1] \rightarrow [0, 1]$ satisfying $h(0) = 0$ and $h(1) = 1$. By the thermodynamic relations $s = -f_{,T}$ and $e = f + Ts$ the entropy and the internal energy can be expressed in terms of (T, \hat{c}, ϕ) . By appropriate assumptions on f , inversely, the temperature can be expressed as a function in $(e, \hat{c}, \phi) = (c, \phi)$ whence also the entropy, $s(c, \phi) = -f_{,T}(T(c, \phi), \hat{c}, \phi)$. Short calculations taking the change of variables into account yield

$$s_{,c}(c, \phi) = -u(c, \phi), \quad s_{,\phi}(c, \phi) = -\frac{f_{,\phi}(T(c, \phi), \hat{c}, \phi)}{T(c, \phi)}.$$

The total entropy of the system is now

$$S(c, \phi) = \int_{\Omega} \left(s(c, \phi) - \left(\delta a(\phi, \nabla \phi) + \frac{1}{\delta} w(\phi) \right) \right) dx.$$

The evolution of the system is determined by a gradient flow of the entropy for the phase field variables coupled to balance equations for the conserved variables such that the second law of thermodynamics is fulfilled. To allow for anisotropy in the mobility of the phase boundaries, again a weighted L^2 -product is used. Given a smooth field $\phi : \Omega \rightarrow \Sigma^M$ let

$$(w, v)_{\omega, \phi} := \int_{\Omega} \delta \omega(\phi, \nabla \phi) w \cdot v \, dx \quad \forall w, v \in C^\infty(\Omega; \mathbb{T}\Sigma^M).$$

The function ω is supposed to be smooth, positive, and homogeneous of degree zero in the second variable, i.e.,

$$\omega(\phi, X) \geq 0 \quad \text{and} \quad \omega(\phi, \eta X) = \omega(\phi, X) \quad \forall (\phi, X, \eta) \in \Sigma^M \times \mathbb{R}^{d \times M} \times \mathbb{R}^+.$$

The evolution of the system is defined by

$$(\partial_t \phi, v)_{\omega, \phi} = \left\langle \frac{\delta S}{\delta \phi}(c, \phi), v \right\rangle \quad \forall v \in C^\infty(\Omega, \mathbb{T}\Sigma^M).$$

Taking the boundary condition

$$a_{, \nabla \phi_\alpha}(\phi, \nabla \phi) \cdot \nu_{ext} = 0, \quad 1 \leq \alpha \leq M, \quad (2.21)$$

into account this means that for all $\alpha \in \{1, \dots, M\}$

$$\delta \omega(\phi, \nabla \phi) \partial_t \phi_\alpha = \delta \nabla \cdot a_{, \nabla \phi_\alpha}(\phi, \nabla \phi) - \delta a_{, \phi_\alpha}(\phi, \nabla \phi) - \frac{1}{\delta} w_{, \phi_\alpha}(\phi) + s_{, \phi_\alpha}(c, \phi) - \lambda \quad (2.22)$$

with the Lagrange factor (due to the constraint $\sum_{\alpha} \phi_\alpha = 1$)

$$\lambda = \frac{1}{M} \sum_{\alpha=1}^M \left(\delta \nabla \cdot a_{, \nabla \phi_\alpha}(\phi, \nabla \phi) - \delta a_{, \phi_\alpha}(\phi, \nabla \phi) - \frac{1}{\delta} w_{, \phi_\alpha}(\phi) + s_{, \phi_\alpha}(c, \phi) \right).$$

It is also possible to consider multi-well potentials of obstacle type (cf. [BE91]). Then the differential equation (2.22) becomes a variational inequality.

The balance equations for the conserved quantities read

$$\partial_t c_i = -\nabla \cdot J_i(c, \phi, \nabla u(c, \phi)) = \nabla \cdot \left(\sum_{j=0}^N L_{ij}(c, \phi) \nabla u_j(c, \phi) \right). \quad (2.23)$$

The fact that the Onsager coefficients $L_{ij}(c, \phi)$ can differ in the different phases may be modelled by interpolating the coefficients $\{L_{ij}^\alpha\}_\alpha$ of the pure phases analogously as done for the free energy. The matrix $L = (L_{ij})_{i,j=0}^N$ then remains symmetric and positive semi-definite. Moreover, the condition $\sum_{i=1}^N L_{ij}(c, \phi) = 0$, $1 \leq j \leq N$, remains satisfied. In addition to initial conditions boundary conditions are imposed which, in the isolated case, are of the form

$$J_i(c, \phi, \nabla u(c, \phi)) \cdot \nu_{ext} = 0, \quad 0 \leq i \leq N. \quad (2.24)$$

In [GNS04] the following entropy inequality is shown:

Theorem 2.9. *If the system under consideration evolves following (2.22) and (2.23) then it holds that*

$$\frac{d}{dt} s(c, \phi) \geq -\nabla \cdot \left(\sum_{i=0}^N (-u_i) J_i - \delta \sum_{\alpha=1}^M a_{, \nabla \phi_\alpha} \partial_t \phi_\alpha \right).$$

If the boundary conditions (2.21) and (2.24) hold then $\frac{d}{dt} S(c, \phi) \geq 0$.

2.4 Example for calibration: binary alloy, two phases

The framework for phase field modelling of alloy solidification presented in the previous subsection generalizes earlier models that have successfully been applied to describe phenomena like dendritic and eutectic growth. By postulating appropriate free energies f , surface terms a and w , Onsager coefficients L_{ij} , and a kinetic mobility function ω , for example, the models used in [Ca89, PF90, WMB92] can be derived (see [GNS04, St05b]). In the following we will exemplify the choices to model non-isothermal solidification of a binary alloy involving a solid and as liquid phase. For more complex cases of multiple phases and components we refer to the article of Nestler and Wendler.

Let $M = 2$ and $N = 2$. According to the model of an ideal solution, the free energy density of the liquid phase is defined by

$$f^{(l)}(T, \hat{c}) := \sum_{i=1}^2 -\frac{L_i}{2} \frac{T - T_i}{T_i} c_i + \frac{R_g}{v_m} T \sum_{i=1}^2 c_i \log(c_i) - c_p T \log\left(\frac{T}{T_{ref}}\right),$$

and the free energy of the solid phase by

$$f^{(s)}(T, \hat{c}) := \sum_{i=1}^2 \frac{L_i}{2} \frac{T - T_i}{T_i} c_i + \frac{R_g}{v_m} T \sum_{i=1}^2 c_i \log(c_i) - c_p T \log\left(\frac{T}{T_{ref}}\right).$$

The quantities L_A and L_B are the latent heats of the pure substances $A = 1$ and $B = 2$, T_A and T_B are the melting temperatures, R_g is the gas constant, v_m the molar volume (supposed to be constant), c_p the specific heat, and T_{ref} some reference temperature, e.g., the mean value of the melting temperatures. In the following, the entropy differences s_A and s_B between the phases will appear. They are defined by $s_i := L_i/T_i$, $i = A, B$. Moreover let $R := R_g/v_m$. For simplicity assume that $L_A = s_A T_A = L_B = s_B T_B =: 2L$.

To simplify the presentation further we now consider dimensionless equations. Whenever thermodynamic quantities appear in the following, we will use the same letters but they are thought to be appropriately rescaled. In particular we are able to set $c_p = 1$ and $T_{ref} = 1$. Interpolating the free energies of the pure phases with the interpolation function $h(\phi) = \phi$ in the sense of (2.20) yields

$$\begin{aligned} f(T, c, \phi) &:= \left(c_1 \frac{s_A}{2} (T_A - T) + c_2 \frac{s_B}{2} (T_B - T) \right) (\phi_1 - \phi_2) \\ &\quad + RT \sum_{i=1}^2 c_i \log(c_i) - T \log(T). \end{aligned}$$

Since $\phi_1 + \phi_2 = 1$ and $c_1 + c_2 = 1$ it is sufficient to consider $\Phi = \phi_1 - \phi_2$ and $C = c_1$ in order to distinguish the phases and to describe the alloy composition. We then have $\Phi = 1$ in the liquid phase, $\Phi = -1$ in the solid phase, and C is the concentration of component A . The free energy density can then be written in the form

$$\begin{aligned} \tilde{f}(T, C, \Phi) &:= f(T, C, 1 - C, \frac{1+\Phi}{2}, \frac{1-\Phi}{2}) \\ &= \frac{1}{2} (C s_A (T_A - T) + (1 - C) s_B (T_B - T)) \Phi \\ &\quad + RT (C \log(C) + (1 - C) \log(1 - C)) - T \log(T) \end{aligned} \quad (2.25)$$

resulting in the internal energy density

$$\tilde{e}(T, C, \Phi) = \frac{1}{2} (C L_A + (1 - C) L_B) \Phi + T =: L \Phi + T.$$

Setting $L_{0i} = L_{i0} := 0$ for $i = 1, 2$ and $L_{00} := K(\Phi)T^2$ the energy flux becomes

$$-L_{00}\nabla u_0 = -K(\Phi)T^2\nabla\frac{-1}{T} = -K(\Phi)\nabla T$$

whence the balance equation for the energy reads

$$\partial_t \tilde{e} = \partial_t T + L\partial_t \Phi = \nabla \cdot (K(\Phi)\nabla T). \quad (2.26)$$

Since $\bar{\mu}_1 = f_{,c_1} - \frac{1}{2}(f_{,c_1} + f_{,c_2}) = \frac{1}{2}(f_{,c_1} - f_{,c_2}) = \frac{1}{2}\tilde{f}_{,C}$ we have

$$-u_2 = u_1 = \frac{\bar{\mu}_1}{T} = \frac{1}{2}\frac{s_B - s_A}{2}\Phi + \frac{R}{2}(\log(C) - \log(1 - C))$$

whence

$$-\nabla u_2 = \nabla u_1 = \frac{1}{2}\left(\frac{s_B - s_A}{2}\nabla\Phi + R\frac{1}{C(1 - C)}\nabla C\right).$$

Choosing $\tilde{D}(\Phi)C(1 - C) =: L_{11} = -L_{12} = -L_{21} = L_{22}$ with some diffusivity coefficient $\tilde{D}(\Phi)$ a short calculation gives

$$\begin{aligned} -\partial_t c_2 = \partial_t c_1 = \partial_t C = \nabla \cdot (\tilde{D}(\Phi)R\nabla C) \\ + \nabla \cdot \left(\tilde{D}(\Phi)C(1 - C)\frac{s_B - s_A}{2}\nabla\Phi\right). \end{aligned} \quad (2.27)$$

Subtracting the equations for the two phase field variables ϕ_1 and ϕ_2 yields

$$\delta^2\omega\partial_t\Phi = \delta^2(\nabla \cdot (a_{,\nabla\phi_1} - a_{,\nabla\phi_2}) - (a_{,\phi_1} - a_{,\phi_2})) - (w_{,\phi_1} - w_{,\phi_2}) - \frac{\delta}{T}(f_{,\phi_1} - f_{,\phi_2}).$$

The standard double-well potential $w(\phi) := 9\gamma\phi_1^2\phi_2^2$ for some $\gamma > 0$ related to the surface tension (see below) gives

$$(w_{,\phi_1} - w_{,\phi_2})\left(\frac{1+\Phi}{2}, \frac{1-\Phi}{2}\right) = \frac{9}{4}\gamma p'(\Phi) \quad \text{where } p(\Phi) = \frac{1}{2}(\Phi^2 - 1)^2.$$

Moreover it holds that

$$-\frac{\delta}{T}(f_{,\phi_1} - f_{,\phi_2}) = -\frac{\delta}{T}2\tilde{f}_{,\Phi} = -\frac{\delta}{T}(Cs_A(T_A - T) + (1 - C)s_B(T_B - T)).$$

The surface gradient term is set to $a(\phi, \nabla\phi) := \gamma|\phi_1\nabla\phi_2 - \phi_2\nabla\phi_1|^2 = \gamma|\frac{1}{4}\nabla\Phi|^2$. Short calculations give

$$a_{,\phi_1} - a_{,\phi_2} = 0, \quad a_{,\nabla\phi_1} - a_{,\nabla\phi_2} = 2\gamma(\phi_1\nabla\phi_2 - \phi_2\nabla\phi_1)(\phi_1 - \phi_2) = \gamma\nabla\Phi.$$

Finally, let $\xi := \frac{2}{3}\delta$, $\alpha := \frac{\omega}{\gamma}$, and replace the surface energy $T\gamma =: \sigma$ by a temperature independent constant (i.e., replace T in that term by some reference temperature T_{ref} and assume that variations of σ in the temperature can be neglected). Then the evolution of the phase field variable is governed by

$$\xi^2\alpha\partial_t\Phi = \xi^2\Delta\Phi - p'(\Phi) - \frac{2\xi}{3\sigma}(Cs_A(T_A - T) + (1 - C)s_B(T_B - T)). \quad (2.28)$$

The model consisting of equations (2.26)–(2.28) and some additional conditions will be used in the following section to sketch the method of relating a phase field model to a sharp interface model and in the last section to describe dendritic solidification.

2.5 Some remarks on the solvability of the phase field model

The reduced grand canonical potential is defined to be the Legendre transform of the negative entropy with respect to the conserved quantities,

$$\psi(u, \phi) = (-s)^*(c(u, \phi), \phi).$$

With its help it is possible to reformulate the differential equations using (u, ϕ) as variables (cf. [St05b]). The parabolic system then has the structure

$$\begin{aligned} \partial_t \psi_{,u_i}(u, \phi) &= \nabla \cdot \left(\sum_{j=0}^N L_{ij}(\psi, u(u, \phi), \phi) \nabla u_j \right), \\ \omega(\phi, \nabla \phi) \partial_t \phi_\alpha &= \nabla \cdot a_{, \nabla \phi_\alpha}(\phi, \nabla \phi) - a_{, \phi_\alpha}(\phi, \nabla \phi) - w_{, \phi_\alpha}(\phi) + \psi_{, \phi_\alpha}(u, \phi) - \lambda \end{aligned}$$

where $0 \leq i \leq N$, $1 \leq \alpha \leq M$. When rigorously analyzing these equations the main difficulties arise from the growth properties of ψ in u and the nonlinearities involving $\nabla \phi$.

An ideal solution formulation of the free energy density has the structure

$$f(T, c) = T \log(T) + T \sum_i c_i \log(c_i) + \dots$$

As a result, in ψ a term $-\log(-u_0)$ appears. In particular, when solving the differential equations it must be shown that $u_0 < 0$ almost everywhere. Moreover, ψ is only of at most linear growth in the u_i , $1 \leq i \leq N$. A control of terms involving $\psi_{,u}$ obtained by standard estimates for parabolic equations do not provide much information of u itself any more. These difficulties have been independently tackled in [AP92] and [LV83] respectively.

Based on those results, the above system including the phase field variables is analyzed in [St05b] by approximating ψ with a perturbed potential of quadratic growth in u . The main task is to derive suitable estimates and, based on the estimates, to develop and apply appropriate compactness arguments in order to go to the limit as the perturbation vanishes. It is assumed that the matrix of Onsager coefficients $L = (L_{ij})_{ij}$ is positive (on a certain subspace) uniformly in their arguments. If a degenerating coefficient matrix is considered as in the previous subsection it may be better to switch to (T, \hat{c}) or (e, \hat{c}) as variables, e.g. cf. [Ec04a].

Managing the phase field variables is kept simple in [St05b] by appropriate assumptions on a , w , and ω . The interesting case of a involving the terms $\phi_\alpha \nabla \phi_\beta - \phi_\beta \nabla \phi_\alpha$ (which give a good approximation of the direction of $\nu_{\alpha\beta}$) is still open. Non-local models have been considered by multiple authors (for instance, we refer to [BS96, SZ03, KRS05]). There, the energy is the only conserved quantity, and the difficulties with the logarithmic term in u_0 are tackled by performing a Moser type iteration to get L^∞ -bounds for u_0 and $1/u_0$.

3 Relation between the approaches and calibration

The relation between the phase field model and the free boundary problem presented in the previous chapter can be established using the method of matched asymptotic expansions. Generalizing methods developed in [CF88, Ca89, BGS98, GNS98] this has been done in [GNS04]. The procedure is as follows: It is assumed that the solution to the phase field model can be expanded in δ -series in the bulk regions occupied by the phases (outer expansions) and, using rescaled coordinates, in the interfacial regions (inner expansion). Given suitable relations between the functions

and parameters of the phase field model on the one hand and the parameters in the free boundary problem on the other hand the functions to leading order of the δ -series solve the governing equations of the free boundary problem. It should be remarked that this procedure is a formal method in the sense that it is not rigorously shown that the assumed expansions in fact exist and converge. But in some cases this ansatz could be verified (cf. [DS95, St96, CC98, Di04]).

If the phase field model is considered as an approximation of the free boundary problem fast convergence with respect to δ is desired. An improvement of the approximation was obtained in [KR98] in the context of thin interface asymptotics. The analysis led to a positive correction term in the kinetic coefficient of the phase field equation balancing undesired terms of order δ in the Gibbs-Thomson condition and raising the stability bound of explicit numerical methods. Besides, the better approximation allows for larger values of δ and, therefore, for coarser grids. In particular, it is possible to consider the limit of vanishing kinetic undercooling which is important in applications. Numerical simulations of appropriate test problems reveal an enormous gain in efficiency thanks to a better approximation.

In [Al99] the analysis was extended to the case of different diffusivities in the phases and both classical and thin interface asymptotics were discussed. By choosing different interpolation functions for the free energy density and the internal energy density (the function h in (2.20)) an approximation of second order could still be achieved but the gradient structure of the model and thermodynamic consistency were lost. Based on those ideas it was shown in [An02] that even an approximation of third order is possible by using high order polynomials for the interpolation. In [MWA00] an approach based on an energy and an entropy functional was used providing more degrees of freedom to tackle the difficulties with unequal diffusivities in the phases while avoiding the loss of the thermodynamic consistency. Both classical and thin asymptotics are discussed in that article as well as the limit of vanishing kinetic undercooling. In a more recent analysis in [RBKD04], a binary alloy also involving different diffusivities in the phases was considered and a better approximation was obtained by adding a small additional term to the mass flux (anti-trapping mass current, the ideas stem from [Ka01]).

We have shown in [GS06] that, for two-phase multi-component systems with arbitrary phase diagrams, there is a correction term to the kinetic coefficient such that the model with moving boundaries is approximated to second order in the small parameter δ . A new feature compared to the existing results is that, in general, this correction term depends on temperature and chemical potentials. Indeed, up to some numerical constants, the latent heat appears in the correction term obtained by Karma and Rappel [KR98]. Analogously, the equilibrium jump in the concentrations enters the correction term when investigating an isothermal binary alloy. But from realistic phase diagrams it is obvious that this jump depends on the temperature leading to a temperature dependent correction term in the non-isothermal case.

In this chapter, the procedure to get an second order approximation will be sketched for a simple model describing solidification of a pure substance. The model is based on the model in Subsection 2.4. There, the small quantity $\xi = \frac{2}{3}\delta$ was introduced and will be used instead of δ . In addition to the free boundary problem which appears as problem to leading order a correction problem to the next order is derived by continuing the asymptotic analysis. The goal is to obtain that fields identically zero solve the correction problem. It turns out that the above mentioned correction term to the kinetic coefficient is necessary to allow for this solution. The model equations including assumptions, asymptotic expansions, and matching conditions are listed in the following subsection. After, the asymptotic analysis is performed. Finally, the leading order problem and the correction problem are stated. In [GS06], numerical tests have been performed to show that a better approximation of the free boundary problem thanks to the kinetic correction term is really obtained.

3.1 The simplified model and assumptions

In order to present the main ideas to obtain a second order approximation a simple model for solidification of a pure substance is considered, namely, the model in Subsection 2.4 where we set $C \equiv 1$. In the definition of the free energy density (2.25) Φ is replaced by a term $h(\Phi)$ with an interpolation function $h : [-1, 1] \rightarrow [0, 1]$ which is symmetric, i.e., $h(-\Phi) = -h(\Phi)$, and fulfills $h'(\pm 1) = 0$. For s_A we simply write s , and T_A is replaced by T_m . The kinetic coefficient splits into a main part and a positive correction term of order ξ , i.e., $\alpha = \alpha_0 + \xi\alpha_1$. The correction term will later be determined and turn out to be crucial to get a higher order approximation of the related free boundary problem. The heat diffusivity K is assumed to be independent of the phase field variable. The governing equations then have the form

$$\xi^2(\alpha_0 + \xi\alpha_1)\partial_t\Phi = \xi^2\Delta\Phi - p'(\Phi) - \frac{2\xi}{3\sigma}(s(T_m - T))h'(\Phi), \quad (3.1)$$

$$\partial_t T + L\partial_t h(\Phi) = K\Delta T. \quad (3.2)$$

To obtain a well-posed problem initial and boundary conditions have to be imposed. Consider a domain $\Omega \subset \mathbb{R}^2$ and a time interval $I_{\mathcal{T}} := (0, \mathcal{T})$. For $\xi > 0$ let $(T(t, x; \xi), \Phi(t, x; \xi))$, $x \in \Omega$, $t \in I_{\mathcal{T}}$, denote smooth solutions to (3.1)–(3.2) given the same initial and boundary conditions. We suppose that, for all times, there exist two phases separated by a diffuse interfacial layer which is bounded away from the boundary of the domain Ω . Here, we do not carry out the asymptotic analysis for the initial and boundary conditions but only give some remarks. That analysis is carried out in [St05b], Section 3.2, and [GS06].

The following procedure of matching asymptotic expansions is outlined with great care in [FP95, DW05]. Here, only the main ideas for the two-dimensional case are sketched. The family

$$\Gamma(t; \xi) := \{x \in \Omega : \Phi(t, x; \xi) = 0\}, \quad \xi > 0, t \in I_{\mathcal{T}}, \quad (3.3)$$

is supposed to be a set of smooth curves in Ω . They are demanded to be uniformly bounded away from $\partial\Omega$ and to depend smoothly on (ξ, t) such that, if $\xi \searrow 0$, some limiting curve $\Gamma(t; 0)$ is obtained. With $\Omega^l(t; \xi)$ and $\Omega^s(t; \xi)$ we denote the regions occupied by the liquid phase (where $\Phi(t, x; \xi) > 0$) and the solid phase (where $\Phi(t, x; \xi) < 0$) respectively.

Let $\gamma(t, s; 0)$ be a parameterization of $\Gamma(t; 0)$ by arc-length s for every $t \in I_{\mathcal{T}}$. The vector $\nu(t, s; 0)$ denotes the unit normal on $\Gamma(t; 0)$ pointing into $\Omega^l(t; 0)$, and $\tau(t, s; 0) := \partial_s \gamma(t, s; 0)$ denotes the unit tangential vector. For ξ small enough the curves $\Gamma(t; \xi)$ can be parametrized over $\Gamma(t; 0)$ using some distance function $d(t, s; \xi)$,

$$\gamma(t, s; \xi) := \gamma(t, s; 0) + d(t, s; \xi)\nu(t, s; 0).$$

Close to $\xi = 0$ we assume that there is the expansion $d(t, s; \xi) = \xi^1 d_1(t, s) + \xi^2 d_2(t, s) + O(\xi^3)$. Also the curvature $\kappa(t, s; \xi)$ and the normal velocity $v(t, s; \xi)$ of $\Gamma(t; \xi)$ are smooth and can be expanded in ξ -series (cf. the Appendix of [GS06]):

$$\kappa(t, s; \xi) = \kappa(t, s; 0) + \xi(\kappa(t, s; 0)^2 d_1(t, s) + \partial_{ss} d_1(t, s)) + O(\xi^2), \quad (3.4)$$

$$v(t, s; \xi) = \partial_t \gamma(t, s; \xi) \cdot \nu(t, s; \xi) = v(t, s; 0) + \xi \partial^\circ d_1(t, s) + O(\xi^2). \quad (3.5)$$

Here, ∂° denotes the normal time derivative, see (A.1) for a definition.

We suppose that in each domain $E \subset \mathbb{R}^2$ such that $\bar{E} \subset \Omega \setminus \Gamma(t; 0)$ the solution can be expanded in a series close to $\xi = 0$ (**outer expansion**):

$$\begin{aligned}
T(t, x; \xi) &= \sum_{k=0}^K \xi^k \theta_k(t, x) + O(\xi^{K+1}), \\
\Phi(t, x; \xi) &= \sum_{k=0}^K \xi^k \varphi_k(t, x) + O(\xi^{K+1}).
\end{aligned} \tag{3.6}$$

Let z be the $\frac{1}{\xi}$ -scaled signed distance of x from $\Gamma(t; 0)$. Hence, in a neighborhood of $\Gamma(t; 0)$ we can write for $z \neq 0$

$$\hat{T}(t, s, z; \xi) := T(t, x(t, s, z); \xi), \quad \hat{\Phi}(t, s, z; \xi) := \Phi(t, x(t, s, z); \xi).$$

An essential assumption is now that \hat{T} and $\hat{\Phi}$ can be expanded in these new variables (**inner expansion**),

$$\hat{T}(t, s, z; \xi) = \sum_{k=0}^K \xi^k T_k(t, s, z) + O(\xi^{K+1}), \tag{3.7}$$

$$\hat{\Phi}(t, s, z; \xi) = \sum_{k=0}^K \xi^k \Phi_k(t, s, z) + O(\xi^{K+1}), \tag{3.8}$$

and that these expansions are valid for $z \in \mathbb{R}$. The notion is that, since the interfacial thickness scales with ξ , one can expect a meaningful convergence behavior when rescaling the space with $1/\xi$ in the normal direction.

Given $x \notin \Gamma(t; 0)$ clearly $z(t, x) = \text{dist}(x, \Gamma(t; 0))/\xi \rightarrow \pm\infty$ as $\xi \searrow 0$. On the other hand, in that limit x is located in one of the two phases, and the closer it lies to the interface $\Gamma(t; 0)$ the better the series of the functions $\theta_k(t, x)$ approximates the value of the temperature on the interface. These facts are reflected by the following matching conditions relating the outer and inner expansions (see [St05b], Section 3.1, and [GS06] for the derivation): As $z \rightarrow \pm\infty$

$$T_0(z) \sim \theta_0(0^\pm), \tag{3.9}$$

$$T_1(z) \sim \theta_1(0^\pm) + (\nabla \theta_0(0^\pm) \cdot \nu)z, \tag{3.10}$$

$$\partial_z T_1(z) \sim \nabla \theta_0(0^\pm) \cdot \nu, \tag{3.11}$$

$$\partial_z T_2(z) \sim \nabla \theta_1(0^\pm) \cdot \nu + ((\nu \cdot \nabla)(\nu \cdot \nabla) \theta_0(0^\pm))z \tag{3.12}$$

and analogously for Φ . Here, for a function $g(t, x) = \hat{g}(t, s, r)$ with the signed distance $r = \text{dist}(x, \Gamma(t; 0))$

$$g(0^+) := \lim_{r \searrow 0} \hat{g}(t, s, r), \quad g(0^-) := \lim_{r \nearrow 0} \hat{g}(t, s, r).$$

3.2 Outer solutions

Away from $\Gamma(t; 0)$, i.e., in domains $E \subset \mathbb{R}^2$ with $\overline{E} \subset \Omega \setminus \Gamma(t; 0)$, the expansions (3.6) are plugged into the differential equations. All terms are expanded in ξ -series.

To leading order ξ^0 equation (3.1) yields the identity $0 = -p'(\varphi_0)$. The only stable solutions are the minima of p , hence $\varphi_0 \equiv \pm 1$. These values distinguish the two phases because, since the result is independent of ξ , necessarily $\varphi_0 = 1$ in Ω^l and $\varphi_0 = -1$ in Ω^s .

To the next order ξ^1 the identity

$$0 = -p''(\varphi_0)\varphi_1 - \frac{2}{3\sigma}s(T_m - \theta_0)h'(\varphi_0)$$

follows. By $h'(\pm 1) = 0$ and $p''(\pm 1) = 4$ we obtain $\varphi_1 \equiv 0$ as the only solution.

The energy balance equation (3.2) yields the heat equation, to leading order for θ_0 and to the next order for θ_1 :

$$\partial_t \theta_k = K \Delta \theta_k, \quad k = 0, 1.$$

Observe that it is possible to replace θ_0 by the internal energies $e^{(l)}(\theta_0) = \theta_0 + L$ of the liquid phase or $e^{(s)} = \theta_0 - L$ of the solid phase.

The initial conditions and boundary conditions on $\partial\Omega$ are independent of ξ and, hence, only enter θ_0 and φ_0 respectively. The higher order corrections fulfill homogeneous initial and boundary conditions. Boundary conditions on $\Gamma(t; 0)$ will be obtained by matching the expansions with the expansions in the interfacial region.

3.3 Inner solutions

Derivatives with respect to (t, x) transform into derivatives with respect to (t, s, z) as follows:

$$\begin{aligned} \frac{d}{dt} &= -\frac{1}{\xi} v \partial_z + \partial^\circ - (\partial^\circ d_1) \partial_z + O(\xi), \\ \Delta_x &= \frac{1}{\xi^2} \partial_{zz} - \frac{1}{\xi} \kappa \partial_z \\ &\quad + (\partial_s d_1)^2 \partial_{zz} - 2\partial_s d_1 \partial_{sz} - (\kappa^2(z + d_1) - \partial_{ss} d_1) \partial_z + \partial_{ss} + O(\xi). \end{aligned}$$

The phase field equation first yields

$$0 = \partial_{zz} \Phi_0 - p'(\Phi_0). \quad (3.13)$$

By (3.3) and the assumption that (3.8) holds true for $\xi = 0$ we have $\Phi_0(z = 0) = 0$. The matching conditions (3.9) imply

$$\Phi_0(t, s, z) \rightarrow \varphi_0(t, s; 0^\pm) = \pm 1 \text{ as } z \rightarrow \pm\infty.$$

Therefore the solution to (3.13) is $\Phi_0(t, s, z) = \tanh(z)$ and only depends on z .

For the conserved variable we get $0 = K \partial_{zz} T_0$ to order ξ^{-2} . By the matching conditions (3.9) T_0 has to be bounded as $z \rightarrow \pm\infty$, hence we see that T_0 must be constant with respect to z which means $T_0 = T_0(t, s)$. The matching condition (3.9) furthermore implies that $T_0(t, s)$ is exactly the value of θ_0 in the point $\gamma(t, s; 0) \in \Gamma(t; 0)$ from both sides of the interface. In particular,

$$\theta_0 \text{ is continuous across the interface } \Gamma(t; 0).$$

To order ξ^1 equation (3.1) yields

$$-\alpha_0 v \partial_z \Phi_0 = \partial_{zz} \Phi_1 - \kappa \partial_z \Phi_0 - p''(\Phi_0) \Phi_1 - \frac{2}{3\sigma} s (T_m - T_0) h'(\Phi_0). \quad (3.14)$$

From the outer solutions we have $\varphi_1(t, s, 0^\pm) = 0$ and $\nabla \varphi_0(t, s, 0^\pm) \cdot \nu = 0$. Due to the matching condition (3.10) we conclude $\Phi_1(t, s, z) \rightarrow 0$ as $z \rightarrow \pm\infty$. The operator $\mathcal{L}(\Phi_0) = \partial_{zz} - w''(\Phi_0)$ is self-adjoint. Differentiating (3.13) with respect to z we obtain that $\partial_z \Phi_0$ lies in the kernel of $\mathcal{L}(\Phi_0)$. Since $\Phi_0(-z) = -\Phi_0(z)$, $\partial_z \Phi_0$ and $h'(\Phi_0)$ are even, (3.14) allows for an even solution. In the following we will assume that Φ_1 indeed is even.

A solvability condition can be deduced by multiplying the equation with $\partial_z \Phi_0$ and integrating over \mathbb{R} with respect to z :

$$\begin{aligned} 0 &= \int_{\mathbb{R}} \left((\kappa - \alpha_0 v) (\partial_z \Phi_0(z))^2 + \frac{2}{3\sigma} s (T_m - T_0) h'(\Phi_0(z)) \partial_z \Phi_0(z) \right) dz \\ &= \frac{4}{3} (\kappa - \alpha_0 v) + \frac{4}{3\sigma} s (T_m - \theta_0) \end{aligned} \quad (3.15)$$

where we used that $\int_{\mathbb{R}} (\partial_z \Phi_0)^2 dz = \frac{4}{3}$. Up to the factor $\frac{4}{3}$ this is the Gibbs-Thomson condition (2.6).

The system (3.2) becomes to the order ξ^{-1}

$$-v\partial_z(T_0 + Lh(\Phi_0)) = K\partial_{zz}T_1.$$

Integrating two times with respect to z furnishes

$$\begin{aligned} T_1 &= -\frac{1}{K} \left(vL \int_0^z h(\Phi_0) dz' + (vT_0 - A)z \right) + \bar{\tau} \\ &\sim -\frac{1}{K} \left((v(T_0 + L) - A)z - vLH \right) + \bar{\tau} \text{ as } z \rightarrow \infty \\ &\sim -\frac{1}{K} \left((v(T_0 - L) - A)z - vLH \right) + \bar{\tau} \text{ as } z \rightarrow -\infty \end{aligned} \quad (3.16)$$

where A and $\bar{\tau}$ are integration constants and

$$H := \int_0^\infty (1 - h(\Phi_0(z'))) dz' = \int_{-\infty}^0 (1 + h(\Phi_0(z'))) dz'.$$

Here, we used the fact that Φ_0 converges to constants exponentially fast, so that the integral \int_0^z has been replaced by \int_0^∞ while the linear terms remain. By (3.10)

$$\theta_1(0^\pm) = \bar{\tau} + \frac{v}{K} LH \quad (3.17)$$

which means, in particular, that

$$\theta_1 \text{ is continuous across } \Gamma(t; 0). \quad (3.18)$$

With (3.11) and $T_0 = \theta_0(0^\pm)$ the following jump condition is obtained on $\Gamma(t; 0)$:

$$[-K\nabla\theta_0]_s^l \cdot \nu = (v(T_0 + L) - A) - (v(T_0 - L) - A) = v[e(\theta_0(0))]_s^l. \quad (3.19)$$

Since Φ_0 only depends on z the phase field equation to order ξ^2 gives

$$\begin{aligned} & -\alpha_0 v \partial_z \Phi_1 - \alpha_1 v \partial_z \Phi_0 - \alpha_0 (\partial^\circ d_1) \partial_z \Phi_0 \\ &= \partial_{zz} \Phi_2 - p''(\Phi_0) \Phi_2 + (\partial_s d_1)^2 \partial_{zz} \Phi_0 - (\kappa^2(z + d_1) + \partial_{ss} d_1) \partial_z \Phi_0 \\ & - \kappa \partial_z \Phi_1 - \frac{1}{2} p'''(\Phi_0) (\Phi_1)^2 + \frac{2}{3\sigma} s(T_m - T_0) h''(\Phi_0) \Phi_1 + \frac{2}{3\sigma} s T_1 h'(\Phi_0). \end{aligned}$$

To guarantee that Φ_2 exists there is again a solvability condition which is obtained by multiplying with $\partial_z \Phi_0$ and integrating over \mathbb{R} with respect to z . The terms involving Φ_1 vanish. For this purpose, equation (3.14) and the assumption that Φ_1 is even is used. Let

$$\begin{aligned} J &:= \int_0^\infty \partial_z (h \circ \Phi_0)(z) \int_0^z (1 - (h \circ \Phi_0)(z')) dz' dz \\ &= \int_{-\infty}^0 \partial_z (h \circ \Phi_0)(z) \int_z^0 (1 + (h \circ \Phi_0)(z')) dz' dz. \end{aligned}$$

Using (3.16) to replace T_1 and, after, (3.17) to replace $\bar{\tau}$ a short calculation shows that the solvability condition becomes (remember that $2L = sT_m$)

$$\begin{aligned} 0 &= \sigma(-\alpha_0 \partial^\circ + \partial_{ss} + \kappa^2) d_1 - s\theta_1 \\ & + v \left(-\sigma\alpha_1 + (H + J) \frac{1}{K} T_m s^2 \right). \end{aligned} \quad (3.20)$$

We remark that $\partial^\circ d_1$ and $(\partial_{ss} + \kappa^2)d_1$ are the first order corrections of the normal velocity and the curvature of $\Gamma(t, s; \xi)$ (see (3.5) and (3.4) respectively). Indeed, when inserting the expansions for $T = \theta_0 + \xi\theta_1 + \dots$ and the interface distance $d = \xi d_1 + \dots$ into the Gibbs-Thomson condition $\sigma\alpha v = \sigma\kappa + s(T_m - T)$ then, to leading order, we get (3.15), and the first line of (3.20) is the equation to first order in ξ .

The goal is to obtain that $\theta_1 \equiv 0$ and $d_1 \equiv 0$ are solutions to the equations they have to fulfill. For this purpose, the second line of (3.20) must vanish. But by suitable choice of the additional correction term α_1 in the kinetic coefficient, namely

$$\alpha_1 = (H + J) \frac{\sigma}{K} T_m s^2, \quad (3.21)$$

this is indeed ensured.

Analogously to the above correction to the Gibbs-Thomson condition we are interested in deriving a first order correction to the jump condition (3.19). The equation (3.2) yields to order ξ^0

$$\begin{aligned} & -v\partial_z(T_1 + Lh'(\Phi_0)\Phi_1) + (\partial^\circ - (\partial^\circ d_1)\partial_z)(T_0 + Lh(\Phi_0)) \\ & = K(\partial_{zz}T_2 - \kappa\partial_zT_1 + \partial_{ss}T_0). \end{aligned}$$

Integrating once with respect to z leads to

$$\begin{aligned} -K\partial_zT_2 = & \underbrace{v(T_1 + Lh'(\Phi_0)\Phi_1) - B}_{(i)} \\ & + \underbrace{\int_0^z (-\partial^\circ + (\partial^\circ d_1)\partial_z)(T_0 + Lh(\Phi_0))dz'}_{(ii)} - \underbrace{\kappa KT_1 + K\partial_{ss}T_0 z}_{(iii)} \end{aligned}$$

where B is an integration constant. We need to collect the terms contributing to $\nabla\theta_1 \cdot \nu$. In view of (3.12) this means that the terms linear in z are not of interest. Applying (3.10) to Φ_1, T_1 and by the assumption $h'(0) = h'(1) = 0$ it holds that

$$(i) \sim v\theta_1 - B + (\dots)z \text{ as } z \rightarrow \pm\infty.$$

Furthermore, since $\partial^\circ\Phi_0 = 0$,

$$\begin{aligned} (ii) & = -\partial^\circ(T_0 \pm L)z + (\partial^\circ d_1)L(h(\Phi_0))\Big|_0^z \\ & \sim -\partial^\circ e^{(l)} + (\partial^\circ d_1)L && \text{as } z \rightarrow \infty, \\ & \sim -\partial^\circ e^{(l)} - (\partial^\circ d_1)L && \text{as } z \rightarrow -\infty. \end{aligned}$$

By (3.10) and (3.18) we get $(iii) = \kappa K\theta_1 + (\dots)z$ as $z \rightarrow \pm\infty$. Finally, the first order correction of the jump condition (3.19) at the interface is

$$[-K\nabla\theta_1]_s^l \cdot \nu = v\theta_1 + 2L(\partial^\circ d_1).$$

3.4 Summary of assumptions and stated problems

Let us now collect the equations. First, the problem to leading order is stated:

(LOP) Find a function $\theta_0 : I_{\mathcal{T}} \times \Omega \rightarrow \mathbb{R}$ and a family of curves $\{\Gamma(t; 0)\}_{t \in I_{\mathcal{T}}}$ separating Ω into two domains $\Omega^l(t; 0)$ and $\Omega^s(t; 0)$ such that

$$\partial_t e^{(p)}(\theta_0) = K\Delta\theta_0, \quad \text{in } \Omega^p(t; 0), \quad t \in I_{\mathcal{T}}, \quad p = s, l,$$

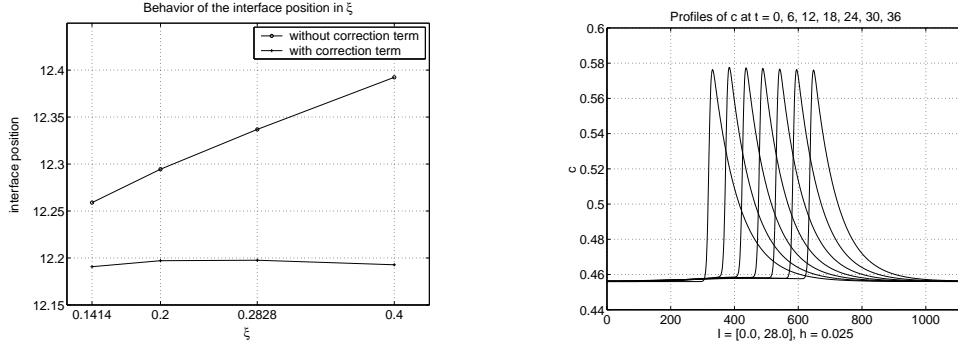


Fig. 3.1. Numerical test of the correction term. On the left: the position of the interface depicted over ξ . On the right: profiles of the concentration c during evolution.

and such that on $\Gamma(t; 0)$ there holds for all $t \in I_{\mathcal{T}}$:

$$\begin{aligned} \theta_0 &\text{ is continuous,} \\ [-K\nabla\theta_0]_s^l \cdot \nu &= v[e(\theta_0)]_s^l, \\ \sigma\alpha_0 v &= \sigma\kappa + s(T_m - \theta_0). \end{aligned}$$

If we define α_1 as in (3.21) then the correction problem reads as follows:

(CP) Let $(\theta_0, \{\Gamma(t; 0)\}_t)$ be a solution to (LOP). Let $l(t)$ be the length of $\Gamma(t; 0)$ and set $S_{I_{\mathcal{T}}} := \{(t, s) : t \in I_{\mathcal{T}}, s \in [0, l(t)]\}$. Then find functions $\theta_1 : I_{\mathcal{T}} \times \Omega \rightarrow \mathbb{R}$ and $d_1 : S_{I_{\mathcal{T}}} \rightarrow \mathbb{R}$ such that

$$\partial_t \theta_1 = K \Delta \theta_1, \quad \text{in } \Omega^p(t; 0), t \in I_{\mathcal{T}}, p = s, l,$$

and such that on $\Gamma(t; 0)$ there holds for all $t \in I_{\mathcal{T}}$:

$$\begin{aligned} \theta_1 &\text{ is continuous,} \\ [-K\nabla\theta_1]_s^l \cdot \nu &= v\theta_1 + (\partial^\circ d_1)[e(\theta_0)]_s^l \\ \sigma\alpha_0 \partial^\circ d_1 &= \sigma(\partial_{ss} + \kappa^2)d_1 - s\theta_1. \end{aligned}$$

Obviously, $(\theta_1, d_1) \equiv 0$ is a solution to the correction problem (as previously remarked, the boundary conditions on $\partial\Omega$ are homogeneous). If this solution is unique then the leading order problem is approximated to second order in ξ by the phase field model. Problem (CP) is in fact the linearization of (LOP), i.e., the problem resulting from (LOP) when inserting the expansions $T = \theta_0 + \xi\theta_1 + \dots$ and $d = \xi d_1 + \dots$. We point out again that the choice (3.21) is crucial in order to guarantee that the undesired terms in (3.20) vanish.

3.5 Numerical example

In [GS06] several numerical tests have been performed revealing that the free boundary problem can indeed be better approximated by the phase field model with the correction term. Fig. 3.1 shows the results for an undercooled binary alloy (the potentials, physical parameters, and initial values are precisely stated in [GS06], Subsection 4.3). A planar solid-liquid front moves into the liquid phase. On the right the figure shows the profiles of the concentration of one component during the solidification. The position of the interface, i.e, the point where $\Phi(t, x; \xi) = 0$, is depicted on the left for several values of ξ , the other parameters being fixed.

Simulating with the correction term (3.21) in the phase field equation and varying ξ the changes in the interface position turned out to be of about 10^{-3} which is smaller than the grid spacing $\Delta x = 0.02$. In contrast, if the correction term was not taken into account changes of several grid points were observed. This behavior in ξ indicates that the approximation of the sharp interface solution is improved thanks to the correction term.

3.6 Remarks on the multi-phase case

When multiple phases are present the asymptotic analysis leads to a leading order problem consisting of the equations (2.3)–(2.6), (2.9), and (2.10) (cf. [GNS98, GNS04]). Indeed, the procedure presented in the previous subsections yields the equations (2.3)–(2.6). To obtain the force balance (2.9) (and, analogously, (2.10)) it is assumed that, away from the triple junction on a diffuse phase boundary, the situation is just as in the case of two phases.

Aiming for a second order approximation of the force balance we observed that, in general, in the interfacial regions not only the phase field variables of the adjacent phases are present but also phase fields corresponding to other phases appear. It turned out that these artificial third phase contributions do not trouble the first order asymptotic analysis but a second order analysis. As a first step we therefore developed and analyzed suitable multi-well potentials w that avoid the third phase contributions (cf. [St05a, GHS06]), smooth potentials as well as potentials of obstacle type.

As an additional feature, the calibration of the phase field model with respect to given surface energies $\sigma_{\alpha\beta}(\nu)$ and mobility coefficients $m_{\alpha\beta}(\nu)$ becomes much simpler. It is shown in [BBR05] that the Γ -limit of (2.19) as $\delta \rightarrow 0$ has the form of the surface contribution in (2.12), and a relation between the $\sigma_{\alpha\beta}$ and the functions a and w is derived. Using matched asymptotic expansions, [St91] for the isotropic case and [GNS98] for the general case proposed the simpler relation

$$\sigma_{\alpha\beta}(\nu) = \inf_p \left\{ \int_{-1}^1 \sqrt{w(p)a(p, p' \otimes \nu)} dy, \right. \\ \left. p \in C^{0,1}([-1, 1]; \Sigma^M), p(-1) = e_\alpha, p(1) = e_\beta \right\}. \quad (3.22)$$

Using numerical simulations they got evidence that this formula seems to hold true for a large class of anisotropies.

The new potentials w are such that solutions to (3.22) exist with $p_i \neq 0$ only if $i = \alpha, \beta$. Moreover, it is possible to adapt coefficients in w and calibration functions in a such that the integral in (3.22) becomes a given surface energy. Similarly, the relation between the $m_{\alpha\beta}(\nu)$ and $\omega(\phi, \nabla\phi)$ becomes much simpler thanks to the new potentials.

4 A homogenized two-scale model for a binary mixture

In this section we apply the theory of homogenization to a simplified physical situation with periodic equiaxed dendritic microstructure which is described by a phase field model for a binary alloy. The resulting model will be a *two-scale model* that consists of a macroscopic heat equation and of microscopic cell problems that describe the evolution of the phases and the microscopic solute transport at each point of the macroscopic domain. In order to justify the formal asymptotic expansion, an estimate is established that compares the solution of the two-scale model to that of the original model.

The phase transition problem to be considered is given by equations (2.26)–(2.28), i.e.,

$$\partial_t T + L \partial_t \Phi - \nabla \cdot (K(\Phi) \nabla T) = 0, \quad (4.1)$$

$$\partial_t C - \nabla \cdot (D_1(\Phi) \nabla C) - \nabla \cdot (D_2(C, \Phi) \nabla \Phi) = 0, \quad (4.2)$$

$$\alpha \xi^2 \partial_t \Phi - \xi^2 \Delta \Phi + p'(\Phi) + q(T, C, \Phi) = 0, \quad (4.3)$$

to be solved in the time-space cylinder $Q_{\mathcal{T}\Omega} := I_{\mathcal{T}} \times \Omega$ with time interval $I_{\mathcal{T}} := [0, \mathcal{T}]$ and domain $\Omega \subset \mathbb{R}^d$. The diffusion tensors are assumed to be Lipschitz-functions of the phase field Φ , they shall be symmetric, $K_{ij} = K_{ji}$, $D_{1,ij} = D_{1,ji}$ for $i, j = 1, \dots, d$, as well as elliptic and bounded,

$$k_0 |z|^2 \leq K_{ij} z_i z_j \leq k_1 |z|^2, \quad d_0 |z|^2 \leq D_{1,ij} z_i z_j \leq d_1 |z|^2 \quad (4.4)$$

for all $z \in \mathbb{R}^d$ with positive constants $k_0 \leq k_1$ and $d_0 \leq d_1$ independent of Φ . Here and in the sequel, the sum convention is used. The function $D_2 : \mathbb{R}^2 \rightarrow \mathbb{R}^{d,d}$ is Lipschitz and bounded. The function p represents the double-well potential $p(\Phi) = \frac{1}{2}(\Phi^2 - 1)^2$, and $q : \mathbb{R}^3 \rightarrow \mathbb{R}$ is a Lipschitz function. The differential equations are supplemented by Dirichlet conditions for the temperature and homogeneous Neumann conditions for concentration and phase field,

$$T = T_{ibc}, \quad (D_1(\Phi) \nabla C + D_2(C, \Phi) \nabla \Phi) \cdot \nu_{ext} = 0, \quad \nabla \Phi \cdot \nu_{ext} = 0 \quad (4.5)$$

on $S_{\mathcal{T}\Omega} := I_{\mathcal{T}} \times \partial\Omega$, and by initial conditions

$$T(0, \cdot) = T_{ibc}, \quad C(0, \cdot) = C_{ic} \quad \text{and} \quad \Phi(0, \cdot) = \Phi_{ic} \quad (4.6)$$

on Ω . For simplicity of the notation the Dirichlet condition and the initial condition of the temperature are given by the same function T_{ibc} that is defined on $Q_{\mathcal{T}\Omega}$.

Let us introduce some notation for function spaces. Spaces of functions with continuous derivatives of order β are denoted by $C^\beta(Q)$, $L_r(Q)$ is the Lebesgue space of functions whose r -th power has an integral, $W_r^k(Q)$ is the Sobolev space of functions with derivatives of order k whose r -th power is integrable, and $H^\beta(Q) = W_2^\beta(Q)$. In anisotropic spaces of the type $C^{k,\ell}(I \times Q)$ or $W_r^{k,\ell}(I \times Q)$ with time interval I , the index k refers to the time variable and ℓ to the space variables.

4.1 Asymptotic expansion and the two-scale model

In order to construct a model that is suitable for a very small scale of the evolving dendritic structures, we consider a sequence of problems of varying scale $\varepsilon > 0$, study the limit $\varepsilon \rightarrow 0$ of their solutions, and construct a limit problem that is valid for the limit of these solutions. This limit problem may be used as an approximation for situations with small but non-vanishing scale ε .

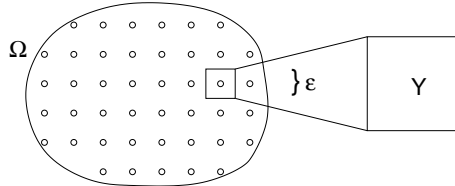


Fig. 4.1. Periodic microstructure

This procedure is done for an idealized equiaxed dendritic microstructure that consists of equiaxed crystals growing at the nodes of a uniform grid with edge length

given by the scale parameter ε , see Fig. 4.1. This situation is generated by the initial data

$$T_{ibc}^{(\varepsilon)}(x) = T_{ibc}^{(0)}(x), \quad C_{ic}^{(\varepsilon)}(x) = C_{ic}^{(0)}\left(x, \frac{x}{\varepsilon}\right) \quad \text{and} \quad \Phi_{ic}^{(\varepsilon)}(x) = \Phi_{ic}^{(0)}\left(x, \frac{x}{\varepsilon}\right) \quad (4.7)$$

with functions $T_{ibc}^{(0)} \in L_2(\Omega)$, $C_{ic}^{(0)}, \Phi_{ic}^{(0)} \in L_2(\Omega; C_{\#}(Y))$. The domain Y is a *unit cell*, by definition this is a bounded, simply connected Lipschitz domain with the property that \mathbb{R}^d can be represented as union of shifted copies of \bar{Y} with no intersection of their interiors. For simplicity of the presentation, the volume of the unit cell is scaled to one. The standard example for Y is the unit cube $Y = [0, 1]^d$. The set $C_{\#}(Y)$ contains all periodic continuous functions in \mathbb{R}^d with periodicity cell Y , the subscript $\#$ indicates periodic boundary conditions with respect to $y \in Y$. Condition (4.7) describes instantaneous nucleation at time $t = 0$ of a periodic distribution of nuclei. In order to obtain a well-defined asymptotic limit for $\varepsilon \rightarrow 0$, it is necessary to scale some given data in dependence of ε . Here it is assumed

$$\xi = \varepsilon \xi_0, \quad \alpha = \varepsilon^{-2} \alpha_0, \quad \text{and} \quad D_\ell = \varepsilon^2 D_\ell^{(0)}, \quad \ell = 1, 2. \quad (4.8)$$

The scaling of ξ is obvious: if the size of a solid crystal is proportional to ε , and if we model this crystal by a diffuse interface model, then the width of the diffuse interface must be bounded by $\text{const} \cdot \varepsilon$ with a constant that is small compared to the size of the crystal. Hence ξ_0 is a small phase field parameter that is fixed in the asymptotic expansion. The relaxation parameter α is scaled such that the total relaxation factor $\alpha \xi^2$ in the phase field equation remains constant. The scaling of the solute diffusivity is motivated by the fact that dendritic structures are created by a competition between a diffusional instability and surface energy. At least one of the diffusivities K or D_1, D_2 has to be scaled in dependence of ε . Since solute diffusivity is usually smaller than heat conductivity, it is natural to scale D_1 and D_2 . The fact that D_ℓ and ξ are both scaled proportional to ε^2 does not indicate that they are of similar size: in fact we expect $D_\ell^{(0)}$ to be of the size 1 and ξ_0 to be small compared to $D_\ell^{(0)}$, but the relation D_ℓ/ξ is kept fixed.

In order to study the limit $\varepsilon \rightarrow 0$, the existence of an asymptotic expansion

$$u_\varepsilon(t, x) = u_0\left(t, x, \frac{x}{\varepsilon}\right) + \varepsilon u_1\left(t, x, \frac{x}{\varepsilon}\right) + \varepsilon^2 u_2\left(t, x, \frac{x}{\varepsilon}\right) + \dots \quad \text{for } u = T, C, \Phi \quad (4.9)$$

is assumed. The existence of such an asymptotic expansion is not guaranteed. The result of the calculation will be justified in the next section. The gradient of a function $x \mapsto u(x, \frac{x}{\varepsilon})$ is given by $\nabla u = \nabla_x u + \frac{1}{\varepsilon} \nabla_y u$, where ∇_x and ∇_y denote the gradients with respect to the first and second variables of u , respectively. The asymptotic expansions (4.9) and the formal relation $\nabla = \nabla_x + \frac{1}{\varepsilon} \nabla_y$ are used in the differential equations (4.1)–(4.3). Then the coefficients of different powers of ε are compared, starting from the lowest order. For the Φ -dependent conductivities we use a Taylor expansion that is abbreviated by $K_\varepsilon = K_0 + \varepsilon K_1 + \varepsilon^2 K_2 + \dots$ with $K_0 = K(\Phi_0)$ and analogous expansions for $D_1^{(0)}(\Phi)$, $D_2^{(0)}(C, \Phi)$. The validity of these expansions with a remainder of order ε^β requires $K, D_1^{(0)} \in C^\beta(\mathbb{R}; \mathbb{R}^{d,d})$ and $D_2^{(0)} \in C^\beta(\mathbb{R}^2; \mathbb{R}^{d,d})$.

The **problem of 1st order** consists of the terms of order ε^{-2} in the heat equation (4.1); these are

$$\begin{aligned} -\nabla_y \cdot (K_0 \nabla_y T_0) &= 0 \quad \text{in } Q_{TY} := I_T \times \Omega \times Y, \\ T_0 &\text{ is } Y\text{-periodic with respect to } y. \end{aligned}$$

The solutions of this problem are constant with respect to y , hence $T_0(t, x, y) = T_0(t, x)$ is independent of y .

The **problem of 2nd order** is given by the terms of order ε^{-1} in the heat equation,

$$\begin{aligned} -\nabla_y \cdot (K_0(\nabla_y T_1 + \nabla_x T_0)) &= 0 \text{ in } Q_{\mathcal{T}\Omega Y}, \\ T_1 &\text{ is } Y\text{-periodic with respect to } y. \end{aligned}$$

This is a linear elliptic equation for T_1 with right hand side defined in terms of T_0 . Its solution can be represented by

$$T_1(t, x, y) = \sum_{j=1}^d H_j(t, x, y) \partial_{x_j} T_0(t, x)$$

with the solutions H_j of the local cell problem

$$-\nabla_y \cdot (K_0 \nabla_y H_j) = \nabla_y \cdot (K_0 e_j), \quad H_j \text{ is } Y\text{-periodic},$$

where e_j is the j -th unit vector of \mathbb{R}^d . Both K_0 and H_j depend on Φ_0 .

The **problem of 3rd order** consists of the terms of order ε^0 in the heat equation, the diffusion equation and the phase field equation,

$$\begin{aligned} \partial_t T_0 + L \partial_t \Phi_0 - \nabla_y \cdot (K_0(\nabla_y T_2 + \nabla_x T_1) + K_1(\nabla_y T_1 + \nabla_x T_0)) \\ - \nabla_x \cdot (K_0(\nabla_y T_1 + \nabla_x T_0)) &= 0, \end{aligned} \quad (4.10)$$

$$\partial_t C_0 - \nabla_y \cdot (D_1^{(0)}(\Phi_0) \nabla_y C_0) - \nabla_y \cdot (D_2^{(0)}(C_0, \Phi_0) \nabla_y \Phi_0) = 0, \quad (4.11)$$

$$\alpha_0 \xi_0^2 \partial_t \Phi_0 - \xi_0^2 \Delta_y \Phi_0 + p'(\Phi_0) + q(T_0, C_0, \Phi_0) = 0 \quad (4.12)$$

on $Q_{\mathcal{T}\Omega Y}$, supplemented by periodic boundary conditions on ∂Y for T_2 , C_0 and Φ_0 . Equations (4.11) and (4.12) do not contain any derivatives with respect to x . Hence they can be interpreted as a set of differential equations defined on $Q_{\mathcal{T}Y} := I_{\mathcal{T}} \times Y$ for every parameter $x \in \Omega$. Equation (4.10) is transformed into a macroscopic equation for $T_0 = T_0(t, x)$ by integration with respect to $y \in Y$. Due to the periodic boundary conditions the ∇_y -term disappears and the homogenized heat equation is obtained,

$$\partial_t T_0 + L \partial_t \bar{\Phi}_0 - \nabla \cdot (K^*(\Phi_0) \nabla T_0) = 0$$

with solid volume fraction $\bar{\Phi}_0(t, x) := \int_Y \Phi_0(t, x, y) dy$ and the effective heat conductivity

$$K_{ij}^*(\Phi_0) := \int_Y \left(K_{ij}(\Phi_0) + \sum_{k=1}^d K_{ik}(\Phi_0) \partial_{y_k} H_j(\Phi_0) \right) dy.$$

The effective heat conductivity K_{ij}^* is symmetric, elliptic and bounded with the same constants k_0 and k_1 as the original matrix K , see e.g. [JKO94] or [Ho97].

Let us sum up the obtained two-scale model. It consists of

- The macroscopic heat equation

$$\partial_t (T_0 + L \bar{\Phi}_0) - \nabla \cdot (K^*(\Phi_0) \nabla T_0) = 0 \text{ in } Q_{\mathcal{T}\Omega} = I_{\mathcal{T}} \times \Omega \quad (4.13)$$

with boundary conditions and initial conditions

$$T_0 = T_{ibc}^{(0)} \text{ on } S_{\mathcal{T}\Omega} = I_{\mathcal{T}} \times \partial\Omega \text{ and } T_0(0, \cdot) = T_{ibc}^{(0)} \text{ in } \Omega.$$

- The definition of the averaged phase field $\bar{\Phi}_0(t, x) = \int_Y \Phi_0(t, x, y) dy$ and the effective heat conductivity

$$K_{ij}^*(\Phi_0) = \int_Y K_{ik}(\Phi_0) (\delta_{jk} + \partial_{y_k} H_j(\Phi_0)) dy \quad (4.14)$$

with the Kronecker symbol δ_{jk} via the solutions $H_j = H_j(\Phi_0)$ of the local cell problems

$$-\nabla_y \cdot (K(\Phi_0)(\nabla_y H_j + e_j)) = 0 \quad \text{in } Y \quad (4.15)$$

with periodic boundary conditions.

- The microscopic problems

$$\partial_t C_0 - \nabla_y \cdot (D_1^{(0)}(\Phi_0) \nabla_y C_0) - \nabla_y \cdot (D_2^{(0)}(C_0, \Phi_0) \nabla_y \Phi_0) = 0, \quad (4.16)$$

$$\alpha_0 \xi_0^2 \partial_t \Phi_0 - \xi_0^2 \Delta_y \Phi_0 + p'(\Phi_0) + q(T_0, C_0, \Phi_0) = 0 \quad (4.17)$$

in $Q_{TY} = I_T \times Y$ with periodic boundary conditions and initial data

$$C_0(0, x, y) = C_{ic}^{(0)}(x, y), \quad \Phi_0(0, x, y) = \Phi_{ic}^{(0)}(x, y) \quad \text{for } y \in Y.$$

These equations must be solved for every point $x \in \Omega$ of the macroscopic domain.

4.2 Analysis of the two-scale model

The existence of weak solutions to the two-scale model is proved in [Ec04c], Theorem 3.3, by a fixed point approach. Uniqueness of the solution is also proved in [Ec04c], Theorems 3.4 and 3.5. The results can be summed up as:

Theorem 4.1. *Let $\Omega \subset \mathbb{R}^d$ be a C^2 -smooth domain of dimension $d = 2$ or $d = 3$, $Y \subset \mathbb{R}^d$ be a unit cell, let $K, D_1 : \mathbb{R} \rightarrow \mathbb{R}^{d,d}$ be Lipschitz, symmetric and satisfy the condition (4.4), let $T_{ibc} \in W_r^{1,2}(Q_{T\Omega}) \cap H^1(I_T; W_s^1(\Omega))$ with $r > d$, $s > 1$ for $d = 2$ and $s > 6/5$ for $d = 3$, $C_{ic}, \Phi_{ic} \in L_\infty(\Omega; W_{\ell\#}^{2-2/\ell}(Y)) \cap W_r^1(\Omega; L_2(Y))$ with $\ell > 1 + d/2$, $0 \leq C_{ic} \leq 1$, suppose $D_2 \in C^{0,1}(\mathbb{R}^2; \mathbb{R}^{d,d})$ with $D_2(C, \Phi) = 0$ for $C \notin [0, 1]$, $p(\Phi) = \frac{1}{2}(\Phi^2 - 1)^2$, $q : \mathbb{R}^3 \rightarrow \mathbb{R}$ is Lipschitz and satisfies the growth condition $|q(T, C, \Phi)| \leq \text{const}(1 + |T| + |C| + |\Phi|)$, and let L, ξ, α be positive constants. Then there exists a unique weak solution (T, C, Φ) of the two-scale model (4.13)–(4.17).*

An estimate for the model error is derived in [Ec04b] under appropriate assumptions concerning the regularity of the solutions for both the original model and the two-scale model. Let $(T_\varepsilon, C_\varepsilon, \Phi_\varepsilon)$ denote the solutions of the original model (4.1)–(4.3), (4.5), (4.7) with the scaling (4.8) of the parameters and (T_0, C_0, Φ_0) be the solutions of the two-scale model (4.13)–(4.17) with initial data $T_{ibc}^{(0)}, C_{ic}^{(0)}, \Phi_{ic}^{(0)}$. The error estimate is done in terms of *macroscopic reconstructions of scale ε* for the solutions of the two-scale model:

$$u_0^\varepsilon(t, x) := u_0(t, x, x/\varepsilon) \quad \text{for } u \in \{T, C, \Phi\}.$$

The required regularity for the solutions of the original model is

$$\begin{aligned} & \|T_\varepsilon\|_{H^{1/2,1}(Q_{T\Omega})} + \|T_\varepsilon\|_{L_\infty(I_T; L_2(\Omega))} + \varepsilon \|C_\varepsilon\|_{H^{1/2,1}(Q_{T\Omega})} \\ & + \varepsilon \|\Phi_\varepsilon\|_{H^{1/2,1}(Q_{T\Omega})} + \|C_\varepsilon\|_{L_\infty(Q_{T\Omega})} + \|\Phi_\varepsilon\|_{L_\infty(Q_{T\Omega})} \leq \text{const}_1 \end{aligned} \quad (4.18)$$

with a constant const_1 independent of ε . The solution of the two-scale model is supposed to satisfy

$$\begin{aligned} T_0 & \in W_r^{1,2}(Q_{T\Omega}) \cap H^{1/2+\beta}(I_T; H^1(\Omega)), \\ C_0, \Phi_0 & \in L_\infty(\Omega; C^{1,2}(Q_{TY})), \quad \nabla_x C_0, \nabla_x \Phi_0 \in L_\infty(\Omega; W_s^{1,2}(Q_{TY})) \end{aligned} \quad (4.19)$$

with parameters $r > d + 2$, $s > d$ and $\beta > 0$.

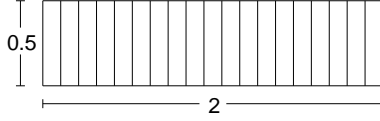


Fig. 4.2. Macroscopic domain of the numerical example

Theorem 4.2. *Let $\Omega \subset \mathbb{R}^d$ be a bounded Lipschitz domain and Y be a unit cell, let $K, D_1^{(0)} \in C^2(\mathbb{R}; \mathbb{R}^{d,d})$ be bounded and elliptic as described in (4.4), $D_2^{(0)} \in C^{0,1}(\mathbb{R}^2; \mathbb{R}^{d,d})$ be bounded, $q: \mathbb{R}^3 \rightarrow \mathbb{R}$ be globally Lipschitz and $p(\Phi) = \frac{1}{2}(\Phi^2 - 1)^2$. The solutions of the original model and the two-scale model satisfy the regularity properties (4.18) and (4.19). Let*

$$T_1^\varepsilon(t, x) := T_0(t, x) + \varepsilon H_j(t, x, \frac{x}{\varepsilon}) \partial_{x_j} T_0(t, x)$$

be the first order term in the asymptotic expansion for the temperature. Then

$$\begin{aligned} & \|T_\varepsilon - T_0\|_{L_\infty(I_T; L_2(\Omega))} + \|C_\varepsilon - C_0^\varepsilon\|_{L_\infty(I_T; L_2(\Omega))} + \|\Phi_\varepsilon - \Phi_0^\varepsilon\|_{L_\infty(I_T; L_2(\Omega))} \\ & + \|T_\varepsilon - T_1^\varepsilon\|_{L_2(I_T; H^1(\Omega))} \leq \text{const } \varepsilon^{1/2} \end{aligned}$$

with const independent of ε .

This theorem guarantees an order of approximation $\varepsilon^{1/2}$ for the two-scale model. The exponent of ε is limited to $\frac{1}{2}$, because the two-scale model does not approximate the original model of scale ε close to the boundary of the domain. It must be expected that the domain of an equiaxed dendritic crystal growing close to the boundary is not a full shifted copy of εY , but a subdomain obtained by intersection with Ω . This generates an additional error of order $\varepsilon^{1/2}$.

4.3 Numerical example

In order to illustrate the two-scale model we present the results of numerical computations for two space dimensions. The computations are done with constant heat conductivity $K = 1$ — hence no elliptic cell problem must be solved, — constant solute diffusivity $D_1(\Phi) = 1$, $D_2(C, \Phi) = -0.05$ and latent heat $2L = 1$. The function q in the phase field model is given by

$$q(\nabla_y \Phi, T, c, \Phi) = (1 - \Phi^2) \cdot 1.2 \cdot \arctan\left(\frac{\xi}{1.2 \cdot \sigma(\nabla_y \Phi)}(T + 10 \cdot C - \frac{1}{2}\Phi - 2)\right).$$

The quantity σ here is correlated with the surface tension for the sharp interface limit $\xi \rightarrow 0$. Its dependence on $\nabla_y \Phi$ is introduced in order to describe the dependence of the surface tension on the orientation of the surface. The problem can be reformulated in terms of the function $\mu = 10 \cdot C - \frac{1}{2}\Phi - 2$ that plays the role of a chemical potential; the diffusion equation then takes the form

$$\partial_t(\mu + \frac{1}{2}\Phi) - \Delta_y \mu = 0,$$

and the constitutive function q in the phase field equation is

$$q(\nabla_y \Phi, T, \mu, \Phi) = (1 - \Phi^2) \cdot 1.2 \cdot \arctan\left(\frac{\xi}{1.2 \cdot \sigma(\nabla_y \Phi)}(\mu + T)\right).$$

The precise form of $\sigma(\nabla \Phi)$ is

$$\sigma(\nabla \Phi) = \sigma_0(1 - (m^2 - 1)\sigma_1 \cos(m(\Theta(\nabla \Phi) - \Theta_0))),$$

where σ_0 describes the average value, σ_1 is the strength of the anisotropy, m describes the symmetry pattern of the dendrites, $\Theta(\nabla \Phi)$ is the angle between $\nabla \Phi$

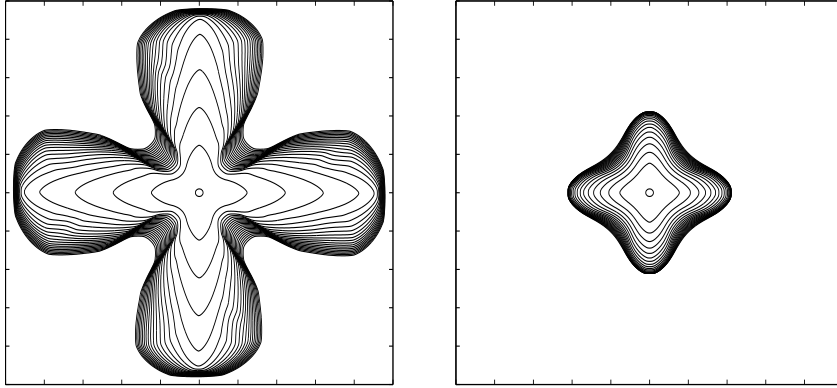


Fig. 4.3. Evolution of left and right crystal for $\Theta_0 = 0$

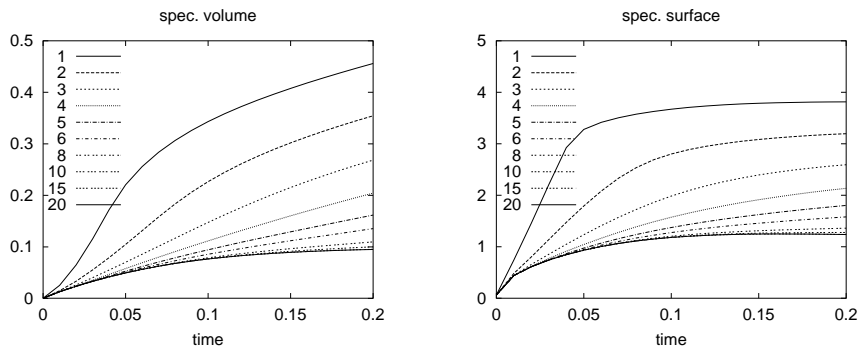
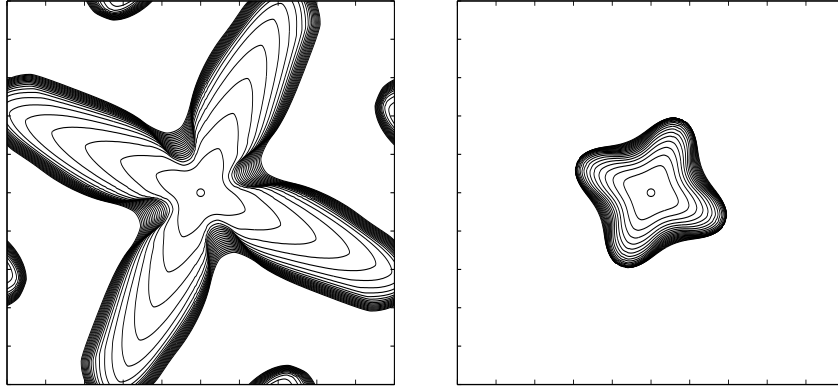
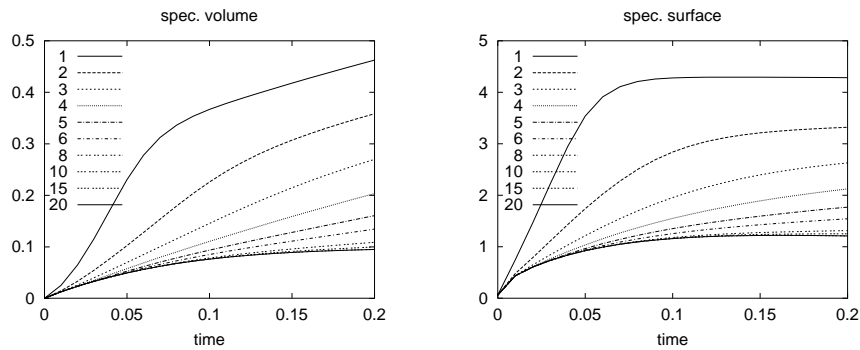


Fig. 4.4. Evolution of specific data for $\Theta_0 = 0$

and the x_1 -axis and Θ_0 is an offset angle. The special choice of q involving the arctan function is chosen in order to ensure that the minima of the potential for fixed $T, \mu, \nabla_y \Phi$ are kept at $\Phi = \pm 1$, even for large deviations from the equilibrium melting point; following the proposition of Kobayashi [Ko93].

Both the global heat equation and the microscopic problems are discretized by bilinear finite elements on uniform rectangular grids. The equations are decoupled by the time discretization in the following way: first a partially linearized version of the phase field equation is solved with temperature, concentration and $\nabla_y \Phi$ taken from the previous time step, then the diffusion equation is solved. This is done for every grid point of the macroscopic grid, then the global heat equation is solved. The decoupled linear equations are discretized with respect to time by the Crank-Nicolson scheme. This gives a semi-implicit time-discretization of the two-scale model, with an implicit discretization of the main parts of the differential operators.

The examples to be presented are computed for $\sigma_0 = 0.0002$, $m = 4$, $\xi = 0.005$, $\alpha = 5$ and $\sigma_1 = 0.05$. The initial conditions are $T = -0.1$ and $\mu(T, c, \Phi) = -0.1$, this adds up to a total initial undercooling of -0.2 . The unit cell for the microscopic problem is $Y = [0, 1]^2$, the initial solid nucleus is a sphere of radius $r = 0.05$ located at the midpoint $(0.5, 0.5)$ of Y . The boundary conditions are periodic boundary conditions for the microscopic problems and given heat fluxes for the macroscopic equations. The macroscopic domain is $\Omega = [0, 2] \times [0, 0.5]$; we prescribe homogeneous heat fluxes $\nabla T \cdot \nu_{ext} = 0$ on $[0, 2] \times \{0\}$, $\{2\} \times [0, 0.5]$ and $[0, 2] \times \{0.5\}$, on the remaining part $\{0\} \times [0, 0.5]$ of the boundary we prescribe the heat flux $\nabla T \cdot \nu_{ext} = -1$. The macroscopic equation is discretized by a uniform rectangular grid with

Fig. 4.5. Evolution of left and right crystal for $\Theta_0 = 0.4$ Fig. 4.6. Evolution of specific data for $\Theta_0 = 0.4$

19×1 elements; it is essentially one-dimensional, the crystals evolving at the same x_1 -position are equal. The microscopic problems are solved with uniform rectangular grids of 300×300 elements. The time step is $\Delta t = 2 \cdot 10^{-5}$, the final time of all computations is $t = 0.2$.

The figures show the results for three different orientations $\Theta_0 = 0$, $\Theta_0 = 0.4$ and $\Theta_0 = \pi/4$ for the anisotropy of the surface tension. Figures 4.3, 4.5 and 4.7 show the evolution of the left and right crystals from the initial time $t = 0$ to $t = 0.2$ in twenty steps. The left crystal is that growing at $x_1 = 0$, the right that at $x_1 = 2$. Due to the boundary cooling at $x_1 = 0$ the left crystal grows quickly, whereas the right one evolves rather slowly; its driving force is limited to the initial undercooling. For the left crystal, the offset angle $\Theta_0 = 0$ leads to shorter dendrites than the other angles, here the interaction of neighboring crystals happens earlier than in the cases $\Theta_0 = 0.4$ and $\Theta_0 = \pi/4$. This effect is not visible for the right crystals which are in an early stage of their evolution. In Figures 4.4, 4.6 and 4.8 the evolution of the specific data (specific volume and specific surface) is depicted for selected crystals in a row in x_1 -direction, the number corresponds to the position of the crystal, starting with position 1 at $x_1 = 0$. Further examples are presented in [Ec04a] and [Ec04b].

4.4 Some remarks on the numerical analysis

Error estimates for simple finite element discretizations of both the original model for scale ε and the two-scale model are derived and compared in [Ec02]. For linear or bilinear finite elements on a grid with mesh size h and a discretization with respect

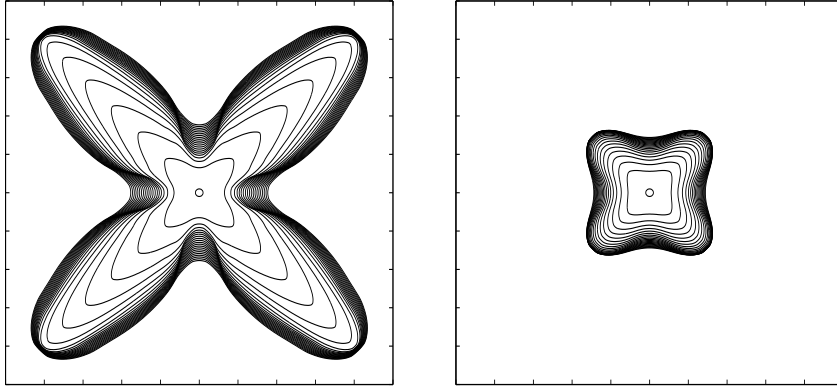


Fig. 4.7. Evolution of left and right crystal for $\Theta_0 = \pi/4$

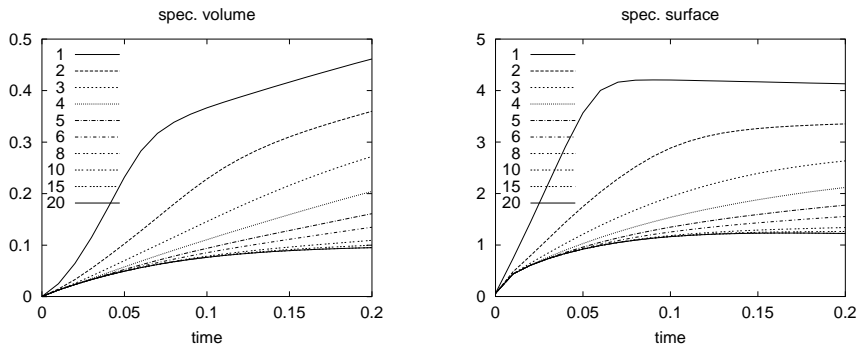


Fig. 4.8. Evolution of specific data for $\Theta_0 = \pi/4$

to time by an implicit Euler scheme with time step Δt , the error for the original model of scale ε is

$$\text{const}_1 \left(\left(\frac{h}{\varepsilon} \right)^2 + \Delta t \right).$$

This estimate reveals the typical convergence properties of the chosen discretization for parabolic equations: convergence of second order with respect to the space variables and of first order with respect to time. The factor $1/\varepsilon$ of the mesh size h accounts for the obvious fact that the microstructure starts to be properly resolved for $h \ll \varepsilon$ only. The discretization of the two-scale model uses a global grid for the macroscopic heat equation defined on Ω , at each node of this global grid the local cell problem defined on Y is solved with a local grid for Y . The mesh size of both grids is related to h_0 , the time step is again Δt . Then the error estimate for the two-scale model is

$$\text{const}_2 (h_0^2 + \Delta t).$$

Obviously no dependence on ε is present here. In order to have comparable computational complexity, the mesh sizes h_0 for the two-scale model and h for the original model should scale according to $h_0 \sim \sqrt{h}$. Respecting also the model error of order $\varepsilon^{1/2}$ for the two-scale model we conclude that the two-scale model is superior, if the mesh size used for the original model is larger than the threshold $h_\varepsilon = \text{const}_3 \varepsilon^{5/4}$ with a suitable const_3 .

4.5 Conclusion

The presented two-scale model is an approximate model for a problem with scale ε of the microstructure, with increasing accuracy for decreasing ε . Numerical computations with this model are valid for a whole range of microscale parameters $\varepsilon \in (0, \varepsilon_0]$ with the appropriate diffusivities. The model is suitable for material with *fast* heat diffusion and *slow* solute diffusion, where the temperature is assumed to be essentially constant on the microscopic scale, while the solute transport is neglected on the macroscopic scale.

Extensions of the presented two-scale model may be possible for more complex physical phenomena, for example phase transitions with convection, and physically more realistic situations, in particular for non-periodic microstructures. The extension to models with convection is probably possible by the application of techniques similar to those presented here to available phase field models that include convection, see e.g. [AMW00], [BDSKT99], [NWRs00]. For phase transitions with density differences between solid and liquid — where convection cannot be avoided — it may be necessary to use a unit cell that is fixed in Lagrangian coordinates but moves and deforms with the flow in an Eulerian description. Non-periodic microstructures can be described by a probabilistic description of the initial conditions, then it is possible to apply techniques of random homogenization of the type described in [JKO94]. A corresponding stochastic version of the two-scale model can be found in [Ec04a].

A Facts on evolving surfaces and transport identities

Let $I_{\mathcal{T}} = (0, \mathcal{T}) \subset \mathbb{R}$ be a time interval and let $m, d \in \mathbb{N}$ with $m \leq d$.

Definition A.1. $(\Sigma_t)_{t \in I_{\mathcal{T}}}$ is an evolving m -dimensional surface in \mathbb{R}^d if

1. for each $t \in I_{\mathcal{T}}$, the surface Σ_t can be parameterized over a fixed smooth orientable submanifold $U \subset \mathbb{R}^{m+1}$,
2. the set $\Sigma' := \{x' = (t, x) : t \in I_{\mathcal{T}}, x \in \Sigma_t\} \subset \mathbb{R} \times \mathbb{R}^d$ is a smooth $m+1$ -dimensional surface,
3. the tangent space $\mathbb{T}_{x'}\Sigma'$ is nowhere purely spatial, i.e., $\mathbb{T}_{x'}\Sigma' \neq \{0\} \times V$ with $V \cong \mathbb{R}^m$.

The spatial tangent space of dimension m in $x \in \Sigma_t$ is denoted by $\mathbb{T}_x\Sigma_t$, the spatial normal space of dimension $d-m$ by $\mathbb{N}_x\Sigma_t := (\mathbb{T}_x\Sigma_t)^\perp$. There is a unique vector field $\mathbf{v}_\Sigma : \Sigma' \rightarrow \mathbb{R}^{d+1}$ such that $(1, \mathbf{v}_\Sigma(t, x)) \in \mathbb{T}_{x'}\Sigma'$ and $\mathbf{v}_\Sigma(t, x) \in \mathbb{N}_x\Sigma_t$; $\mathbf{v}_\Sigma(t, x)$ is the vectorial normal velocity of the evolving surface. It can be verified that

$$\begin{aligned} \mathbb{T}_{x'}\Sigma' &= \{(s, s\mathbf{v}_\Sigma(x')) + (0, \tau) : s \in \mathbb{R}, \tau \in \mathbb{T}_x\Sigma_t\}, \\ \mathbb{N}_{x'}\Sigma' &= \{(-\mathbf{v}_\Sigma(x') \cdot \nu, \nu) : \nu \in \mathbb{N}_x\Sigma_t\}. \end{aligned}$$

Let φ be a smooth scalar field on Σ' . The derivative

$$\partial^\circ \varphi(x') := \partial_{(1, \mathbf{v}_\Sigma(x'))} \varphi(x') \text{ in } x' = (t, x) \in \Sigma', \quad (\text{A.1})$$

is the normal time derivative of φ in x' and describes the variation of φ when following the curve $\delta \mapsto c(\delta) \in \Sigma_{t+\delta}$ defined by $c(0) = x$ and $\partial_\delta c(\delta) = \mathbf{v}_\Sigma(t+\delta, c(\delta))$, $\delta \in (t - \delta_0, t + \delta_0)$ with some small $\delta_0 > 0$.

Let $(\tau_k(t, x))_{k=1}^m$ be an orthonormal basis of $\mathbb{T}_x\Sigma_t$. By $\partial_{\tau_k} \varphi(x)$ the differential of φ into direction $(0, \tau_k) \in \mathbb{T}_{x'}\Sigma'$ is denoted. The surface gradient of φ in x' is defined by $\nabla_\Sigma \varphi(x') := \sum_{k=1}^m \partial_{\tau_k} \varphi(x') \tau_k \in \mathbb{T}_x\Sigma_t$. Let $\boldsymbol{\varphi}$ be a smooth vector field on Σ' . The surface divergence of $\boldsymbol{\varphi}$ in x' is defined by $\nabla_\Sigma \cdot \boldsymbol{\varphi}(x') := \sum_{k=1}^m \partial_{\tau_k} \boldsymbol{\varphi}(x') \cdot \tau_k$.

If $m = d-1$ the normal space $N_x \Sigma_t$ has dimension one, and Σ' is orientable. Then there is a smooth vector field ν_Σ of unit normals, $\nu_\Sigma(x') \in N_x \Sigma_t$, $|\nu_\Sigma(x')|_2 = 1$. The (scalar) curvature and the curvature vector then are defined by

$$\kappa_\Sigma := -\nabla_\Sigma \cdot \nu_\Sigma, \quad \boldsymbol{\kappa}_\Sigma := \kappa_\Sigma \nu_\Sigma. \quad (\text{A.2})$$

Moreover, the (scalar) normal velocity then is defined by

$$v_\Sigma = \mathbf{v}_\Sigma \cdot \nu_\Sigma, \quad (\text{A.3})$$

and the following relation, derived in [Gu00], Chapter 15b, holds:

$$\partial^\circ \nu_\Sigma = -\nabla_\Sigma v_\Sigma. \quad (\text{A.4})$$

Definition A.2. $\Gamma' := (\Gamma_t)_t$ is an evolving m -dimensional subsurface of Σ' if

1. the set Γ_t is a relatively open connected subset of Σ_t for each $t \in I_\mathcal{T}$,
2. the boundary $\partial\Gamma' := (\partial\Gamma_t)_t$ consists of a finite number of evolving $m-1$ -dimensional surfaces such that, locally for each $t \in I_\mathcal{T}$, $\partial\Gamma_t$ is the graph of a Lipschitz continuous map.

A vectorial normal velocity $\mathbf{v}_{\partial\Gamma}$ can be assigned to the pieces of $\partial\Gamma'$ while Γ' obviously has the same vectorial normal velocity as Σ' , namely \mathbf{v}_Σ .

In some point $x \in \partial\Gamma_t$ the tangent cone on Γ_t is denoted by $\mathbb{T}_x \Gamma_t$. If x is in the interior of one of the pieces the cone is a half-space of $\mathbb{T}_x \Sigma_t$. Besides then the boundary of $\mathbb{T}_x \Gamma_t$ in $\mathbb{T}_x \Sigma_t$ coincides with the tangent space of the boundary $\partial\Gamma_t$, i.e., $\partial\mathbb{T}_x \Gamma_t = \mathbb{T}_x \partial\Gamma_t$. In such points x there is a unique unit vector $\tau_\Gamma \in \mathbb{T}_x \Sigma_t \cap N_x \partial\Gamma_t$ with $\tau_\Gamma \cdot \tilde{\tau} \leq 0$ for all $\tilde{\tau} \in \mathbb{T}_x \Gamma_t$. This vector τ_Γ is said to be the external unit normal of Γ_t with respect to Σ_t .

Let $m = d-1$ and $d \leq 3$. First, a divergence theorem is stated for a smooth surface with piecewise smooth Lipschitz boundary like Γ_t as in Definition A.2:

Theorem A.3. ([Be86], Corollary 4) *In the above situation there is the following identity:*

$$\int_{\Gamma_t} (\nabla_\Sigma \cdot \boldsymbol{\varphi} + \boldsymbol{\kappa}_\Sigma \cdot \boldsymbol{\varphi}) d\mathcal{H}^m(x) = \int_{\partial\Gamma_t} \boldsymbol{\varphi} \cdot \tau_\Gamma d\mathcal{H}^{m-1}.$$

If $\boldsymbol{\varphi}$ is a tangent vector field then $\boldsymbol{\kappa}_\Sigma \cdot \boldsymbol{\varphi} = 0$ so that one gets the usual divergence theorem on surfaces. It should be remarked that the proof in [Be86] is performed for smooth $\partial\Gamma_t$ but there is a brief note on the above case of a piecewise smooth boundary at the end of Section II(2). Finally, a transport identity is stated:

Theorem A.4. ([Be86], Theorem 1) *In the above situation it holds for every $t \in I_\mathcal{T}$ that*

$$\frac{d}{dt} \left(\int_{\Gamma_t} \boldsymbol{\varphi} d\mathcal{H}^m \right) \Big|_t = \int_{\Gamma_t} (\partial^\circ \boldsymbol{\varphi} - \boldsymbol{\varphi} \mathbf{v}_\Sigma \cdot \boldsymbol{\kappa}_\Sigma) d\mathcal{H}^m + \int_{\partial\Gamma_t} (\boldsymbol{\varphi} \mathbf{v}_{\partial\Gamma} \cdot \tau_\Gamma) d\mathcal{H}^{m-1}.$$

Remark A.5. If $\mathbf{v}_\Sigma = 0$ and $\boldsymbol{\kappa}_\Sigma = 0$ then Γ_t is flat, ∂° reduces to ∂_t and $\mathbf{v}_{\partial\Gamma}$ is tangential. Altogether, the Reynold's transport theorem is obtained.

References

- [Al99] Almgren, R.F.: Second-order phase field asymptotics for unequal conductivities. SIAM J. Appl. Math. **59**, 2086–2107 (1999)
- [AP92] Alt, H.W., Pawlow, I.: Existence of solutions for non-isothermal phase separation. Adv. Math. Sci. Appl. **1**, 319–409 (1992)

- [AP96] Alt, H.W., Pawlow, I.: On the entropy principle of phase transition models with a conserved order parameter. *Adv. Math. Sci. Appl.* **6** 291–376 (1996)
- [An02] Andersson, C.: Third order asymptotics of a phase-field model. TRITA-NA-0217, Dep. of Num. Anal. and Comp. Sc., Royal Inst. of Technology, Stockholm (2002)
- [AMW00] Anderson, D.M., McFadden, G.B., Wheeler, A.A.: A phase field model for solidification with convection. *Physica D* **135**, 175–194 (2000)
- [BGN06] Barrett, J.W., Garcke, H., Nürnberg, R.: On the Variational Approximation of Combined Second and Fourth Order Geometric Evolution Equations. Preprint No. 07/2006, Faculty of Mathematics, University of Regensburg.
- [BBR05] Bellettini, G., Braides, A., Riey, G.: Variational Approximation of Anisotropic Functionals on Partitions. *Ann. Mat.* **184**, 75–93 (2002)
- [BDSKT99] Beckermann, C., Diepers, H.-J., Steinbach, I., Karma, A., Tong, X.: Modeling melt convection in phase field simulations of solidification. *J. Comput. Phys.* **154**, 468–496 (1999)
- [Be86] Betounes, D.E.: Kinematics of submanifolds and the mean curvature normal. *Arch. Rat. Mech. Anal.* **96**, 1–27 (1986)
- [BE91] Blowey, J.F., Elliott, C.M.: The Cahn-Hilliard gradient theory for phase separation with nonsmooth free energy. I. Mathematical analysis. *Europ. J. Appl. Math.* **2**, 233–280 (1991)
- [BS96] Brokate, M., Sprekels, J.: *Hysteresis and Phase Transitions*. *Appl. Math. Sc.* **121**, Springer (1996)
- [BGS98] Bronsard, L., Garcke, H., Stoth, B.: A multi-phase Mullins–Sekerka system: Matched asymptotic expansions and an implicit time discretization for the geometric evolution problem. *Proc. Roy. Soc. Edinburgh Sect. A* **128**, 481–506 (1998)
- [CC98] Caginalp, G., Chen, X.: Convergence of the phase field model to its sharp interface limits. *Europ. J. Appl. Math.* **9**, 417–445 (1998)
- [CF88] Caginalp, G., Fife, P.C.: Dynamics of layered interfaces arising from phase boundaries. *SIAM J. Appl. Math.* **48**, 506–518 (1988)
- [Ca89] Caginalp, G.: Stefan and Hele Shaw type models as asymptotic limits of the phase field equations. *Phys. Rev. A* **39**, 5887–5896 (1989)
- [CH74] Cahn, J.W., Hoffmann, D.W.: A vector thermodynamics for anisotropic surfaces II. Curved and faceted surfaces. *Acta Metall. Mater.*, **22**, 1205–1214 (1974)
- [Da01] Davis, S.H.: *Theory of solidification*. Cambridge University Press (2001)
- [DS95] De Mottoni, P., Schatzman, M.: Geometrical evolution of developed interfaces. *Trans. Amer. Math. Soc.* **347**, 1533–1589 (1995)
- [Di04] Dirr, N.: A Stefan problem with surface tension as the sharp interface limit of a nonlocal system of phase-field type. *J. Statist. Phys.* **114**, 1085–1113 (2004)
- [DW05] Dreyer, W., Wagner, B.: Sharp-interface model for eutectic alloys, Part I: Concentration dependent surface tension. *Interf. Free Bound.* **7**, 199–227 (2005)
- [Ec02] Eck, C.: Finite element error estimates for a two-scale phase field model describing liquid–solid phase transitions with equiaxed dendritic microstructure. SPP 1095 Mehrskalprobleme, Preprint 67 (2002) <http://www1.am.uni-erlangen.de/~eck/papers/pfhee.pdf>
- [Ec04a] Eck, C.: A two-scale phase field model for liquid-solid phase transitions of binary mixtures with dendritic microstructure. Habilitation Thesis, Universität Erlangen (2004)
- [Ec04b] Eck, C.: Homogenization of a phase field model for binary mixtures. *Multiscale Modeling and Simulation* **3**(1), 1–27 (2004)
- [Ec04c] Eck, C.: Analysis of a two-scale phase field model for liquid-solid phase transitions with equiaxed dendritic microstructures. *Multiscale Modeling and Simulation* **3**(1), 28–49 (2004)
- [FP90] Fife, P.C., Penrose, O.: Thermodynamically consistent models of phase-field type for the kinetics of phase transitions. *Physica D* **43**, 44–62 (1990)
- [FP95] Fife, P.C., Penrose, O.: Interfacial dynamics for thermodynamically consistent phase-field models with nonconserved order parameter. *EJDE* 1995 **16**, 1–49 (1995)

- [GHS06] Garcke, H., Haas, R., Stinner, B.: On Ginzburg-Landau type free energies for multi-phase systems. In preparation.
- [GNS04] Garcke, H., Nestler, B., Stinner, B.: A diffuse interface model for alloys with multiple components and phases. *SIAM J. Appl. Math.*, **64**, 775–799 (2004)
- [GNS98] Garcke, H., Nestler, B., Stoth, B.: On anisotropic order parameter models for multi-phase systems and their sharp interface limits. *Phys. D* **115**, 87–108 (1998)
- [GNS99] Garcke, H., Nestler, B., Stoth, B.: A multi phase field concept: numerical simulations of moving phase boundaries and multiple junctions. *SIAM J. Appl. Math.* **60**, 295–315 (1999)
- [GS06] Garcke, H., Stinner, B.: Second order phase field asymptotics for multi-component systems. To appear in *Interf. Free Bound.* (2006)
- [Gi77] Giusti, E.: Minimal surfaces and functions of bounded variation. *Notes on Pure Math.* **10**, Austr. Nat. Univ. Canberra (1977)
- [Gu00] Gurtin, M.E.: Configurational forces as basic concepts of continuum physics. *Appl. Math. Sc.* **137**, Springer (2000)
- [Ha94] Haasen, P.: *Physikalische Metallkunde*. 3. ed., Springer (1994)
- [Ha06] Haas, R.: Modelling and analysis for general non-isothermal convective phase field systems. In preparation.
- [Ho97] Hornung, U. (ed.): *Homogenization and Porous Media*. Springer, New York (1997)
- [JKO94] Jikov, V.V., Kozlov, S.M., Oleinik, O.A.: *Homogenization of Differential Operators and Integral Functionals*, Springer, Berlin - Heidelberg (1994)
- [KR98] Karma, A., Rappel, J.-W.: Quantitative phase-field modeling of dendritic growth in two and three dimensions. *Phys. Rev. E* **57**, 4323–4349 (1998)
- [KY87] Kirkaldy, J.S., Young, D.J.: *Diffusion in the condensed state*. The Institute of Metals, London (1987)
- [Ka01] Karma, A.: Phase-field formulation for quantitative modeling of alloy solidification. *Phys. Rev. Lett.* **87**, 115701–1-4 (2001)
- [Ko93] Kobayashi, R.: Modeling and numerical simulation of dendritic crystal growth. *Physica D* **63** 410–423 (1993)
- [KRS05] Krejčí, P., Rocca, E., Sprekels, J.: Nonlocal temperature-dependent phase-field models for non-isothermal phase transitions. *WIAS Preprint No.* 1006 (2005)
- [LG50] Landau, L.D., Ginzburg, V.I.: K teorii sverkhrovodimosti. *Zh. Eksp. Teor. Fiz* **20**, 1064–1082 (1950), english translation: On the theory of superconductivity, *Collected Papers of L.D. Landau*, D. ter Haar (ed.), Pergamon, Oxford, UK, 626–633 (1965)
- [LV83] Luckhaus, S., Visintin, A.: Phase transition in multicomponent systems. *Man. Math.* **43**, 261–288 (1983)
- [MWA00] McFadden, G.B., Wheeler, A.A., Anderson, D.M.: Thin interface asymptotics for an energy/entropy approach to phase-field models with unequal conductivities. *Phys. D* **144**, 154–168 (2000)
- [Mu01] Müller, I.: *Grundzüge der Thermodynamik*. 3. ed., Springer (2001)
- [NWR00] Nestler, B., Wheeler, A.A., Ratke, L., Stöcker, C.: Phase-field model for solidification of a monotectic alloy with convection. *Physica D* **141**, 133–154 (2000)
- [On31] Onsager, L.: Reciprocal relations in irreversible processes I. *Phys. Rev.*, **37**, 405–426 (1931)
- [PF90] Penrose, O., Fife, P.C.: Thermodynamically consistent models of phase field type for the kinetics of phase transition. *Phys. D* **43**, 44–62 (1990)
- [RBKD04] Ramirez, J.C., Beckermann, C., Karma, A., Diepers, H.-J.: Phase-field modeling of binary alloy solidification with coupled heat and solute diffusion. *Phys. Rev. E* **69**, 51607–1-16 (2004)
- [SZ03] Sprekels, J., Zheng, S.: Global existence and asymptotic behaviour for a nonlocal phase-field model for non-isothermal phase transitions. *J. Math. Anal. Appl.* **279**, 97–110 (2003)
- [St91] Sternberg, P.: Vector-valued local minimizers of nonconvex variational problems. *Rocky Mountain J. Math.* **21**, 799–807 (1991)
- [St05a] Stinner, B.: Surface energies in multi phase systems with diffuse phase boundaries. To appear in the *Proc. of the conference on Free Boundary Problems in Coimbra, Portugal* (2005)

- [St05b] Stinner, B.: Derivation and analysis of a phase field model for alloy solidification. Doctoral Thesis, Universität Regensburg (2005).
- [St96] Stoth, B.: A sharp interface limit of the phase field equations, one-dimensional and axisymmetric. *Europ. J. Appl. Math.* **7**, 603–633 (1996)
- [Vi96] Visintin, A.: Models of phase transitions. *Progr. Nonlin. Diff. Eq. Appl.* **28**, Birkhäuser, Boston (1996)
- [WMB92] Wheeler, A.A., McFadden, G.B., Boettinger, W.J.: Phase-field model for isothermal phase transitions in binary alloys, *Phys. Rev. A* **45**, 7424–7439 (1992)
- [WM97] Wheeler, A.A., McFadden, G.B.: On the notion of a ξ -vector and a stress tensor for a general class of anisotropic diffuse interface models. *Proc. Roy. Soc. London Ser. A* **453**, 1611–1630 (1997)

