

# Derivation and Analysis of a Phase Field Model for Alloy Solidification

Dissertation zur Erlangung des  
Doktorgrades der Naturwissenschaften  
(Dr. rer. nat.)  
der Naturwissenschaftlichen Fakultät I - Mathematik  
der Universität Regensburg

vorgelegt von

Björn Stinner

Regensburg, Oktober 2005

Promotionsgesuch eingereicht am 10. Oktober 2005

Die Arbeit wurde angeleitet von Prof. Dr. H. Garcke

Prüfungsausschuss:	Vorsitzender:	Prof. Dr. Janssen
	1. Gutachter:	Prof. Dr. Garcke
	2. Gutachter:	Priv.-Doz. Dr. Eck
	weiterer Prüfer:	Prof. Dr. Finster Zirker

# Contents

<b>1 Alloy Solidification</b>	<b>11</b>
1.1 Irreversible thermodynamics . . . . .	11
1.1.1 Thermodynamics for a single phase . . . . .	11
1.1.2 Multi-phase systems . . . . .	15
1.1.3 Derivation of the Gibbs-Thomson condition . . . . .	18
1.2 The general sharp interface model . . . . .	24
1.3 Non-negativity of entropy production . . . . .	25
1.4 Calibration . . . . .	28
1.4.1 Phase diagrams . . . . .	28
1.4.2 Mass diffusion . . . . .	30
<b>2 Phase Field Modelling</b>	<b>33</b>
2.1 The general phase field model . . . . .	34
2.2 Non-negativity of entropy production . . . . .	38
2.3 Examples . . . . .	39
2.3.1 Possible choices of the surface terms . . . . .	39
2.3.2 Relation to the Penrose-Fife model . . . . .	40
2.3.3 A linearised model . . . . .	41
2.3.4 Relation to the Caginalp model . . . . .	42
2.3.5 Relation to the Warren-McFadden-Boettinger model . . . . .	43
2.4 The reduced grand canonical potential . . . . .	44
2.4.1 Motivation and introduction . . . . .	44
2.4.2 Example . . . . .	46
2.4.3 Reformulation of the model . . . . .	47
<b>3 Asymptotic Analysis</b>	<b>49</b>
3.1 Expansions and matching conditions . . . . .	51
3.2 First order asymptotics of the general model . . . . .	55
3.2.1 Outer solution . . . . .	56
3.2.2 Inner expansion . . . . .	57
3.2.3 Jump and continuity conditions . . . . .	59
3.2.4 Gibbs-Thomson relation and force balance . . . . .	60
3.3 Second order asymptotics in the two-phase case . . . . .	64
3.3.1 The modified two-phase model . . . . .	64
3.3.2 Outer solutions . . . . .	65
3.3.3 Inner solutions . . . . .	66
3.3.4 Summary of the leading order problem and the correction problem . . . . .	69
3.4 Numerical simulations of test problems . . . . .	71
3.4.1 Scalar case in 1D . . . . .	71
3.4.2 Scalar case in 2D . . . . .	74
3.4.3 Binary isothermal systems . . . . .	75

3.4.4	Binary non-isothermal case . . . . .	76
<b>4</b>	<b>Existence of Weak Solutions</b>	<b>79</b>
4.1	Quadratic reduced grand canonical potentials . . . . .	81
4.1.1	Assumptions and existence result . . . . .	81
4.1.2	Galerkin approximation . . . . .	84
4.1.3	Uniform estimates . . . . .	86
4.1.4	First convergence results . . . . .	89
4.1.5	Strong convergence of the gradients of the phase fields . . . . .	90
4.1.6	Initial values for the phase fields . . . . .	92
4.1.7	Additional a priori estimates . . . . .	94
4.2	Linear growth in the chemical potentials . . . . .	97
4.2.1	Assumptions and existence result . . . . .	98
4.2.2	Solution to the perturbed problem . . . . .	99
4.2.3	Properties of the Legendre transform . . . . .	101
4.2.4	Compactness of the conserved quantities . . . . .	104
4.2.5	Convergence statements . . . . .	107
4.3	Logarithmic temperature term . . . . .	109
4.3.1	Assumptions and existence result . . . . .	110
4.3.2	Solution to the perturbed problem . . . . .	112
4.3.3	Estimate of the conserved quantities . . . . .	114
4.3.4	Strong convergence of temperature and chemical potentials . . . . .	118
4.3.5	Convergence statements . . . . .	122
<b>A</b>	<b>Notation</b>	<b>123</b>
<b>B</b>	<b>Equilibrium thermodynamics</b>	<b>125</b>
<b>C</b>	<b>Facts on evolving surfaces and transport identities</b>	<b>129</b>
<b>D</b>	<b>Several functional analytical results</b>	<b>131</b>

# Introduction

The subject of the present work is the derivation and the analysis of a phase field model to describe solidification phenomena on a microscopic length scale occurring in alloys of iron, aluminium, copper, zinc, nickel, and other materials which are of importance in industrial applications. Mechanical properties of castings and the quality of workpieces can be traced back to the structure on an intermediate length scale of some  $\mu m$  between the atomic scale of the crystal lattice (typically of some  $nm$ ) and the typical size of the workpiece. This so-called microstructure consists of grains which may only differ in the orientation of the crystal lattice, but it is also possible that there are differences in the crystalline structure or the composition of the alloy components. In the first case the system is named homogeneous, in the latter case heterogeneous. The homogeneous parts in heterogeneous systems are named phases. These phases itself are in thermodynamic equilibrium but the boundaries separating the grains of the present phases are not in equilibrium and comprise excess free energy. Following [Haa94], Chapter 3, the microstructure is defined to be the totality of all crystal defects which are not in thermodynamic equilibrium.

The fact that the thermodynamic equilibrium is not attained results from the process of solidification. When a melt is cooled down solid germs appear and grow into the liquid phase. The type of the solid phase and the evolution of the solid-liquid phase boundaries depends on the local concentrations of the components and on the local temperature. But also the surface energy of the solid-liquid interface plays an important role. Not only the typical size of the microstructure is determined by the surface energy. Its anisotropy, together with certain (possibly also anisotropic) mobility coefficients, and the fact that the solid-liquid interface is unstable leads to the formation of dendrites as in Fig. 1. The properties as the number of tips, the tip velocity, and the tip curvature are of special interest in materials science.

During the growth, the primary solid phases can meet forming grain boundaries which involve surface energies of their own. In eutectic alloys, lamellar eutectic growth as in Fig. 2 on the left can be observed, i.e., layers of solid phases enriched with two different components grow into a melt of an intermediate composition. The strength and robustness of workpieces thanks to that fine microstructure make such alloys of particular interest in industry. The typical width of the grains and its dependence on composition and cooling rate is of interest as well as the appearance of patterns like, for example, eutectic colonies (cf. Fig. 2 on the right). At an even later stage of solidification, when essentially the whole melt is solidified, coarsening and ripening processes involving a motion of the grain boundaries on a larger timescale are observed.

In the following, the distinction between phase and grain will be dropped, and the notation "phase" will be used for an atomic arrangement in thermodynamic equilibrium as well as a domain occupied by a certain phase, i.e., a grain of the phase. As a consequence, the notation "phase boundary" will be used for interfaces separating grains of the same phase, too.

When modelling solidification processes, classically, the occurring phase boundaries are moving hypersurfaces meeting in triple lines or moving curves meeting in triple points if the problem is essentially two dimensional as in thin films. The Gibbs-Thomson condition couples the form and the motion of the interface to its surface energy and to the local thermodynamic potentials. In the Stefan problem (cf. [Dav01], Section 2.2) for a pure material, for example, the Gibbs-Thomson condition states that the deviation of the temperature from its equilibrium value  $u = c(T - T_m)$

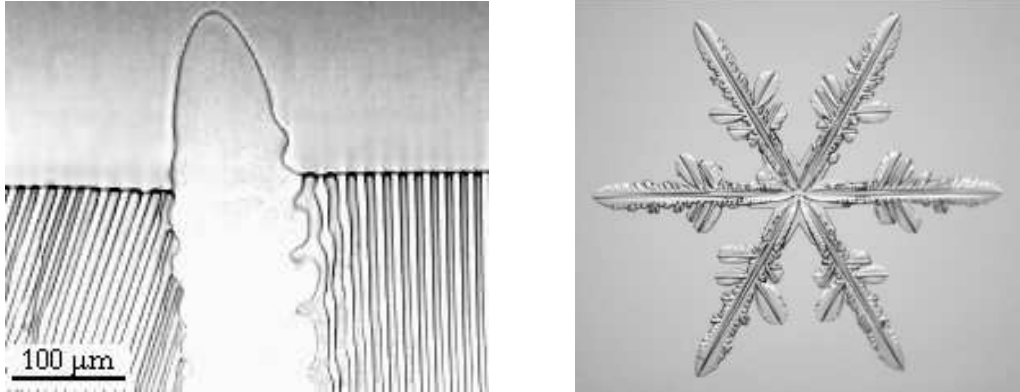


Figure 1: On the left: growth of a primary dendrite with intermediate eutectic microstructure into some hypo-eutectic  $C_2Cl_6$ - $CBr_4$ -alloy (Akamatsu and Faivre, picture from <http://www.gps.jussieu.fr/gps/surfaces/lamel.htm>); on the right: ice crystal (Libbrecht, picture from <http://www.its.caltech.edu/atomic/snowcrystals/photos/photos.htm>)

on the solid-liquid interface ( $T$  being the interfacial temperature,  $T_m$  the melting temperature, and  $c$  some material dependent constant) is proportional to the surface tension  $\sigma$  multiplied with the curvature  $\kappa$  of the interface,

$$u = \sigma\kappa.$$

In addition, balance equations for the energy and the components must be considered. In the context of irreversible thermodynamics (cf. [Mül01], see also Section 1.1.1 for a brief introduction) this leads to diffusion equations for the heat and the components in the pure phases, coupled to jump conditions on the phase boundaries taking, for example, the release of latent heat during solidification and the segregation of components into account (cf. [Dav01], Section 3.1). In the already mentioned Stefan problem the diffusion equation for the heat reads

$$\partial_t u = D\Delta u$$

with some diffusion coefficient  $D$ , and the jump condition on the solid-liquid interface

$$lv_\nu = [-D\nabla u] \cdot \nu$$

where the constant  $l$  is proportional to the latent heat,  $\nu$  is a unit normal on the interface,  $v_\nu$  is the velocity of the interface in direction  $\nu$ , and  $[\cdot]$  denotes the jump of the quantity in the brackets when crossing the interface in direction  $\nu$ .

The idea of introducing order parameters enables to state a weak formulation of the free boundary problem and, possibly, to solve it (for example, [Luc91] for the Stefan problem). To each possible phase an order parameter  $\phi$ , in the following also called phase field variable, is introduced to describe the presence of the corresponding phase, i.e., in a pure phase the phase field variable of the corresponding phase is one while the other phase field variables vanish, and on the phase boundaries they are not defined but jump across the interface. As long as the phase field variables are of bounded variation, the surface energy is given as an integral of terms of their spatial gradients over the considered domain. In the case of a system with two phases occupying a domain  $\Omega$  a scalar phase field variable  $\phi \in BV(\Omega)$  is sufficient, and the surface energy is then

$$E_{\text{sharp}} = \int_{\Omega} \sigma |\nabla \phi| dx$$

where  $|\nabla \phi| dx$  has to be understood in the sense of a measure with support on the phase boundary. Adding further thermodynamic potentials to the energy (depending on the temperature, for

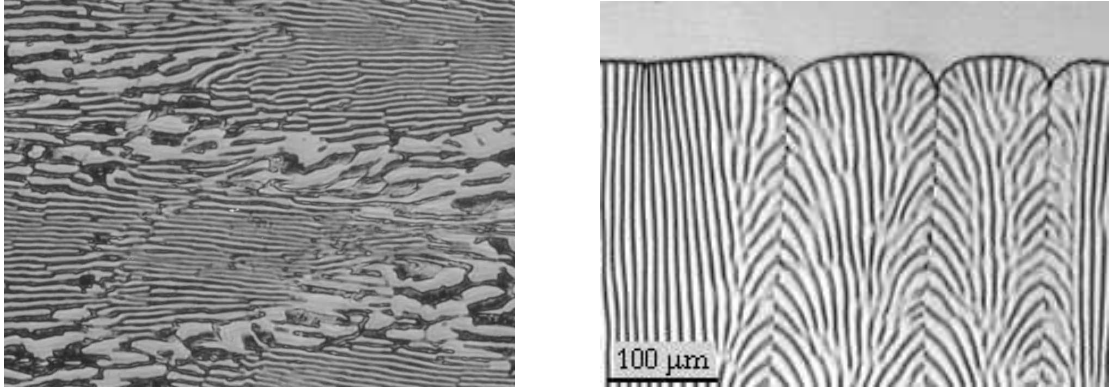


Figure 2: On the left: eutectic structures of some *Ru-Al-Mo*-alloy (Rosset, Cefalu, Varner, Johnson, picture from [https://engineering.purdue.edu/MSE/FACULTY/RESEARCH\\_FOCUS/Def\\_Fract\\_Ruth.whtml](https://engineering.purdue.edu/MSE/FACULTY/RESEARCH_FOCUS/Def_Fract_Ruth.whtml)); on the right: eutectic grains, so-called colonies (Akamatsu and Faivre, picture from <http://www.gps.jussieu.fr/gps/surfaces/lamel.htm>)

example), the evolution of the phase boundaries can be defined as an appropriate gradient flow of the free energy in the isothermal case or, with the opposite sign, of the entropy in the general case.

In the phase field approach, a length scale  $\varepsilon$  smaller than the typical size of the microstructure to be described is introduced. Instead of jumping across the phase boundaries, the phase field variables change smoothly in a transition layer whose thickness is determined by the new small length scale  $\varepsilon$ . This leads to the notion of a diffuse interface. The smooth profiles of the phase fields in the interfacial layer are obtained by replacing the sharp interface energy/entropy by a Ginzburg-Landau type energy/entropy involving a gradient term and a multi-well potential  $w$ . In the case of two phases it may be of the form

$$E_{\text{diffuse}} = \int_{\Omega} \left( \varepsilon \sigma |\nabla \phi|^2 + \frac{\sigma}{\varepsilon} w(\phi) \right) dx.$$

In the corresponding gradient flow, leading to systems of Allen-Cahn equations (cf., for example, [TC94]), the gradient term models diffusion trying to smooth out the phase field variables while the multi-well potential term is a counter-player and tries to separate the values. Of particular interest is the limit when the small length scale  $\varepsilon$  related to the thickness of the interfacial layer tends to zero. In quite general settings, the  $\Gamma$ -limit of the Ginzburg-Landau energy is known (cf. [Mod87, BBR05]), and for the time dependent case there are results establishing a relation between the Allen-Cahn equations and motion by curvature. Much less is known in the case that additional evolution equations are coupled to the Allen-Cahn equations as, for example, balance equations in models for solidification. Nevertheless, using the method of matched asymptotic expansions, often a sharp interface model related to the phase field model can be found.

The use of such smoothly varying phase field variables dates back to ideas of van der Waals [vdW83] and Landau and Ginzburg [LG50]. Langer [Lan86] and Caginalp [Cag89] introduced the idea in the context of solidification on which [OKS01] gives a summary. An overview on other applications of the phase field approach can be found in [Che02]. The phase field is not always considered as a mathematical device allowing for a reformulation of a free boundary problem. In other models, the phase field variables stand for physical quantities as, for example, the concentrations in the model of Cahn and Hilliard [CH58] or the mass density. There, the phase transitions are regarded as being diffuse from the beginning, i.e., they have a thickness of some atomic layers, and the sharp interface model is considered as an approximation on a larger length scale.

Independent of the interpretation of the phase field variables and the question whether the diffuse interface model is the natural one or an approximation of a free boundary problem, one advantage

of the phase field approach is that the numerical implementation of phase field models is much simpler than of sharp interface models. The fact that phases can disappear and phase boundaries can coalesce must be taken into account. The numerical handling of such singularities is difficult for the sharp interface model but not impossible (cf. [Sch98]). This problem is overcome in the phase field approach since there are only parabolic differential equations to solve. Furthermore, the extension of the interface by one dimension does not really cause high additional effort as long as adaptive methods are applied since the transition layers where the phase field variables strongly vary are very thin.

In the following, a short overview on the content of the present work is given. Intentionally, it is kept brief since each chapter starts with a careful and detailed introduction on its goals, difficulties, and results.

In Chapter 1, the sharp interface modelling of solidification in alloy systems is revised. Based on irreversible thermodynamics, the governing set of equations is derived providing a general framework (cf. Section 1.2). The main task is the derivation of the Gibbs-Thomson condition from a localised gradient flow of the entropy. To obtain a model for a specific material, the framework has to be calibrated by postulating suitable free energy densities for the possible phases and inserting material properties and parameters such as the surface energies and diffusivities.

In Chapter 2, a general framework for phase field modelling of solidification is presented. An entropy functional of Ginzburg-Landau type in the phase field variables plays the central role. Balance equations for the conserved quantities are coupled to a gradient flow like evolution equation for the phase fields in such a way that an entropy inequality can be derived. The general character becomes clear by demonstrating that the governing equations of earlier models are obtained by appropriate calibration. For the following analysis it turns out that the so-called reduced grand canonical potential density is a good thermodynamic quantity to formulate the general model. It is defined to be the Legendre transform of the negative entropy density.

The relation between the phase field model of the second chapter and the sharp interface model of the first chapter in the sense of a sharp interface limit is shown in Chapter 3. First, the procedure of matching asymptotic expansions is outlined. Afterwards, the main result on the relation is stated and proven. The quality of the approximation is of interest, too, and it is demonstrated that in certain cases a higher order approximation is possible taking additional correction terms in the phase field model into account. Numerical simulations support the theoretical results.

Chapter 4 is dedicated to the rigorous analysis of the partial differential equations of the phase field model. The parabolic system has the structure

$$\begin{aligned}\partial_t b(u, \phi) &= \nabla \cdot L \nabla u, \\ \partial_t \phi &= \nabla \cdot a'(\nabla \phi) - w'(\phi) + g(u, \phi)\end{aligned}$$

for a function  $u$  related to thermodynamic quantities and a set of phase field variables  $\phi$ . The first equation describes conservation of conserved quantities while the second one is the gradient flow of the entropy. The function  $b$  is the derivative of the reduced grand canonical potential  $\psi$  which is a convex function with respect to  $u$ , i.e.,  $b$  is monotone in  $u$ , and also the coupling term  $g$  is related to  $\psi$ . Existence of weak solutions to the parabolic system of equations is shown. The focus lies on tackling difficulties caused by the growth properties of the reduced grand canonical potential  $\psi$  in  $u$ , namely, potentials  $\psi$  involving terms like  $-\ln(-u)$  or of at most linear growth in  $u$  are of interest. The idea is to use a perturbation technique. The perturbed problem is solved making a Galerkin ansatz. The main task is then 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.



### **Acknowledgement**

I want to thank everyone who contributed to this work and supported me to finish it. My deepest thanks go to my supervisor Harald Garcke for his ideas and help to tackle all the challenges. Furthermore, I thank Britta Nestler and Christof Eck for the fruitful discussions on solidification phenomena and applications and, respectively, on the existence theory of weak solutions to partial differential equations.

I gratefully acknowledge the German Research Foundation (DFG) for the financial support within the priority program "Analysis, Modeling and Simulation of Multiscale Problems".



# Chapter 1

## Alloy Solidification

In applications, the production of certain microstructural morphologies in alloys is often achieved by imposing appropriate conditions just 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 as initial and boundary values or as additional forces and parameters in the equations governing the evolution. Starting from thermodynamic principles for irreversible processes, a framework for continuum modelling of alloy solidification is derived in Section 1.1.

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 localising an appropriate gradient flow of the entropy. For this purpose, variations of the entropy by deforming the interface in a small ball around a point on the phase boundary are considered. Since only variations are admissible such that the energy and mass remain conserved, the motion law is obtained by letting the radius of the small ball converge to zero after suitable rescaling.

It turns out that 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 local entropy production is non-negative and to derive an entropy inequality. This is presented in Section 1.3 after stating the total set of governing equations in Section 1.2.

Finally, in Section 1.4, it is discussed how material parameters can enter the framework such that a certain alloy is described. This step is called calibration. Bulk material properties and physical parameters as latent heats and melting temperatures of the components can be taken into account by postulating appropriate free energies of the possible phases. Their relation to the phase diagram describing the solidification behaviour of the considered alloy is briefly clarified. Experimentally measurable diffusion coefficients can enter the equations via suitable definition of the fluxes for the conserved quantities.

In this chapter, 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  $e$ .

### 1.1 Irreversible thermodynamics

#### 1.1.1 Thermodynamics for a single phase

An alloy of  $N \in \mathbb{N}$  components occupying an open domain  $\Omega \in \mathbb{R}^d$  during some time interval  $I = (0, T)$  is considered. In applications  $d = 3$ , but in the following chapters sometimes problems are examined which effectively are one or two dimensional, hence  $d \in \{1, 2, 3\}$ . There are no phase boundaries present, only the distributions of temperature and composition of the alloy are

of interest. The following assumptions are made:

- S1 The system is closed, there is no mass flux across the external boundary  $\partial\Omega$ .
- S2 The pressure is constant.
- S3 The only transport mechanism is diffusion. There are no forces present leading to flows or deformations.
- S4 The mass density is constant.

The domain  $\Omega$  remains undeformed during evolution. In applications, the changes in pressure or volume are often small and can be neglected (cf. [Haa94], Section 5.1) which motivates the second assumption. Models with constant mass density like the Stefan problem of the Introduction have been very successfully applied to describe microstructural evolution. But other effects as, for example, convection in liquid phases, can strongly influence the growing structures (cf. [Dav01]). The applicability of the model presented in the following is therefore restricted to cases where such effects can be neglected. Before deriving the governing set of equations some objects are defined for later use.

**1.1 Definition** For  $K \in \mathbb{N}$  define the sets

$$\mathbb{H}\Sigma^K := \left\{ v \in \mathbb{R}^K : \sum_{i=1}^K v_i = 1 \right\}, \quad (1.1a)$$

$$\Sigma^K := \left\{ v \in \mathbb{H}\Sigma^K : v_i \geq 0 \quad \forall i \right\}. \quad (1.1b)$$

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

$$\mathbb{T}_v\mathbb{H}\Sigma^K \cong \mathbb{T}\Sigma^K := \left\{ w \in \mathbb{R}^K : \sum_{i=1}^K w_i = 0 \right\}. \quad (1.1c)$$

The map  $\mathcal{P}^K : \mathbb{R}^K \rightarrow \mathbb{T}\Sigma^K$  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  $\text{Id}_K$  is the identity on  $\mathbb{R}^K$ .

Observe that  $\text{Id}_K - \frac{1}{K} \mathbf{1}_K \otimes \mathbf{1}_K$  is symmetric and  $\mathcal{P}^K w = w$  for all  $w \in \mathbb{T}\Sigma^K$ .

By the first law of thermodynamics, energy and mass are conserved quantities. By  $e$  or  $c_0$  the internal energy density (with respect to volume) is denoted. Let  $N$  be the number of components. Then  $c_i$  is the concentration of component  $i \in \{1, \dots, N\}$ . Writing  $\hat{c} = (c_1, \dots, c_N)$ , the (mass) concentrations are demanded to fulfil the constraint

$$\hat{c} \in \Sigma^N. \quad (1.2)$$

Following [Mül01], Section 11.2, the evolution is governed by balance equations for the conserved quantities. By the above Assumptions S2-S4 they simplify to

$$\partial_t e = -\nabla \cdot J_0, \quad \partial_t c_i = -\nabla \cdot J_i, \quad 1 \leq i \leq N, \quad (1.3)$$

with fluxes  $J_0$  for the energy and  $J_i$  for concentration  $c_i$ . For (1.2) being fulfilled the constraint

$$\sum_{i=1}^N J_i = 0 \quad (1.4)$$

is imposed. 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  $s$  is a function of the conserved quantities. Its derivatives are the inverse temperature and the chemical potential difference reduced by the temperature (see Appendix B), i.e.,

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

By  $\mu_i$  the chemical potential divided by the (by Assumption S4 constant) mass density corresponding to component  $i$  is denoted. In the above equation the identity  $\bar{\mu} = \mathcal{P}^N \mu$  was used where  $\mu = (\mu_1, \dots, \mu_N)$ . The scalar field  $T$  is the temperature. The fluxes are postulated to be linear combinations of the thermodynamic forces  $\nabla \frac{1}{T}$  and  $\nabla \frac{-\bar{\mu}_j}{T}$ ,  $1 \leq j \leq N$ , i.e.,

$$J_i = L_{i0} \nabla \frac{1}{T} + \sum_{j=1}^N L_{ij} \nabla \frac{-\bar{\mu}_j}{T}, \quad 0 \leq i \leq N \quad (1.5)$$

with coefficients  $L_{ij}$  which may depend on the thermodynamic potentials  $\frac{1}{T}$  and  $\frac{-\bar{\mu}}{T}$  or on the conserved quantities  $e$  and  $\hat{c}$ . This phenomenological theory was already introduced in [Ons31]. It is assumed that

$$L = (L_{ij})_{i,j=0}^N \text{ is positive semi-definite.} \quad (1.6a)$$

In Section 1.3 it is shown in a more general context that then local entropy production indeed is non-negative. To fulfil (1.4) it is required that

$$\sum_{i=1}^N L_{ij} = 0, \quad \forall j \in \{1, \dots, N\}. \quad (1.6b)$$

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 by the constraint (1.4). 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). A simple calculation shows that then due to the symmetry of the matrix  $(L_{ij})_{i,j}$

$$\sum_{j=1}^N L_{ij} \nabla \frac{-\bar{\mu}_j}{T} = \sum_{j=1}^N L_{ij} \nabla \frac{-\mu_j}{T}.$$

Another short calculation, more precisely considering  $J_i - J_N$ , shows that the definition of the fluxes as above is equivalent to the definition in [Mül01], Section 11.2.

The equations (1.3) are coupled to initial conditions at  $t = 0$  and boundary conditions on the external boundary  $\partial\Omega$ . As the system is closed it holds that  $J_i \cdot \nu_{ext} = 0$  for all  $i \in \{1, \dots, N\}$ ,  $\nu_{ext}$  is the external unit normal. If not otherwise stated the same is assumed for the energy flux, i.e., the system is adiabatic.

The equations (1.3) can also be interpreted as gradient flow of the entropy with respect to a weighted  $H^{-1}$ -product. Let

$$M : L^1(\Omega, \mathbb{R} \times \mathbb{T}\Sigma^N) \rightarrow \mathbb{R} \times \mathbb{T}\Sigma^N, \quad M(f) = \left( 0, \int_{\Omega} f_1(x) dx, \dots, \int_{\Omega} f_N(x) dx \right)$$

and consider the following problem: Given some function  $f \in L^2(\Omega, \mathbb{R} \times \mathbb{T}\Sigma^N)$  find  $h \in H^{1,2}(\Omega, \mathbb{R} \times \mathbb{T}\Sigma^N)$  with  $M(h) = 0$  such that

$$\int_{\Omega} \nabla v : L \nabla h := \int_{\Omega} \sum_{i,j=0}^N \nabla v_i \cdot L_{ij} \nabla h_j = \int_{\Omega} v \cdot f \quad (1.7)$$

## CHAPTER 1. ALLOY SOLIDIFICATION

---

for all test functions  $v \in H^{1,2}(\Omega, \mathbb{R} \times \text{T}\Sigma^N)$  with  $M(v) = 0$ . Using the Lax-Milgram theorem (cf. [Alt99], Theorem 4.2) it can be shown that this problem has a unique solution provided the following conditions are satisfied:

L1 The functions  $L_{ij}$  are essentially bounded, i.e.,  $L_{ij} \in L^\infty(\Omega)$ ,  $0 \leq i, j \leq N$ ,

L2 the core of the matrix  $L = (L_{ij})_{i,j=0}^N$  is the space  $(\mathbb{R} \times \text{T}\Sigma^N)^\perp$ , i.e., the space spanned by  $(0, 1, \dots, 1) \in \mathbb{R}^{N+1}$ .

If  $L$  depends on  $e$ ,  $\hat{c}$ ,  $T$ , or  $\bar{\mu}$  then, given a situation in form of measurable fields  $(e, \hat{c}, T, \bar{\mu})$ , it is assumed that the  $L_{ij}(e, \hat{c}, T, \bar{\mu})$  fulfils these properties. Observe that by the second assumption the matrix  $L$  is positive definite when restricted on  $\mathbb{R} \times \text{T}\Sigma^N$  so that the left hand side of (1.7) is coercive. Let  $\mathcal{G}$  be the operator that assigns to each  $f \in L^2(\Omega, \mathbb{R} \times \text{T}\Sigma^N)$  the solution  $h$  of (1.7). By

$$(f_1, f_2)_L := (\mathcal{G}(f_1), f_2)_{L^2} \tag{1.8}$$

a scalar product on  $L^2(\Omega, \mathbb{R} \times \text{T}\Sigma^N)$  is well-defined. Indeed, the symmetry follows from the symmetry of  $L$  and

$$\begin{aligned} (f_1, f_2)_L &= \int_{\Omega} \mathcal{G}(f_1) \cdot f_2 = \int_{\Omega} \nabla \mathcal{G}(f_1) : L \nabla \mathcal{G}(f_2) \\ &= \int_{\Omega} \nabla \mathcal{G}(f_2) : L \nabla \mathcal{G}(f_1) = \int_{\Omega} \mathcal{G}(f_2) \cdot f_1 = (f_2, f_1)_L, \end{aligned}$$

and the positivity from assumption L2.

If the system is isolated mass and energy in the whole system are constant, i.e.,  $M((e, \hat{c})^T(t)) = M((e, \hat{c})^T(t=0))$  and  $M(\partial_t(e, \hat{c})^T(t)) = 0$  for all  $t \in I$ . Therefore, when computing the variation of the entropy, only directions  $v \in L^2(\Omega, \mathbb{R} \times \text{T}\Sigma^N)$  with  $M(v) = 0$  are allowed. The gradient flow reads

$$(\partial_t(e, \hat{c})^T, v)_L = \left\langle \frac{\delta S}{\delta(e, \hat{c})}(e, \hat{c}), v \right\rangle = \int_{\Omega} \left( \frac{1}{T}, \frac{-\bar{\mu}}{T} \right)^T \cdot v =: - \int_{\Omega} u \cdot v.$$

For the second identity the relations  $s_{,e} = \frac{1}{T}$  and  $s_{,\hat{c}} = \frac{-\bar{\mu}}{T}$  were used. For some  $w \in L^2(\Omega, \mathbb{R} \times \text{T}\Sigma^N)$  the function  $w - M(w)$  is an allowed test function. By (1.8)

$$\begin{aligned} \int_{\Omega} \left( \mathcal{G}(\partial_t(e, \hat{c})^T) - M(\mathcal{G}(\partial_t(e, \hat{c})^T)) \right) \cdot w &= \int_{\Omega} \mathcal{G}(\partial_t(e, \hat{c})^T) \cdot (w - M(w)) \\ &= (\partial_t(e, \hat{c})^T, w - M(w))_L = - \int_{\Omega} u \cdot (w - M(w)) = - \int_{\Omega} (u - M(u)) \cdot w \end{aligned}$$

so that  $\mathcal{G}(\partial_t(e, \hat{c})^T) = -u + M(u - \mathcal{G}(\partial_t(e, \hat{c})^T))$ . Since  $\nabla M(\mathcal{G}(\partial_t(e, \hat{c})^T)) = 0$  equation (1.7) yields for  $v \in L^2(\Omega, \mathbb{R} \times \text{T}\Sigma^N)$  with  $M(v) = 0$  the identity

$$\int_{\Omega} v \cdot \partial_t(e, \hat{c})^T = \int_{\Omega} \nabla v : L \nabla \mathcal{G}(\partial_t(e, \hat{c})^T) = \int_{\Omega} \nabla v : L \nabla(-u).$$

The corresponding strong formulation is (1.3) with the fluxes defined in (1.5).

If the system not isolated but closed and, for example, Dirichlet boundary conditions are imposed for the temperature then of course a different solution space must be considered for problem (1.7), whence the above facts and conclusions read different.

### 1.1.2 Multi-phase systems

Let  $M \in \mathbb{N}$  be the number of possible phases. The domain  $\Omega$  is now decomposed into subdomains  $\Omega_1(t), \dots, \Omega_M(t)$ ,  $t \in I$ , which are called phases (and, more precisely, correspond to grains in applications; see the discussion in the Introduction). The phases are not necessarily connected but it is assumed that each one consists of a finite number of connected subdomains. The phase boundaries

$$\Gamma_{\alpha\beta}(t) := \overline{\Omega_\alpha(t)} \cap \overline{\Omega_\beta(t)}, \quad 1 \leq \alpha, \beta \leq M, \alpha \neq \beta,$$

are supposed to be piecewise smoothly evolving points, curves or hypersurfaces, depending on the dimension (cf. Definition C.1 in Appendix C). The unit normal on  $\Gamma_{\alpha\beta}$  pointing into phase  $\beta$  is denoted by  $\nu_{\alpha\beta}$ . The external boundary of phase  $\Omega_\alpha$  is denoted by

$$\Gamma_{\alpha,ext} := \overline{\Omega_\alpha(t)} \cap \partial\Omega.$$

If  $d \geq 2$  the intersections of the curves or hypersurfaces are defined by (for pairwise different  $\alpha, \beta, \delta \in \{1, \dots, M\}$ )

$$T_{\alpha\beta\delta}(t) := \overline{\Omega_\alpha(t)} \cap \overline{\Omega_\beta(t)} \cap \overline{\Omega_\delta(t)}.$$

Besides the phase boundaries can hit the external boundary. The sets of these points are denoted 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 smoothly evolving points. If  $d = 3$  triple lines can appear which are piecewise smoothly evolving curves. The triple lines can intersect and form quadruple junctions. Then the following sets are well-defined for pairwise different  $\alpha, \beta, \delta, \zeta \in \{1, \dots, M\}$ :

$$Q_{\alpha\beta\delta\zeta}(t) := \overline{\Omega_\alpha(t)} \cap \overline{\Omega_\beta(t)} \cap \overline{\Omega_\delta(t)} \cap \overline{\Omega_\zeta(t)}.$$

Besides the triple lines can hit the external boundary. The sets of these points are denoted by

$$Q_{\alpha\beta\delta,ext}(t) := \overline{\Omega_\alpha(t)} \cap \overline{\Omega_\beta(t)} \cap \overline{\Omega_\delta(t)} \cap \partial\Omega.$$

**1.2 Remark** During evolution, it may happen that one of the connected subdomains of a phase or even a whole phase 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. The latter configuration is not in mechanical equilibrium and will instantaneously split up forming new phase boundaries.

It is supposed that such singularities only occur at finitely many times  $t \in I$  during the evolution. This is why only piecewise smooth evolution is assumed. The following evolution equations are stated for times at which no singularity occurs.

In each phase  $\Omega_\alpha$ ,  $\alpha \in \{1, \dots, M\}$ , the smooth fields as in the previous Subsection 1.1.1 are present. They are denoted by  $c_i^\alpha$ ,  $e^\alpha$ ,  $\mu_i^\alpha$ ,  $T^\alpha$  and  $s^\alpha$  (here,  $\alpha$  is always an index, no exponent). Additionally, surface fields on the phase boundaries  $\Gamma_{\alpha\beta}$  are taken into account. The surface tension  $\sigma_{\alpha\beta}(\nu_{\alpha\beta})$  and a capillarity coefficient  $\gamma_{\alpha\beta}(\nu_{\alpha\beta})$  can depend on the orientation of the interface given by  $\nu_{\alpha\beta}$ . Both  $\sigma_{\alpha\beta}$  and  $\gamma_{\alpha\beta}$  are one-homogeneously extended to  $\mathbb{R}^d \setminus \{0\}$ , i.e.,

$$\sigma_{\alpha\beta}(l\nu) = l\sigma_{\alpha\beta}(\nu), \quad \gamma_{\alpha\beta}(l\nu) = l\gamma_{\alpha\beta}(\nu) \quad \forall l > 0.$$

Then the gradient  $\nabla\gamma_{\alpha\beta}(\nu)$  is well-defined whenever  $\nu \neq 0$ . Furthermore there is a mobility coefficient  $m_{\alpha\beta}(\nu_{\alpha\beta})$  that can also depend on the orientation of the interface. It is zero-homogeneously extended to  $\mathbb{R}^d \setminus \{0\}$ , i.e.,

$$m_{\alpha\beta}(l\nu) = m_{\alpha\beta}(\nu) \quad \forall l > 0.$$

Besides it is assumed that for all  $\alpha \neq \beta$

$$\sigma_{\alpha\beta}(\nu_{\alpha\beta}) = \sigma_{\alpha\beta}(-\nu_{\alpha\beta}) = \sigma_{\beta\alpha}(\nu_{\beta\alpha})$$

and analogously for  $\gamma_{\alpha\beta}$  and  $m_{\alpha\beta}$  so that the anisotropic surface fields are even and do not depend on the order of the indices. This assumption is not really necessary but shortens the following presentation and analysis.

The surface tensions  $\sigma_{\alpha\beta}$  and the mobilities  $m_{\alpha\beta}$  are physical quantities that may be measured in experiments. Given some reference temperature  $T_{ref}$ , the capillarity coefficients are related to the surface tensions by setting

$$\gamma_{\alpha\beta}(\nu_{\alpha\beta}) := \frac{\sigma_{\alpha\beta}(\nu_{\alpha\beta})}{T_{ref}}. \quad (1.9)$$

Based on ideas of [WSW<sup>+</sup>93] (see the Remark 1.3 below) the entropy is defined by

$$S(t) = \sum_{\alpha=1}^M \int_{\Omega_{\alpha}(t)} s^{\alpha}(e^{\alpha}, \hat{c}^{\alpha}) d\mathcal{L}^d - \sum_{\alpha < \beta, \alpha, \beta=1}^M \int_{\Gamma_{\alpha\beta}(t)} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) d\mathcal{H}^{d-1} \quad (1.10)$$

**1.3 Remark** Surface tensions usually decrease if temperature is increased. Similarly there can be a dependence on the concentrations of the adjacent phases  $\Omega_{\alpha}$  and  $\Omega_{\beta}$  or on the chemical potential. In [Gur93] the case of a pure material in two dimensions is considered. Temperature dependent surface fields for free energy, entropy and internal energy are defined and analysed yielding analogous relations as valid for the bulk fields. In particular, there is a contribution to the internal energy by the present surfaces which must be taken into account in the energy balance and which leads to additional terms in the jump condition for the energy (1.13c). These terms are often supposed to be small and are neglected (cf. [Dav01], Section 2.2.1). But in the following Gibbs-Thomson condition (1.14) the  $\gamma$ -term is necessary to generate capillarity effects leading to structures as in Fig. 1 and 2.

If the surface tension is linear in the temperature, i.e.,  $\sigma = \frac{\gamma}{T_{ref}}T$ , then following [Gur93] there is indeed no surface contribution to the internal energy, and the surface entropy, given by  $-\partial_T \sigma$ , is independent of the temperature as defined in (1.10). This yields the desired capillarity term in (1.14) without changing (1.13c). The following chapters deal with phase field models, and in that context such a definition of the entropy is motivated in [WSW<sup>+</sup>93]. The analysis of a more general dependence of  $\sigma$  on  $T$  and also on  $\bar{\mu}$  is left for future research.

The evolution must be defined in such a way that energy and mass are conserved and that local entropy production is non-negative. In every phase  $\alpha$  balance equations hold for the conserved quantities, i.e.

$$\partial_t e^{\alpha} = -\nabla \cdot J_0^{\alpha}, \quad \partial_t c_i^{\alpha} = -\nabla \cdot J_i^{\alpha}, \quad 1 \leq i \leq N, \quad (1.11)$$

and the coefficients of the fluxes which are defined as in the previous Subsection 1.1.1 can depend on the phase:

$$J_0^{\alpha} = L_{00}^{\alpha} \nabla \frac{1}{T^{\alpha}} - \sum_{j=1}^N L_{0j}^{\alpha} \nabla \frac{\bar{\mu}_j^{\alpha}}{T^{\alpha}}, \quad (1.12a)$$

$$J_i^{\alpha} = L_{i0}^{\alpha} \nabla \frac{1}{T^{\alpha}} - \sum_{j=1}^N L_{ij}^{\alpha} \nabla \frac{\bar{\mu}_j^{\alpha}}{T^{\alpha}}, \quad 1 \leq i \leq N. \quad (1.12b)$$

These equations are coupled to conditions on the moving phase boundaries  $\Gamma_{\alpha\beta}$ . To ensure conservation of  $e$  and the  $c_i$  the potentials  $\frac{1}{T}$  and  $\frac{\bar{\mu}_j}{T}$ ,  $1 \leq j \leq N$ , (or, equivalently, temperature



## 1.1. IRREVERSIBLE THERMODYNAMICS

and generalised chemical potential difference) are continuous and jump conditions (or Rankine-Hugoniot-conditions) have to be satisfied (cf., for example, [Smo94]):

$$T^\alpha = T^\beta, \quad (1.13a)$$

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta \quad \forall i, \quad (1.13b)$$

$$[e]_\alpha^\beta v_{\alpha\beta} = [J_0]_\alpha^\beta \cdot \nu_{\alpha\beta}, \quad (1.13c)$$

$$[c_i]_\alpha^\beta v_{\alpha\beta} = [J_i]_\alpha^\beta \cdot \nu_{\alpha\beta} \quad \forall i. \quad (1.13d)$$

Here,  $h^\alpha$  stands for the limit of the field  $h$  from the adjacent phase  $\alpha$  and  $[\cdot]_\alpha^\beta$  denotes the jump of the quantity in brackets across  $\Gamma_{\alpha\beta}$ , e.g.,  $[e]_\alpha^\beta = e^\beta - e^\alpha$ . The quantity  $v_{\alpha\beta}$  is the normal velocity towards  $\nu_{\alpha\beta}$ .

The evolution of the phase boundaries is coupled to the thermodynamic fields by the Gibbs-Thomson condition. To ensure that entropy is maximised during evolution a gradient flow of the entropy is considered to describe the phase boundary motion. Computing the variation of the entropy (1.10) under the constraint that energy and mass are conserved (see the next subsection) yields the following condition on  $\Gamma_{\alpha\beta}$ :

$$m_{\alpha\beta}(\nu_{\alpha\beta})v_{\alpha\beta} = -\nabla_\Gamma \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) + \frac{1}{T} \left[ f(T, \hat{c}) - \bar{\mu}(T, \hat{c}) \cdot \hat{c} \right]_\alpha^\beta. \quad (1.14)$$

The field  $f^\alpha$  is the (Helmholtz) free energy density of phase  $\alpha$ . 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  $-\nabla_\Gamma \cdot \nabla \gamma_{\alpha\beta}(\nu) = \bar{\gamma}_{\alpha\beta} \kappa_{\alpha\beta}$  where  $\kappa_{\alpha\beta}$  is the mean curvature (see Section 1.3). In thermodynamic equilibrium the right hand side of (1.14) vanishes.

To obtain a well-posed problem for the evolution of the  $\Gamma_{\alpha\beta}(t)$  initial boundaries  $\Gamma_{\alpha\beta}^0$  are given. Besides if  $d = 2, 3$  certain angle conditions in points where a phase boundary of  $\Gamma_{\alpha\beta}$  hits  $\partial\Omega$  or another phase boundary are satisfied. As mass density is constant and there is not transport (except diffusion) mechanical equilibrium is ensured. The angle conditions are due to local force balance or, equivalently, local minimisation of the surface energy (cf. [GN00], Section 2). The surface tensions are demanded to fulfil the constraint

$$\sigma_{\alpha\beta} + \sigma_{\beta\delta} > \sigma_{\alpha\delta} \quad \text{for pairwise different } \alpha, \beta, \delta$$

uniformly in their arguments. Otherwise undesired wetting effects could appear (cf. [Haa94], Section 3.4, for a discussion and references).

On a phase boundary belonging to  $\Gamma_{\alpha\beta}$  there is the vector field

$$\xi_{\alpha\beta}(\nu_{\alpha\beta}) := \nabla \sigma_{\alpha\beta}(\nu_{\alpha\beta}) = \sigma_{\alpha\beta}(\nu_{\alpha\beta})\nu_{\alpha\beta} + \nabla_\Gamma \sigma_{\alpha\beta}(\nu_{\alpha\beta}) \quad (1.15)$$

where  $\nabla_\Gamma$  is the surface gradient. The identity  $\nabla = \nabla_\Gamma + \nu_{\alpha\beta} \cdot \nabla$  was used as well as the fact that  $\sigma_{\alpha\beta}$  is one-homogeneously extended implying

$$\nabla \sigma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \nu_{\alpha\beta} = \sigma_{\alpha\beta}(\nu_{\alpha\beta}). \quad (1.16)$$

The idea of using those  $\xi$ -vectors originally stems from [CH74] where also the relation to the capillary forces acting on the phase boundary is established. For a short outline, [WM97] is a suitable reference.

In the three-dimensional case  $T_{\alpha\beta\delta}$  consists of triple lines that can be oriented so that, to each point  $x$  on the triple line, a unit tangent vector  $\tau_{\alpha\beta\delta}(x)$  can be assigned. If the whole space is cut with the plane orthogonal to  $\tau_{\alpha\beta\delta}(x)$  through  $x$  then the picture in Fig. 1.1 is obtained. Observe that this plane is spanned by the vectors  $\nu_{\alpha\beta}(x)$  and  $\tau_{\alpha\beta}(x)$ . The force with that  $\Gamma_{\alpha\beta}$  acts on  $x$  is given by  $\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \times \tau_{\alpha\beta\delta}(x)$ ,  $\times : \mathbb{R}^3 \times \mathbb{R}^3 \rightarrow \mathbb{R}^3$  being the vector product. Since  $(\tau_{\alpha\beta}(x), \nu_{\alpha\beta}(x), \tau_{\alpha\beta\delta}(x))$  is an oriented orthonormal system of  $\mathbb{R}^3$  it follows that (evaluation at  $x$  which is omitted here)

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

whence for the force there results the identity

$$\begin{aligned}\xi_{\alpha\beta}(\nu_{\alpha\beta}) \times \tau_{\alpha\beta\delta} &= (\nabla\sigma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \tau_{\alpha\beta})(\tau_{\alpha\beta} \times \tau_{\alpha\beta\delta}) + (\nabla\sigma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \nu_{\alpha\beta})(\nu_{\alpha\beta} \times \tau_{\alpha\beta\delta}) \\ &= (\nabla\sigma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \tau_{\alpha\beta})(-\nu_{\alpha\beta}) + \sigma_{\alpha\beta}(\nu_{\alpha\beta})\tau_{\alpha\beta}.\end{aligned}\tag{1.17a}$$

Mechanical equilibrium means that the sum of the capillary forces acting on  $x$  is zero, i.e., setting  $\mathcal{A} := \{(\alpha, \beta), (\beta, \delta), (\delta, \alpha)\}$ :

$$0 = \sum_{(i,j) \in \mathcal{A}} \xi_{ij}(\nu_{ij}(x)) \times \tau_{\alpha\beta\delta}(x).\tag{1.17b}$$

The set  $\Gamma_{\alpha\beta}(t) \cap \partial\Omega$  consists of lines to that a unit tangent vector  $\tau_{\alpha\beta,ext}(x)$  can be assigned to every point  $x \in \Gamma_{\alpha\beta}(t) \cap \partial\Omega$  similarly as  $\tau_{\alpha\beta\delta}(x)$  as before. The force acting on  $x$  is given by

$$\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \times \tau_{\alpha\beta,ext}(x).\tag{1.17c}$$

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

$$\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \cdot \nu_{ext}(x) = 0\tag{1.17d}$$

because then  $\xi_{\alpha\beta}(\nu_{\alpha\beta}(x))$  is tangential to  $\partial\Omega$  implying that the force  $\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \times \tau_{\alpha\beta,ext}(x)$  is normal to  $\partial\Omega$ .

The two-dimensional case can be handled by extending identically the situation into the third dimension such that one gets  $\tau_{\alpha\beta\delta} = (0, 0, 1)$ . The conditions (1.17b) and (1.17d) hold true also in this case. Observe that then  $\nabla\sigma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \tau_{\alpha\beta} = \nabla_{\Gamma}\sigma_{\alpha\beta}(\nu_{\alpha\beta})$ .

All the identities that are derived for the  $\sigma_{\alpha\beta}$  hold also true for the  $\gamma_{\alpha\beta}$  by the relation (1.9). A full list of the equations governing the evolution is given in Section (1.2).

**1.4 Remark** The principle of local thermodynamic equilibrium implies that the entropy locally is maximised, hence its variation should vanish. This yields a Gibbs-Thomson condition (1.14) with  $m_{\alpha\beta} \equiv 0$ . But it turned out that a mobility coefficient is necessary to describe certain phenomena (cf. the introduction of the kinetic coefficient in [Dav01] in Section 2.1.4; in Section 5 also its anisotropy is motivated). But there may be situations where the kinetic term can be neglected, cf., for example, [JH66], Section III.

### 1.1.3 Derivation of the Gibbs-Thomson condition

In this section a physical motivation of the Gibbs-Thomson condition (1.14) based on thermodynamic principles is given. The idea is to define the motion of the phase boundaries as a gradient flow of the entropy. If only surface entropy contributions are present a procedure as outlined in [TC94] can be applied. On the set of admissible surfaces (see Definition 1.5 below) the tangent space of a surface is defined by the smooth real valued functions  $f$  on the surface supplied with a (possibly weighted)  $L^2$ -product. A variation of the surface entropy in the direction  $f$  is then the change rate of the entropy when deforming the surface towards its normal with a strength given by  $f$ .

In the general situation also bulk entropy is present, and variations must be such that total energy  $E = \sum_{\alpha} \int_{\Omega_{\alpha}} e^{\alpha}$  and total mass  $\hat{C} = \sum_{\alpha} \int_{\Omega_{\alpha}} \hat{c}^{\alpha}$  are conserved. In general, a deformation of a phase boundary also 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 (1.14) is a local motion law, only local deformations of an  $\varepsilon$ -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. But in the limit as  $\varepsilon \rightarrow 0$  all terms become local after appropriate scaling so that the desired equation is obtained.

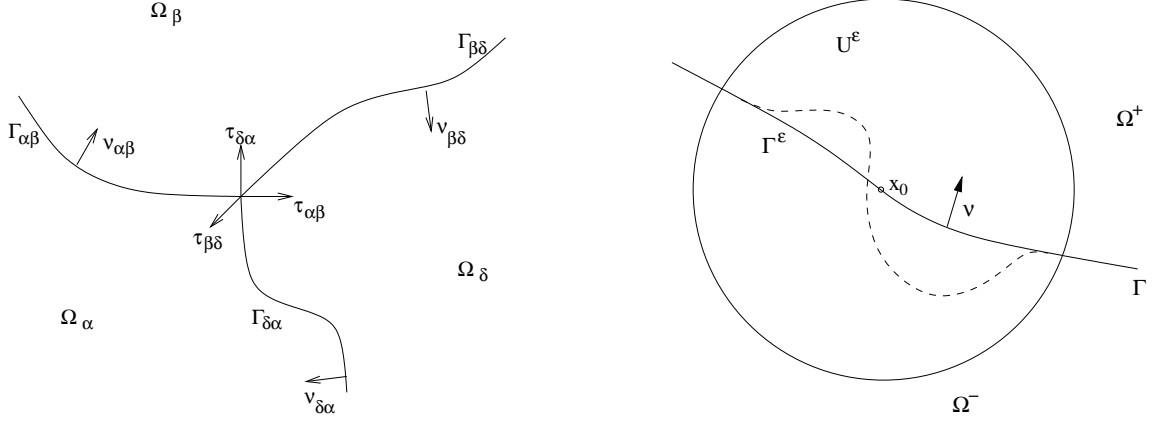


Figure 1.1: On the left: triple junction  $x$  with orientations of the forming curves; such a picture is also obtained in the 3D-case by cutting the space with the plane spanned by  $\nu_{\alpha\beta}(x)$ ,  $\tau_{\alpha\beta}(x)$ . On the right: local situation around a point  $x_0$  on a phase boundary for the derivation of the Gibbs-Thomson condition; a local deformation is indicated by the dashed line.

For simpler presentation, not the general situation as in the previous Subsection 1.1.2 is considered but the following one. Let  $\Gamma$  be a smooth compactly embedded  $d - 1$ -dimensional hypersurface separating two phases  $\Omega^+$  and  $\Omega^-$  and let  $\nu$  be the unit normal pointing into  $\Omega^+$ . Such a surface respectively configuration is called admissible.

**1.5 Definition** 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.

According to (1.10) the entropy is given by

$$S = \int_{\Omega^+ \cup \Omega^-} s(e^0, \hat{c}^0) - \int_\Gamma \gamma(\nu). \quad (1.18)$$

The bulk fields for energy density and concentrations, here denoted by  $e^0$  and  $\hat{c}^0$  respectively, are allowed to suffer jump discontinuities across  $\Gamma$ , but the potentials  $s_{,e} = \frac{1}{T}$  and  $s_{,\hat{c}} = \frac{-\mu}{T}$  are supposed to be Lipschitz continuous. Within the phases  $\Omega^+$  and  $\Omega^-$  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  $\{U^\varepsilon\}_{\varepsilon>0}$  around  $x_0$  with radius  $\varepsilon$  as in Fig. 1.1. Given arbitrary functions  $\xi^\varepsilon \in C_0^1(U^\varepsilon)$  it is shown in [Giu77], Section 10.5, that there are a vector fields

$$\vec{\xi}^\varepsilon \in C_0^1(U^\varepsilon, \mathbb{R}^d) \quad \text{with } \vec{\xi}^\varepsilon = \xi^\varepsilon \nu \text{ on } \Gamma^\varepsilon := \Gamma \cap U^\varepsilon. \quad (1.19)$$

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

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

$\theta^\varepsilon_{,\delta}$  being the partial derivative of  $\theta^\varepsilon$  with respect to  $\delta$ , yields a local deformation of  $U^\varepsilon$ . The restriction of  $\delta$  is such that  $\Gamma^\varepsilon := U^\varepsilon \cap \Gamma$  remains a smooth surface imbedded into  $U^\varepsilon$ , i.e., the sets

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

define an evolving  $d - 1$ -dimensional surface in  $U^\varepsilon$  in the sense of Definition C.1.

The following identity is proven in [Gar02]:

$$\frac{d}{d\delta} \det \theta_{,x}^\varepsilon(\delta, x) = \nabla \cdot \vec{\xi}^\varepsilon(\theta^\varepsilon(\delta, x)) \det \theta_{,x}^\varepsilon(\delta, x). \quad (1.20)$$

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

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

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

**1.6 Definition** *The energy density under the local deformation  $\theta^\varepsilon$  of  $U^\varepsilon$  is defined by*

$$e(\delta, y) := e^0(\theta^\varepsilon(-\delta, y)) - \mathcal{M}^\varepsilon(e^0(\theta^\varepsilon(-\delta, \cdot)) - e^0(\cdot)), \quad y \in U^\varepsilon. \quad (1.21a)$$

Analogously, the concentration vector under the deformation is defined by

$$\hat{c}(\delta, y) := \hat{c}^0(\theta^\varepsilon(-\delta, y)) - \mathcal{M}^\varepsilon(\hat{c}^0(\theta^\varepsilon(-\delta, \cdot)) - \hat{c}^0(\cdot)), \quad y \in U^\varepsilon. \quad (1.21b)$$

The local entropy under the deformation consists of the bulk part

$$S_B^\varepsilon(\delta) := \int_{U^\varepsilon} s(e(\delta, y), \hat{c}(\delta, y)) dy \quad (1.22a)$$

and the surface part

$$S_S^\varepsilon(\delta) := - \int_{\Gamma_\delta^\varepsilon} \gamma(\nu(\delta)) d\mathcal{H}^{d-1}. \quad (1.22b)$$

Lagrange multipliers as  $\mathcal{M}^\varepsilon(e^0(\theta^\varepsilon(-\delta, \cdot)) - e^0(\cdot))$  in (1.21a) ensure that energy and mass are conserved under the deformation. For example, concerning the energy:  $\int_{U^\varepsilon} e(\delta, y) dy = \int_{U^\varepsilon} e^0(x) dx$  for all  $\delta$ .

**1.7 Lemma** *The derivative of the bulk entropy (1.22a) with respect to  $\delta$  in  $\delta = 0$  is*

$$\frac{d}{d\delta} S_B^\varepsilon(0) = \int_{U^\varepsilon} \left( s(e^0, \hat{c}^0) - \mathcal{M}^\varepsilon\left(\frac{1}{T}\right) e^0 - \mathcal{M}^\varepsilon\left(\frac{-\bar{\mu}}{T}\right) \cdot \hat{c}^0 \right) \nabla \cdot \vec{\xi}^\varepsilon dx.$$

**Proof:** By the definitions (1.21a) and (1.21b), the bulk entropy (1.22a) is

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

where for the last identity the transformation  $y = \theta^\varepsilon(\delta, x)$  was used. The equation (1.20) yields together with  $\theta^\varepsilon(0, x) = x$  and  $\det(\theta_{,x}^\varepsilon(0, x)) = \det \text{Id} = 1$

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

An analogous identity holds true with  $\hat{c}^0$  instead of  $e^0$ . With  $s_{,e} = \frac{1}{T}$  and  $s_{,\hat{c}} = \frac{-\bar{\mu}}{T}$  it follows that

$$\begin{aligned}
 \frac{d}{d\delta} S_B^\varepsilon(0) &= \int_{U^\varepsilon} s\left(e^0(x) - \mathcal{M}^\varepsilon(e^0(\theta^\varepsilon(0, \cdot)) - e^0), \hat{c}^0(x) - \mathcal{M}^\varepsilon(\hat{c}^0(\theta^\varepsilon(0, \cdot)) - \hat{c}^0)\right) \nabla \cdot \vec{\xi}^\varepsilon(x) dx \\
 &\quad - \int_{U^\varepsilon} s_{,e}(e^0(x), \hat{c}^0(x)) \frac{d}{d\delta} \int_{U^\varepsilon} e^0(\theta^\varepsilon(-(\cdot), z)) dz \Big|_{\delta=0} dx \\
 &\quad - \int_{U^\varepsilon} s_{,\hat{c}}(e^0(x), \hat{c}^0(x)) \cdot \frac{d}{d\delta} \int_{U^\varepsilon} \hat{c}^0(\theta^\varepsilon(-(\cdot), z)) dz \Big|_{\delta=0} dx \\
 &= \int_{U^\varepsilon} s(e^0(x), \hat{c}^0(x)) \nabla \cdot \vec{\xi}^\varepsilon(x) dx \\
 &\quad - \int_{U^\varepsilon} \frac{1}{T(x)} dx \int_{U^\varepsilon} e^0(x) \nabla \cdot \vec{\xi}^\varepsilon(x) dx \\
 &\quad - \int_{U^\varepsilon} \frac{-\bar{\mu}(x)}{T(x)} dx \cdot \int_{U^\varepsilon} \hat{c}^0(x) \nabla \cdot \vec{\xi}^\varepsilon(x) dx \\
 &= \int_{U^\varepsilon} \left( s(e^0, \hat{c}^0) - \mathcal{M}^\varepsilon\left(\frac{1}{T}\right) e^0 - \mathcal{M}^\varepsilon\left(\frac{-\bar{\mu}}{T}\right) \cdot \hat{c}^0 \right) \nabla \cdot \vec{\xi}^\varepsilon(x) dx
 \end{aligned}$$

which is the desired identity.  $\square$

**1.8 Lemma** *The derivative of the surface entropy (1.22b) with respect to  $\delta$  in  $\delta = 0$  is*

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

Here,  $\nabla_\Gamma$  is the surface gradient,  $\nabla_\Gamma \cdot$  the surface divergence.

**Proof:** Interpreting  $\{\Gamma_\delta^\varepsilon\}_\delta$  as evolving surface, the normal velocity is  $\xi^\varepsilon$  and the vectorial normal velocity is  $\vec{\xi}^\varepsilon = \xi^\varepsilon \nu$ . The curvature is denoted by  $\kappa_\Gamma$ . Applying Theorem C.4 from Appendix C yields (observe that the boundary integrals over  $\partial\Gamma^\varepsilon$  vanish as the velocity  $\vec{\xi}^\varepsilon$  has a compact support in  $U^\varepsilon$  and vanishes there)

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

which is using (C.5), (C.4), (C.6) and the one-homogeneity of  $\gamma$

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

Applying Theorem C.3 on  $\vec{\varphi} = \nabla \gamma(\nu) \xi^\varepsilon$  (again the boundary integral vanishes) and again (C.4) on the last term it follows that

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

which is the desired result.  $\square$

As stated at the beginning of this section, the goal is to define the motion as a localised version of a gradient flow similarly to  $(v, \xi)_\Gamma = \langle \delta S, \xi \rangle$  for all  $\xi$  as in [TC94]. This is realised in the following definition.

**1.9 Definition** Let  $|\Gamma^\varepsilon| = \mathcal{H}^{d-1}(\Gamma^\varepsilon)$ . The motion of the phase boundary  $\Gamma$  is defined as follows: In each point  $x_0 \in \Gamma$  the identity

$$\lim_{\varepsilon \rightarrow 0} \frac{1}{|\Gamma^\varepsilon|} (v, \xi^\varepsilon)_\Gamma = \lim_{\varepsilon \rightarrow 0} \frac{1}{|\Gamma^\varepsilon|} \frac{d}{d\delta} (S_B^\varepsilon + S_S^\varepsilon)(0) \quad (1.23)$$

holds for all families of functions  $\xi^\varepsilon \in C_0^1(U^\varepsilon)$  where  $S_B^\varepsilon(\delta)$  and  $S_S^\varepsilon(\delta)$  are defined by (1.22a) and (1.22b) respectively.

**1.10 Theorem** The localised gradient flow (1.23) yields the Gibbs-Thomson condition (1.14).

To prove the theorem the following lemma is useful:

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

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

where the functions  $\vec{\xi}^\varepsilon$  are uniformly bounded and satisfy condition (1.19). By  $g^+$  the limit of  $g$  in  $x \in \Gamma$  when approximated from the side  $\Omega^+$  is denoted. Analogously  $g^-$  is defined when approximating  $x \in \Gamma$  from  $\Omega^-$ , and  $[g]_{-}^{\pm} = g^+ - g^-$  is the difference.

**Proof:** For a given small  $\varepsilon > 0$  consider the function

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

Let  $\zeta$  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  $\xi^\varepsilon$  by the convolution of  $\tilde{\xi}^\varepsilon$  with  $\varepsilon^{-3d} \zeta(\cdot/\varepsilon^3)$ , i.e.,

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

Then for  $\varepsilon$  small enough  $\xi^\varepsilon = z$  on  $\Gamma \cap U^{\varepsilon - 2\varepsilon^2} =: \tilde{\Gamma}^\varepsilon$ . The functions  $\vec{\xi}^\varepsilon$  constructed from the  $\xi^\varepsilon$  as in [Giu77], Section 10.5, satisfy the demanded properties.

Observe that thanks to the smoothness of  $\Gamma$  the  $\mathcal{H}^{d-1}$ -measure of  $\Gamma^\varepsilon \setminus \tilde{\Gamma}^\varepsilon$  is of order  $\varepsilon^d$  so that

$$\frac{\mathcal{H}^{d-1}(\Gamma^\varepsilon \setminus \tilde{\Gamma}^\varepsilon)}{\mathcal{H}^{d-1}(\Gamma^\varepsilon)} = O(\varepsilon) \quad \text{as } \varepsilon \rightarrow 0.$$

The function  $f = [g]_{-}^{\pm}$  is Lipschitz continuous on  $\Gamma$ . It holds that

$$\int_{\Gamma^\varepsilon} f \xi^\varepsilon \, d\mathcal{H}^{d-1} = \int_{\Gamma^\varepsilon} f z \, d\mathcal{H}^{d-1} + \int_{\Gamma^\varepsilon} f (\xi^\varepsilon - z) \, d\mathcal{H}^{d-1}.$$

The first term on the right hand side converges to  $f(x_0)z$  as  $\varepsilon \rightarrow 0$ . The second term vanishes in that limit:

$$\begin{aligned} & \left| \int_{\Gamma^\varepsilon} f (\xi^\varepsilon - z) \, d\mathcal{H}^{d-1} \right| \\ & \leq \|f\|_{L^\infty(\Gamma^\varepsilon)} \frac{1}{|\Gamma^\varepsilon|} \int_{\Gamma^\varepsilon} |\xi^\varepsilon - z| \, d\mathcal{H}^{d-1} \\ & = \|f\|_{L^\infty(\Gamma^\varepsilon)} \frac{1}{|\Gamma^\varepsilon|} \int_{\Gamma^\varepsilon \setminus \tilde{\Gamma}^\varepsilon} |\xi^\varepsilon - z| \, d\mathcal{H}^{d-1} \\ & \leq \|f\|_{L^\infty(\Gamma^\varepsilon)} \|\xi^\varepsilon - z\|_{L^\infty(\Gamma^\varepsilon)} \frac{\mathcal{H}^{d-1}(\Gamma^\varepsilon \setminus \tilde{\Gamma}^\varepsilon)}{\mathcal{H}^{d-1}(\Gamma^\varepsilon)} = O(\varepsilon) \quad \text{as } \varepsilon \rightarrow 0. \end{aligned}$$

## 1.1. IRREVERSIBLE THERMODYNAMICS

As moreover the  $\mathcal{L}^d$ -measure of  $U^\varepsilon$  is of order  $\varepsilon^d$  but the  $\mathcal{H}^{d-1}$ -measure of  $\Gamma^\varepsilon$  is of order  $\varepsilon^{d-1}$  and since  $|\nabla g \cdot \vec{\xi}^\varepsilon|$  is bounded in  $U^\varepsilon$  the assertion on the limiting behaviour as  $\varepsilon \rightarrow 0$  is obtained.

To show the first identity the divergence theorem is applied on the two parts  $U^\varepsilon \cap \Omega^+$  and  $U^\varepsilon \cap \Omega^-$  of  $U^\varepsilon$ . As  $\vec{\xi}^\varepsilon$  vanishes on the external boundary  $\partial U^\varepsilon$  there only remain some boundary terms on  $\Gamma^\varepsilon$ . Whenever boundary integrals appear in the following computation then  $\nu_{ext}$  denotes the external unit normal of the domain corresponding to the boundary. On  $\Gamma^\varepsilon$  of course it is identical to  $\pm\nu$ .

$$\begin{aligned}
\int_{U^\varepsilon} g \nabla \cdot \vec{\xi}^\varepsilon \, dx &= \int_{U^\varepsilon \cap \Omega^+} g \nabla \cdot \vec{\xi}^\varepsilon \, dx + \int_{U^\varepsilon \cap \Omega^-} g \nabla \cdot \vec{\xi}^\varepsilon \, dx \\
&= - \int_{U^\varepsilon \cap \Omega^+} \nabla g \cdot \vec{\xi}^\varepsilon \, dx + \int_{\partial(U^\varepsilon \cap \Omega^+)} g \vec{\xi}^\varepsilon \cdot \nu_{ext} \, d\mathcal{H}^{d-1} \\
&\quad - \int_{U^\varepsilon \cap \Omega^-} \nabla g \cdot \vec{\xi}^\varepsilon \, dx + \int_{\partial(U^\varepsilon \cap \Omega^-)} g \vec{\xi}^\varepsilon \cdot \nu_{ext} \, d\mathcal{H}^{d-1} \\
&= - \int_{U^\varepsilon} \nabla g \cdot \vec{\xi}^\varepsilon \, dx + \int_{\Gamma^\varepsilon} g^+ \vec{\xi}^\varepsilon \cdot (-\nu) \, d\mathcal{H}^{d-1} + \int_{\Gamma^\varepsilon} g^- \vec{\xi}^\varepsilon \cdot \nu \, d\mathcal{H}^{d-1} \\
&= - \int_{U^\varepsilon} \nabla g \cdot \vec{\xi}^\varepsilon \, dx - \int_{\Gamma^\varepsilon} [g]_-^+ \xi^\varepsilon \, d\mathcal{H}^{d-1}
\end{aligned}$$

where for the last identity (1.19) was used. □

**Proof:** (Theorem 1.10) First, observe that  $\mathcal{M}^\varepsilon(\frac{1}{T}) \rightarrow \frac{1}{T(x_0)}$  and  $\mathcal{M}^\varepsilon(\frac{-\bar{\mu}}{T}) \rightarrow \frac{-\bar{\mu}(x_0)}{T(x_0)}$  as  $\varepsilon \rightarrow 0$  because  $T$  and  $\bar{\mu}$  are Lipschitz continuous.

Choose some arbitrary  $z \in \mathbb{R}$  and a family of functions  $\{\xi^\varepsilon\}_{\varepsilon>0}$  as in Lemma 1.11 and let  $\{\vec{\xi}^\varepsilon\}_{\varepsilon>0}$  be the corresponding vector fields. Then, using Lemma 1.11,

$$\begin{aligned}
\frac{1}{|\Gamma^\varepsilon|} \int_{U^\varepsilon} \mathcal{M}^\varepsilon\left(\frac{1}{T}\right) e^0(x) \nabla \cdot \vec{\xi}^\varepsilon(x) \, dx &= \mathcal{M}^\varepsilon\left(\frac{1}{T}\right) \frac{1}{|\Gamma^\varepsilon|} \int_{U^\varepsilon} e^0(x) \nabla \cdot \vec{\xi}^\varepsilon(x) \, dx \\
&\rightarrow \frac{1}{T(x_0)} [e^0(x_0)]_-^+ z = \left[\frac{e^0}{T}\right]_-^+(x_0) z.
\end{aligned}$$

An analogous result is obtained when replacing  $\mathcal{M}^\varepsilon(\frac{1}{T})e^0$  by  $\mathcal{M}^\varepsilon(\frac{-\bar{\mu}}{T}) \cdot \hat{c}^0$ . The limit of the right hand side of (1.23) is, using the Lemmata 1.7, 1.8, and 1.11,

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

where for the last identity the relation  $e = f + sT \Rightarrow \frac{f}{T} = -s + \frac{e}{T}$  was applied. The left hand side of (1.23) yields in the limit as  $\varepsilon \rightarrow 0$

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

Since  $z \in \mathbb{R}$  and  $x_0 \in \Gamma$  can be chosen arbitrarily the condition (1.14) follows. □

## 1.2 The general sharp interface model

In this section, the variables and the governing set of equations are listed for completeness.

There are the following bulk fields in the phases  $\Omega_\alpha$ ,  $\alpha \in \{1, \dots, M\}$ :

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

On the phase boundaries  $\Gamma_{\alpha\beta}$  with  $\alpha \neq \beta$ ,  $\alpha, \beta \in \{1, \dots, M\}$  there are the following surface fields:

$$\begin{aligned}
 \nu_{\alpha\beta} &: \text{unit normal pointing into } \Omega_\beta, \\
 \sigma_{\alpha\beta}(\nu_{\alpha\beta}) &: \text{surface tension,} \\
 \gamma_{\alpha\beta}(\nu_{\alpha\beta}) &: \text{capillarity coefficient,} \\
 m_{\alpha\beta}(\nu_{\alpha\beta}) &: \text{mobility coefficient,} \\
 v_{\alpha\beta} &: \text{normal velocity towards } \nu_{\alpha\beta}, \\
 \kappa_{\alpha\beta} &: \text{curvature.}
 \end{aligned}$$

The matrix of surface tensions  $(\sigma_{\alpha\beta}(\nu))_{\alpha,\beta}$  is symmetric for every unit vector  $\nu$  (the diagonal entries are not of interest and may be set to zero). The relation between surface tension and capillarity coefficient is given by (1.9), i.e.,

$$\gamma_{\alpha\beta}(\nu_{\alpha\beta}) = \frac{\sigma_{\alpha\beta}(\nu_{\alpha\beta})}{T_{ref}} \quad (1.24a)$$

with some reference temperature  $T_{ref}$ . The surface tensions are one-homogeneous in their argument and fulfil the constraint

$$\sigma_{\alpha\beta} + \sigma_{\beta\delta} > \sigma_{\alpha\delta}. \quad (1.24b)$$

The mobilities  $m_{\alpha\beta}(\nu_{\alpha\beta})$  are zero-homogeneous in their arguments.

For the conserved quantities energy and mass the balance equations

$$\partial_t c_i^\alpha = -\nabla \cdot J_i^\alpha = \nabla \cdot \left( \sum_{j=0}^N L_{ij}^\alpha \nabla u_j^\alpha \right), \quad 0 \leq i \leq N, \quad (1.24c)$$

hold in every phase  $\Omega_\alpha(t)$  (compare (1.11), (1.12a), (1.12b)). On the phase boundaries  $\Gamma_{\alpha\beta}$  the continuity conditions (1.13a), (1.13b)

$$[u_i]_\alpha^\beta = 0, \quad 0 \leq i \leq N, \quad (1.24d)$$

as well as the jump conditions (1.13c), (1.13d)

$$[c_i]_\alpha^\beta v_{\alpha\beta} = [J_i]_\alpha^\beta \cdot \nu_{\alpha\beta}, \quad 0 \leq i \leq N, \quad (1.24e)$$

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

$$m_{\alpha\beta}(\nu_{\alpha\beta}) v_{\alpha\beta} = -\nabla_\Gamma \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) + \left[ -u_0 f(T, \hat{c}) + \sum_{i=1}^N u_i c_i \right]_\alpha^\beta. \quad (1.24f)$$



### 1.3. NON-NEGATIVITY OF ENTROPY PRODUCTION

In points where three phases  $\Omega_\alpha$ ,  $\Omega_\beta$ , and  $\Omega_\delta$  meet or where a phase boundary  $\Gamma_{\alpha\beta}$  meets the external boundary forces are in equilibrium. Following (1.17b) and (1.17d) this is expressed by

$$0 = \sum_{(i,j) \in \mathcal{A}} \xi_{ij}(\nu_{ij}(x)) \times \tau_{\alpha\beta\delta}(x) \quad (1.24g)$$

where  $\mathcal{A} := \{(\alpha, \beta), (\beta, \delta), (\delta, \alpha)\}$  and by

$$\xi_{\alpha\beta}(\nu_{\alpha\beta}(x)) \cdot \nu_{ext}(x) = 0 \quad (1.24h)$$

respectively. To obtain a well-posed problem, additionally, initial data and boundary conditions must be provided. If not otherwise stated, the isolated case

$$J_i^\alpha \cdot \nu_{ext} = 0 \text{ on } \partial\Omega, \quad 0 \leq i \leq N, 1 \leq \alpha \leq M, \quad (1.24i)$$

is considered.

### 1.3 Non-negativity of entropy production

In this section it is shown that the equations governing the evolution imply locally positive entropy production. For this purpose some definitions and facts on evolving surfaces are necessary, in particular, a divergence theorem and a transport theorem on surfaces. These facts are listed in Appendix C and are based on [Bet86].

An entropy inequality is derived at times  $t \in I$  such that the following holds true in an open time interval  $I' = (t - \delta_0, t + \delta_0)$  around  $t$ :

- If  $d = 1$  then the sets  $\Gamma_{\alpha\beta}$  consist of smoothly evolving points (0-dimensional surfaces).
- If  $d = 2$  then the sets  $\Gamma_{\alpha\beta}$  consist of smoothly evolving 1-dimensional subsurfaces. More precisely, there are evolving curves ending in points that belong to  $T_{\alpha\beta,ext}$  or  $T_{\alpha\beta\delta}$  for some  $\delta \neq \alpha, \beta$ . These endpoints also smoothly evolve, and the curves can be extended over the endpoints so that the curve except the endpoints can be seen as a subcurve as in Definition C.2. In particular, the external unit normal vectors in the endpoints (i.e., the vectors  $\tau_\Gamma$  discussed just after Definition C.2) are well-defined.
- If  $d = 3$  then the sets  $\Gamma_{\alpha\beta}$  consist of smoothly evolving 2-dimensional subsurfaces that meet in smoothly evolving curves belonging to  $T_{\alpha\beta,ext}$  or  $T_{\alpha\beta\delta}$  for some  $\delta \neq \alpha, \beta$ . Also here, it is assumed that the external unit normal vectors in points on the endcurves are well-defined.

It may happen during evolution that phases disappear and boundaries vanish. Times with such singularities are excluded.

By  $\int_{\Gamma_{\alpha\beta}(t)}$  the integral over all surfaces included in the set  $\Gamma_{\alpha\beta}$  at time  $t$  with respect to the surface measure  $\mathcal{H}^{d-1}$  is denoted in the following. Analogously  $\int_{\Omega_\alpha(t)}$  and  $\int_{T_{\alpha\beta\delta}(t)}$  are defined. Also expressions like  $\nabla_{\Gamma_{\alpha\beta}}$  or  $\vec{v}_{\partial\Gamma_{\alpha\beta}}$  must be interpreted in that context. Besides for shortening the presentation set  $\bar{\mu}_0 := -1$ .

**1.12 Theorem** *At times  $t \in I$  when the above assumption is fulfilled the entropy (1.10) satisfies*

$$\frac{d}{dt} S(t) = \int_{\Omega(t)} \sum_{i,j=0}^N \nabla \frac{-\bar{\mu}_i}{T} \cdot L_{ij} \nabla \frac{-\bar{\mu}_j}{T} d\mathcal{L}^d + \sum_{1 \leq \alpha < \beta \leq M} \int_{\Gamma_{\alpha\beta}(t)} m_{\alpha\beta} (v_{\alpha\beta})^2 d\mathcal{H}^{d-1} \geq 0. \quad (1.25)$$

**Proof:** First, the bulk terms are considered. Let  $\alpha \in \{1, \dots, M\}$ . By (1.12a), (1.12b) and (B.4)

$$\partial_t s^\alpha(e^\alpha, \hat{c}^\alpha) = \partial_e s^\alpha(e^\alpha, \hat{c}^\alpha) \partial_t e^\alpha + \nabla_c s^\alpha(e^\alpha, \hat{c}^\alpha) \cdot \partial_t \hat{c}^\alpha = - \left( \frac{1}{T} \nabla \cdot J_0^\alpha + \sum_{i=1}^N \frac{-\bar{\mu}_i}{T} \nabla \cdot J_i^\alpha \right).$$

Furthermore, the boundary

$$\partial\Omega_\alpha(t) = \bigcup_{\beta \neq \alpha} \Gamma_{\alpha\beta}(t) \cup \Gamma_{\alpha,ext}(t)$$

piecewise consists of evolving  $d - 1$ -dimensional surfaces and satisfies the Lipschitz condition in Definition C.2 (the  $\Gamma_t$  there corresponds to  $\Omega_\alpha(t)$ , and the vector  $\tau_\Gamma = \tau_{\Omega_\alpha}$  appearing in the following discussion there is nothing else than the external unit normal of  $\Omega_\alpha$  in regular boundary points; one may write  $\tau_{\Omega_\alpha} = \nu_{\partial\Omega_\alpha}$ ). On  $\Gamma_{\alpha\beta}(t)$  it holds that  $\vec{v}_{\partial\Omega_\alpha} \cdot \tau_{\Omega_\alpha} = \nu_{\alpha\beta}$ , and on  $\Gamma_{\alpha,ext}(t)$  obviously  $\vec{v}_{\partial\Omega_\alpha} \cdot \tau_{\Omega_\alpha} = 0$  since the domain  $\Omega$  is fixed in time. Hence, using Reynold's transport theorem (see Remark C.5) and integrating by parts:

$$\begin{aligned} & \left. \frac{d}{dt} \left( \int_{\Omega_\alpha} s^\alpha(e^\alpha, \hat{c}^\alpha) d\mathcal{L}^d \right) \right|_t \\ &= \int_{\Omega_\alpha(t)} \partial_t s^\alpha(e^\alpha, \hat{c}^\alpha) d\mathcal{L}^d + \int_{\partial\Omega_\alpha(t)} s^\alpha(e^\alpha, \hat{c}^\alpha) \vec{v}_{\partial\Omega_\alpha} \cdot \tau_{\Omega_\alpha} d\mathcal{H}^{d-1} \\ &= - \int_{\Omega_\alpha(t)} \sum_{i=0}^N \frac{-\bar{\mu}_i^\alpha}{T^\alpha} \nabla \cdot J_i^\alpha d\mathcal{L}^d + \sum_{\beta \neq \alpha} \int_{\Gamma_{\alpha\beta}(t)} s^\alpha \nu_{\alpha\beta} d\mathcal{H}^{d-1} \\ &= \int_{\Omega_\alpha(t)} \sum_{i=0}^N \nabla \frac{-\bar{\mu}_i^\alpha}{T^\alpha} \cdot J_i^\alpha d\mathcal{L}^d - \int_{\Gamma_{\alpha,ext}(t)} \left( \frac{1}{T^\alpha} J_0^\alpha + \sum_i \frac{-\bar{\mu}_i^\alpha}{T^\alpha} J_i^\alpha \right) \cdot \nu_{ext} d\mathcal{H}^{d-1} \\ & \quad + \sum_{\beta \neq \alpha} \int_{\Gamma_{\alpha\beta}(t)} \left( s^\alpha \nu_{\alpha\beta} - \left( \frac{1}{T^\alpha} J_0^\alpha + \sum_i \frac{-\bar{\mu}_i^\alpha}{T^\alpha} J_i^\alpha \right) \cdot \nu_{\alpha\beta} \right) d\mathcal{H}^{d-1} \end{aligned}$$

By (1.24i) the second term vanishes. Summing up over  $\alpha$  and using the jump and continuity conditions (1.13a)-(1.13d) as well as the definitions of the fluxes (1.12a), (1.12b) and relation (B.3) it follows that

$$\begin{aligned} & \left. \frac{d}{dt} \left( \int_{\Omega} s(e, \hat{c}) d\mathcal{L}^d \right) \right|_t \\ &= \sum_{\alpha} \int_{\Omega_\alpha(t)} \left( \nabla \frac{1}{T^\alpha} \cdot J_0^\alpha + \sum_{i=1}^N \nabla \frac{-\bar{\mu}_i^\alpha}{T^\alpha} \cdot J_i^\alpha \right) d\mathcal{L}^d \\ & \quad + \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}(t)} \left( -[s]_\alpha^\beta \nu_{\alpha\beta} + \left[ \frac{1}{T} J_0 + \sum_{i=1}^N \frac{-\bar{\mu}_i}{T} J_i \right]_\alpha^\beta \cdot \nu_{\alpha\beta} \right) d\mathcal{H}^{d-1} \\ &= \int_{\Omega(t)} \left( \nabla \frac{-\bar{\mu}_0}{T} \cdot J_0 + \sum_{i=1}^N \nabla \frac{-\bar{\mu}_i}{T} \cdot J_i \right) d\mathcal{L}^d \\ & \quad + \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}(t)} \left( -[s]_\alpha^\beta \nu_{\alpha\beta} + \frac{1}{T} [e]_\alpha^\beta \nu_{\alpha\beta} + \sum_{i=1}^N \frac{-\bar{\mu}_i}{T} [c_i]_\alpha^\beta \nu_{\alpha\beta} \right) d\mathcal{H}^{d-1} \\ &= \int_{\Omega(t)} \sum_{i,j=0}^N \nabla \frac{-\bar{\mu}_i}{T} \cdot L_{ij} \nabla \frac{-\bar{\mu}_j}{T} d\mathcal{L}^d + \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}(t)} \frac{1}{T} \left[ f - \sum_i \bar{\mu}_i c_i \right]_\alpha^\beta \nu_{\alpha\beta} d\mathcal{H}^{d-1}. \quad (1.26a) \end{aligned}$$

Next, the surface contribution to (1.10) of one set  $\Gamma_{\alpha\beta}$  is considered. Theorem C.4 implies

$$\begin{aligned} \left. \frac{d}{dt} \left( - \int_{\Gamma_{\alpha\beta}} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) d\mathcal{H}^{d-1} \right) \right|_t &= - \int_{\Gamma_{\alpha\beta}(t)} \left( \partial^\circ \gamma_{\alpha\beta}(\nu_{\alpha\beta}) - \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \vec{v}_{\Gamma_{\alpha\beta}} \cdot \vec{\kappa}_{\Gamma_{\alpha\beta}} \right) d\mathcal{H}^{d-1} \\ & \quad - \int_{\partial\Gamma_{\alpha\beta}(t)} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \vec{v}_{\partial\Gamma_{\alpha\beta}} \cdot \tau_{\Gamma_{\alpha\beta}} d\mathcal{H}^{d-2}. \quad (1.26b) \end{aligned}$$

### 1.3. NON-NEGATIVITY OF ENTROPY PRODUCTION

Using (C.6), Theorem C.3 and the identities (C.4), (C.5) and (1.16) (observe that by (1.9) this also holds true for  $\gamma_{\alpha\beta}$ ) the first term becomes

$$\begin{aligned}
& - \int_{\Gamma_{\alpha\beta}(t)} \left( \partial^\circ \gamma_{\alpha\beta}(\nu_{\alpha\beta}) - \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \vec{v}_{\Gamma_{\alpha\beta}} \cdot \vec{\kappa}_{\Gamma_{\alpha\beta}} \right) d\mathcal{H}^{d-1} \\
&= - \int_{\Gamma_{\alpha\beta}(t)} \left( \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot (-\nabla \Gamma_{\alpha\beta} \nu_{\alpha\beta}) - \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \nu_{\alpha\beta} v_{\alpha\beta} \kappa_{\alpha\beta} \right) d\mathcal{H}^{d-1} \\
&= - \int_{\Gamma_{\alpha\beta}(t)} \left( (\nabla_{\Gamma_{\alpha\beta}} \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta})) v_{\alpha\beta} + \vec{\kappa}_{\Gamma_{\alpha\beta}} \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) v_{\alpha\beta} - \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \vec{\kappa}_{\Gamma_{\alpha\beta}} v_{\alpha\beta} \right) d\mathcal{H}^{d-1} \\
&+ \int_{\partial \Gamma_{\alpha\beta}(t)} \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) v_{\alpha\beta} \cdot \tau_{\Gamma_{\alpha\beta}} d\mathcal{H}^{d-2} \\
&= - \int_{\Gamma_{\alpha\beta}(t)} (\nabla_{\Gamma_{\alpha\beta}} \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta})) v_{\alpha\beta} d\mathcal{H}^{d-1} + \int_{\partial \Gamma_{\alpha\beta}(t)} \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) v_{\alpha\beta} \cdot \tau_{\Gamma_{\alpha\beta}} d\mathcal{H}^{d-2}. \tag{1.26c}
\end{aligned}$$

Since

$$\partial \Gamma_{\alpha\beta}(t) = \bigcup_{\delta \neq \alpha, \beta} T_{\alpha\beta\delta}(t) \cup T_{\alpha\beta, ext}(t),$$

the second terms of (1.26b) and (1.26c) together yield using (1.17a) and (1.17c) divided by  $T_{ref}$

$$\begin{aligned}
& - \int_{\partial \Gamma_{\alpha\beta}(t)} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \vec{v}_{\partial \Gamma_{\alpha\beta}} \cdot \tau_{\Gamma_{\alpha\beta}} d\mathcal{H}^{d-2} + \int_{\partial \Gamma_{\alpha\beta}(t)} \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) v_{\alpha\beta} \cdot \tau_{\Gamma_{\alpha\beta}} d\mathcal{H}^{d-2} \\
&= \int_{\partial \Gamma_{\alpha\beta}(t)} \left( - (\nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \nu_{\alpha\beta}) (\vec{v}_{\partial \Gamma_{\alpha\beta}} \cdot \tau_{\Gamma_{\alpha\beta}}) + (\vec{v}_{\Gamma_{\alpha\beta}} \cdot \nu_{\alpha\beta}) (\nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \tau_{\Gamma_{\alpha\beta}}) \right) d\mathcal{H}^{d-2} \\
&= \int_{\partial \Gamma_{\alpha\beta}(t)} \vec{v}_{\partial \Gamma_{\alpha\beta}} \cdot \left( - \tau_{\Gamma_{\alpha\beta}} (\nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \nu_{\alpha\beta}) + \nu_{\alpha\beta} (\nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \cdot \tau_{\Gamma_{\alpha\beta}}) \right) d\mathcal{H}^{d-2} \\
&= \sum_{\delta \neq \alpha, \beta} \int_{T_{\alpha\beta\delta}(t)} -\vec{v}_{T_{\alpha\beta\delta}} \cdot (\xi_{\alpha\beta}(\nu_{\alpha\beta}) \times \tau_{\alpha\beta\delta}) \frac{1}{T_{ref}} d\mathcal{H}^{d-2} \\
&+ \int_{T_{\alpha\beta, ext}(t)} -\vec{v}_{T_{\alpha\beta, ext}} \cdot (\xi_{\alpha\beta}(\nu_{\alpha\beta}) \times \tau_{\alpha\beta, ext}) \frac{1}{T_{ref}} d\mathcal{H}^{d-2}. \tag{1.26d}
\end{aligned}$$

The last term vanishes as by (1.17d) the force  $\xi_{\alpha\beta} \times \tau_{\alpha\beta\delta}$  is normal and  $\vec{v}_{\partial \Gamma_{\alpha\beta}} = \vec{v}_{T_{\alpha\beta, ext}}$  is tangential so that

$$\vec{v}_{T_{\alpha\beta, ext}} \cdot (\xi_{\alpha\beta} \times \tau_{\alpha\beta, ext}) = 0 \quad \text{on } T_{\alpha\beta, ext}.$$

Therefore, (1.26b), (1.26c) and (1.26d) yield

$$\begin{aligned}
\frac{d}{dt} \left( - \int_{\Gamma_{\alpha\beta}} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) d\mathcal{H}^{d-1} \right) \Big|_t &= - \int_{\Gamma_{\alpha\beta}(t)} (\nabla_{\Gamma_{\alpha\beta}} \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta})) v_{\alpha\beta} d\mathcal{H}^{d-1} \\
&- \sum_{\delta \neq \alpha, \beta} \int_{T_{\alpha\beta\delta}(t)} \vec{v}_{T_{\alpha\beta\delta}} \cdot (\xi_{\alpha\beta}(\nu_{\alpha\beta}) \times \tau_{\alpha\beta\delta}) \frac{1}{T_{ref}} d\mathcal{H}^{d-2}.
\end{aligned}$$

Summing up over all pairs  $\alpha < \beta$  the last term reads

$$\begin{aligned}
& - \sum_{\alpha < \beta} \sum_{\delta \neq \alpha, \beta} \int_{T_{\alpha\beta\delta}(t)} \vec{v}_{T_{\alpha\beta\delta}} \cdot (\xi_{\alpha\beta}(\nu_{\alpha\beta}) \times \tau_{\alpha\beta\delta}) \frac{1}{T_{ref}} d\mathcal{H}^{d-2} \\
&= - \sum_{\alpha < \beta < \delta} \int_{T_{\alpha\beta\delta}(t)} \vec{v}_{T_{\alpha\beta\delta}} \cdot \underbrace{\sum_{(i,j) \in \mathcal{A}} (\xi_{ij}(u_{ij}) \times \tau_{\alpha\beta\delta})}_{=0 \text{ by (1.17b)}} \frac{1}{T_{ref}} d\mathcal{H}^{d-2},
\end{aligned}$$

hence

$$\frac{d}{dt} \left( - \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) d\mathcal{H}^{d-1} \right) \Big|_t = - \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}(t)} (\nabla_{\Gamma_{\alpha\beta}} \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta})) \nu_{\alpha\beta} d\mathcal{H}^{d-1}. \quad (1.26e)$$

Finally, (1.26a) and (1.26e) yield, using the Gibbs-Thomson condition (1.14), the desired result

$$\begin{aligned} \frac{d}{dt} S(t) &= \frac{d}{dt} \left( \int_{\Omega} s(e, \hat{c}) d\mathcal{L}^d - \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) d\mathcal{H}^{d-1} \right) \Big|_t \\ &= \int_{\Omega(t)} \sum_{i,j} \nabla \frac{-\bar{\mu}_i}{T} \cdot L_{ij} \nabla \frac{-\bar{\mu}_j}{T} d\mathcal{L}^d \\ &\quad + \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}(t)} \left( \frac{1}{T} [f - \bar{\mu} \cdot \hat{c}]_{\alpha}^{\beta} - \nabla_{\Gamma_{\alpha\beta}} \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \right) \nu_{\alpha\beta} d\mathcal{H}^{d-1} \\ &= \int_{\Omega(t)} \sum_{i,j} \nabla \frac{-\bar{\mu}_i}{T} \cdot L_{ij} \nabla \frac{-\bar{\mu}_j}{T} d\mathcal{L}^d + \sum_{\alpha < \beta} \int_{\Gamma_{\alpha\beta}(t)} m_{\alpha\beta}(\nu_{\alpha\beta})^2 d\mathcal{H}^{d-1}. \end{aligned}$$

By (1.6a) the last line is non-negative.  $\square$

## 1.4 Calibration

### 1.4.1 Phase diagrams

In materials science, the solidification behaviour of alloys is described by phase diagrams. Such diagrams indicate at which composition and temperature a certain phase is preferred. Often, unstable regions appear as, instead of forming one homogeneous phase, it is energetically favourable to form several phases with different compositions. The fact that energy is necessary to create boundaries between the phases is not taken into account.

The phase diagram of a specific alloy can experimentally be determined. In theory, alloys are modelled by postulating free energies of the possible phases. Keeping the temperature fixed, the system is in equilibrium if the free energy is minimised over the set of possible compositions; every point on the lower convex hull of the free energies can be realised. Given the composition of the alloy, either one of the free energies realises the lower convex hull (then the phase corresponding to that energy is stable) or the convex hull is strictly lower than each free energy. In the latter case the point on the convex hull can be found by interpolating certain points on the graphs of different free energies. But this means that forming phases corresponding to those points (with volume fractions such that the mass of the whole system is not changed) yields a lower free energy than the free energy of each homogeneous phase at the given composition. In the following, the above procedure is more precisely described and exemplarily done for a binary alloy.

It is shown in Appendix B, Lemma B.3 that, given a fixed temperature  $T$ , two phases which labelled with  $\alpha$  and  $\beta$  are in equilibrium if and only if (1.13b) and (1.14) with  $\nu_{\alpha\beta} = 0$  and  $-\nabla_{\Gamma} \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) = 0$  (the phase boundary doesn't move and is flat) are fulfilled. Postulating free energy densities of the phases, from those conditions pairs of concentration vectors  $\hat{c}^{\alpha}$  and  $\hat{c}^{\beta}$  can be computed such that the phases are in equilibrium.

From statistical thermodynamics (cf., for example, [Haa94], Section 5.2 and the references therein) the model of ideal solution can be derived for the free energy density:

$$f_{id}^{\alpha}(T, \hat{c}) = \sum_{i=1}^N \left( L_i^{\alpha} \frac{T - T_i^{\alpha}}{T_i^{\alpha}} c_i + \frac{R_g}{v_m} T c_i \ln(c_i) - c_i T \left( \ln\left(\frac{T}{T_{ref}}\right) - 1 \right) c_i \right). \quad (1.27)$$

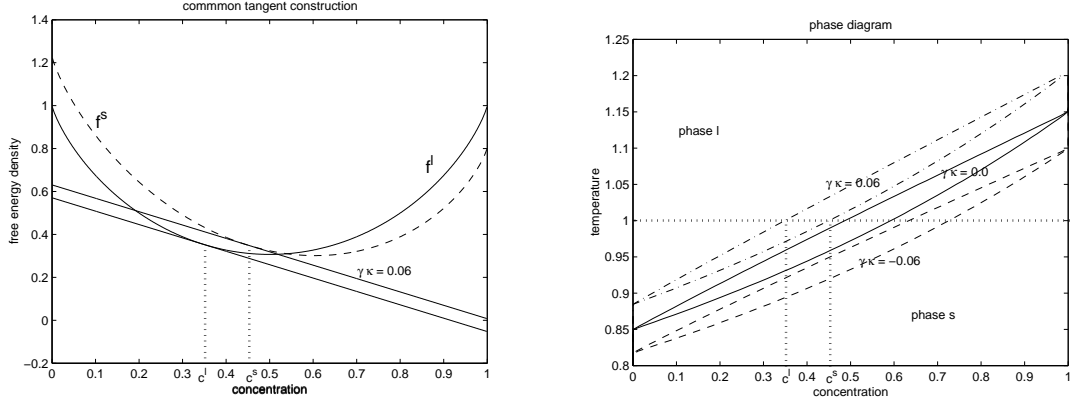


Figure 1.2: On the left: tangents with equal slope and given distance  $\gamma\kappa = 0.06$  on two free energy densities for phases  $l$  and  $s$ , the corresponding concentrations are drawn in the phase diagram; on the right: additional terms in the Gibbs-Thomson condition shift the phase diagram. The parameters do not correspond to a certain material.

$L_i^\alpha$  and  $T_i^\alpha$  are the latent heat respectively the melting temperature of component  $i$  in phase  $\alpha$ ,  $R_g$  is the gas constant,  $v_m$  the molar volume (which is supposed to be constant) and  $c_v$  the specific heat capacity (constant, too; observe that  $c_v = c_p$  due to the assumptions in Subsection 1.1.1 that volume and pressure are fixed, cf. [Mül01], Section 2.4.3). It is clear that  $f_{id}^\alpha$  is strictly concave in the temperature and convex in the concentrations which can be used for Legendre transformations.

The more general model of subregular solution takes the Redlich-Kister terms (cf. [RK48]) into account and reads

$$f_{sr}^\alpha = f_{id}^\alpha + \sum_{i=1}^N \sum_{j=1}^N c_i c_j \sum_{n=0}^K M_{ij}^{(n)} (c_i - c_j)^n \quad (1.28)$$

with interaction coefficients  $M_{ij}^{(n)}$ . In the case  $K = 0$ , the model of regular solution is obtained. The property of convexity in  $c$  may be lost because of the additional terms. Then more than one pair of concentration vectors may be found such that the equilibrium conditions are satisfied.

In the case of a binary alloy, i.e.,  $N = 2$ , the concentration of the second component is given by  $c_2 = 1 - c_1$ . It holds that  $\mathcal{P}^2 e_1 = \frac{1}{2}(e_1 - e_2)$  and  $\mathcal{P}^2 e_2 = \frac{1}{2}(e_2 - e_1)$ , hence, as  $\bar{\mu}_i = \nabla_c f \cdot \mathcal{P}^2 e_i$  (see Appendix B, Lemma B.2),

$$\bar{\mu}_1 = \frac{1}{2}(\partial_{c_1} f - \partial_{c_2} f) = -\bar{\mu}_2.$$

Writing  $\tilde{c} := c_1$  and setting  $\tilde{f}(T, \tilde{c}) := f(T, \tilde{c}, 1 - \tilde{c})$  implies  $\bar{\mu}_1(T, \tilde{c}) = \frac{1}{2}\partial_{\tilde{c}}\tilde{f}(T, \tilde{c})$ . Given (1.13a), i.e.,  $T = T^\alpha = T^\beta$ , the conditions (1.13b) reduce to

$$\partial_{\tilde{c}}\tilde{f}^\alpha(T, \tilde{c}^\alpha) = \partial_{\tilde{c}}\tilde{f}^\beta(T, \tilde{c}^\beta). \quad (1.29)$$

Besides

$$\begin{aligned} f(T, \tilde{c}) - \bar{\mu}(T, \tilde{c}) \cdot c &= \tilde{f}(T, \tilde{c}) - \bar{\mu}_1(T, \tilde{c})\tilde{c} - \bar{\mu}_2(T, S\tilde{c})(1 - \tilde{c}) \\ &= \tilde{f}(T, \tilde{c}) - \partial_{\tilde{c}}\tilde{f}(T, \tilde{c})\tilde{c} + \frac{1}{2}\partial_{\tilde{c}}\tilde{f}(T, \tilde{c}) \end{aligned}$$

so that with (1.29) the Gibbs-Thomson condition (1.14) becomes

$$\tilde{f}^\alpha(T, \tilde{c}^\alpha) = \tilde{f}^\beta(T, \tilde{c}^\beta) + \partial_{\tilde{c}}\tilde{f}^\beta(T, \tilde{c}^\beta)(\tilde{c}^\alpha - \tilde{c}^\beta). \quad (1.30)$$

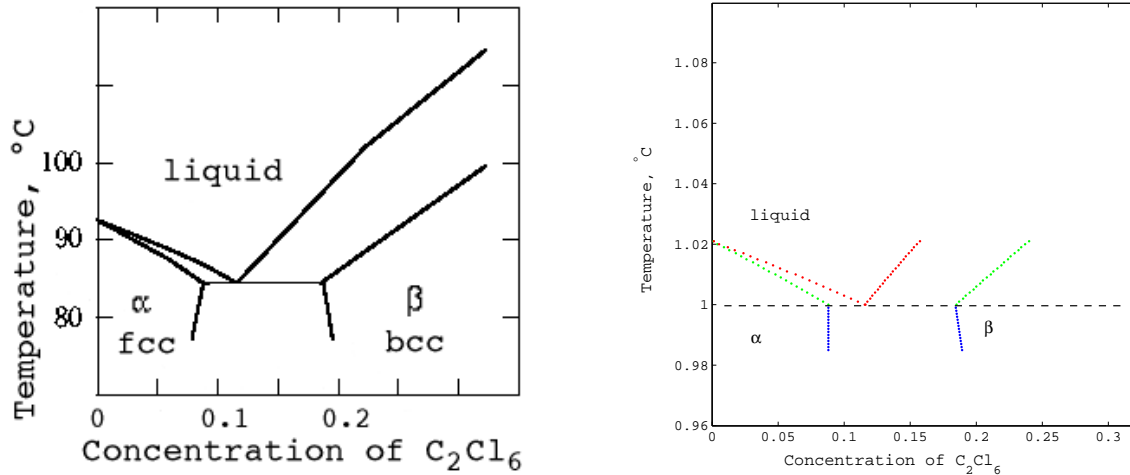


Figure 1.3: On the left: original phase diagram of  $C_2Cl_6-CBr_4$ , from <http://www.gps.jussieu.fr/engl/exper.htm>; on the right: numerically computed phase diagram with dimensionless temperature.

Equations (1.29) and (1.30) being satisfied means that there is a common tangent touching  $\tilde{f}^\alpha$  and  $\tilde{f}^\beta$  in  $\tilde{c}^\alpha$  and  $\tilde{c}^\beta$  respectively. The numerically computed diagrams in the figures 1.2 and 1.3 were obtained by solving (1.29) and (1.30) for several temperatures and plotting the computed concentrations with MATLAB. Lens shaped regions with unstable states are observed. Given a point  $(\tilde{c}, T)$  in that region, both  $\tilde{f}^l(T, \tilde{c})$  and  $\tilde{f}^s(T, \tilde{c})$  are higher than the value on the lower convex envelope of the free energy densities. These points can be realised by appropriate linear combinations of  $\tilde{f}^l(T, \tilde{c}^l)$  and  $\tilde{f}^s(T, \tilde{c}^s)$ ,  $\tilde{c}^l$  and  $\tilde{c}^s$  being computed from the above equilibrium conditions. In points  $(\tilde{c}, T)$  outside of the lens one of the free energy densities corresponds to the lower convex envelope and realises the energetically lowest possible value.

If the phase boundary is not in equilibrium and the  $v_{\alpha\beta}$ -term or the  $\gamma_{\alpha\beta}$ -term is present in (1.14) then the phase diagram is shifted. More precisely, for a given temperature the task is not any more to find a common tangent but to find tangents that have the same slope since (1.29) remains fulfilled and that have a distance given by the additional term appearing in (1.30). This is shown in Fig. 1.2. In particular, this is why the limit concentrations on a moving or curved phase boundary from the adjacent phases can differ from equilibrium concentrations. This allows for effects as, for example, solute trapping. Such an effect occurs (and can be measured) at relatively high velocities, and it is not clear whether in such a regime thermodynamics of irreversible processes involving the assumption of local equilibrium is still applicable.

In Fig. 1.3, the eutectic phase diagram of  $C_2Cl_6-CBr_4$  is approximated by postulating free energy densities of the form (1.27) for the three possible phases  $\alpha$ ,  $\beta$  and  $l$ . In the following table, the dimensionless parameters are listed.  $B$  corresponds to component  $C_2Cl_6$  and  $A$  to  $CBr_4$ . The values  $T_A^\beta$  and  $L_A^\beta$  are fit parameters as pure  $CBr_4$  is not stable in the structure of the  $\beta$ -phase so that these values cannot be measured. The same holds true analogously for  $T_B^\alpha$  and  $L_B^\alpha$ .

$CBr_4$	$T_A^\alpha = 1.021$	$L_A^\alpha = 1.5$	$T_A^\beta = 0.93$	$L_A^\beta = 1.075$
$C_2Cl_6$	$T_B^\alpha = 0.568$	$L_B^\alpha = 0.358$	$T_B^\beta = 1.28$	$L_B^\beta = 2.13$

### 1.4.2 Mass diffusion

In this section some relations are established between the Onsager coefficients  $L_{ij}$  and diffusion coefficients that are often experimentally measured and given in literature. For simplicity, the temperature is fixed and the influence of temperature gradients on mass fluxes is not considered

but only cross effects due to the presence of several components. Since in the present model mass diffusion is a bulk phenomenon (enhanced diffusion in the phase boundaries is not taken into account but can easily be involved, cf. [NGS05]) only one phase is considered. The flux (1.5) becomes with  $T$ , being fixed, entering the coefficients

$$J_i = \sum_{j=1}^N L_{ij} \nabla(-\mu_j).$$

According to Fick's law, diffusion is often modelled by a linear relation between diffusive flux and concentration gradients (cf. [TÅV03], Section 2.4 and the discussion therein). If the diffusivity  $D_{ik}$  models the influence of gradients of component  $k$  on the flux of component  $i$  then

$$J_i = - \sum_{k=1}^N D_{ik} \nabla c_k.$$

For (1.4) to be fulfilled,

$$\sum_{i=1}^N D_{ik} = 0, \quad 1 \leq k \leq N,$$

is supposed. Often, one component (w.l.o.g. component  $N$ ) is considered as solvent for the others which only appear in a minor concentration. Since  $c_N = 1 - \sum_{i=1}^{N-1} c_i$  it holds that

$$J_i = - \sum_{k=1}^N D_{ik} \nabla c_k = - \sum_{k=1}^{N-1} (D_{ik} - D_{iN}) \nabla c_k =: - \sum_{k=1}^{N-1} D_{ik}^N \nabla c_k$$

with coefficients  $D_{ik}^N = D_{ik} - D_{iN}$  that are often given in literature. In particular, cross effects are possible in the sense that concentration gradients of one species causes another species to diffuse. An example is the Darken effect [Dar49] for diffusion of carbon in steel under the influence of silicon (cf. again [TÅV03], Section 2.4).

Considering  $\mu$  as a function in  $\hat{c}$  (cf. Appendix B) yields

$$J_i = \sum_{j=1}^N L_{ij} \nabla(-\mu_j) = \sum_{j=1}^N L_{ij} \sum_{k=1}^N (-\partial_{c_k} \mu_j) \nabla c_k = - \sum_{k=1}^N \left( \sum_{j=1}^N L_{ij} \partial_{c_k} \mu_j \right) \nabla c_k$$

and therefore

$$D_{ik} = \sum_{j=1}^N L_{ij} \partial_{c_k} \mu_j \quad \text{or, shortly,} \quad D = L \partial_c \mu. \quad (1.31)$$

In particular,  $\sum_i D_{ik} = 0$  is obtained from the corresponding condition on the  $L_{ij}$ . In Subsection 1.1.1 it is mentioned that  $L$  can be chosen to be symmetric. Then  $D$  is not symmetric in general. Furthermore,

$$D_{ik}^N = \sum_{j=1}^N L_{ij} (\partial_{c_k} - \partial_{c_N}) \mu_j.$$

The fact that  $L$  is symmetric imposes constraints on the  $D_{ij}^N$  and on the dependence of the  $\mu_j$  on the concentrations.

Instead of using the  $D_{ik}^N$ , alternatively to each species an atomic diffusivity or bare mobility  $D_i(\hat{c})$  can be assigned. Defining

$$D_{ik} = D_i(\hat{c}) \delta_{ik} - \frac{D_i(\hat{c}) c_i}{\sum_l D_l(\hat{c}) c_l} D_k(\hat{c})$$

## CHAPTER 1. ALLOY SOLIDIFICATION

---

it is easy to derive that  $\sum_{i=1}^N D_{ik} = 0$  and, by (1.31),  $\sum_{i=1}^N L_{ij} = 0$ . Using  $c_N = 1 - \sum_{i=1}^{N-1} c_i$  it holds that

$$\begin{aligned}
 J_i &= - \sum_{k=1}^N D_{ik} \nabla c_k \\
 &= - D_i(\hat{c}) \nabla c_i + \frac{D_i(\hat{c}) c_i}{\sum_l D_l(\hat{c}) c_l} \sum_{k=1}^N D_k(\hat{c}) \nabla c_k \\
 &= - D_i(\hat{c}) \nabla c_i + \frac{D_i(\hat{c}) c_i}{\sum_l D_l(\hat{c}) c_l} \sum_{k=1}^{N-1} (D_k(\hat{c}) - D_N(\hat{c})) \nabla c_k,
 \end{aligned}$$

whence there results the following relation to the  $D_{ik}^N$ :

$$D_{ik}^N = D_i(\hat{c}) \delta_{ik} - \frac{D_i(\hat{c}) c_i}{\sum_l D_l(\hat{c}) c_l} (D_k(\hat{c}) - D_N(\hat{c})), \quad 1 \leq i \leq N, 1 \leq k \leq N-1.$$



## Chapter 2

# Phase Field Modelling

In this chapter, a general framework based on the phase field approach is presented to describe the microstructure formation occurring during alloy solidification. In the preceding chapter, an entropy functional played a central role involving bulk and surface contributions. Introducing phase field variables and replacing the surface terms by a Ginzburg-Landau type entropy, the motion of the (diffuse) phase boundaries or, respectively, the evolution of the phase fields can be defined by a gradient flow of the entropy which yields a set of partial differential equations of parabolic type (see Section 2.1). As before, the evolution is coupled to bulk equations balancing the conserved quantities energy and mass. In particular, a small length scale is involved related to the thickness of the interfacial layers.

To take kinetic anisotropy of the phase boundaries into account, a deviation from the gradient flow structure is allowed by introducing a positive mobility function depending on the phase fields and their gradients. In spite of this deviation, an entropy inequality can be derived again (see Section 2.2).

To clarify the generality of the developed framework, it is shown in Section 2.3 that, by appropriate calibration, i.e., choosing free energies for the phases and suitable potentials for the Ginzburg-Landau part of the entropy as well as Onsager coefficients for the fluxes, the governing equations of models are obtained which have been used earlier. More precisely, the models of Caginalp [Cag89] (various asymptotic limits are discussed in this paper), Penrose-Fife [PF90] (in this work, thermodynamic consistency is discussed), and Wheeler-Boettinger-McFadden [WMB92] (as one of the first phase field models for an alloy) are derived.

The general framework is formulated in terms of the phase fields and the conserved quantities. Instead of the latter the thermodynamic potentials, namely, the negative inverse temperature and generalised chemical potential differences divided by the temperature, may be used. Since these potentials are continuous across the phase boundaries in the related sharp interface model, the asymptotic analysis in the following chapter is simplified. The use of the thermodynamic potentials instead of the conserved quantities is also motivated by the discussion in [KKS99]. There it was found that, when taking the concentration as variable, in the diffuse interfacial region an extra amount of free energy appears which is due to the interpolation properties in the concentration and the phase field variable. It plays no role in the sharp interface limit since it scales proportional to the small length scale related to the interface thickness. But if one is interested in a quantitative description of a specific alloy and in numerical simulations with, necessarily, relatively high interface thicknesses then, depending on the material, it is possible that this extra potential cannot be ignored any more. By using the chemical potential as a variable instead of the concentration, the additional potential is avoided.

A good thermodynamic quantity to reformulate the diffusion equations is the reduced grand canonical potential, defined to be the Legendre transform of the negative entropy with respect to the conserved quantities energy and concentrations. After its introduction and an example, the

reformulated general phase field model is presented in Section 2.4.

As in the previous chapter, derivatives sometimes are denoted by subscripts after a comma. For example,  $s_{,\phi}(c, \phi)$  is the derivative of the function  $s = s(c, \phi)$  in a point  $(c, \phi)$  with respect to the variables corresponding to  $\phi$ .

## 2.1 The general phase field model

A system with  $M$  possible phases and  $N$  components is considered. The entropy (1.10) is replaced by an entropy functional of the form

$$S(c, \phi) = \int_{\Omega} \left( s(c, \phi) - (\varepsilon a(\phi, \nabla \phi) + \frac{1}{\varepsilon} w(\phi)) \right) dx. \quad (2.1)$$

The vector  $\phi = (\phi_{\alpha})_{\alpha=1}^M$  consists of phase field variables. Each variable  $\phi_{\alpha}$  describes the local fraction of the corresponding phase  $\alpha$ . They are required to fulfil the constraint

$$\phi \in \Sigma^M \quad (2.2)$$

analogously to the constraint (1.2) imposed on the concentrations. Here,

$$c := (e, c_1, \dots, c_N) \in \mathbb{R} \times \Sigma^N \quad (2.3a)$$

denotes the vector of all conserved variables including the internal energy  $e = c_0$ . The pure concentration vector is denoted by

$$\hat{c} := (c_1, \dots, c_N) \in \Sigma^N. \quad (2.3b)$$

The bulk entropy contribution  $s(c, \phi)$  will later be motivated (see (2.13)). The interfacial contribution in (1.10), namely

$$- \sum_{\alpha < \beta, \alpha, \beta=1}^M \int_{\Gamma_{\alpha\beta}} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) d\mathcal{H}^{d-1}, \quad (2.4)$$

is replaced by a Ginzburg-Landau type functional (cf. [LG50]) of the form

$$- \int_{\Omega} \left( \varepsilon a(\phi, \nabla \phi) + \frac{1}{\varepsilon} w(\phi) \right) dx. \quad (2.5)$$

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, non-negative, and homogeneous of degree two in the second variable, i.e.,

$$a(\phi, X) \geq 0 \quad \text{and} \quad a(\phi, \eta X) = \eta^2 a(\phi, X) \quad \forall (\phi, X) \in \Sigma^M \times (\mathbb{T}\Sigma^M)^d \quad \text{and} \quad \forall \eta \in \mathbb{R}^+, \quad (2.6a)$$

and  $w : \Sigma^M \rightarrow \mathbb{R}$  is a smooth function with 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.,

$$w(\phi) \geq 0, \quad \text{and} \quad w(\phi) = 0 \Leftrightarrow \phi = e_{\beta} \text{ for some } \beta \in \{1, \dots, M\}. \quad (2.6b)$$

Observe that the  $e_{\beta}$  are the corners of the set  $\Sigma^M$  onto which  $\phi$  maps by (2.2). Possible choices for  $a$  and  $w$  are given in Section 2.3.

For the case of two phases it is shown in [Mod87] under appropriate assumptions on  $a$  that the functional (2.5)  $\Gamma$ -converges to the perimeter functional (2.4) when  $\varepsilon$  converges to zero. This result was generalised to more general surface energies (cf. [AB98]) which motivates the replacement. It should be remarked that the rigorous treatment of the case of several order parameters is still an open problem because of the appearance of triple points or lines, and so far only formal results exist (see the following chapter).

## 2.1. THE GENERAL PHASE FIELD MODEL

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. As shown in the following section the coupling is such that an entropy inequality holds, and the second law of thermodynamics is fulfilled.

To compute the variational derivative of the entropy with respect to the phase field variables let  $v : \Omega \rightarrow \mathbb{T}\Sigma^M$  be a smooth test function and  $\phi : \Omega \rightarrow \text{int}(\Sigma^M)$  be smooth where  $\text{int}(\Sigma^M)$  is the interior of  $\Sigma^M$  with respect to the induced topology on  $\mathbb{H}\Sigma^M$  from  $\mathbb{R}^M$ . Observe that then  $S(c, \phi + \delta v)$  is well-defined for  $\delta$  small enough.

$$\begin{aligned} \left\langle \frac{\delta S}{\delta \phi}(c, \phi), v \right\rangle &= \frac{d}{d\delta} \int_{\Omega} \left( s(c, \phi + \delta v) - (\varepsilon a(\phi + \delta v, \nabla \phi + \delta \nabla v) + \frac{1}{\varepsilon} w(\phi + \delta v)) \right) dx \Big|_{\delta=0} \\ &= \int_{\Omega} \sum_{\alpha=1}^M \left( s_{,\phi_\alpha}(c, \phi) v_\alpha - \varepsilon a_{,\phi_\alpha}(\phi, \nabla \phi) v_\alpha - \varepsilon a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) \cdot \nabla v_\alpha - \frac{1}{\varepsilon} w_{,\phi_\alpha}(\phi) v_\alpha \right) dx \\ &= \int_{\Omega} \sum_{\alpha=1}^M \left( \varepsilon \nabla \cdot a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) - \varepsilon a_{,\phi_\alpha}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi_\alpha}(\phi) + s_{,\phi_\alpha}(c, \phi) \right) v_\alpha dx. \end{aligned}$$

To obtain the last identity the boundary conditions

$$a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) \cdot \nu_{ext} = 0, \quad 1 \leq \alpha \leq M, \quad (2.7)$$

were imposed.

To allow for anisotropy in the mobility of the phase boundaries, analogously as in Definition 1.5 in Subsection 1.1.3 the  $L^2$  product is weighted. Given a smooth field  $\phi : \Omega \rightarrow \Sigma^M$  let

$$(w, v)_{\omega, \phi} := \int_{\Omega} \varepsilon \omega(\phi, \nabla \phi) w \cdot v dx \quad \forall w, v \in C^\infty(\Omega; \mathbb{T}\Sigma^M). \quad (2.8a)$$

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

$$\omega(\phi, X) \geq 0 \quad \text{and} \quad \omega(\phi, \eta X) = \omega(\phi, X) \quad \forall (\phi, X) \in \Sigma^M \times \mathbb{R}^{d \times M} \text{ and } \forall \eta \in \mathbb{R}^+. \quad (2.8b)$$

The evolution is of the system, defined by

$$(\partial_t \phi, v)_{\omega, \phi} = \left\langle \frac{\delta S}{\delta \phi}(c, \phi), v \right\rangle \quad \forall v \in C^\infty(\Omega, \mathbb{T}\Sigma^M), \quad (2.9)$$

yields for all test function  $v : \Omega \rightarrow \mathbb{T}\Sigma^M$

$$\begin{aligned} \int_{\Omega} \varepsilon \omega(\phi, \nabla \phi) \partial_t \phi \cdot v dx \\ = \int_{\Omega} \left( \varepsilon \nabla \cdot a_{,\nabla \phi}(\phi, \nabla \phi) - \varepsilon a_{,\phi}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi}(\phi) + s_{,\phi}(c, \phi) \right) \cdot v dx. \end{aligned} \quad (2.10)$$

Observe that since the weight  $\omega$  of the  $L^2$  product depends on  $\phi$  this is no gradient flow of the entropy as in the sharp interface model. If  $v : \Omega \rightarrow \mathbb{R}^M$  is an arbitrary test function, then  $v - \mathcal{P}^M v$  maps onto  $\mathbb{T}\Sigma^M$ ,  $\mathcal{P}^M$  being the projection defined in (1.1c). Inserting  $v - \mathcal{P}^M v$  and using

$$\int_{\Omega} \xi \cdot (v - \mathcal{P}^M v) dx = \int_{\Omega} (\xi - \mathcal{P}^M \xi) \cdot v dx$$

for another test function  $\xi : \Omega \rightarrow \mathbb{R}^M$  which holds thanks to the symmetry of  $\mathcal{P}^M = \frac{1}{M} \mathbf{1}_M \otimes \mathbf{1}_M$  gives for the left hand side of (2.10)

$$\int_{\Omega} \varepsilon \omega(\phi, \nabla \phi) \partial_t \phi \cdot (v - \mathcal{P}^M v) dx = \int_{\Omega} \varepsilon \omega(\phi, \nabla \phi) \partial_t \phi \cdot v dx$$

since  $\partial_t \phi(t, x) \in \text{T}\Sigma^M$  implying  $\mathcal{P}^M \partial_t \phi = 0$ . The right hand side of (2.10) becomes when inserting the function  $v - \mathcal{P}^M v$

$$\int_{\Omega} \sum_{\alpha} \left( \varepsilon \nabla \cdot a_{,\nabla \phi_{\alpha}}(\phi, \nabla \phi) - \varepsilon a_{,\phi_{\alpha}}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi_{\alpha}}(\phi) + s_{,\phi_{\alpha}}(c, \phi) - \lambda \right) v_{\alpha} \, dx$$

where the Lagrange factor  $\lambda$  is given by

$$\begin{aligned} \lambda &= \frac{1}{M} \mathbf{1}_M \cdot \left( \varepsilon \nabla \cdot a_{,\nabla \phi}(\phi, \nabla \phi) - \varepsilon a_{,\phi}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi}(\phi) + s_{,\phi}(c, \phi) \right) \\ &= \frac{1}{M} \sum_{\alpha=1}^M \left( \varepsilon \nabla \cdot a_{,\nabla \phi_{\alpha}}(\phi, \nabla \phi) - \varepsilon a_{,\phi_{\alpha}}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi_{\alpha}}(\phi) + s_{,\phi_{\alpha}}(c, \phi) \right). \end{aligned} \quad (2.11)$$

Finally, (2.9) yields

$$\varepsilon \omega(\phi, \nabla \phi) \partial_t \phi = \varepsilon \nabla \cdot a_{,\nabla \phi}(\phi, \nabla \phi) - \varepsilon a_{,\phi}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi}(\phi) + s_{,\phi}(c, \phi) - \lambda \mathbf{1}_M.$$

The balance equations for the conserved quantities read

$$\partial_t c_i = -\nabla \cdot J_i(c, \phi, \nabla u(c, \phi)), \quad 0 \leq i \leq N,$$

with the fluxes

$$J_i(c, \phi, \nabla u(c, \phi)) = \sum_{j=0}^N L_{ij}(c, \phi) \nabla(-u_j(c, \phi)).$$

Similarly as done in Subsection 1.1.1 it can be shown that this is a gradient flow of the entropy with respect to a weighted  $H^{-1}$ -product. The different phases are taken into account by letting the potentials and the coefficients depend on the smooth phase field variables. This may be done as follows:

The 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.

$$f(T, \hat{c}, \phi) = \sum_{\alpha=1}^M f^{\alpha}(T, \hat{c}) h(\phi_{\alpha}) \quad (2.12)$$

with an interpolation function  $h : [0, 1] \rightarrow [0, 1]$  satisfying  $h(0) = 0$  and  $h(1) = 1$ . By  $s = -f_{,T}$  and  $e = f + Ts = f - Tf_{,T}$  (see Appendix B) the internal energy can be expressed as a function in  $(T, \hat{c}, \phi)$ . By appropriate assumptions on  $f$  the temperature inversely can be expressed as a function in  $(e, \hat{c}, \phi) = (c, \phi)$ . Let

$$\Phi : \mathbb{R}^+ \times \text{int}(\Sigma^N) \times \text{int}(\Sigma^M) \rightarrow \mathbb{R} \times \text{int}(\Sigma^N) \times \text{int}(\Sigma^M), \quad (T, \hat{c}, \phi) \mapsto (e(T, \hat{c}, \phi), \hat{c}, \phi)$$

be this change of variables. Using  $\bar{\mu} = f_{,\hat{c}}$  (see Appendix B) and again  $e = f - Tf_{,T}$  yields

$$e_{,T} = -Tf_{,TT}, \quad e_{,\hat{c}} = \bar{\mu} - T\bar{\mu}_{,T}, \quad e_{,\phi} = f_{,\phi} - Tf_{,T\phi}.$$

Then  $D\Phi(T, \hat{c}, \phi) : \mathbb{R} \times \text{T}\Sigma^N \times \text{T}\Sigma^M \rightarrow \mathbb{R} \times \text{T}\Sigma^N \times \text{T}\Sigma^M$  is given by

$$D\Phi(T, \hat{c}, \phi) = \begin{pmatrix} -Tf_{,TT} & \bar{\mu} - T\bar{\mu}_{,T} & f_{,\phi} - Tf_{,T\phi} \\ 0 & \text{Id}_{\text{T}\Sigma^N} & 0 \\ 0 & 0 & \text{Id}_{\text{T}\Sigma^M} \end{pmatrix}$$

where  $\text{Id}_{\text{T}\Sigma^K}$  is the identity on  $\text{T}\Sigma^K$ . Assuming that  $Tf_{,TT} \neq 0$  the inverse function theorem implies

$$D(\Phi^{-1})(e, \hat{c}, \phi) = \frac{-1}{Tf_{,TT}} \begin{pmatrix} 1 & -(\bar{\mu} - T\bar{\mu}_{,T}) & -(f_{,\phi} - Tf_{,T\phi}) \\ 0 & -Tf_{,TT} \text{Id}_{\text{T}\Sigma^N} & 0 \\ 0 & 0 & -Tf_{,TT} \text{Id}_{\text{T}\Sigma^M} \end{pmatrix}$$

## 2.1. THE GENERAL PHASE FIELD MODEL

where  $f$  and its derivatives are evaluated at  $(T(e, \hat{c}, \phi), \hat{c}, \phi)$ . In the first line the derivatives of  $T$  with respect to  $e$ ,  $\hat{c}$  and  $\phi$  can be found. Considering the entropy density as a function in the new variables  $(e, \hat{c}, \phi) = (c, \phi)$ , i.e.

$$s(e, \hat{c}, \phi) = -f_{,T}(T(e, \hat{c}, \phi), \hat{c}, \phi), \quad (2.13)$$

the derivatives of  $s$  with respect to  $(c, \phi)$  can be computed:

$$\begin{aligned} s_{,c_0}(c, \phi) &= s_{,e}(e, \hat{c}, \phi) = -f_{,TT}T_{,e} = -f_{,TT} \frac{-1}{Tf_{,TT}} = \frac{1}{T} &= -u_0, \\ s_{,\hat{c}}(c, \phi) &= s_{,\hat{c}}(e, \hat{c}, \phi) = -f_{,T\hat{c}} - f_{,TT}T_{,\hat{c}} = -\bar{\mu}_{,T} - f_{,TT} \frac{\bar{\mu} - T\bar{\mu}_{,T}}{Tf_{,TT}} = \frac{-\bar{\mu}}{T} &=: -\hat{u}, \\ s_{,\phi}(c, \phi) &= s_{,\phi}(e, \hat{c}, \phi) = -f_{,T\phi} - f_{,TT}T_{,\phi} = -f_{,T\phi} - f_{,TT} \frac{f_{,\phi} - Tf_{,T\phi}}{Tf_{,TT}} &= -\frac{f_{,\phi}}{T}. \end{aligned}$$

The identity in the last line can be inserted into (2.10) and the following equations. Moreover  $u_0 = \frac{-1}{T}$  and  $\hat{u} = \frac{\bar{\mu}}{T}$  are expressed in terms of  $(c, \phi)$ .

The coefficients  $L_{ij}$  and the diffusivities (see Subsection 1.4.2) can distinguish in the different phases, too. This may be modelled by interpolating the coefficients  $\{L_{ij}^\alpha\}_\alpha$  of the pure phases analogously as done for the free energy. The matrix  $L(c, \phi) = (L_{ij}(c, \phi))_{i,j=0}^N$  remains symmetric. From (1.6a) and (1.6b) the conditions

$$L = (L_{ij}(c, \phi))_{i,j=0}^N \text{ is positive semi-definite,} \quad (2.14a)$$

$$\sum_{i=1}^N L_{ij}(c, \phi) = 0 \quad \forall j \in \{1, \dots, N\} \quad (2.14b)$$

can be deduced. Altogether, the above computations motivate the following definition of the model:

**2.1 Definition** *The evolution of the system is governed by the partial differential equations*

$$\partial_t c_i = -\nabla \cdot J_i(c, \phi, \nabla u(c, \phi)) = \nabla \cdot \left( \sum_{j=0}^N L_{ij}(c, \phi) \nabla u_j(c, \phi) \right), \quad (2.15a)$$

$$\varepsilon \omega(\phi, \nabla \phi) \partial_t \phi_\alpha = \varepsilon \nabla \cdot a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) - \varepsilon a_{,\phi_\alpha}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi_\alpha}(\phi) - \frac{f_{,\phi_\alpha}(T(c, \phi), \hat{c}, \phi)}{T(c, \phi)} - \lambda \quad (2.15b)$$

where  $0 \leq i \leq N$  and  $1 \leq \alpha \leq M$  with  $\lambda$  given by

$$\lambda = \frac{1}{M} \sum_{\alpha=1}^M \left( \varepsilon \nabla \cdot a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) - \varepsilon a_{,\phi_\alpha}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi_\alpha}(\phi) - \frac{f_{,\phi_\alpha}(T(c, \phi), \hat{c}, \phi)}{T(c, \phi)} \right). \quad (2.15c)$$

The differential equations are subject to initial conditions

$$c(t=0) = c_{ic}, \quad \phi(t=0) = \phi_{ic} \quad (2.15d)$$

and boundary conditions

$$J_i(c, \phi, \nabla u(c, \phi)) \cdot \nu_{ext} = 0, \quad 1 \leq i \leq N, \quad (2.15e)$$

$$a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) \cdot \nu_{ext} = 0, \quad 1 \leq \alpha \leq M. \quad (2.15f)$$

If not otherwise stated, additionally the boundary condition

$$J_0(c, \phi, \nabla u(c, \phi)) \cdot \nu_{ext} = 0 \quad (2.15g)$$

is imposed.

**2.2 Remark** The boundary condition (2.15e) implies that the system is closed as there is no mass flux across the external boundary. If (2.15g) holds true there is no energy flux across the external boundary and the system is adiabatic. Instead of (2.15g) one may impose different conditions that, for example, correspond to Dirichlet conditions for the temperature. Such boundary conditions can, for example, model the cooling of the system to a certain temperature.

## 2.2 Non-negativity of entropy production

Analogously as done in Section 1.3, it is shown in the following that the equations in Definition 2.1 governing the evolution imply a locally non-negative entropy production which is the second law of thermodynamics. The calculation is much easier than in Section 1.3 as no jumps of fields across phase boundaries are involved but only smooth fields appear.

The time derivative of the integrand of the entropy (2.1) is

$$\begin{aligned} \partial_t \left( s(c, \phi) - \varepsilon a(\phi, \nabla \phi) - \frac{1}{\varepsilon} w(\phi) \right) \\ = \underbrace{s_{,c} \cdot \partial_t c}_I + \underbrace{s_{,\phi} \cdot \partial_t \phi - \varepsilon (a_{,\phi} \cdot \partial_t \phi + a_{,\nabla \phi} : \nabla \partial_t \phi) - \frac{1}{\varepsilon} w_{,\phi} \cdot \partial_t \phi}_{II}. \end{aligned}$$

Using (2.15a) and  $s_{,c} = -u$  yields for  $I$  (the dependence of the functions on  $c$  and  $\phi$  is omitted here and in the following for a shorter presentation)

$$\begin{aligned} I &= \sum_{i=0}^N u_i \nabla \cdot \left( \sum_{j=0}^N L_{ij} \nabla (-u_j) \right) \\ &= \nabla \cdot \left( \sum_{i,j=0}^N u_i L_{ij} \nabla (-u_j) \right) - \sum_{i,j=0}^N \nabla u_i \cdot L_{ij} \nabla (-u_j) \\ &= \nabla \cdot \left( \sum_{i=0}^N u_i J_i \right) + \sum_{i,j=0}^N \nabla (-u_i) \cdot L_{ij} \nabla (-u_j). \end{aligned}$$

Using (2.15b) it holds for the second term that

$$\begin{aligned} II &= \sum_{\alpha=1}^M \left( s_{,\phi_\alpha} \partial_t \phi_\alpha - \varepsilon a_{,\phi_\alpha} \partial_t \phi_\alpha - \varepsilon a_{,\nabla \phi_\alpha} \cdot \nabla (\partial_t \phi_\alpha) - \frac{1}{\varepsilon} w_{,\phi_\alpha} \partial_t \phi_\alpha \right) \\ &= \sum_{\alpha=1}^M \left( -\frac{f_{,\phi_\alpha}}{T} - \varepsilon a_{,\phi_\alpha} + \varepsilon \nabla \cdot a_{,\nabla \phi_\alpha} - \frac{1}{\varepsilon} w_{,\phi_\alpha} \right) \partial_t \phi_\alpha - \sum_{\alpha=1}^M \varepsilon \nabla \cdot (a_{,\nabla \phi_\alpha} \partial_t \phi_\alpha) \\ &= \varepsilon \omega(\phi, \nabla \phi) \sum_{\alpha=1}^M (\partial_t \phi_\alpha)^2 + \underbrace{\sum_{\alpha=1}^M \lambda \partial_t \phi_\alpha}_{=\lambda \partial_t \sum \phi_\alpha = 0} - \varepsilon \sum_{\alpha=1}^M \nabla \cdot (a_{,\nabla \phi_\alpha} \partial_t \phi_\alpha). \end{aligned}$$

Integrating  $I$  and  $II$  with respect to the space gives, using the divergence theorem,

$$\begin{aligned} \partial_t S(c, \phi) &= \int_{\Omega} (I + II) \, dx \\ &= \int_{\Omega} \left( \sum_{i,j=0}^N \nabla (-u_i) \cdot L_{ij} \nabla (-u_j) + \varepsilon \omega(\phi, \nabla \phi) \sum_{\alpha=1}^M (\partial_t \phi_\alpha)^2 \right) \, dx \end{aligned} \quad (2.16a)$$

$$- \int_{\partial \Omega} \left( \sum_{i=0}^N (-u_i) J_i + \varepsilon (a_{,\nabla \phi_\alpha} \partial_t \phi_\alpha) \right) \cdot \nu_{ext} \, d\mathcal{H}^{d-1}. \quad (2.16b)$$

From (2.16a) and using Assumptions (2.14a) and (2.8b) it is clear that the local entropy production is non-negative,

$$\sum_{i,j=0}^N \nabla (-u_i) \cdot L_{ij} \nabla (-u_j) + \varepsilon \omega(\phi, \nabla \phi) \varepsilon \sum_{\alpha=1}^M (\partial_t \phi_\alpha)^2 \geq 0.$$

Moreover, (2.16b) implies that the entropy flux

$$J_s := \sum_{i=0}^N (-u_i) J_i + \varepsilon \sum_{\alpha=1}^M a_{,\nabla\phi_\alpha} \partial_t \phi_\alpha$$

consists of two terms. The first one is due to energy and mass diffusion and the second one due to moving phase boundaries (cf. [AP92]). With the boundary conditions (2.15e), (2.15g), and (2.7) it holds that

$$\partial_t S(c, \phi) \geq 0$$

which is the desired entropy inequality for an isolated system.

## 2.3 Examples

The phase field model from Definition 2.1 generalises earlier models that have successfully been applied to describe such phenomena as mentioned in the Introduction. In the next subsections this is exemplarily shown for the models used in [Cag89, PF90, WMB92] by postulating suitable functions  $a$ ,  $w$ , and  $f$ .

### 2.3.1 Possible choices of the surface terms

First, some examples for the terms modelling interfacial contributions to the entropy are given. The simplest form of the gradient energy is

$$a(\phi, \nabla\phi) = \tilde{\gamma} |\nabla\phi|^2 = \tilde{\gamma} \sum_{\alpha=1}^M |\nabla\phi_\alpha|^2$$

or, more generally,

$$a(\phi, \nabla\phi) = \sum_{\alpha < \beta} \tilde{g}_{\alpha\beta} \nabla\phi_\alpha \cdot \nabla\phi_\beta \tag{2.17a}$$

with constants  $\tilde{\gamma}$  and  $\tilde{g}_{\alpha\beta}$ ,  $\alpha, \beta \in \{1, \dots, M\}$ . However, as shown in [SPN<sup>+</sup>96, GNS99a], gradient energies of the form

$$a(\phi, \nabla\phi) = \sum_{\alpha < \beta} A_{\alpha\beta} (\phi_\alpha \nabla\phi_\beta - \phi_\beta \nabla\phi_\alpha), \tag{2.17b}$$

where the  $A_{\alpha\beta}$  are convex functions that are homogeneous of degree two, are more convenient with respect to the calibration of parameters in the phase field model to the surface terms in the sharp interface model. A choice that leads to isotropic surface terms is

$$a(\phi, \nabla\phi) = \sum_{\alpha < \beta} \frac{\tilde{\gamma}_{\alpha\beta}}{\tilde{m}_{\alpha\beta}} |\phi_\alpha \nabla\phi_\beta - \phi_\beta \nabla\phi_\alpha|^2$$

with constants  $\tilde{\gamma}_{\alpha\beta}$  and  $\tilde{m}_{\alpha\beta}$  that can be related to  $\gamma_{\alpha\beta}$  and  $m_{\alpha\beta}$  (cf. [GNS98]).

Possible choices for the mobility function (2.8b) are given and discussed in [GNS99b, NGS05]. A general form is

$$\omega(\phi, \nabla\phi) = \omega_0 + \sum_{\alpha < \beta} B_{\alpha\beta} (\phi_\alpha \nabla\phi_\beta - \phi_\beta \nabla\phi_\alpha)$$

where the  $B_{\alpha\beta}$  are smooth functions that are homogeneous of degree zero and that can be related to the mobility coefficient  $m_{\alpha\beta}(\nu)$  of the  $\alpha$ - $\beta$ -phase transition (see the following chapter).

For the bulk potential one may take the standard multi-well potential

$$w_{st}(\phi) = 9 \sum_{\alpha < \beta} \tilde{m}_{\alpha\beta} \tilde{\gamma}_{\alpha\beta} \phi_\alpha^2 \phi_\beta^2 \quad (2.18)$$

or a higher order variant

$$\tilde{w}_{st}(\phi) = w_{st}(\phi) + \sum_{\alpha < \beta < \delta} \gamma_{\alpha\beta\delta} \phi_\alpha^2 \phi_\beta^2 \phi_\delta^2.$$

For numerical computations, the obstacle potential with multiple wells yields good calibration properties. It is defined by

$$w_{ob}(\phi) = \begin{cases} \frac{16}{\pi^2} \sum_{\alpha < \beta} \tilde{m}_{\alpha\beta} \tilde{\gamma}_{\alpha\beta} \phi_\alpha \phi_\beta & \text{if } \phi \in \Sigma^M, \\ \infty & \text{elsewhere,} \end{cases}$$

with a higher order variant

$$\tilde{w}_{ob}(\phi) = \begin{cases} w_{ob}(\phi) + \sum_{\alpha < \beta < \delta} \gamma_{\alpha\beta\delta} \phi_\alpha \phi_\beta \phi_\delta & \text{if } \phi \in \Sigma^M, \\ \infty & \text{elsewhere.} \end{cases}$$

The calibration properties of the presented multi-well potentials are discussed in [GNS99b] and [GHS05].

### 2.3.2 Relation to the Penrose-Fife model

Now, it is demonstrated that the general model includes the model of Penrose and Fife [PF90] as a special case. There is only one component, and the variable  $\hat{c}$  can be neglected. There are two phases, a solid one and a liquid one, hence the equations can be written down in terms of the solid fraction  $\varphi = \phi_1$ . Then, by (2.2),  $\phi_2 = 1 - \varphi$ . Moreover, instead of using the density of the internal energy as variable, the temperature is taken.

The first phase, the solid one, is characterised by  $\phi = e_1$  of, equivalently,  $\varphi = 1$ . Its free energy density is postulated to be

$$f^s(T) = L \frac{T - T_m}{T_m} - c_v T (\ln(T) - 1),$$

where  $T_m$  is the melting temperature and  $L$  the latent heat of the solid-liquid phase transition. The second phase, the liquid one, is characterised by  $\phi = e_2 \Leftrightarrow \varphi = 0$ , and its free energy density is postulated to be

$$f^l(T) = -c_v T (\ln(T) - 1).$$

Setting

$$f(T, \varphi, 1 - \varphi) = L \frac{T - T_m}{T_m} h(\varphi) - c_v T (\ln(T) - 1) \quad (2.19)$$

it holds that  $s(T, \varphi, 1 - \varphi) = -\frac{L}{T_m} h(\varphi) + c_v \ln(T)$  and

$$e(T, \varphi, 1 - \varphi) = -Lh(\varphi) + c_v T.$$



The evolution equation (2.15a) for the energy yields

$$c_v \partial_t T - Lh'(\varphi) \partial_t \varphi = -\nabla \cdot \left( L_{00} \nabla \frac{1}{T} \right).$$

Choosing  $L_{00} = c_v K_2 T^2$  the right hand side becomes  $c_v K_2 \Delta T$ .

Furthermore, the simple gradient entropy term

$$a(\phi, \nabla \phi) = \frac{\tilde{\gamma}}{2} |\nabla \phi|^2 = \frac{\tilde{\gamma}}{2} (|\nabla \phi_1|^2 + |\nabla \phi_2|^2) = \tilde{\gamma} |\nabla \varphi|^2$$

where  $\tilde{\gamma} = \frac{\kappa_1 c_v}{\varepsilon}$  for some constant  $\kappa_1$  is taken. Then  $a_{,\nabla \phi_\alpha} = \tilde{\gamma} \nabla \phi_\alpha$ ,  $\nabla \cdot a_{,\nabla \phi_\alpha} = \tilde{\gamma} \Delta \phi_\alpha$  and  $a_{,\phi_\alpha} = 0$ . Inserting this into the phase field equations (2.15b) yields

$$\varepsilon \omega \partial_t \phi_1 = \varepsilon \tilde{\gamma} \Delta \phi_1 - \frac{1}{\varepsilon} w_{,\phi_1} - \frac{1}{T} f_{,\phi_1} - \lambda, \quad (2.20a)$$

$$\varepsilon \omega \partial_t \phi_2 = \varepsilon \tilde{\gamma} \Delta \phi_2 - \frac{1}{\varepsilon} w_{,\phi_2} - \frac{1}{T} f_{,\phi_2} - \lambda \quad (2.20b)$$

with

$$\lambda = \frac{1}{2} \left( \varepsilon \tilde{\gamma} \Delta \phi_1 - \frac{1}{\varepsilon} w_{,\phi_1} - \frac{1}{T} f_{,\phi_1} + \varepsilon \tilde{\gamma} \Delta \phi_2 - \frac{1}{\varepsilon} w_{,\phi_2} - \frac{1}{T} f_{,\phi_2} \right).$$

Since  $\varphi = \phi_1 = 1 - \phi_2$  it holds that  $\partial_t \phi_1 = \partial_t \varphi$ ,  $\partial_t \phi_2 = -\partial_t \varphi$ ,  $\Delta \phi_1 = \Delta \varphi$  and  $\Delta \phi_2 = -\Delta \varphi$ . Moreover,

$$\begin{aligned} w_{,\phi_1}(\varphi, 1 - \varphi) - w_{,\phi_2}(\varphi, 1 - \varphi) &= \partial_\varphi w(\varphi, 1 - \varphi), \\ f_{,\phi_1}(T, \varphi, 1 - \varphi) - f_{,\phi_2}(T, \varphi, 1 - \varphi) &= \partial_\varphi f(T, \varphi, 1 - \varphi). \end{aligned}$$

Subtracting (2.20b) from (2.20a) gives

$$2\varepsilon \omega \partial_t \varphi = 2\varepsilon \tilde{\gamma} \Delta \varphi - \frac{1}{\varepsilon} \partial_\varphi w(\varphi, 1 - \varphi) - \frac{1}{T} \partial_\varphi f(T, \varphi, 1 - \varphi). \quad (2.21)$$

By (2.19),  $-\frac{1}{T} \partial_\varphi f(T, \varphi, 1 - \varphi) = L \left( \frac{1}{T} - \frac{1}{T_m} \right) h'(\varphi)$ . Setting  $\omega \equiv \frac{1}{2\varepsilon}$ ,  $K_1 = \frac{c_v}{2\varepsilon}$  and defining

$$s_0(\varphi) := -\frac{1}{\varepsilon c_v} w(\varphi, 1 - \varphi) - \frac{L}{c_v T_m} h(\varphi), \quad \lambda(\varphi) := Lh'(\varphi)/c_v$$

the equations (2.21) and (2.15a) become

$$\begin{aligned} \partial_t \varphi &= K_1 \left( \frac{\lambda(\varphi)}{T} + s'_0(\varphi) + \kappa_1 \Delta \varphi \right), \\ \partial_t T - \lambda(\varphi) \partial_t \varphi &= K_2 \Delta T \end{aligned}$$

which is the model in [PF90], Chapter 6.

### 2.3.3 A linearised model

In this subsection the general model is partially linearised. This is done in such a way that the evolution equations in the pure phases are linear, i.e., they reduce to standard linear diffusion equations. Only a binary system is considered, but a generalisation to multi-component systems is straightforward.

By  $\tilde{c} = c_1$  the concentration of the first component is denoted, hence  $c_2 = 1 - \tilde{c}$ . The fact that  $L$  is symmetric and the algebraic constraints (2.14b) give

$$L_{01} = L_{10} = -L_{02} = -L_{20} \quad \text{and} \quad L_{11} = L_{22} = -L_{12} = -L_{21}.$$

Setting  $\tilde{f}(T, \tilde{c}) = f(T, \tilde{c}, 1 - \tilde{c})$  gives as in Subsection 1.4.1

$$\tilde{f}_{,\tilde{c}} = \bar{\mu}_1 - \bar{\mu}_2.$$

Therefore  $L_{i1}\nabla(-\bar{\mu}_1) + L_{i2}\nabla(-\bar{\mu}_2) = L_{i1}\nabla\tilde{f}_{,\tilde{c}}$ ,  $i = 0, 1, 2$ , and the conservation laws for energy and concentration read

$$\partial_t e = -\nabla \cdot L_{00}\nabla\frac{1}{T} - \nabla \cdot L_{10}\nabla\frac{-\tilde{f}_{,\tilde{c}}}{T}, \quad (2.22a)$$

$$\partial_t \tilde{c} = -\nabla \cdot L_{10}\nabla\frac{1}{T} - \nabla \cdot L_{11}\nabla\frac{-\tilde{f}_{,\tilde{c}}}{T}. \quad (2.22b)$$

Defining  $\tilde{e}(T, \tilde{c}) := \tilde{f}(T, \tilde{c}) - T\tilde{f}_{,T}(T, \tilde{c})$  and choosing

$$L_{11} = D\frac{T}{\tilde{f}_{,\tilde{c}\tilde{c}}}, \quad L_{10} = L_{01} = \tilde{e}_{,\tilde{c}}D\frac{T}{\tilde{f}_{,\tilde{c}\tilde{c}}}, \quad \text{and} \quad L_{00} = \tilde{e}_{,\tilde{c}}^2D\frac{T}{\tilde{f}_{,\tilde{c}\tilde{c}}} + KT^2,$$

the equations (2.22a) and (2.22b) become after a short calculation

$$\partial_t \tilde{e} = \nabla \cdot \left( K\nabla T + \tilde{e}_{,\tilde{c}}D\nabla\tilde{c} + \tilde{e}_{,\tilde{c}}D\frac{\tilde{f}_{,\tilde{c}\phi}}{\tilde{f}_{,\tilde{c}\tilde{c}}}\nabla\phi \right), \quad (2.22c)$$

$$\partial_t \tilde{c} = \nabla \cdot \left( D\nabla\tilde{c} + D\frac{\tilde{f}_{,\tilde{c}\phi}}{\tilde{f}_{,\tilde{c}\tilde{c}}}\nabla\phi \right). \quad (2.22d)$$

The diffusivity coefficients  $K$  and  $D$  may depend on  $\phi$ . It remains to couple equations (2.22c) and (2.22d) to the equations for the phase field variables (2.15b).

If the internal energy density is affine linear in the variables  $(T, \tilde{c})$ , i.e.,

$$\tilde{e}(T, \tilde{c}) = c_v T + e_{,\tilde{c}}\tilde{c} \quad \text{with } e_{,\tilde{c}} \text{ constant,}$$

then the system (2.22c)–(2.22d) reduces in regions where  $\phi$  is constant, i.e., in the pure phases (where, the diffusivities  $K$  and  $D$  are constants), to

$$c_v \partial_t T = \nabla \cdot K\nabla T = K\Delta T, \quad \partial_t \tilde{c} = \nabla \cdot D\nabla\tilde{c} = D\Delta\tilde{c}.$$

These are classical linear diffusion equations for temperature (Fourier's law) and concentration (Fick's law).

### 2.3.4 Relation to the Caginalp model

Further linearisation of the model leads to a generalisation of the original phase field model [Cag89] to the case of alloy solidification. Let  $M = 3$ ,  $N = 2$  (a three-phase system for a binary alloy is considered) and choose the free energy density

$$\tilde{f}(T, \tilde{c}, \phi) = \left( \kappa\frac{\tilde{c}}{2} - \sum_{\alpha=1}^3 L_1^\alpha \phi_\alpha \right) \tilde{c} T - c_v T \left( \ln\left(\frac{T}{T_{ref}}\right) - 1 \right) - \sum_{\alpha=1}^3 L_2^\alpha \phi_\alpha,$$

where  $L_2^\alpha$  are latent heat coefficients and  $L_1^\alpha$  and  $\kappa$ , respectively, are coefficients entering the chemical potentials. As in the preceding subsection,  $\tilde{c} = c_1$  and  $c_2 = 1 - c_1 = 1 - \tilde{c}$ . Then

$$s = -\tilde{f}_{,T} = -\left( \kappa\frac{\tilde{c}}{2} - \sum_{\alpha=1}^3 L_1^\alpha \phi_\alpha \right) \tilde{c} + c_v \ln\left(\frac{T}{T_{ref}}\right),$$

$$\tilde{e} = \tilde{f} + Ts = c_v T - \sum_{\alpha} L_2^\alpha \phi_\alpha,$$

$$\frac{\bar{\mu}_1 - \bar{\mu}_2}{T} = \frac{\tilde{f}_{,\tilde{c}}}{T} = \kappa\tilde{c} - \sum_{\alpha} L_1^\alpha \phi_\alpha,$$

$$\frac{\tilde{f}_{,\phi_\alpha}}{T} = -L_1^\alpha \tilde{c} - \frac{L_2^\alpha}{T}.$$

The mobility matrix is chosen as in the previous subsection leading to

$$\begin{aligned}\partial_t \tilde{e} &= \partial_t \left( c_v T - \sum_{\alpha} L_2^{\alpha} \phi_{\alpha} \right) = \nabla \cdot (K \nabla T), \\ \partial_t \tilde{c} &= \nabla \cdot D \nabla \left( \kappa \tilde{c} - \sum_{\alpha} L_1^{\alpha} \phi_{\alpha} \right).\end{aligned}$$

For the gradient energy the isotropic function  $a(\phi, \nabla \phi) = \frac{\tilde{\gamma}}{2} \sum_{\alpha} |\nabla \phi_{\alpha}|^2$  is taken as in Subsection 2.3.2. Then the equations for the phase field variables are of the form

$$\omega \varepsilon \partial_t \phi_{\alpha} = \varepsilon \tilde{\gamma} \Delta \phi_{\alpha} - \frac{1}{\varepsilon} w_{,\phi_{\alpha}}(\phi) + L_1^{\alpha} \tilde{c} + \frac{L_2^{\alpha}}{T} - \lambda,$$

The term  $\frac{1}{T}$  can be linearised around a reference temperature  $T_m$ : so that

$$\omega \varepsilon \partial_t \phi_{\alpha} = \varepsilon \tilde{\gamma} \Delta \phi_{\alpha} - \frac{1}{\varepsilon} w_{,\phi_{\alpha}}(\phi) + L_1^{\alpha} \tilde{c} + L_2^{\alpha} \left( \frac{1}{T_m} - \frac{1}{T_m^2} (T - T_m) \right) - \lambda.$$

The equations for  $(T, \tilde{c})$  are linear, and all terms in the equation for  $\phi$  are linear except the term  $w_{,\phi_{\alpha}}$ .

It should be remarked that the above choice of the free energy density leads to a linearised phase diagram. In particular, the magnitude of the jump of the concentration in the sharp interface model is constant for each of the phase boundaries (cf. equations (1.29) and (1.30) in Subsection 1.4.1).

### 2.3.5 Relation to the Warren-McFadden-Boettinger model

In the model used in [WMB92] double-well potentials are used with coefficients depending on the concentration. The presented general model is not intended for a concentration dependence of  $w$ . But it turns out that, if the constants  $W_A$  and  $W_B$  in equations (8) and (9) of [WMB92] are equal (let  $W_A = W_B =: W$ ), then the concentration dependence of the double-well potential drops out. In the following derivation it is restricted to the latter case.

A binary alloy involving two phases is considered. Diffusion of heat is supposed to be much faster than the relaxation of the phase boundaries and the mass diffusion. Therefore the energy equation is not considered and a constant temperature is assumed. The variables  $\varphi = \phi_1$  and  $\tilde{c} = c_1$  introduced in the Subsection 2.3.2 and 2.3.3 are used again. Component 1 corresponds to component  $B$  in [WMB92]. As in Subsection 2.3.2, the gradient entropy term

$$a(\phi, \nabla \phi) = \frac{K}{2} |\nabla \phi|^2$$

leads to the phase field equation

$$2\varepsilon \omega \partial_t \varphi = 2\varepsilon K \Delta \varphi - \frac{1}{\varepsilon} \partial_{\varphi} w(\varphi, 1 - \varphi) - \frac{1}{T} \partial_{\varphi} \tilde{f}(\tilde{c}, \varphi, 1 - \varphi).$$

Setting  $\omega = \frac{1}{M_1}$  and  $K = \delta^2$  this becomes

$$\partial_t \varphi = M_1 \left( \delta^2 \Delta \varphi - \frac{1}{2\varepsilon^2} \partial_{\varphi} w(\varphi, 1 - \varphi) - \frac{1}{2\varepsilon T} \partial_{\varphi} \tilde{f}(\tilde{c}, \varphi, 1 - \varphi) \right).$$

If the multi-well potential

$$w(\phi_1, \phi_2) = \frac{\varepsilon^2 W}{2} \phi_1^2 \phi_2^2$$

is chosen then  $\frac{1}{2\varepsilon^2} \partial_{\varphi} w(\varphi, 1 - \varphi) = W \tilde{w}'(\varphi)$  with  $\tilde{w}(\varphi) = \frac{1}{4} \varphi^2 (1 - \varphi)^2$ , and the phase field equation reads

$$\partial_t \varphi = M_1 \left( \delta^2 \Delta \varphi - W \tilde{w}'(\varphi) - \frac{1}{2\varepsilon T} \partial_{\varphi} \tilde{f}(\tilde{c}, \varphi, 1 - \varphi) \right).$$

The free energy density is postulated to be

$$\tilde{f}(\tilde{c}, \varphi, 1 - \varphi) = \frac{\varepsilon W}{3} (\tilde{c} \beta_B(T) + (1 - \tilde{c}) \beta_A(T)) T h(\varphi) + \frac{2R}{v_m} T (\tilde{c} \ln(\tilde{c}) + (1 - \tilde{c}) \ln(1 - \tilde{c}))$$

where  $h(\varphi) = (3 - 2\varphi)\varphi^2$  and the functions  $\beta_B(T)$  and  $\beta_A(T)$  are explained in [WMB92] just below equation (7). Then

$$\frac{1}{2\varepsilon T} \partial_\varphi \tilde{f}(\tilde{c}, \varphi, 1 - \varphi) = \frac{W}{6} (\tilde{c} \beta_B(T) + (1 - \tilde{c}) \beta_A(T)) h'(\varphi)$$

and hence the phase field equation reads

$$\partial_t \varphi = M_1 \left( \delta^2 \Delta \varphi - W \tilde{w}'(\varphi) - \frac{W}{6} (\tilde{c} \beta_B(T) + (1 - \tilde{c}) \beta_A(T)) h'(\varphi) \right)$$

which is equation (17) from [WMB92] (for the case  $W_A = W_B = W$ ). Since

$$\begin{aligned} \tilde{f}_{,\tilde{c}\phi_1}(\tilde{c}, \varphi, 1 - \varphi) &= \frac{W}{3} (\beta_B(T) - \beta_A(T)) T h'(\varphi), \\ \tilde{f}_{,\tilde{c}\phi_2}(\tilde{c}, \varphi, 1 - \varphi) &= 0, \\ \tilde{f}_{,\tilde{c}\tilde{c}}(\tilde{c}, \varphi, 1 - \varphi) &= \frac{2R}{v_m} \frac{T}{\tilde{c}(1 - \tilde{c})}, \end{aligned}$$

and choosing  $L_{11} = D \frac{T}{f_{,\tilde{c}\tilde{c}}}$  as in Subsection 2.3.3, (2.22d) becomes

$$\begin{aligned} \partial_t \tilde{c} &= \nabla \cdot \left( D \nabla \tilde{c} + D \frac{v_m}{R} \frac{\tilde{c}(1 - \tilde{c})}{2} \frac{W}{3} (\beta_B(T) - \beta_A(T)) T h'(\varphi) \nabla \varphi \right) \\ &= D \Delta \tilde{c} + M_2 \nabla \cdot \left( \tilde{c}(1 - \tilde{c}) \nabla \left( \frac{W}{6} (\beta_B(T) - \beta_A(T)) h(\varphi) \right) \right) \end{aligned}$$

with  $M_2 = \frac{D v_m}{R}$  which is equation (18) from [WMB92]. Since the equations (17) and (18) govern the evolution in [WMB92] it is shown that their model can be recovered by the presented general one under the mentioned condition  $W_A = W_B$ .

## 2.4 The reduced grand canonical potential

### 2.4.1 Motivation and introduction

In Subsection 1.4.1 the relation between free energies and phase diagrams is established. The following chapters motivate that, sometimes, the reduced grand canonical potential is more appropriate for the analysis. The entropy is a function in the conserved variables internal energy and concentrations (cf. (B.4) in Appendix B) and the reduced grand canonical potential is defined to be the Legendre transform (cf. [ET99]) of the negative entropy. Some structural assumptions on the entropy are necessary. As usual let

$$e := c_0, \quad c := (c_0, c_1, \dots, c_N) \quad \rightsquigarrow \quad s = s(c).$$

Let  $\text{int}(\Sigma^N)$  be the interior of  $\Sigma^N$  with respect to the induced topology on  $\text{H}\Sigma^N \subset \mathbb{R}^N$  and assume that

R1  $(-s) : C := E \times \text{int}(\Sigma^N) \rightarrow \mathbb{R}$  with an open interval  $E \subset \mathbb{R}$  is smooth and strictly convex,

R2  $\nabla(-s) : C \rightarrow U$  is a  $C^\infty$ -diffeomorphism into a convex open set  $U \subset \mathbb{R} \times \text{T}\Sigma^N$ .

## 2.4. THE REDUCED GRAND CANONICAL POTENTIAL

---

In Assumption R2, the tangent space  $T_c C$  on  $C$  in  $c \in C$  is identified with  $\mathbb{R} \times T\Sigma^N$  according to Definition 1.1. Observe that  $E \times \text{int}(\Sigma^N)$  is a convex subset of an affine linear subspace. Assumption R1 implies that  $D^2(-s)(c)$ , acting on  $(\mathbb{R} \times T\Sigma^N)^2$ , is positive and has full rank so that, locally, Assumption R2 is already satisfied.

In the following, the sets  $C$  and  $U$  are considered as subsets of  $\mathbb{R}^{N+1}$ , and  $c \cdot u$  is the standard scalar product on  $\mathbb{R}^{N+1}$  for elements  $c \in C$  and  $u \in U$ .

**2.3 Lemma** *With the Assumptions R1 and R2 the Legendre transform of the entropy density*

$$(-s)^*(u) := \sup_{c \in C} \{c \cdot u + s(c)\}, \quad u \in U,$$

is a real valued smooth function  $(-s)^* : U \rightarrow \mathbb{R}$ . Besides

$$\nabla(-s)^*(u) = c.$$

**Proof:** For given  $u$ ,  $c = c(u) := (\nabla(-s))^{-1}(u)$  exists by Assumption R2. From the convexity of  $s$  in Assumption R1 it follows that this is the only critical point of  $c \mapsto c \cdot u + s(c)$  and that this is the global maximum. Hence  $(-s)^*(u) = c(u) \cdot u + s(c(u))$ . The identity for the derivative follows easily using  $\nabla(-s)(c) = u$ .  $\square$

**2.4 Definition** *If the entropy density  $s$  satisfies the Assumptions R1 and R2 then the density of the reduced grand canonical potential is defined by*

$$\psi : U \rightarrow \mathbb{R}, \quad \psi(u) = (-s)^*(u).$$

Analogously as in [ET99] it can be shown that

$$(-s)^{**} = \psi^* = -s. \tag{2.23}$$

Besides the preceding computations motivate to write

$$\psi = c \cdot u + s, \quad d\psi = c \cdot du = edu_0 + \sum_{i=1}^N c_i du_i. \tag{2.24}$$

A relation to the grand canonical potential  $b$  (see (B.5) in Appendix B) can be derived as follows:

$$\begin{aligned} \psi &= s + u \cdot c = s + \frac{-1}{T} \left( e - \sum_{i=1}^N \bar{\mu}_i c_i \right) \\ &= s + \frac{-1}{T} (f + sT - \sum_{i=1}^N \bar{\mu}_i c_i) = \frac{-1}{T} (f - \bar{\mu}_i c_i) \\ &= \frac{1}{T} b = -u_0 b. \end{aligned} \tag{2.25}$$

Using that (B.8) is equivalent to (1.13b) and (1.14) for a fixed temperature the equilibrium conditions on a phase boundary between two phases  $\alpha$  and  $\beta$  transform into

$$u^\alpha = u^\beta, \quad \psi^\alpha = \psi^\beta. \tag{2.26}$$

### 2.4.2 Example

For a binary alloy with components  $A$  and  $B$  the free energy density

$$f(T, c_1, c_2) = L_A \frac{T - T_A}{T_A} c_1 + L_B \frac{T - T_B}{T_B} c_2 + \tilde{R}T(c_1 \ln(c_1) + c_2 \ln(c_2)) - c_v T \left( \ln\left(\frac{T}{T_{ref}}\right) - 1 \right)$$

is postulated (cf. (1.27)). Then

$$s = -f_{,T} = -\left(\frac{L_A}{T_A} c_1 + \frac{L_B}{T_B} c_2\right) - \tilde{R}(c_1 \ln(c_1) + c_2 \ln(c_2)) + c_v \ln\left(\frac{T}{T_{ref}}\right).$$

Moreover

$$e = f + Ts = -L_A c_1 - L_B c_2 + c_v T,$$

and, hence, the temperature can be written as a function in  $(e, c_1, c_2)$ :

$$T = \frac{1}{c_v}(e + L_A c_1 + L_B c_2).$$

Then also  $-s$  can be written as a function in  $c = (e, c_1, c_2)$

$$-s(c) = \left(\frac{L_A}{T_A} c_1 + \frac{L_B}{T_B} c_2\right) + \tilde{R}(c_1 \ln(c_1) + c_2 \ln(c_2)) - c_v \ln\left(\frac{1}{c_v T_{ref}}(e + L_A c_1 + L_B c_2)\right).$$

Since  $u = \nabla_c(-s)(c) \in \mathbb{R} \times \mathbb{T}\Sigma^2$  it is obvious that  $u_0 = \nabla_c(-s)(c) \cdot (1, 0, 0)^\perp$ . Moreover  $u_1 = -u_2$ , hence  $2u_1 = u_1 - u_2 = \nabla_c(-s)(c) \cdot (0, 1, -1)^\perp$ . The above function for  $-s(c)$  yields

$$\begin{aligned} u_0 &= -\frac{c_v}{e + L_A c_1 + L_B c_2}, \\ 2u_1 &= L_A \left( \frac{1}{T_A} - \frac{c_v}{e + L_A c_1 + L_B c_2} \right) - L_B \left( \frac{1}{T_B} - \frac{c_v}{e + L_A c_1 + L_B c_2} \right) + \tilde{R} \ln\left(\frac{c_1}{c_2}\right). \end{aligned}$$

Using  $c_2 = 1 - c_1$  the above functions can be inverted, and  $c$  can be written as a function in  $u$ . A short calculation yields

$$\begin{aligned} e(u) &= -\frac{c_v}{u_0} - L_A \frac{1}{1 + e^{v_1(u)}} - L_B \frac{1}{1 + e^{v_2(u)}}, \\ c_1(u) &= \frac{1}{1 + e^{v_1(u)}}, \\ c_2(u) &= \frac{1}{1 + e^{v_2(u)}} \end{aligned}$$

where

$$\begin{aligned} v_1(u) &= \frac{1}{\tilde{R}} \left( L_A(u_0 - u_A) - L_B(u_0 - u_B) - 2u_1 \right), \\ v_2(u) &= \frac{1}{\tilde{R}} \left( L_B(u_0 - u_B) - L_A(u_0 - u_A) - 2u_2 \right) = -v_1(u) \end{aligned}$$

with  $u_A := \frac{-1}{T_A}$  and  $u_B := \frac{-1}{T_B}$ . The entropy density becomes

$$s(c(u)) = \left( \frac{L_A u_A}{1 + e^{v_1(u)}} + \frac{L_B u_B}{1 + e^{v_2(u)}} \right) + \tilde{R} \left( \frac{\ln(1 + e^{v_1(u)})}{1 + e^{v_1(u)}} + \frac{\ln(1 + e^{v_2(u)})}{1 + e^{v_2(u)}} \right) - c_v \ln(-u_0 T_{ref}).$$

## 2.4. THE REDUCED GRAND CANONICAL POTENTIAL

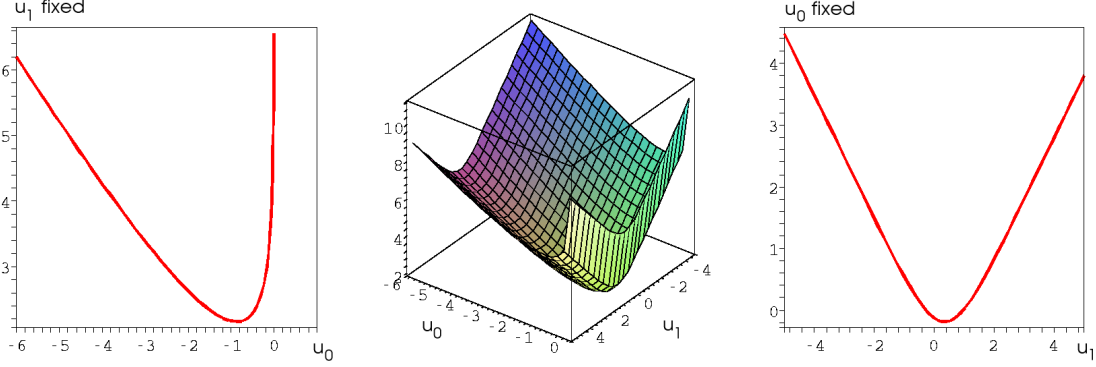


Figure 2.1: Reduced grand canonical potential  $\psi$  from the example in Subsection 2.4.2 as a function in  $u_0$  and  $u_1 = -u_2$ . The parameters are given in (2.27).

Inserting this and  $c(u)$  into (2.24) gives the reduced grand canonical potential density

$$\begin{aligned}
 \psi(u) &= c(u) \cdot u + s(c(u)) \\
 &= -c_v - \frac{L_A u_0}{1 + e^{v_1(u)}} - \frac{L_B u_0}{1 + e^{v_2(u)}} + \frac{u_1}{1 + e^{v_1(u)}} + \frac{u_2}{1 + e^{v_2(u)}} \\
 &\quad + \left( \frac{L_A u_A}{1 + e^{v_1(u)}} + \frac{L_B u_B}{1 + e^{v_2(u)}} \right) + \tilde{R} \left( \frac{\ln(1 + e^{v_1(u)})}{1 + e^{v_1(u)}} + \frac{\ln(1 + e^{v_2(u)})}{1 + e^{v_2(u)}} \right) - c_v \ln(-u_0 T_{ref}) \\
 &= \left( \frac{L_A (u_A - u_0)}{1 + e^{v_1(u)}} + \frac{L_B (u_B - u_0)}{1 + e^{v_2(u)}} \right) \\
 &\quad + \left( \frac{u_1 + \tilde{R} \ln(1 + e^{v_1(u)})}{1 + e^{v_1(u)}} + \frac{u_2 + \tilde{R} \ln(1 + e^{v_2(u)})}{1 + e^{v_2(u)}} \right) - c_v (1 + \ln(-u_0 T_{ref})).
 \end{aligned}$$

Fig. 2.1 shows this potential for the following values:

$$L_A = 1.0, \quad L_B = 1.2, \quad u_A = 0.8, \quad u_B = 1.4, \quad \tilde{R} = 1.0, \quad c_v = 1.0, \quad T_{ref} = 1.0. \quad (2.27)$$

Up to the last term, the growth in  $u$  is nearly linear while the last term tends to infinity as  $u_0 \nearrow 0$ .

### 2.4.3 Reformulation of the model

The aim is now to write down the equations governing the evolution in terms of  $(u, \phi)$  instead of  $(c, \phi)$ . For this purpose, the density of the reduced grand canonical potential  $\psi$  including its derivatives is used.

In the preceding section it is shown how the reduced grand canonical potential density of a phase can be computed given the free energy density of the phase. In a multi-phase system there are therefore densities  $\psi^\alpha : U_\alpha \rightarrow \mathbb{R}$ ,  $1 \leq \alpha \leq M$ , for the possible phases with  $U_\alpha \subset \mathbb{R} \times \mathbb{T}\Sigma^N$  defined in Assumption R2 in Section 2.4. Assume that  $U = \bigcap_{\alpha=1}^M U_\alpha$  is non-empty. The function  $\psi : U \times \Sigma^M \rightarrow \mathbb{R}$  is obtained as a suitable interpolation of the  $\psi^\alpha$  such that  $\psi(u, e_\alpha) = \psi^\alpha(u)$ , for example (see also the Remark 2.6 below)

$$\psi : U \times \Sigma^M \rightarrow \mathbb{R}, \quad \psi(u, \phi) = \sum_{\alpha=1}^M \psi^\alpha(u) h(\phi_\alpha) \quad (2.28)$$

with an interpolation function

$$h : [0, 1] \rightarrow [0, 1] \quad \text{satisfying } h(0) = 0, \quad h(1) = 1. \quad (2.29)$$

It is assumed that the Legendre transformation in Lemma 2.3 as well as the backward transformation (2.23) is possible after adapting the domains  $U_\phi$  and  $C_\phi$  in dependence of  $\phi$ . Let  $\phi \in \Sigma^M$  be fixed. Given  $\psi$ , sufficient conditions for the backward transformation to obtain  $s$  read similarly as the Assumptions R1 and R2 in Section 2.4 for the forward transformation. Hence

$$s(c, \phi) = \psi(u(c, \phi), \phi) - c \cdot u(c, \phi) \quad (2.30a)$$

where

$$c = \nabla_u \psi(u, \phi) = (\nabla_u \psi(\cdot, \phi))(u) \Leftrightarrow u = (\nabla \psi(\cdot, \phi))^{-1}(c). \quad (2.30b)$$

If the dependence of  $\psi$  on  $\phi$  is smooth then also the domains  $U_\phi$  and  $C_\phi$  depend smoothly on  $\phi$  in the following sense: Given  $u \in U_\phi$  and  $c = \psi_{,u}(u, \phi) \in C_\phi$  there is a small ball  $B_\kappa(\phi) \subset \Sigma^M$  of radius  $\kappa$  around  $\phi$  such that  $u \in U_{\tilde{\phi}}$  and  $c \in C_{\tilde{\phi}}$  for all  $\tilde{\phi} \in B_\kappa(\phi)$ . Thus, varying  $\phi$  is possible in (2.30a) which with (2.30b) provides the identity

$$s_{,\phi}(c, \phi) \cdot v = \sum_{\alpha=1}^M \left( u_{,\phi_\alpha} \cdot \underbrace{\psi_{,u}(u, \phi)}_{=c} + \psi_{,\phi_\alpha}(u, \phi) - u_{,\phi_\alpha} \cdot c \right) v_\alpha = \psi_{,\phi}(u, \phi) \cdot v \quad (2.31)$$

for every  $v \in \text{T}\Sigma^M$ . Using this, the identity  $s_{,\phi} = -\frac{f_{,\phi}}{T}$ , and (2.30b), the model in Definition 2.1 can be reformulated considering  $(u, \phi)$  as variables:

**2.5 Definition** *The evolution of the system is governed by the partial differential equations*

$$\partial_t \psi_{,u_i}(u, \phi) = -\nabla \cdot J_i(\psi_{,u}(u, \phi), \phi, \nabla u) = \nabla \cdot \left( \sum_{j=0}^N L_{ij}(\psi_{,u}(u, \phi), \phi) \nabla u_j \right), \quad (2.32a)$$

$$\varepsilon \omega(\phi, \nabla \phi) \partial_t \phi_\alpha = \varepsilon \nabla \cdot a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) - \varepsilon a_{,\phi_\alpha}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi_\alpha}(\phi) + \psi_{,\phi_\alpha}(u, \phi) - \lambda \quad (2.32b)$$

where  $0 \leq i \leq N$  and  $1 \leq \alpha \leq M$  with  $\lambda$  given by

$$\lambda = \frac{1}{M} \sum_{\alpha=1}^M \left( \varepsilon \nabla \cdot a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) - \varepsilon a_{,\phi_\alpha}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi_\alpha}(\phi) + \psi_{,\phi_\alpha}(u, \phi) \right). \quad (2.32c)$$

The differential equations are subject to initial conditions

$$u(t=0) = u_{ic}, \quad \phi(t=0) = \phi_{ic} \quad (2.32d)$$

and boundary conditions

$$J_i(\psi_{,u}(u, \phi), \phi, \nabla u) \cdot \nu_{ext} = 0, \quad 1 \leq i \leq N, \quad (2.32e)$$

$$a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) \cdot \nu_{ext} = 0, \quad 1 \leq \alpha \leq M. \quad (2.32f)$$

If not otherwise stated, additionally the boundary condition

$$J_0(\psi_{,u}(u, \phi), \phi, \cdot) \cdot \nu_{ext} = 0 \quad (2.32g)$$

is imposed.

**2.6 Remark** Of course it is possible to choose interpolation functions in (2.28) involving  $u$ . Indeed, instead of interpolating the densities of the reduced grand canonical potentials, first, the free energy densities could be interpolated similarly to (2.12), and after the procedure as in the example of the previous section could be carried out to gain  $\psi$  from  $f$ . It turns out that, for the limiting model as  $\varepsilon \rightarrow 0$ , it does not matter which interpolation is chosen. But in numerical simulations more complicated interpolations involve more computational effort and, since in applications feasible values for  $\varepsilon$  have to be chosen (the smaller  $\varepsilon$  the higher the costs), different results may be obtained.



## Chapter 3

# Asymptotic Analysis

This chapter is dedicated to the limit of the general phase field model as  $\varepsilon \rightarrow 0$ . It is demonstrated that the relation between the phase field model presented in Subsection 2.4.3 and the sharp interface model presented in Section 1.2 can be established using the method of matched asymptotic expansions. For this purpose, methods developed in [CF88, BGS98, GNC00, GNS98] are generalised. It is supposed that, in the bulk regions of the pure phases as well as in the interfacial regions, the solution to the phase field model can be expanded in  $\varepsilon$ -series. In Section 3.1 necessary conditions are derived for that these expansions match. It turns out that the coefficient functions to leading order of the  $\varepsilon$  expansions in the bulk regions exactly fulfil the governing equations of the sharp interface model (see Section 3.2).

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 or converge respectively. But in some cases, this ansatz could be verified (cf. [ABC94, CC98, MS95, Sto96]).

In the following Section 3.3 the quality of the approximation of the sharp interface is of interest. The approximation obtained in Section 3.2 is of first order in the small parameter  $\varepsilon$ . For example, expanding the temperature in the pure phases in the form  $T = T_0 + \varepsilon T_1 + O(\varepsilon^2)$  the asymptotic analysis yields that  $T_0$  satisfies the equations of the sharp interface problem. But if  $T_1$  vanishes the approximation of  $T_0$  is of second order in  $\varepsilon$ . To see whether this is possible, the asymptotic analysis has to be continued in order to derive the equations  $T_1$  has to fulfil which leads to the notion of an  $O(\varepsilon)$ -correction problem.

An improvement of the approximation was obtained in [KR98] in the context of a thin interface asymptotic analysis. The analysis led to a positive correction term in the kinetic coefficient of the phase field equation balancing undesirable  $O(\varepsilon)$ -terms in the Gibbs-Thomson condition and raising the stability bound of explicit numerical methods. Besides, the better approximation allows for larger values of  $\varepsilon$  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 [Alm99] 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 an approximation of second order could still be achieved but the gradient structure of the model and thermodynamic consistency were lost. In [And02] it was shown, based on [Alm99], that even an approximation of third order is possible by using high order polynomials for the interpolation. McFadden, Wheeler, and Anderson [MWA00] used an approach based on an energy and an entropy functional 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 the paper 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

## CHAPTER 3. ASYMPTOTIC ANALYSIS

---

was obtained by adding a small additional term to the mass flux (anti-trapping mass current, the ideas stem from [Kar01]).

In the present work it is shown 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. A new feature compared to the existing results is that, in general, this correction term depends on  $u$ , i.e., 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.

To investigate the gain in efficiency thanks to the better approximation results of numerical simulations to the phase field model with and without correction term are compared in Section 3.4.

For the derivations, some assumptions on the occurring functions are necessary:

A1 The core of the matrix  $L = (L_{ij})_{i,j=0}^N$  of Onsager coefficients is the space orthogonal to  $\mathbb{R} \times \text{T}\Sigma^N$  (cf. assumption L2 in Subsection 1.1.1), i.e.,

$$\ker(L) = \text{span}\{(0, 1, \dots, 1)\} \subset \mathbb{R}^{N+1} = (Y^N)^\perp$$

where

$$Y^N = \mathbb{R} \times \text{T}\Sigma^N.$$

Then, for each  $v \in Y^N$ , there is a unique solution  $\xi \in Y^N$  of the equation  $L\xi = v$ . The solution is denoted by  $L^{-1}v$ .

A2 In addition to (2.29), the interpolation functions fulfil

$$h'(0) = h'(1) = 0.$$

A3 Around its minima  $e_\beta$ ,  $1 \leq \beta \leq M$ , the function  $w$  is strictly convex. This means that

$$w_{,\phi\phi}(e_\beta) > 0, \quad 1 \leq \beta \leq M.$$

This chapter only treats the two dimensional case (i.e.,  $d = 2$ ). The generalisation to the three dimensional case is straightforward. The differentials along curves simply become surface gradients or surface divergences.

Several times the homogeneity of  $a$  is used. This is why the following facts are stated at the beginning of this chapter: It holds that

$$a_{,\phi}(\phi, \eta \nabla \phi) = \eta^2 a_{,\phi}(\phi, \nabla \phi), \quad a_{,\nabla \phi}(\phi, \eta \nabla \phi) = \eta a_{,\nabla \phi}(\phi, \nabla \phi), \quad (3.1a)$$

and, moreover,

$$a(\phi, 0) = 0, \quad a_{,\phi}(\phi, 0) = 0, \quad a_{,\nabla \phi}(\phi, 0) = 0, \quad a_{,\nabla \phi}(\phi, \nabla \phi) : \nabla \phi = 2a(\phi, \nabla \phi) \quad (3.1b)$$

for all  $\phi \in \Sigma^M$ ,  $\nabla \phi \in (\text{T}\Sigma^M)^d$ , and  $\eta > 0$ .

### 3.1 Expansions and matching conditions

The matching procedure for asymptotic expansions in the context of phase field models is outlined with great care in [FP95]. Here, only the main ideas are sketched.

Consider a time interval  $I = (0, t_{end})$  and an interfacial region in a domain  $D \subset \mathbb{R}^2$  where two phases meet. The family of curves  $\{\Gamma(t; \varepsilon)\}_{\varepsilon > 0, t \in I}$  is supposed to be a set of smooth curves in  $D$  which are uniformly bounded away from  $\partial D$  and depend smoothly on  $(\varepsilon, t)$  such that, if  $\varepsilon \rightarrow 0$ , some smooth limiting curve  $\Gamma(t; 0)$  is obtained. By  $D^l(t; \varepsilon)$  and  $D^s(t; \varepsilon)$  the regions occupied by the two phases are denoted. The limiting curve  $\Gamma(t; 0)$  corresponds to the sharp interface between the phases in the sense of Section 1.2, i.e., to some curve of a phase boundary  $\Gamma_{sl}$ , while the approximating curves  $\Gamma(t; \varepsilon)$  are given somehow as level sets of the phase field variables. In the model of Definition 2.1 in Section 2.1, for example, if  $(\phi(t, x; \varepsilon), c(t, x; \varepsilon))$  is the solution of (2.15a)–(2.15g), then  $\Gamma(t; \varepsilon)$  may be defined by

$$\Gamma(t; \varepsilon) := \left\{ x \in D : \phi_l(t, x; \varepsilon) = \phi_s(t, x; \varepsilon) \right\}, \quad \varepsilon > 0, t \in I. \quad (3.2)$$

Let  $\gamma(t, s; 0)$  be a parametrisation of  $\Gamma(t; 0)$  by arc-length  $s \in [0, l(t)]$  for every  $t \in I$ ,  $l(t)$  being the length of  $\Gamma(t; 0)$ . The vector  $\nu(t, s; 0)$  denotes the unit normal on  $\Gamma(t; 0)$  pointing into  $D^l(t; 0)$ , and the vector  $\tau(t, s; 0) := \partial_s \gamma(t, s; 0)$  denotes the unit tangent vector towards the parametrisation. The orientation is such that  $(\nu, \tau)$  is positively oriented.

Using some distance function  $d(t, s; \varepsilon)$ , the curves  $\Gamma(t; \varepsilon)$  can be parametrised over  $\Gamma(t; 0)$  by

$$\gamma(t, s; \varepsilon) := \gamma(t, s; 0) + d(t, s; \varepsilon)\nu(t, s; 0). \quad (3.3)$$

Close to  $\varepsilon = 0$  it is assumed that there is the expansion  $d(t, s; \varepsilon) = d_0(t, s) + \varepsilon^1 d_1(t, s) + \varepsilon^2 d_2(t, s) + O(\varepsilon^3)$ . Since  $d(t, s; 0) \equiv 0$  the expansion becomes

$$d(t, s; \varepsilon) = \varepsilon^1 d_1(t, s) + \varepsilon^2 d_2(t, s) + O(\varepsilon^3). \quad (3.4)$$

Near  $\Gamma(t; 0)$ , the coordinates  $(s, r)$  are well-defined,  $r$  being the signed distance of  $x$  from  $\Gamma(t; 0)$  (positive towards  $\nu$ , i.e., if  $x \in D^l(t; 0)$ ). Let  $z = \frac{r}{\varepsilon}$  and  $\varepsilon_0 > 0$ . For each  $t \in I$  and  $\varepsilon \in (0, \varepsilon_0)$  there are the diffeomorphisms

$$F_\varepsilon(t, s, z) := (t, \gamma(t, s; 0) + (\varepsilon z + d(t, s; \varepsilon))\nu(t, s))$$

mapping an open set  $V(t; \varepsilon) \subset \mathbb{R}^2$  onto an open tube  $B(t)$  around  $\Gamma(t; 0)$ . The coordinates  $(t, s, z)$  are such that the curve  $\Gamma(t; \varepsilon)$  is given by the set  $\{F_\varepsilon(t, s, z) | z = 0\}$ . It is supposed that, uniformly in  $t$  and  $\varepsilon$ , the tube  $B(t)$  is large enough such that values for  $z$  lying in a fixed interval around zero are allowed as arguments for  $z$ . To obtain expressions for  $\nabla_{(t,x)} z(t, x)$  and  $\nabla_{(t,x)} s(t, x)$  it is necessary to compute the inverse of the derivative of  $F_\varepsilon$ .

Let  $\kappa := \kappa(t, s; 0)$  be the curvature of  $\Gamma(t; 0)$  defined by  $\partial_s \tau = \kappa \nu$  or, equivalently, by  $\partial_s \nu = -\kappa \tau$ . Furthermore let

$$v = v(t, s; 0) = \partial_t \gamma(t, s; 0) \cdot \nu(t, s; 0) \quad (\text{normal velocity, intrinsic}), \quad (3.5a)$$

$$v_\tau = v_\tau(t, s; 0) = \partial_t \gamma(t, s; 0) \cdot \tau(t, s; 0) \quad (\text{tangential velocity, non-intrinsic}). \quad (3.5b)$$

Hence, writing  $d_\varepsilon = d(t, s; \varepsilon)$ ,

$$\begin{aligned} DF_\varepsilon(t, s, z) &= \begin{pmatrix} \partial_t t(t, s, z) & \partial_s t(t, s, z) & \partial_z t(t, s, z) \\ \partial_t x(t, s, z) & \partial_s x(t, s, z) & \partial_z x(t, s, z) \end{pmatrix} \\ &= \begin{pmatrix} 1 & 0 & 0 \\ \partial_t \gamma + (\varepsilon z + d_\varepsilon) \partial_t \nu + (\partial_t d_\varepsilon) \nu & \tau - (\varepsilon z + d_\varepsilon) \kappa \tau + (\partial_s d_\varepsilon) \nu & \varepsilon \nu \end{pmatrix} \end{aligned}$$

and, using (3.5a) and (3.5b),

$$\begin{aligned} D(F_\varepsilon^{-1})(t, x) &= (DF_\varepsilon)^{-1}(t, x) = \begin{pmatrix} \partial_t t(t, x) & \nabla_x t(t, x) \\ \partial_t s(t, x) & \nabla_x s(t, x) \\ \partial_t z(t, x) & \nabla_x z(t, x) \end{pmatrix} \\ &= \begin{pmatrix} 1 & (0, 0) \\ -\frac{1}{1-\kappa(\varepsilon z + d_\varepsilon)}(v_\tau + (\varepsilon z + d_\varepsilon)\tau \cdot \partial_t \nu) & \frac{1}{1-\kappa(\varepsilon z + d_\varepsilon)}\tau^T \\ \frac{1}{\varepsilon} \left( -\partial_t d_\varepsilon + \frac{\partial_s d_\varepsilon(\varepsilon z + d_\varepsilon)}{1-\kappa(\varepsilon z + d_\varepsilon)}\tau \cdot \partial_t \nu + \frac{\partial_s d_\varepsilon}{1-\kappa(\varepsilon z + d_\varepsilon)}v_\tau - v \right) & \frac{1}{\varepsilon}\nu^T - \frac{\partial_s d_\varepsilon}{\varepsilon(1-\kappa(\varepsilon z + d_\varepsilon))}\tau^T \end{pmatrix} \end{aligned}$$

with  $\partial_t \gamma$ ,  $\partial_t \nu$ ,  $\nu$ ,  $\tau$ ,  $\kappa$ ,  $v_\tau$  and  $v$  evaluated at  $(t, s; 0)$ . The ansatz (3.4) yields the expansion

$$\frac{1}{1-\kappa(\varepsilon z + d_\varepsilon)} = 1 + \varepsilon \kappa(z + d_1) + \varepsilon^2(\kappa d_2 + \kappa^2(z + d_1)^2) + O(\varepsilon^3),$$

whence

$$\begin{aligned} \partial_t s(t, x) &= -v_\tau + O(\varepsilon), \\ \nabla_x s(t, x) &= \left(1 + \varepsilon \kappa(z + d_1) + \varepsilon^2(\kappa d_2 + \kappa^2(z + d_1)^2) + O(\varepsilon^3)\right)\tau, \\ \partial_t z(t, x) &= -\frac{1}{\varepsilon}v - (\partial_t d_1 - \partial_s d_1 v_\tau) + O(\varepsilon), \\ \nabla_x z(t, x) &= \frac{1}{\varepsilon}\nu - \left(\partial_s d_1 + \varepsilon(\partial_s d_2 + \partial_s d_1 \kappa(z + d_1))\right)\tau \\ &\quad - \varepsilon^2 \left(\partial_s d_3 + \partial_s d_2 \kappa(z + d_1) + \partial_s d_1 \kappa d_2 + \partial_s d_1 \kappa^2(z + d_1)^2\right)\tau + O(\varepsilon^3). \end{aligned}$$

A short calculation shows that for a function  $B(t, s, z)$  and for a vector field  $\vec{B}(t, s, z)$  it holds that

$$\frac{d}{dt} B = -\frac{1}{\varepsilon}v \partial_z B + \partial^\circ B - (\partial^\circ d_1) \partial_z B + O(\varepsilon), \quad (3.6a)$$

$$\begin{aligned} \nabla_x B &= \frac{1}{\varepsilon} \partial_z B \nu + (\partial_s B - \partial_s d_1 \partial_z B) \tau \\ &\quad + \varepsilon(\kappa(z + d_1) \partial_s B - (\partial_s d_2 + \partial_s d_1 \kappa(z + d_1)) \partial_z B) \tau + O(\varepsilon^2), \end{aligned} \quad (3.6b)$$

$$\begin{aligned} \nabla_x \cdot \vec{B} &= \frac{1}{\varepsilon} \partial_z \vec{B} \cdot \nu + (\partial_s \vec{B} - \partial_s d_1 \partial_z \vec{B}) \cdot \tau \\ &\quad + \varepsilon(\kappa(z + d_1) \partial_s \vec{B} - (\partial_s d_2 + \partial_s d_1 \kappa(z + d_1)) \partial_z \vec{B}) \cdot \tau + O(\varepsilon^2), \end{aligned} \quad (3.6c)$$

$$\begin{aligned} \Delta_x B &= \frac{1}{\varepsilon^2} \partial_{zz} B - \frac{1}{\varepsilon} \kappa \partial_z B \\ &\quad + (\partial_s d_1)^2 \partial_{zz} B - 2\partial_s d_1 \partial_{sz} B - \kappa^2(z + d_1) \partial_z B - \partial_{ss} d_1 \partial_z B + \partial_{ss} B + O(\varepsilon) \end{aligned} \quad (3.6d)$$

where  $\partial^\circ = \partial_t - v_\tau \partial_s$  is the (intrinsic) normal-time-derivative (see Appendix C). This identity is motivated by the following calculation: Consider a field  $f(t, x)$  in  $I \times D$  and write  $\tilde{f}(t, s) = f(t, \gamma(t, s))$  for  $f$  restricted on  $\Gamma(t; 0)$ . Then it holds with (C.1)

$$\begin{aligned} &\partial_t \tilde{f}(t, s) - v_\tau \partial_s \tilde{f}(t, s) \\ &= \frac{d}{dt} f(t, \gamma(t, s)) - \partial_t \gamma(t, s) \cdot \tau(t, s) \partial_s f(t, \gamma(t, s)) \\ &= \partial_t f(t, \gamma(t, s)) + \partial_t \gamma(t, s) \cdot \nabla_x f(t, \gamma(t, s)) - \partial_t \gamma(t, s) \cdot \tau(t, s) \nabla_x f(t, \gamma(t, s)) \cdot \tau(t, s) \\ &= \partial_t f(t, \gamma(t, s)) + \left( (\partial_t \gamma(t, s) \cdot \nu(t, s)) \nu(t, s) + (\partial_t \gamma(t, s) \cdot \tau(t, s)) \tau(t, s) \right) \cdot \nabla_x f(t, \gamma(t, s)) \\ &\quad - (\partial_t \gamma(t, s) \cdot \tau(t, s)) \tau(t, s) \cdot \nabla_x f(t, \gamma(t, s)) \\ &= \partial_t f(t, \gamma(t, s)) + v(t, s) \nu(t, s) \cdot \nabla_x f(t, \gamma(t, s)) \\ &= \partial_{(1, (v\nu)(t, s))} f(t, \gamma(t, s)) \\ &= \partial^\circ f(t, \gamma(t, s)). \end{aligned}$$

### 3.1. EXPANSIONS AND MATCHING CONDITIONS

Now assume that the normal velocity and the curvature of  $\Gamma(t; \varepsilon)$  can be expanded in  $\varepsilon$ -series,

$$\begin{aligned} v(t, s; \varepsilon) &= v_0(t, s; 0) + \varepsilon v_1(t, s; 0) + \varepsilon^2 v_2(t, s; 0) + \dots, \\ \kappa(t, s; \varepsilon) &= \kappa_0(t, s; 0) + \varepsilon \kappa_1(t, s; 0) + \varepsilon^2 \kappa_2(t, s; 0) + \dots \end{aligned}$$

The first order corrections  $v_1$  and  $\kappa_1$  can be written in terms of  $d_1$ :

**3.1 Lemma** *It holds that*

$$\kappa(t, s; \varepsilon) = \kappa(t, s; 0) + \varepsilon(\kappa(t, s; 0)^2 d_1(t, s) + \partial_{ss} d_1(t, s)) + O(\varepsilon^2), \quad (3.7a)$$

$$v(t, s; \varepsilon) = v(t, s; 0) + \varepsilon \partial^0 d_1(t, s) + O(\varepsilon^2). \quad (3.7b)$$

**Proof:** The unit tangent vector and the unit normal vector are

$$\begin{aligned} \tau(t, s; \varepsilon) &= \frac{\partial_s \gamma_\varepsilon}{|\partial_s \gamma_\varepsilon|} = \frac{(1 - \kappa d_\varepsilon)\tau + (\partial_s d_\varepsilon)\nu}{((1 - \kappa d_\varepsilon)^2 + (\partial_s d_\varepsilon)^2)^{1/2}}, \\ \nu(t, s; \varepsilon) &= \frac{\partial_s \gamma_\varepsilon^\perp}{|\partial_s \gamma_\varepsilon|} = \frac{(1 - \kappa d_\varepsilon)\nu - (\partial_s d_\varepsilon)\tau}{((1 - \kappa d_\varepsilon)^2 + (\partial_s d_\varepsilon)^2)^{1/2}} \end{aligned}$$

where  $\partial_s \gamma_\varepsilon^\perp$  is the rotation of  $\partial_s \gamma_\varepsilon$  by 90 degree such that  $(\partial_s \gamma_\varepsilon^\perp, \partial_s \gamma_\varepsilon)$  is positively oriented. Inserting the expansion (3.4) yields

$$\left( (1 - \kappa d_\varepsilon)^2 + (\partial_s d_\varepsilon)^2 \right)^{-1/2} = 1 + \varepsilon \kappa d_1(t, s) + O(\varepsilon^2)$$

and for  $v(t, s; \varepsilon)$  the expansion

$$\begin{aligned} v(t, s; \varepsilon) &= \partial_t \gamma_\varepsilon \cdot \nu(t, s; \varepsilon) \\ &= \frac{(\partial_t \gamma(t, s; 0) + \partial_t d_\varepsilon \nu + d_\varepsilon \partial_t \nu) \cdot ((1 - \kappa d_\varepsilon)\nu - (\partial_s d_\varepsilon)\tau)}{((1 - \kappa d_\varepsilon)^2 + (\partial_s d_\varepsilon)^2)^{1/2}} \\ &= \frac{(1 - \kappa d_\varepsilon)v + \partial_t d_\varepsilon(1 - \kappa d_\varepsilon) - \partial_s d_\varepsilon v_\tau - d_\varepsilon \partial_s d_\varepsilon \partial_t \nu \cdot \tau}{((1 - \kappa d_\varepsilon)^2 + (\partial_s d_\varepsilon)^2)^{1/2}} \\ &= v + \varepsilon \partial^0 d_1 + O(\varepsilon^2) \end{aligned}$$

where  $\partial_t \nu \cdot \nu = \frac{1}{2} \partial_t |\nu|^2 = 0$  was used. To compute the expansion of  $\kappa(t, s; \varepsilon)$ , the identity

$$\partial_{ss} \gamma(t, s; \varepsilon) = -\left( 2(\partial_s d_\varepsilon)\kappa + d_\varepsilon(\partial_s \kappa) \right) \tau + \left( \kappa + \partial_{ss} d_\varepsilon - \kappa^2 d_\varepsilon \right) \nu$$

implies

$$\det(\partial_s \gamma(t, s; \varepsilon), \partial_{ss} \gamma(t, s; \varepsilon)) = -(1 - \kappa d_\varepsilon)(\kappa + \partial_{ss} d_\varepsilon - \kappa^2 d_\varepsilon) - (\partial_s d_\varepsilon)(2(\partial_s d_\varepsilon)\kappa + d_\varepsilon(\partial_s \kappa)),$$

and with

$$|\partial_s \gamma_\varepsilon|^{-3} = (1 - 2\kappa d_\varepsilon + \kappa^2 d_\varepsilon^2 + (\partial_s d_\varepsilon)^2)^{-3/2} = 1 + \varepsilon 3\kappa d_1 + O(\varepsilon^2)$$

this gives

$$\kappa(t, s; \varepsilon) = \frac{-\det(\partial_s \gamma_\varepsilon, \partial_{ss} \gamma_\varepsilon)}{|\partial_s \gamma_\varepsilon|^3} = \kappa + \varepsilon(\kappa^2 d_1 + \partial_{ss} d_1) + O(\varepsilon^2).$$

□

Consider some function  $b(t, x)$  (in the next subsections,  $b$  corresponds to  $\phi$ ,  $c$  or  $u$ ). Suppose that, in each domain  $\tilde{D} \subset\subset D \setminus \Gamma(t; 0)$ , the function  $b$  can be expanded in a series close to  $\varepsilon = 0$  (**outer expansion**): For some  $K \geq 2$

$$b(t, x; \varepsilon) = \sum_{k=0}^K \varepsilon^k b^{(k)}(t, x) + O(\varepsilon^{K+1}). \quad (3.8)$$

Hence, in a neighbourhood of  $\Gamma(t; 0)$ , the functions

$$\hat{b}(t, s, r; \varepsilon) := b(t, x; \varepsilon). \quad (3.9)$$

are well-defined for  $r \neq 0$ . To be more precise, the expansion

$$\hat{b}(t, s, r; \varepsilon) = \sum_{k=0}^K \varepsilon^k \hat{b}^{(k)}(t, s, r) + O(\varepsilon^{K+1}) \quad (3.10)$$

is assumed to be valid uniformly on

$$V_{out}^\alpha := \left\{ (t, s, r; \varepsilon) : t \in I, s \in [0, l(t)], r \in (\varepsilon^\alpha \frac{\delta_0}{2}, \delta_0], \varepsilon \in (0, \varepsilon_0] \right\}$$

for every  $\alpha \in (0, 1)$ . Furthermore it is assumed that function  $\hat{b}^{(k)}$  can be smoothly and uniformly extended onto  $\Gamma(t; 0)$  from both sides, i.e., as  $r \searrow 0$  and  $r \nearrow 0$  respectively.

Let  $B(t, s, z; \varepsilon) := \hat{b}(t, s, r; \varepsilon)$  with  $r = \varepsilon z$ . Suppose that the function  $B$  can be expanded in a series as follows (**inner expansion**):

$$B(t, s, z; \varepsilon) = \sum_{k=0}^K \varepsilon^k B^{(k)}(t, s, z) + O(\varepsilon^{K+1}). \quad (3.11)$$

It is assumed that the functions  $B^{(k)}(t, s, z)$  are well-defined for  $t \in I$ ,  $s \in [0, l(t)]$  and  $z \in \mathbb{R}$ , and that they approximate some polynomial in  $z$  uniformly in  $t, s$  for large  $z$ , i.e.,

$$B^{(k)}(t, s, z) \approx B_{k,0}^\pm(t, s) + B_{k,1}^\pm(t, s)z + B_{k,2}^\pm(t, s)z^2 + \cdots + B_{k,n_k}^\pm(t, s)z^{n_k}, \quad z \rightarrow \pm\infty, \quad (3.12)$$

with  $n_k \in \mathbb{N}$  for all  $k$ . Moreover, the expansion (3.11) shall be valid uniformly on

$$V_{inn}^\alpha := \left\{ (t, s, z; \varepsilon) : t \in I, s \in [0, l(t)], z \in \varepsilon^{\alpha-1}[-\delta_0, \delta_0], \varepsilon \in (0, \varepsilon_0] \right\}$$

for every  $\alpha \in (0, 1)$ .

**3.2 Definition** (cf. [LP88]) *Let  $\zeta \in (\frac{\delta_0}{2}, \delta_0)$ ,  $\varepsilon \in (0, \varepsilon_0]$  and  $\alpha \in (0, 1)$ .*

1. *The variable  $\zeta\varepsilon^\alpha$  is called intermediate variable.*
2. *The expansions (3.10) and (3.11) are said to match if the following holds:  
When replacing  $r$  in (3.10) and  $z$  in (3.11) by an arbitrary intermediate variable, i.e.,  $r = \zeta\varepsilon^\alpha$  and  $z = r/\varepsilon = \zeta\varepsilon^{\alpha-1}$ , then, in the limit as  $\varepsilon \rightarrow 0$ , the coefficients agree to every order in  $\varepsilon$  and  $\zeta$ .*

**3.3 Lemma** *For that the two expansions (3.8) and (3.11) of  $b$  match in the limit as  $\varepsilon \rightarrow 0$  the following conditions must be fulfilled: As  $z \rightarrow \pm\infty$*

$$B^{(0)}(z) \approx b^{(0)}(0^\pm), \quad (3.13a)$$

$$B^{(1)}(z) \approx b^{(1)}(0^\pm) + (\nabla b^{(0)}(0^\pm) \cdot \nu)z, \quad (3.13b)$$

$$\partial_z B^{(1)}(z) \approx \nabla b^{(0)}(0^\pm) \cdot \nu, \quad (3.13c)$$

$$\partial_z B^{(2)}(z) \approx \nabla b^{(1)}(0^\pm) \cdot \nu + (\nu \cdot D^2 b^{(0)}(0^\pm)\nu)z. \quad (3.13d)$$

Here,  $b(0^+)$  denotes the limit of  $b(t, x)$  if  $r(t, x) = \text{dist}(x, \Gamma(t; 0)) \rightarrow 0$  where  $x \in D^l(t; 0)$  which is equivalent to  $r \searrow 0$ ; analogously,  $b(0^-)$  is defined considering  $x \in D^s(t; 0)$  or  $r \nearrow 0$ .

### 3.2. FIRST ORDER ASYMPTOTICS OF THE GENERAL MODEL

**Proof:** An expansion of the functions  $\hat{b}^{(k)}$  in (3.10) in Taylor series at  $r = 0$  yields

$$\hat{b}^{(k)}(t, s, r) = \hat{b}^{(k)}(t, s, 0^+) + \partial_r \hat{b}^{(k)}(t, s, 0^+)r + \frac{1}{2} \partial_{rr} \hat{b}^{(k)}(t, s, 0^+)r^2 + O(r^3), \quad r \in (0, \delta_0], \quad (3.14a)$$

$$\hat{b}^{(k)}(t, s, r) = \hat{b}^{(k)}(t, s, 0^-) + \partial_r \hat{b}^{(k)}(t, s, 0^-)r + \frac{1}{2} \partial_{rr} \hat{b}^{(k)}(t, s, 0^-)r^2 + O(r^3), \quad r \in [-\delta_0, 0). \quad (3.14b)$$

If  $r$  is replaced by an intermediate variable  $\zeta \varepsilon^\alpha$  then, for  $\varepsilon$  small enough,  $r = \zeta \varepsilon^\alpha$  indeed is small, and the above expansion (3.14a) is valid and gives for (3.10) (dropping the dependence on  $(t, s)$ )

$$\begin{aligned} \hat{b}(\zeta \varepsilon^\alpha; \varepsilon) &= \varepsilon^0 \hat{b}^{(0)}(0^+) + \varepsilon^\alpha \partial_r \hat{b}^{(0)}(0^+) \zeta + \varepsilon^{2\alpha} \frac{1}{2} \partial_{rr} \hat{b}^{(0)}(0^+) \zeta^2 + O(\varepsilon^{3\alpha}) \\ &\quad + \varepsilon^1 \hat{b}^{(1)}(0^+) + \varepsilon^{1+\alpha} \partial_r \hat{b}^{(1)}(0^+) \zeta + \varepsilon^{1+2\alpha} \frac{1}{2} \partial_{rr} \hat{b}^{(1)}(0^+) \zeta^2 + O(\varepsilon^{1+3\alpha}) \\ &\quad + \varepsilon^2 \hat{b}^{(2)}(0^+) + \varepsilon^{2+\alpha} \partial_r \hat{b}^{(2)}(0^+) \zeta + \varepsilon^{2+2\alpha} \frac{1}{2} \partial_{rr} \hat{b}^{(2)}(0^+) \zeta^2 + O(\varepsilon^{2+3\alpha}) \\ &\quad + O(\varepsilon^3 + \varepsilon^{4\alpha}). \end{aligned}$$

Equation (3.14b) yields the same with  $0^+$  replaced by  $0^-$  if  $-\zeta \in (\frac{\delta_0}{2}, \delta_0)$ .

The expansion (3.11) is valid for  $z = \zeta \varepsilon^{\alpha-1}$ . Using (3.12) and again dropping the dependence on  $(t, s)$  gives

$$\begin{aligned} B(\zeta \varepsilon^{\alpha-1}; \varepsilon) &= \varepsilon^0 B_{0,0}^+ + \varepsilon^{\alpha-1} B_{0,1}^+ \zeta + \dots + \varepsilon^{n_0(\alpha-1)} B_{0,n_0}^+ \zeta^{n_0} \\ &\quad + \varepsilon^1 B_{1,0}^+ + \varepsilon^{1+\alpha-1} B_{1,1}^+ \zeta + \dots + \varepsilon^{1+n_1(\alpha-1)} B_{1,n_1}^+ \zeta^{n_1} \\ &\quad + \varepsilon^2 B_{2,0}^+ + \varepsilon^{2+\alpha-1} B_{2,1}^+ \zeta + \dots + \varepsilon^{2+n_2(\alpha-1)} B_{2,n_2}^+ \zeta^{n_2} + \dots \end{aligned}$$

The same holds true for  $-\zeta \in (\frac{\delta_0}{2}, \delta_0)$  with  $B^+$  replaced by  $B^-$ .

By Definition 3.2 the expansions of  $B$  and  $\hat{b}$  are said to match if, in the limit  $\varepsilon \rightarrow 0$ , the coefficients to every order in  $\varepsilon$  and  $\zeta$  agree for every  $\alpha \in (0, 1)$ . Comparing the two series yields the following relations between the coefficients  $B_{k,n}^+$  on the one hand and the derivatives  $\partial_r^j u(0^+)$  on the other hand for  $k \leq 2$ :

$$\begin{aligned} B_{0,0}^+ &= \hat{b}^{(0)}(0^+), & B_{0,i}^+ &= 0, \quad 1 \leq i \leq n_0, \\ B_{1,0}^+ &= \hat{b}^{(1)}(0^+), & B_{1,1}^+ &= \partial_r \hat{b}^{(0)}(0^+), & B_{1,i}^+ &= 0, \quad 2 \leq i \leq n_1, \\ B_{2,0}^+ &= \hat{b}^{(2)}(0^+), & B_{2,1}^+ &= \partial_r \hat{b}^{(1)}(0^+), & B_{2,2}^+ &= \frac{1}{2} \partial_{rr} \hat{b}^{(0)}(0^+), & B_{2,i}^+ &= 0, \quad 3 \leq i \leq n_2. \end{aligned}$$

It is obvious from the definition of  $r$  and (3.9) that a derivative of  $\hat{b}$  with respect to  $r$  corresponds to the derivative of  $b$  with respect to  $x$  towards  $\nu = \nu(t, s(t, x); 0)$ . Hence,  $\partial_r \hat{b}^{(k)} = \nabla_x b^{(k)} \cdot \nu$  and, since  $\nu$  is independent of  $r$ ,  $\partial_{rr} \hat{b}^{(k)} = \nu \cdot D_x^2 b^{(k)} \nu$ . Using (3.12) again yields the following matching conditions corresponding to (3.13a)–(3.13d): As  $z \rightarrow +\infty$

$$\begin{aligned} B^{(0)}(z) &\approx b^{(0)}(0^+), \\ B^{(1)}(z) &\approx b^{(1)}(0^+) + (\nabla b^{(0)}(0^+) \cdot \nu) z, \\ \partial_z B^{(1)}(z) &\approx \nabla b^{(0)}(0^+) \cdot \nu, \\ \partial_z B^{(2)}(z) &\approx \nabla b^{(1)}(0^+) \cdot \nu + (\nu \cdot D^2 b^{(0)}(0^+) \nu) z. \end{aligned}$$

Analogously, the result for  $0^-$  can be shown. □

## 3.2 First order asymptotics of the general model

The goal of this section is to figure out the limit of the general phase field system (2.32a), (2.32b), (2.32e)–(2.32g) as  $\varepsilon \rightarrow 0$ , i.e., the limit of the equations

$$\varepsilon \omega(\phi, \nabla \phi) \partial_t \phi = \mathcal{P}^M \left( \varepsilon \nabla \cdot a_{\nabla \phi}(\phi, \nabla \phi) - \varepsilon a_{,\phi}(\phi, \nabla \phi) - \frac{1}{\varepsilon} w_{,\phi}(\phi) + \psi_{,\phi}(u, \phi) \right), \quad (3.15a)$$

$$\partial_t c(u, \phi) = -\nabla \cdot J(c(u, \phi), \phi, \nabla u) = \nabla \cdot (L(c(u, \phi), \phi) \nabla u), \quad (3.15b)$$

subject to the boundary conditions

$$J_i(c(u, \phi), \phi, \nabla u) \cdot \nu_{ext} = 0, \quad 0 \leq i \leq N, \quad (3.15c)$$

$$a_{\nabla \phi_\alpha}(\phi, \nabla \phi) \cdot \nu_{ext} = 0, \quad 1 \leq \alpha \leq M. \quad (3.15d)$$

For this purpose, the method of matched asymptotic expansions is used. Expansions of the variables  $u$  and  $\phi$  of the form (3.8) and (3.11) are plugged into the governing equations and matched according to the conditions in Lemma 3.3.

**3.4 Theorem** *Let  $\{u(t, x; \varepsilon), \phi(t, x; \varepsilon)\}_\varepsilon$  denote a family of solutions to the system (3.15a)–(3.15d). Consider phase boundaries  $\Gamma_{\alpha\beta}$ ,  $\alpha < \beta$ ,  $\alpha, \beta \in \{1, \dots, M\}$ , and assume that the solutions can be expanded according to (3.8) in the adjacent bulk regions. Then the coefficient function  $u^{(0)}$  and the motion of the phase boundaries  $\Gamma_{\alpha\beta}$  satisfy the following equations:*

*In the bulk regions  $\Omega_\alpha$ ,  $\alpha \in \{1, \dots, M\}$ , the balance equations*

$$\partial_t c_i^\alpha(u^{(0)}) = -\nabla \cdot J_i^\alpha(c(u^{(0)}), \nabla u^{(0)}) = \nabla \cdot \left( \sum_{j=0}^N L_{ij}^\alpha(c^\alpha(u^{(0)})) \nabla u_j^{(0)} \right), \quad 0 \leq i \leq N, \quad (3.16a)$$

*are fulfilled. On the phase boundaries  $\Gamma_{\alpha\beta}$  it holds that*

$$[u_i^{(0)}]_\alpha^\beta = 0, \quad 0 \leq i \leq N, \quad (3.16b)$$

$$[c_i(u^{(0)})]_\alpha^\beta \nu_{\alpha\beta} = [J_i(c(u^{(0)}), \nabla u^{(0)})]_\alpha^\beta \cdot \nu_{\alpha\beta}, \quad 0 \leq i \leq N, \quad (3.16c)$$

$$m_{\alpha\beta}(\nu_{\alpha\beta}) \nu_{\alpha\beta} = -\nabla_\Gamma \cdot \nabla \gamma_{\alpha\beta}(\nu_{\alpha\beta}) + [\psi(u^{(0)})]_\alpha^\beta. \quad (3.16d)$$

*There is no flux across the external boundary,*

$$J_i^\alpha(c(u^{(0)}), \nabla u^{(0)}) \cdot \nu_{ext} = 0 \quad \text{on } \partial\Omega_\alpha, \quad 0 \leq i \leq N, \quad 1 \leq \alpha \leq M, \quad (3.16e)$$

*and the angle conditions (1.24g) and (1.24h) are satisfied.*

**Proof:** The equations are derived in the following subsections, namely (3.16a) and (3.16e) in 3.2.1, (3.16b) and (3.16c) in 3.2.3, and (3.16d) in 3.2.4. The angle conditions (1.24g) and (1.24h) can be derived as in [GNS98].

### 3.2.1 Outer solution

Based on experiences from numerical simulations it is known that, when solving the equations of Definition 2.5, several phases arise which are separated by diffuse interfaces with a thickness of order  $\varepsilon$ . In such a phase, away from an interface to another phase, an outer expansion is considered. An ansatz according to (3.8) is made:

$$u(t, x; \varepsilon) = \sum_{k=0}^K \varepsilon^k u^{(k)}(t, x) + O(\varepsilon^{K+1}), \quad \phi(t, x) = \sum_{k=0}^K \varepsilon^k \phi^{(k)}(t, x) + O(\varepsilon^{K+1}), \quad (3.17)$$

where, for the constraints  $\phi \in \Sigma^M$  and  $u \in Y^N$  to be satisfied,

$$\begin{aligned} \phi^{(0)} &\in \mathbf{H}\Sigma^M, & \phi^{(k)} &\in \mathbf{T}\Sigma^M, & k &\geq 1, \\ u^{(k)} &\in Y^N, & & & k &\geq 0. \end{aligned}$$

The components of the vectors are denoted by  $u_j^{(k)}$ ,  $0 \leq j \leq N$ , and  $\phi_\alpha^{(k)}$ ,  $1 \leq \alpha \leq M$ , respectively.

First the equation (3.15a) for the phase field variables is considered. Expanding  $\mathcal{P}^M w_{,\phi}(\phi)$  gives

$$\mathcal{P}^M w_{,\phi}(\phi) = \mathcal{P}^M w_{,\phi}(\phi^{(0)}) + \varepsilon (\mathcal{P}^M w_{,\phi}, \phi)(\phi^{(0)}) \cdot \phi^{(1)} + O(\varepsilon^2).$$



### 3.2. FIRST ORDER ASYMPTOTICS OF THE GENERAL MODEL

---

To leading order  $O(\varepsilon^{-1})$  equation (3.15a) becomes

$$0 = \mathcal{P}^M w_{,\phi}(\phi^{(0)}) = w_{,\phi}(\phi^{(0)}) - \frac{1}{M} \left( \sum_{\alpha=1}^M w_{,\phi_\alpha}(\phi^{(0)}) \right) \mathbf{1}. \quad (3.18)$$

If  $a$  is expanded analogously to  $w$  in  $(\phi^{(0)}, \nabla\phi^{(0)})$  then the boundary conditions (3.15d) become to leading order  $O(\varepsilon^0)$

$$0 = a_{,\nabla\phi}(\phi^{(0)}, \nabla\phi^{(0)}) \cdot \nu_{ext}. \quad (3.19)$$

Since only stable solutions are of interest,  $\phi^{(0)}$  is constant (here, the homogeneity of  $a$  resulting in (3.1b) is used for the boundary conditions) and one of the minima of  $w$ , i.e., in view of (2.6b) one of the base vectors  $\{e_\beta\}_{1 \leq \beta \leq M}$ . This means that the whole domain  $\Omega$  is partitioned into phases to leading order which are characterised by the  $M$  possible values of  $\phi^{(0)}$ .

To the next order  $O(\varepsilon^0)$  equation (3.15a) becomes

$$0 = -(\mathcal{P}^M w_{,\phi}, \phi(\phi^{(0)})) \cdot \phi^{(1)} + \mathcal{P}^M \psi_{,\phi}(u^{(0)}, \phi^{(0)}). \quad (3.20)$$

Inserting  $\phi^{(0)} = e_\beta$  for some  $\beta \in \{1, \dots, M\}$  gives  $w_{,\phi\phi}(\phi^{(0)}) > 0$  due to assumption A3. Moreover, by (2.28) and assumption A2 it holds that  $\psi_{,\phi}(u^{(0)}, \phi^{(0)}) = 0$ . Hence, the only solution to (3.20) is  $\phi^{(1)} = 0$ . This solution is consistent with the boundary conditions for  $\phi^{(1)}$  resulting from equation (3.15d) to order  $O(\varepsilon^1)$  which reads

$$0 = \left( (a_{,\nabla\phi}, \phi(\phi^{(0)}, \nabla\phi^{(0)})) \cdot \phi^{(1)} + (a_{,\nabla\phi}, \nabla\phi(\phi^{(0)}, \nabla\phi^{(0)})) : \nabla\phi^{(1)} \right) \cdot \nu_{ext}. \quad (3.21)$$

The  $O(\varepsilon^0)$ -equations for the conserved variables are

$$\partial_t c_i(u^{(0)}, \phi^{(0)}) = \nabla \cdot \sum_{j=0}^N L_{ij}(c(u^{(0)}, \phi^{(0)}), \phi^{(0)}) \nabla u_j^{(0)}, \quad 0 \leq i \leq N. \quad (3.22)$$

It should be noted that the fields  $c_i(u^{(0)}, \phi^{(0)})$  and the coefficients  $L_{ij}$  were expanded analogously to  $\mathcal{P}^M w_{,\phi}$ . Boundary conditions at the external boundary result from (3.15c) which is to order  $O(\varepsilon^0)$ :

$$J_i(c(u^{(0)}, \phi^{(0)}), \phi^{(0)}, \nabla u^{(0)}) \cdot \nu_{ext} = 0, \quad 0 \leq i \leq N. \quad (3.23)$$

In the following subsections, boundary conditions on the moving phase boundaries between the phases are derived by matching with inner expansions of the variables in interfacial regions.

In phase  $\alpha$ , the equations (1.24c) and (1.24i) are obtained by inserting  $\phi^{(0)} = e_\alpha$  into (3.22) which gives

$$\partial_t c_i(u^{(0)}, e_\alpha) = \nabla \cdot \sum_{j=0}^N L_{ij}(c(u^{(0)}, e_\alpha), e_\alpha) \nabla u_j^{(0)}, \quad 0 \leq i \leq N,$$

and into (3.23) which yields

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

#### 3.2.2 Inner expansion

Now, an interfacial region is considered where, without loss of generality,  $\phi^{(0)} = e_1$  in one of the adjacent phases, denoted by  $\Omega_1$ , and  $\phi^{(0)} = e_2$  in the other one, denoted by  $\Omega_2$ . These two phases are supposed to be separated by a family  $\{\Gamma(t; \varepsilon)\}_{\varepsilon > 0, t \in I}$  of evolving smooth curves defined as in (3.2) with  $\phi_l$  replaced by  $\phi_1$  and  $\phi_s$  by  $\phi_2$ .

### CHAPTER 3. ASYMPTOTIC ANALYSIS

In the interfacial region, the functions  $u$  and  $\phi$  are expanded according to (3.11):

$$u(t, x; \varepsilon) = \sum_{k=0}^K \varepsilon^k U^{(k)}(t, s, z) + O(\varepsilon^{K+1}), \quad \phi(t, x; \varepsilon) = \sum_{k=0}^K \varepsilon^k \Phi^{(k)}(t, s, z) + O(\varepsilon^{K+1}), \quad (3.24)$$

where

$$\begin{aligned} \Phi^{(0)} &\in \Sigma^M, & \Phi^{(k)} &\in \mathbb{T}\Sigma^M, & k &\geq 1, \\ U^{(k)} &\in Y^N, & & & k &\geq 0, \end{aligned}$$

to ensure that the constraints on  $\phi$  and  $u$  are satisfied. Taking a Taylor expansion of  $c_i$  and  $L_{ij}$  around  $(U^{(0)}, \Phi^{(0)})$  and writing  $L_{ij}^{0,in} = L_{ij}(c(U^{(0)}, \Phi^{(0)}), \Phi^{(0)})$ , the conservation laws for mass and energy give to lowest order  $O(\varepsilon^{-2})$

$$0 = \nu \cdot \frac{d}{dz} \left( \sum_{j=0}^N L_{ij}^{0,in} \partial_z U_j^{(0)} \nu \right) = \frac{d}{dz} \left( \sum_{j=0}^N L_{ij}^{0,in} \partial_z U_j^{(0)} \right), \quad 0 \leq i \leq N, \quad (3.25)$$

where  $\partial_z \nu = 0$  was used. Integrating with respect to  $z$  over  $\mathbb{R}$  yields

$$L^{0,in} \partial_z U^{(0)} = k \quad (3.26)$$

for some vector  $k \in \mathbf{R}^{N+1}$ .

The  $O(\varepsilon^{-1})$ -equations of the conserved quantities (3.15b) are with (3.6a)–(3.6c) and  $\partial_s \nu = -\kappa \tau$

$$\begin{aligned} -v \partial_z c_i(U^{(0)}, \Phi^{(0)}) &= \tau \cdot \left( \frac{d}{ds} - \partial_s d_1 \frac{d}{dz} \right) \left( \sum_{j=0}^N L_{ij}^{0,in} \partial_z U_j^{(0)} \nu \right) \\ &+ \nu \cdot \frac{d}{dz} \left( \sum_{j=0}^N L_{ij}^{0,in} \left( \partial_z U_j^{(1)} \nu + (\partial_s - \partial_s d_1 \partial_z) U_j^{(0)} \tau \right) \right) \\ &+ \nu \cdot \frac{d}{dz} \left( \sum_{j=0}^N \left( \text{terms involving derivatives of } L_{ij} \right) \partial_z U_j^{(0)} \nu \right) \\ &= -\kappa \left( \sum_{j=0}^N L_{ij}^{0,in} \partial_z U_j^{(0)} \right) + \frac{d}{dz} \left( \sum_{j=0}^N L_{ij}^{0,in} \partial_z U_j^{(1)} \right) \\ &+ \frac{d}{dz} \left( \sum_{j=0}^N \left( \text{terms involving derivatives of } L_{ij} \right) \partial_z U_j^{(0)} \right). \end{aligned} \quad (3.27)$$

Considering the equations for the phase field variables, similarly as done in [GNS98], the  $a$ -terms are expanded in  $(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu)$ . Using (3.6b) and (3.6c) the expansions

$$\begin{aligned} \mathcal{P}^M a_{,\phi}(\phi, \nabla \phi) &= \frac{1}{\varepsilon^2} \mathcal{P}^M a_{,\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \\ &+ \frac{1}{\varepsilon} (\mathcal{P}^M a_{,\phi})_{,\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \cdot \Phi^{(1)} \\ &+ \frac{1}{\varepsilon} (\mathcal{P}^M a_{,\phi})_{,\nabla \phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau + \partial_z \Phi^{(1)} \otimes \nu) \\ &+ O(\varepsilon^0) \end{aligned}$$

### 3.2. FIRST ORDER ASYMPTOTICS OF THE GENERAL MODEL

and

$$\begin{aligned}
\mathcal{P}^M(\nabla \cdot a_{,\nabla\phi}(\phi, \nabla\phi)) &= \nabla \cdot (\mathcal{P}^M a_{,\nabla\phi}(\phi, \nabla\phi)) \\
&= \frac{1}{\varepsilon^2} \frac{d}{dz} \left( \mathcal{P}^M a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \right) \nu \\
&\quad + \frac{1}{\varepsilon} \frac{d}{dz} \left( (\mathcal{P}^M a_{,\nabla\phi})_{,\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \cdot \Phi^{(1)} \right) \nu \\
&\quad + \frac{1}{\varepsilon} \frac{d}{dz} \left( (\mathcal{P}^M a_{,\nabla\phi})_{,\nabla\phi} : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau + \partial_z \Phi^{(1)} \otimes \nu) \right) \nu \\
&\quad + \frac{1}{\varepsilon} \left( \frac{d}{ds} - \partial_s d_1 \frac{d}{dz} \right) \left( \mathcal{P}^M a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \right) \tau \\
&\quad + O(\varepsilon^0)
\end{aligned}$$

hold. The  $w$ -term is expanded in  $\Phi^{(0)}$  and the  $\psi$ -term in  $(U^{(0)}, \Phi^{(0)})$ .

To leading order  $O(\varepsilon^{-1})$  equation (3.15a) reads

$$0 = \frac{d}{dz} \left( \mathcal{P}^M a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \right) \nu - \mathcal{P}^M a_{,\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) - \mathcal{P}^M w_{,\phi}(\Phi^{(0)}). \quad (3.28)$$

Multiplying this equation with  $\partial_z \Phi^{(0)} \in T\Sigma^M$  gives (the projection  $\mathcal{P}^M$  can be dropped)

$$\begin{aligned}
0 &= \frac{d}{dz} \left( a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \right) : (\partial_z \Phi^{(0)} \otimes \nu) \\
&\quad - a_{,\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \cdot \partial_z \Phi^{(0)} - w_{,\phi}(\Phi^{(0)}) \cdot \partial_z \Phi^{(0)} \\
&= \frac{d}{dz} \left( a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) : (\partial_z \Phi^{(0)} \otimes \nu) \right) - a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) : (\partial_{zz} \Phi^{(0)} \otimes \nu) \\
&\quad - a_{,\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \cdot \partial_z \Phi^{(0)} - \frac{d}{dz} \left( w(\Phi^{(0)}) \right) \\
&= \frac{d}{dz} \left( a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) : (\partial_z \Phi^{(0)} \otimes \nu) - a(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) - w(\Phi^{(0)}) \right). \quad (3.29)
\end{aligned}$$

The equation to order  $O(\varepsilon^0)$  is with (3.6a)

$$\begin{aligned}
-\omega(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \nu \partial_z \Phi^{(0)} &= \frac{d}{dz} \left( (\mathcal{P}^M a_{,\nabla\phi})_{,\phi} \cdot \Phi^{(1)} + (\mathcal{P}^M a_{,\nabla\phi})_{,\nabla\phi} : (\partial_z \Phi^{(1)} \otimes \nu) \right) \nu \\
&\quad + \frac{d}{dz} \left( (\mathcal{P}^M a_{,\nabla\phi})_{,\nabla\phi} : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau) \right) \nu \\
&\quad - (\mathcal{P}^M a_{,\phi})_{,\phi} \cdot \Phi^{(1)} - (\mathcal{P}^M a_{,\phi})_{,\nabla\phi} : (\partial_z \Phi^{(1)} \otimes \nu) \\
&\quad - (\mathcal{P}^M a_{,\phi})_{,\nabla\phi} : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau) \\
&\quad + \left( \frac{d}{ds} - \partial_s d_1 \frac{d}{dz} \right) \left( \mathcal{P}^M a_{,\nabla\phi} \right) \tau \\
&\quad - (\mathcal{P}^M w_{,\phi})_{,\phi} \cdot \Phi^{(1)} + \mathcal{P}^M \psi_{,\phi}(U^{(0)}, \Phi^{(0)}), \quad (3.30)
\end{aligned}$$

where  $w$  and all its derivatives are evaluated at  $\Phi^{(0)}$  and  $a$  and its derivatives in  $(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu)$ .

#### 3.2.3 Jump and continuity conditions

Throughout this subsection, for  $u^{(0)}$  in the outer expansions (3.17) in the phases  $\Omega_1$  and  $\Omega_2$  the superscripts  $u^{(0),1}$  and  $u^{(0),2}$  are used.

First the matching conditions are applied to the functions  $U_j^{(0)}$ ,  $0 \leq j \leq N$ , solving the differential equations (3.26). By assumption A1

$$\partial_z U^{(0)} = (L^{0,in})^{-1} k.$$

Thanks to the matching condition (3.13a) the function  $U^{(0)}$  must be bounded if  $|z| \rightarrow \infty$  since  $u^{(0)}(0^\pm)$  is finite. Hence  $\partial_z U^{(0)}(z) \rightarrow 0$  as  $z \rightarrow \pm\infty$ . Since  $L^{0,in} = L(U^{(0)}, \Phi^{(0)}) \rightarrow L(u^{(0),1}, e_1) \neq 0$  as  $z \rightarrow \infty$  and  $L^{0,in} \rightarrow L(u^{(0),2}, e_2) \neq 0$  as  $z \rightarrow -\infty$ , by assumption A1 necessarily  $k = 0$  so that  $U^{(0)}$  is constant. But due to (3.13a) this means that  $u^{(0),1}(0^+) = u^{(0),2}(0^-)$  which is condition (1.24d).

Since  $\partial_z U^{(0)} = 0$ , the  $O(\varepsilon^{-1})$ -equations (3.27) for the conserved variables simplify to

$$-v \partial_z c_i(U^{(0)}, \Phi^{(0)}) = \frac{d}{dz} \left( \sum_{j=0}^N L_{ij}^{0,in} \partial_z U_j^{(1)} \right).$$

Integrating with respect to  $z$  from  $-\infty$  to  $\infty$  (or, more precisely, integrating from  $-R$  to  $R$  and then considering the limit as  $R \rightarrow \infty$ ) and using that  $v(t, s)$  is independent of  $z$ , yields

$$v \left[ c_i(U^{(0)}, \Phi^{(0)}) \right]_{z \searrow -\infty}^{z \nearrow \infty} = - \left[ \sum_{j=0}^N L_{ij}(U^{(0)}, \Phi^{(0)}) \partial_z U_j^{(1)} \right]_{z \searrow -\infty}^{z \nearrow \infty}.$$

The matching condition (3.13a) for  $\phi$  and  $u$  implies on the one hand

$$v \left[ c_i(U^{(0)}, \Phi^{(0)}) \right]_{z \searrow -\infty}^{z \nearrow \infty} = v(c_i(u^{(0),1}, e_1) - c_i(u^{(0),2}, e_2)) = v[c_i]_2^1.$$

On the other hand, thanks to the matching condition (3.13c),

$$\begin{aligned} & - \left[ \sum_{j=0}^N L_{ij}(c(U^{(0)}, \Phi^{(0)}, \Phi^{(0)}) \partial_z U_j^{(1)}) \right]_{z \searrow -\infty}^{z \nearrow \infty} \\ &= - \left( \sum_{j=0}^N L_{ij}(c(u^{(0),1}, e_1), e_1) \nabla_x u_j^{(0),1} \cdot \nu \right)(0^+) - \left( \sum_{j=0}^N L_{ij}(c(u^{(0),2}, e_2), e_2) \nabla_x u_j^{(0),2} \cdot \nu \right)(0^-) \\ &= \left( J_i(c(u^{(0),1}, e_1), e_1, \nabla u^{(0),1})(0^+) - J_i(c(u^{(0),2}, e_2), e_2, \nabla u^{(0),2})(0^-) \right) \cdot \nu \\ &= [J_i]_2^1 \cdot \nu. \end{aligned}$$

Altogether this is the desired jump condition (1.24e).

### 3.2.4 Gibbs-Thomson relation and force balance

In the bulk regions  $\Omega_1$  and  $\Omega_2$  adjacent to the interfacial region under consideration it holds that  $\phi^{(0)} = e_\alpha$ ,  $\alpha \in \{1, 2\}$ . Due to (3.13a), for each  $s \in [0, l(t)]$  equation (3.28) has to be solved subject to the boundary conditions

$$\Phi^{(0)}(z) \rightarrow e_1 \text{ as } z \rightarrow \infty, \quad \Phi^{(0)}(z) \rightarrow e_2 \text{ as } z \rightarrow -\infty. \quad (3.31)$$

Integrating (3.29) with respect to  $z$  and using (3.1b) and  $w(e_1) = w(e_2) = 0$  the equation

$$0 = a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) : (\partial_z \Phi^{(0)} \otimes \nu) - a(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) - w(\Phi^{(0)}).$$

is obtained. With the last identity in (3.1b) this implies

$$a(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) = w(\Phi^{(0)}),$$

which is known as equipartition of energy. Setting

$$C_{\alpha\beta}^{0,1}([-1, 1], \Sigma^M) := \left\{ p \in C^{0,1}([-1, 1]; \Sigma^M) \mid p(-1) = e_\alpha \text{ and } p(1) = e_\beta \right\},$$

### 3.2. FIRST ORDER ASYMPTOTICS OF THE GENERAL MODEL

the surface entropy in direction  $e \in \mathbf{R}^d$  is proposed to be

$$\gamma_{\alpha\beta}(e) = \inf \left\{ 2 \int_{-1}^1 \sqrt{w(p)} \sqrt{a(p, p' \otimes e)}(y) dy \mid p \in C_{\alpha\beta}^{0,1} \right\}. \quad (3.32)$$

This representation was introduced in [Ste91] for isotropic surface energies and in [GNS98] for the general case. It is shown that, if a minimiser exists for  $e = \nu(t, s)$ , then a reparametrisation of the minimiser fulfils (3.28) and, in addition,

$$\gamma_{2,1}(\nu) = \int_{-\infty}^{\infty} \left( a(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) + w(\Phi^{(0)}) \right) dz. \quad (3.33)$$

In [BBR05] the  $\Gamma$ -limit of a functional of the form (2.5) was computed. Besides a rigorous representation formula for  $\gamma_{\alpha\beta}(\nu)$  was found from which it is not known whether it coincides with (3.32). For applications and numerical simulations it is therefore strictly necessary to test the calibration properties of the chosen potentials  $a$  and  $w$ .

The goal is now to deduce the Gibbs–Thomson law. First observe that due to the matching conditions (3.13b) and (3.13c)

$$\partial_z \Phi^{(0)}(z) \rightarrow 0, \quad \Phi^{(1)}(t, s, z) \rightarrow 0, \quad \partial_z \Phi^{(1)}(t, s, z) \rightarrow 0 \quad \text{as } z \rightarrow \pm\infty. \quad (3.34)$$

The equation (3.28) for  $\Phi^{(0)}$  is multiplied by  $\partial_z \Phi^{(1)} \in \text{T}\Sigma^M$  and the equation (3.30) for  $\Phi^{(1)}$  by  $\partial_z \Phi^{(0)} \in \text{T}\Sigma^M$ . Again the projections  $\mathcal{P}^M$  can be dropped. Then the two equations are summed and integrated from  $-\infty$  to  $\infty$  with respect to  $z$ . Altogether

$$\int_{-\infty}^{\infty} \left( (3.28) \cdot \partial_z \Phi^{(1)} + (3.30) \cdot \partial_z \Phi^{(0)} \right) dz \quad (3.35)$$

is computed. The terms involving  $w$  and its derivatives vanish:

$$\begin{aligned} & - \int_{-\infty}^{\infty} ((w, \phi), \phi \cdot \Phi^{(1)}) \cdot \partial_z \Phi^{(0)} && \text{from (3.30)} \\ & - \int_{-\infty}^{\infty} w, \phi \cdot \partial_z \Phi^{(1)} && \text{from (3.28)} \\ & = - \int_{-\infty}^{\infty} ((w, \phi), \phi \cdot \partial_z \Phi^{(0)}) \cdot \Phi^{(1)} + \int_{-\infty}^{\infty} \partial_z (w, \phi) \cdot \Phi^{(1)} - [w, \phi \cdot \Phi^{(1)}]_{-\infty}^{\infty} \\ & = - [w, \phi(\Phi^{(0)}) \cdot \Phi^{(1)}]_{-\infty}^{\infty} = 0, \end{aligned}$$

since by (3.31)  $w, \phi(\Phi^{(0)}) \rightarrow w, \phi(e_{1,2}) = 0$  and by (3.34)  $\Phi^{(1)}$  is bounded as  $z \rightarrow \pm\infty$ . Concerning the  $a$ -terms, evaluated at  $(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu)$ , the contribution from (3.30) to (3.35) is

$$\begin{aligned} & \int_{-\infty}^{\infty} \partial_z ((a, \nabla \phi), \phi \cdot \Phi^{(1)}) : (\partial_z \Phi^{(0)} \otimes \nu) dz + \int_{-\infty}^{\infty} \partial_z ((a, \nabla \phi), \nabla \phi : (\partial_z \Phi^{(1)} \otimes \nu)) : (\partial_z \Phi^{(0)} \otimes \nu) dz \\ & + \int_{-\infty}^{\infty} \partial_z ((a, \nabla \phi), \nabla \phi : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \nu)) : (\partial_z \Phi^{(0)} \otimes \nu) dz \\ & - \int_{-\infty}^{\infty} ((a, \phi), \phi \cdot \Phi^{(1)}) \cdot \partial_z \Phi^{(0)} dz - \int_{-\infty}^{\infty} ((a, \phi), \nabla \phi : (\partial_z \Phi^{(1)} \otimes \nu)) \cdot \partial_z \Phi^{(0)} dz \\ & - \int_{-\infty}^{\infty} ((a, \phi), \nabla \phi : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau)) \cdot \partial_z \Phi^{(0)} dz \\ & + \int_{-\infty}^{\infty} ((\partial_s - \partial_s d_1 \partial_z) a, \nabla \phi) : (\partial_z \Phi^{(0)} \otimes \tau) dz \end{aligned}$$

$$\begin{aligned}
 &= \underbrace{\left[ ((a, \nabla \phi), \phi \cdot \Phi^{(1)}) : (\partial_z \Phi^{(0)} \otimes \nu) \right]_{-\infty}^{\infty}}_{=:(t1)} - \underbrace{\int_{-\infty}^{\infty} ((a, \nabla \phi), \phi \cdot \Phi^{(1)}) : (\partial_{zz} \Phi^{(0)} \otimes \nu) dz}_{=:(t2)} \\
 &+ \underbrace{\left[ ((a, \nabla \phi), \nabla \phi : (\partial_z \Phi^{(1)} \otimes \nu)) : (\partial_z \Phi^{(0)} \otimes \nu) \right]_{-\infty}^{\infty}}_{=:(t3)} \\
 &- \underbrace{\int_{-\infty}^{\infty} ((a, \nabla \phi), \nabla \phi : (\partial_z \Phi^{(1)} \otimes \nu)) : (\partial_{zz} \Phi^{(0)} \otimes \nu) dz}_{=:(t4)} \\
 &+ \underbrace{\left[ ((a, \nabla \phi), \nabla \phi : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau)) : (\partial_z \Phi^{(0)} \otimes \nu) \right]_{-\infty}^{\infty}}_{=:(t5)} \\
 &- \int_{-\infty}^{\infty} ((a, \nabla \phi), \nabla \phi : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau)) : (\partial_{zz} \Phi^{(0)} \otimes \nu) dz \\
 &- \underbrace{\int_{-\infty}^{\infty} ((a, \phi), \phi \cdot \Phi^{(1)}) \cdot \partial_z \Phi^{(0)} dz}_{=:(t6)} - \underbrace{\int_{-\infty}^{\infty} ((a, \phi), \nabla \phi : (\partial_z \Phi^{(1)} \otimes \nu)) \cdot \partial_z \Phi^{(0)} dz}_{=:(t7)} \\
 &- \int_{-\infty}^{\infty} ((a, \phi), \nabla \phi : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau)) \cdot \partial_z \Phi^{(0)} dz \\
 &+ \int_{-\infty}^{\infty} ((\partial_s - \partial_s d_1 \partial_z) a, \nabla \phi) : (\partial_z \Phi^{(0)} \otimes \tau) dz,
 \end{aligned}$$

while the contribution from (3.28) to (3.35) is

$$\begin{aligned}
 &\int_{-\infty}^{\infty} (\partial_z a, \nabla \phi) : (\partial_z \Phi^{(1)} \otimes \nu) dz - \int_{-\infty}^{\infty} a, \phi \cdot \partial_z \Phi^{(1)} dz \\
 &= \underbrace{\int_{-\infty}^{\infty} ((a, \nabla \phi), \phi \cdot \partial_z \Phi^{(0)}) : (\partial_z \Phi^{(1)} \otimes \nu) dz}_{=:(t7)} + \underbrace{\int_{-\infty}^{\infty} ((a, \nabla \phi), \nabla \phi : (\partial_{zz} \Phi^{(0)} \otimes \nu)) : (\partial_z \Phi^{(1)} \otimes \nu) dz}_{=:(t4)} \\
 &- \underbrace{\left[ a, \phi \cdot \Phi^{(1)} \right]_{-\infty}^{\infty}}_{=:(t8)} + \underbrace{\int_{-\infty}^{\infty} ((a, \phi), \phi \cdot \partial_z \Phi^{(0)}) \cdot \Phi^{(1)} dz}_{=:(t6)} + \underbrace{\int_{-\infty}^{\infty} ((a, \phi), \nabla \phi : (\partial_{zz} \Phi^{(0)} \otimes \nu)) \cdot \Phi^{(1)} dz}_{=:(t2)}.
 \end{aligned}$$

Using (3.1b), (3.31) and (3.34), the boundary terms (t1), (t3), (t5) and (t8) vanish. Since the terms (t2), (t4), (t6), and (t7) appear in the contributions from both equations (3.30) and (3.28) but with opposite signs, the  $a$ -terms in (3.35) are

$$\begin{aligned}
 &- \int_{-\infty}^{\infty} ((a, \nabla \phi), \nabla \phi : (\partial_{zz} \Phi^{(0)} \otimes \nu)) : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau) dz \\
 &- \int_{-\infty}^{\infty} ((a, \nabla \phi), \phi \cdot \partial_z \Phi^{(0)}) : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau) dz \\
 &+ \int_{-\infty}^{\infty} ((\partial_s - \partial_s d_1 \partial_z) a, \nabla \phi) : (\partial_z \Phi^{(0)} \otimes \tau) dz \\
 &= - \int_{-\infty}^{\infty} (\partial_z a, \nabla \phi) : ((\partial_s - \partial_s d_1 \partial_z) \Phi^{(0)} \otimes \tau) dz \\
 &+ \int_{-\infty}^{\infty} (\partial_s a, \nabla \phi) : (\partial_z \Phi^{(0)} \otimes \tau) dz - \partial_s d_1 \int_{-\infty}^{\infty} (\partial_z a, \nabla \phi) : (\partial_z \Phi^{(0)} \otimes \tau) dz
 \end{aligned}$$

### 3.2. FIRST ORDER ASYMPTOTICS OF THE GENERAL MODEL

$$\begin{aligned}
&= - [a_{,\nabla\phi} : (\partial_s \Phi^{(0)} \otimes \tau)]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} a_{,\nabla\phi} : (\partial_{zs} \Phi^{(0)} \otimes \tau) dz + \int_{-\infty}^{\infty} (\partial_s a_{,\nabla\phi}) : (\partial_z \Phi^{(0)} \otimes \tau) dz \\
&= \frac{d}{ds} \left( \int_{-\infty}^{\infty} a_{,\nabla\phi} \cdot \partial_z \Phi^{(0)} dz \right) \tau
\end{aligned}$$

where the boundary term again vanishes thanks to (3.1b) and (3.34).

Finally, (3.35) yields the following solvability condition for equation (3.30):

$$\begin{aligned}
&-v \int_{-\infty}^{\infty} \omega(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) (\partial_z \Phi^{(0)})^2 \\
&= \frac{d}{ds} \left( \int_{-\infty}^{\infty} a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \cdot \partial_z \Phi^{(0)} dz \right) \tau - \int_{-\infty}^{\infty} \psi_{,\phi}(U^{(0)}, \Phi^{(0)}) \cdot \partial_z \Phi^{(0)} dz. \quad (3.36)
\end{aligned}$$

Using that  $U^{(0)}$  is independent of  $z$ , the last term becomes using (3.13a)

$$\begin{aligned}
\int_{-\infty}^{\infty} \psi_{,\phi}(U^{(0)}, \Phi^{(0)}) \cdot \partial_z \Phi^{(0)} dz &= \int_{-\infty}^{\infty} \partial_z (\psi(U^{(0)}, \Phi^{(0)})) dz \\
&= [\psi(U^{(0)}, \Phi^{(0)})]_{z \searrow -\infty}^{z \nearrow \infty} = \psi(u^{(0),1}, e_1) - \psi(u^{(0),2}, e_2) = [\psi(u^{(0)})]_2^1
\end{aligned}$$

with the notation  $u^{(0),1}$  and  $u^{(0),2}$  as in the preceding Subsection (3.2.3).

The derivative of  $\gamma_{2,1}$  with respect to  $\nu$  is with (3.33)

$$\nabla \gamma_{2,1}(\nu) = \int_{-\infty}^{\infty} a_{,\nabla\phi}(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) \cdot \partial_z \Phi^{(0)} dz.$$

Setting

$$m(\nu) = \int_{-\infty}^{\infty} \omega(\Phi^{(0)}, \partial_z \Phi^{(0)} \otimes \nu) (\partial_z \Phi^{(0)})^2 dz,$$

the solvability condition reduces to (observe that  $\tau \cdot \partial_s$  is the surface divergence on the curve  $\Gamma(t; 0)$ )

$$m(\nu)v = -\nabla_s \cdot \nabla \gamma_{2,1}(\nu) + [\psi(u^{(0)})]_2^1.$$

This is the desired condition (1.24f), which can be seen using the identities (2.25) and (B.5).

Considering  $\nu$  and  $\gamma$  as functions in an angle  $\theta \in [0, 2\pi)$ , i.e., setting  $\nu(\theta) = (\cos(\theta), \sin(\theta))$  and  $\hat{\gamma}(\theta) = \gamma(\nu(\theta))$ , one can derive (cf. [GNS98])

$$\nabla_s \cdot D\gamma_{2,1}(\nu) = -(\hat{\gamma}_{2,1}(\theta) + \hat{\gamma}_{2,1}''(\theta))\kappa.$$

Inserting this identity into the solvability condition gives

$$m(\nu)v = (\hat{\gamma}_{2,1}(\theta) + \hat{\gamma}_{2,1}''(\theta))\kappa + [\psi(u^{(0)})]_2^1.$$

To obtain the full set of equations governing the evolution in Section 1.2 it remains to derive the force balance conditions (1.24g) and (1.24h). But this can be done as in [GNS98]. Therefore, all equations defining the sharp interface model are derived by formally matched asymptotic expansions.  $\square$

### 3.3 Second order asymptotics in the two-phase case

In the preceding section it is shown that the phase field model can be related to a corresponding sharp interface model by matching asymptotic expansions. To improve the quality of this approximation, namely, to obtain an approximation to second order in  $\varepsilon$ , ideas of [KR98] are applied and generalised to the case of an arbitrary number of conserved quantities. First of all the governing equations of the two phase model are stated in Subsection 3.3.1. Thereafter the technique of matched asymptotic expansions is applied again (Subsections 3.3.2 and 3.3.3) to deduce a linear parabolic  $O(\varepsilon)$ -correction problem. The problem to leading order as well as the correction problem are stated in Subsection 3.3.4. Given appropriate initial and boundary conditions, zero is a solution to the correction problem.

#### 3.3.1 The modified two-phase model

The problem consists of finding smooth functions

$$\varphi : I \times D \rightarrow \mathbb{R}, \quad u = (u_0, \dots, u_N) : I \times D \rightarrow Y^N$$

that solve the partial differential equations

$$(\omega_0 + \varepsilon\omega_1(u))\partial_t\varphi = \sigma\Delta\varphi - \frac{\sigma}{\varepsilon^2}w'(\varphi) + \frac{1}{2\varepsilon}h'(\varphi)\Psi(u), \quad (3.37a)$$

$$\partial_t\psi_{\varphi,u}(u, \varphi) = \left( \nabla \cdot \sum_{j=0}^N L_{ij} \nabla u_j \right)_{i=0}^N = \nabla \cdot (L \nabla u). \quad (3.37b)$$

The first equation can be obtained from (3.15a) by setting  $\phi_1 = \varphi$ ,  $\phi_2 = 1 - \phi_1 = 1 - \varphi$ . The procedure is outlined in Subsection 2.3.2. The precise coupling to the thermodynamic quantities via the last term in that equation is clarified below. The function  $\omega_1 : Y^N \rightarrow \mathbb{R}$  is a certain correction term in order to obtain quadratic convergence and will be defined during the analysis. The following definitions and assumptions are made:

B1  $\omega_0$  and  $\sigma$  are positive constants. If not stated otherwise,  $\sigma = 1$ .

B2 The function  $w : \mathbb{R} \rightarrow \mathbb{R}^+$  is some non-negative, smooth double-well potential which attains its global minima in 0 and 1, more precisely it is required that

$$\begin{aligned} w(\varphi) &> 0 && \text{if } \varphi \notin \{0, 1\}, \\ w(0) = w(1) &= 0, && w'(0) = w'(1) = 0, \quad w''(0) = w''(1) > 0. \end{aligned}$$

Besides  $w$  is axis-symmetric with respect to  $\frac{1}{2}$ , i.e.,  $w(\frac{1}{2} + \varphi) = w(\frac{1}{2} - \varphi) \forall \varphi \in \mathbb{R}$ .

B3 In addition to assumption A2, the interpolation function  $h : \mathbb{R} \rightarrow \mathbb{R}$  is monotone and point-symmetric with respect to  $(\frac{1}{2}, \frac{1}{2})$ , i.e.,

$$\frac{1}{2} + h(\frac{1}{2} + \varphi) = \frac{1}{2} - h(\frac{1}{2} - \varphi), \quad h'(\varphi) \geq 0.$$

B4 The reduced grand canonical potential density  $\psi : Y^N \times \mathbb{R} \rightarrow \mathbb{R}$  is smooth and given as interpolation between the reduced grand canonical potentials of the two possible phases  $s$  and  $l$ , i.e.,

$$\psi(u, \varphi) = \psi_s(u) + \tilde{h}(\varphi)(\psi_l(u) - \psi_s(u))$$

with a function  $\tilde{h}$  satisfying assumption B3. Observe that in the case  $\tilde{h} \neq h$  the model lacks thermodynamic consistency, and an entropy inequality might not hold (cf. [PF90, KR98, Alm99]). In (3.37a) the abbreviation

$$\Psi(u) := \psi_l(u) - \psi_s(u)$$

was used.



### 3.3. SECOND ORDER ASYMPTOTICS IN THE TWO-PHASE CASE

B5 In addition to assumption A1, the matrix  $L = (L_{ij})_{i,j=0}^N$  is constant. The handling of a dependence on  $u$  is straightforward (cf. also the remark in Subsection 3.3.4 for the result), and a dependence of the diffusivities on the phase has already been considered in [Alm99]. Therefore, the analysis is restricted to this simple case.

For some  $\varepsilon > 0$ , a smooth solution to (3.37a) and (3.37b) is denoted by  $(u(t, x; \varepsilon), \varphi(t, x; \varepsilon))$ . The family of curves  $\{\Gamma(t; \varepsilon)\}_{\varepsilon > 0, t \in I}$  appearing in Section 3.1 and determining the position of the phase boundary in the diffuse interface model is defined by

$$\Gamma(t; \varepsilon) := \left\{ x \in D : \varphi(t, x; \varepsilon) = \frac{1}{2} \right\}, \quad \varepsilon > 0, t \in I. \quad (3.38)$$

To avoid the handling of the boundary values it is supposed that the curves are bounded away from the boundary  $\partial D$  of the considered domain uniformly in  $(t; \varepsilon)$ . By  $D^l(t; \varepsilon)$  and  $D^s(t; \varepsilon)$  the regions occupied by the liquid phase (where  $\varphi(t, x; \varepsilon) > \frac{1}{2}$ ) and the solid phase (where  $\varphi(t, x; \varepsilon) < \frac{1}{2}$ ) respectively are denoted.

Finally, to obtain a well-posed problem, initial conditions

$$\varphi(t = 0) = \varphi_{ic}, \quad u(t = 0) = u_{ic}$$

and boundary conditions

$$(L\nabla u) \cdot \nu_{ext} = 0, \quad (3.39a)$$

$$\nabla \varphi \cdot \nu_{ext} = 0 \quad (3.39b)$$

are imposed.

#### 3.3.2 Outer solutions

According to (3.8), the ansatz

$$u(t, x; \varepsilon) = \sum_{k=0}^K \varepsilon^k u^{(k)}(t, x; \varepsilon) + O(\varepsilon^{K+1}), \quad \varphi(t, x; \varepsilon) = \sum_{k=0}^K \varepsilon^k \varphi^{(k)}(t, x; \varepsilon) + O(\varepsilon^{K+1})$$

is plugged into the differential equations (3.37a) and (3.37b) away from the phase boundary  $\Gamma(t; 0)$ . All functions and terms that appear are expanded in  $\varepsilon$ -series.

The results from the phase field equation (3.37a) are consistent with the results obtained for the general model. To leading order  $O(\varepsilon^{-2})$  there is the identity  $0 = -w'(\varphi^{(0)})$ , and the only stable solutions to this equation subject to the leading order boundary condition  $\nabla \varphi^{(0)} \cdot \nu_{ext} = 0$  are the minima of  $w$ , hence  $\varphi^{(0)} = 0$  or  $\varphi^{(0)} = 1$ . It is assumed that the set  $D^s(t; 0)$  corresponds to the set of all points with  $\varphi^{(0)} = 0$  and similarly  $D^l(t; 0)$  with  $\varphi^{(0)} = 1$ . The equation to the next order yields again  $\varphi^{(1)} = 0$  as in Subsection 3.2.1.

To leading order  $O(\varepsilon^0)$  equation (3.37b) is

$$\partial_t(\psi_{,u}(u^{(0)}, \varphi^{(0)})) = L\Delta u^{(0)}. \quad (3.40)$$

Depending on the value of  $\varphi^{(0)}$  it holds that  $\psi_{,u}(u^{(0)}, \varphi^{(0)}) = (\psi_l)_{,u}(u^{(0)})$  or  $\psi_{,u}(u^{(0)}, \varphi^{(0)}) = (\psi_s)_{,u}(u^{(0)})$ . In both cases (3.40) is a parabolic equation for  $u^{(0)}$  by assumption B4.

To order  $O(\varepsilon^1)$  equation (3.37b) reads

$$\partial_t((\psi_{,uu})(u^{(0)}, \varphi^{(0)})u^{(1)}) = L\Delta u^{(1)} \quad (3.41)$$

where  $\varphi^{(1)} = 0$  was inserted. Assumption B4 states that  $\psi$  is convex so that (3.41) is a linear parabolic equation for  $u^{(1)}$ .

Boundary conditions for (3.40) and (3.41) on  $\Gamma(t; 0)$  are derived in the following subsection. On the external boundary of  $D$  it holds from (3.39a) that

$$(L\nabla u^{(0)}) \cdot \nu_{ext} = 0, \quad (L\nabla u^{(1)}) \cdot \nu_{ext} = 0.$$

### 3.3.3 Inner solutions

Analogously as in Subsection 3.2.2, expansions of the form (3.11) for  $u$  and  $\varphi$  are plugged into the differential equations. For shorter presentation, the constants  $\omega_0$  and  $\sigma$  are dropped, but in the next subsection they reappear in the formulations of the deduced problems. In the expansion for the phase field variable  $\varphi$ ,

$$\varphi(t, x; \varepsilon) = \sum_{k=0}^K \varepsilon^k \Phi^{(k)}(t, s, z) + O(\varepsilon^{K+1})$$

again the functions  $\Phi^{(k)}$  appear. But in contrast to Subsection 3.2.2 they are scalar functions.

To leading order  $O(\varepsilon^{-2})$  equation (3.37a) is

$$0 = \partial_{zz} \Phi^{(0)} - w'(\Phi^{(0)}). \quad (3.42)$$

Definition (3.38) yields  $\Phi^{(0)}(0) = \frac{1}{2}$ . The matching condition (3.13a) implies for  $\varphi$

$$\begin{aligned} \Phi^{(0)}(t, s, z) &\rightarrow \varphi(t, s; 0^+) = 1 \text{ as } z \rightarrow \infty, \\ \Phi^{(0)}(t, s, z) &\rightarrow \varphi(t, s; 0^-) = 0 \text{ as } z \rightarrow -\infty. \end{aligned}$$

Therefore  $\Phi^{(0)}(z)$  only depends on  $z$ . Furthermore,  $\Phi^{(0)}$  is monotone, approximates the values at  $\pm\infty$  exponentially and fulfils

$$\Phi^{(0)}(-z) = 1 - \Phi^{(0)}(z). \quad (3.43)$$

For the conserved variables the equation to leading order is

$$0 = L\partial_{zz} U^{(0)}. \quad (3.44)$$

As shown in Subsection 3.2.3,  $U^{(0)}$  must be constant in  $z$  which means  $U^{(0)} = U^{(0)}(t, s)$ . The matching condition (3.13a) implies that  $U^{(0)}(t, s)$  is exactly the value of  $u^{(0)}$  in the point  $\gamma(t, s; 0) \in \Gamma(t; 0)$  from both sides of the interface. As a consequence

$$u^{(0)} \text{ is continuous across the interface } \Gamma(t; 0). \quad (3.45)$$

To order  $O(\varepsilon^{-1})$  equation (3.37a) yields

$$-v\partial_z \Phi^{(0)} = \partial_{zz} \Phi^{(1)} - \kappa \partial_z \Phi^{(0)} - w''(\Phi^{(0)})\Phi^{(1)} + \frac{1}{2}h'(\Phi^{(0)})\Psi(U^{(0)}). \quad (3.46)$$

From the outer solutions it is known that  $\varphi^{(1)}(t, s, 0^\pm) = 0$  and  $\nabla\varphi^{(0)}(t, s, 0^\pm) \cdot \nu = 0$ , since  $\varphi^{(0)}$  is constant. The matching condition (3.13b) implies  $\Phi^{(1)} \rightarrow 0$  as  $z \rightarrow \pm\infty$ .

The operator  $\mathcal{L}(\Phi^{(0)})b = \partial_{zz}b - w''(\Phi^{(0)})b$  is self-adjoint with respect to the  $L^2$ -product over  $\mathbb{R}$ . Differentiating (3.42) with respect to  $z$  reveals that  $\partial_z \Phi^{(0)}$  lies in the core of  $\mathcal{L}(\Phi^{(0)})$ . Since  $\Phi^{(0)}(-z) = 1 - \Phi^{(0)}(z)$  the functions  $\partial_z \Phi^{(0)}$  and  $h'(\Phi^{(0)})$  are even thanks to assumption B3, hence (3.46) allows for an even solution.

$$\text{In the following it is assumed that } \Phi^{(1)} \text{ is even.} \quad (3.47)$$

Analogously to the procedure in Section 3.2.4, a solvability condition can be derived by multiplying the equation (3.46) by  $\partial_z \Phi^{(0)}$  and integrating over  $\mathbb{R}$  with respect to  $z$ :

$$\begin{aligned} 0 &= \int_{\mathbb{R}} \left( (\kappa - v)(\partial_z \Phi^{(0)}(z))^2 - \frac{1}{2}\Psi(U^{(0)})h'(\Phi^{(0)}(z))\partial_z \Phi^{(0)}(z) \right) dz \\ &= (\kappa - v) \int_{\mathbb{R}} (\partial_z \Phi^{(0)}(z))^2 dz - \frac{1}{2}\Psi(U^{(0)}) = (\kappa - v)I - \frac{1}{2}\Psi(U^{(0)}) \end{aligned} \quad (3.48)$$

### 3.3. SECOND ORDER ASYMPTOTICS IN THE TWO-PHASE CASE

where

$$I = \int_{\mathbb{R}} (\partial_z \Phi^{(0)})^2 dz.$$

The system (3.37b) reads to the order  $O(\varepsilon^{-1})$

$$-v\partial_z \psi_{,u}(U^{(0)}, \Phi^{(0)}) = -v\partial_z ((\psi_s)_{,u}(U^{(0)}) + \tilde{h}(\Phi^{(0)})\Psi_{,u}(U^{(0)})) = L\partial_{zz}U^{(1)}. \quad (3.49)$$

As  $U^{(0)}$  only depends on  $t$  and  $s$  it holds that  $\Psi_{,u}(U^{(0)}) = [\psi_{,u}(u^{(0)})]_s^l = (\psi_l)_{,u}(u^{(0)}) - (\psi_s)_{,u}(u^{(0)})$  for all  $z$ . After integrating two times with respect to  $z$  equation (3.49) gives

$$U^{(1)} = -L^{-1} \left( v \int_0^z \psi_{,u}(U^{(0)}, \Phi^{(0)}) dz' - Az \right) + \bar{u} \quad (3.50a)$$

$$\sim -L^{-1} \left( v(\psi_l)_{,u}(U^{(0)})z - Az - v[\psi_{,u}(u^{(0)})]_s^l \tilde{H} \right) + \bar{u} \text{ as } z \rightarrow \infty \quad (3.50b)$$

$$\sim -L^{-1} \left( v(\psi_s)_{,u}(U^{(0)})z - Az - v[\psi_{,u}(u^{(0)})]_s^l \tilde{H} \right) + \bar{u} \text{ as } z \rightarrow -\infty \quad (3.50c)$$

where  $A \in \mathbb{R} \times \Sigma^N$  (observe that then  $v\psi_{,u} - A \in Y^N$  which allows for using assumption B5) and  $\bar{u} \in Y^N$  are two integration constants and

$$\tilde{H} = \int_0^\infty (1 - \tilde{h}(\Phi^{(0)}(z))) dz = \int_{-\infty}^0 \tilde{h}(\Phi^{(0)}(z)) dz.$$

Here, since  $\Phi^{(0)}$  exponentially converges to constants as  $z \rightarrow \pm\infty$ , the integral  $\int_0^z$  was replaced by  $\int_0^\infty$  while the linear terms remained. Using (3.13b) it holds that

$$u^{(1)}(t, s, 0^\pm) = \bar{u} + vL^{-1}[\psi_{,u}(u^{(0)})]_s^l \tilde{H} \quad (3.51)$$

which means in particular that

$$u^{(1)} \text{ is continuous across } \Gamma(t; 0). \quad (3.52)$$

Since from (3.50a) or equivalently from integrating (3.49) once

$$-L\partial_z U^{(1)} = v\psi_{,u}(U^{(0)}, \Phi^{(0)}) - A,$$

with (3.13c) the following jump condition is obtained at the interface:

$$\begin{aligned} [-L\nabla u^{(0)}]_s^l \cdot \nu &:= -L\nabla u^{(0)}(t, s, 0^+) \cdot \nu + L\nabla u^{(0)}(t, s, 0^-) \cdot \nu \\ &= \left( v(\psi_l)_{,u}(u^{(0)}) - A \right) - \left( v(\psi_s)_{,u}(u^{(0)}) - A \right) \\ &= v[\psi_{,u}(u^{(0)})]_s^l. \end{aligned} \quad (3.53)$$

Using the fact that  $\Phi^{(0)}$  only depends on  $z$ , the phase field equation to order  $O(\varepsilon^0)$  reads (the identity (3.6d) is used for the second order derivatives)

$$\begin{aligned} &-v\partial_z \Phi^{(1)} - \omega_1(u^{(0)})v\partial_z \Phi^{(0)} - (\partial^\circ d_1)\partial_z \Phi^{(0)} \\ &= \partial_{zz}\Phi_2 - w''(\Phi^{(0)})\Phi_2 + (\partial_s d_1)^2 \partial_{zz}\Phi^{(0)} - \kappa^2(z + d_1)\partial_z \Phi^{(0)} - \partial_{ss}d_1 \partial_z \Phi^{(0)} + \\ &- \kappa \partial_z \Phi^{(1)} - \frac{1}{2}w'''(\Phi^{(0)})(\Phi^{(1)})^2 + \frac{1}{2}\Psi(U^{(0)})h''(\Phi^{(0)})\Phi^{(1)} + \frac{1}{2}\Psi_{,u}(U^{(0)}) \cdot U^{(1)}h'(\Phi^{(0)}). \end{aligned}$$

To guarantee that  $\Phi_2$  exists there is again a solvability condition which can be obtained by multiplying with  $\partial_z \Phi^{(0)}$  and integrating over  $\mathbb{R}$  with respect to  $z$ . The  $\Phi^{(1)}$ -terms in this condition vanish which can be seen as follows:

$$\begin{aligned} &\int_{\mathbb{R}} \left( (\kappa - v)\partial_z \Phi^{(1)} + \frac{1}{2}w'''(\Phi^{(0)})(\Phi^{(1)})^2 - \frac{1}{2}\Psi(U^{(0)})h''(\Phi^{(0)})\Phi^{(1)} \right) \partial_z \Phi^{(0)} dz \\ &= \int_{\mathbb{R}} \left( (\kappa - v)\partial_z \Phi^{(1)} \partial_z \Phi^{(0)} - w''(\Phi^{(0)})\Phi^{(1)} \partial_z \Phi^{(1)} + \frac{1}{2}\Psi(U^{(0)})h'(\Phi^{(0)})\partial_z \Phi^{(1)} \right) dz \\ &= 2(\kappa - v) \int_{\mathbb{R}} \partial_z \Phi^{(1)} \partial_z \Phi^{(0)} dz - \int_{\mathbb{R}} \partial_{zz}\Phi^{(1)} \partial_z \Phi^{(1)} dz \end{aligned}$$

**CHAPTER 3. ASYMPTOTIC ANALYSIS**

---

where (3.46) was used to obtain the last identity. Since by (3.43) and (3.47) the functions  $z \mapsto \partial_z \Phi^{(1)}(z) \cdot \partial_z \Phi^{(0)}(z)$  and  $z \mapsto \partial_{zz} \Phi^{(1)}(z) \cdot \partial_z \Phi^{(1)}(z)$  are odd, the integrals in the last line vanish. Now, define the constants

$$\begin{aligned} H &:= \int_0^\infty z \partial_z (h \circ \Phi^{(0)})(z) dz = - \int_{-\infty}^0 z \partial_z (h \circ \Phi^{(0)})(z) dz, \\ J &:= \int_0^\infty \partial_z (h \circ \Phi^{(0)})(z) \int_0^z (1 - (\tilde{h} \circ \Phi^{(0)})(z')) dz' dz \\ &= \int_{-\infty}^0 \partial_z (h \circ \Phi^{(0)})(z) \int_z^0 (\tilde{h} \circ \Phi^{(0)})(z') dz' dz, \end{aligned}$$

where the equalities holds thanks to the symmetries of  $h$  and  $\tilde{h}$  in assumption B3 and B4. By the identity (3.50a) for the  $U^{(1)}$ -term the following holds (using the superscript  $^0$  for a dependence on  $U^{(0)}$  which is independent of  $z$  and equal to  $u^{(0)}(0^\pm)$ ):

$$\begin{aligned} & - \int_{\mathbb{R}} \frac{1}{2} \Psi_{,u}^0 \cdot U^{(1)} \partial_z (h \circ \Phi^{(0)}) dz \\ &= - \int_{\mathbb{R}} \frac{1}{2} \Psi_{,u}^0 \cdot \left( -L^{-1} \left( v \int_0^z \psi_{,u}(U^{(0)}, \Phi^{(0)}) dz' - Az \right) + \bar{u} \right) \partial_z (h \circ \Phi^{(0)}) dz. \end{aligned}$$

Using assumption B4,  $\Psi_{,u} = (\psi_l)_{,u} - (\psi_s)_{,u}$ , and that  $U^{(0)}$  is constant this yields

$$\begin{aligned} &= \int_{\mathbb{R}} \frac{1}{2} \Psi_{,u}^0 \cdot \left( L^{-1} \left( v \int_0^z ((\psi_s)_{,u}^0 + \Psi_{,u}(U^{(0)}) \tilde{h}(\Phi^{(0)}(z'))) dz' - Az \right) - \bar{u} \right) \partial_z (h \circ \Phi^{(0)}) dz \\ &= - \int_{\mathbb{R}} \frac{1}{2} \Psi_{,u}^0 \cdot \bar{u} \partial_z (h \circ \Phi^{(0)}) dz \\ &+ \int_0^\infty \frac{1}{2} \Psi_{,u}^0 \cdot L^{-1} \left( v (\psi_l)_{,u}^0 z - Az - v \Psi_{,u}^0 \int_0^z (1 - (\tilde{h} \circ \Phi^{(0)})(z')) dz' \right) \partial_z (h \circ \Phi^{(0)}) dz \\ &+ \int_{-\infty}^0 \frac{1}{2} \Psi_{,u}^0 \cdot L^{-1} \left( v (\psi_s)_{,u}^0 z - Az - v \Psi_{,u}^0 \int_z^0 (\tilde{h} \circ \Phi^{(0)})(z') dz' \right) \partial_z (h \circ \Phi^{(0)}) dz \\ &= - \frac{1}{2} [\psi_{,u}(u^{(0)})]_s^l \cdot \bar{u} \\ &+ \frac{1}{2} [\psi_{,u}(u^{(0)})]_s^l \cdot L^{-1} \left( (v (\psi_l)_{,u}(u^{(0)}) - A) H + (v (\psi_s)_{,u}(u^{(0)}) - A) (-H) - 2 [\psi_{,u}(u^{(0)})]_s^l J \right) \\ &= - \frac{1}{2} [\psi_{,u}(u^{(0)})]_s^l \cdot \left( \bar{u} + v L^{-1} [\psi_{,u}(u^{(0)})]_s^l \tilde{H} \right) + v [\psi_{,u}(u^{(0)})]_s^l \cdot L^{-1} [\psi_{,u}(u^{(0)})]_s^l \frac{H + \tilde{H} - 2J}{2} \end{aligned}$$

and inserting the relation (3.51)

$$= - \frac{1}{2} [\psi_{,u}(u^{(0)})]_s^l \cdot u^{(1)} + v [\psi_{,u}(u^{(0)})]_s^l \cdot L^{-1} [\psi_{,u}(u^{(0)})]_s^l \frac{H + \tilde{H} - 2J}{2}.$$

Hence, the whole solvability condition for  $\Phi_2$  becomes

$$\begin{aligned} 0 &= [-\partial^\circ + \partial_{ss} + \kappa^2] d_1 I - \frac{1}{2} [\psi_{,u}(u^{(0)})]_s^l u^{(1)} \\ &+ v \left( -\omega_1(u^{(0)}) I + [\psi_{,u}(u^{(0)})]_s^l \cdot L^{-1} [\psi_{,u}(u^{(0)})]_s^l \frac{H + \tilde{H} - 2J}{2} \right). \end{aligned} \quad (3.54)$$

Observe that, by (3.7b) and (3.7a),  $\partial^\circ d_1$  and  $(\partial_{ss} + \kappa^2) d_1$  are the first order corrections of the normal velocity and the curvature of  $\Gamma(t, s; \varepsilon)$ .

In the following, whenever  $\psi$  and its derivatives are evaluated at  $(U^{(0)}, \Phi^{(0)})$  this is denoted by the superscript  $^0$ . The conservation laws (3.37b) yield to order  $O(\varepsilon^0)$

$$-v \partial_z (\psi_{,uu}^0 U^{(1)} + \psi_{,u\varphi}^0 \Phi^{(1)}) + \partial^\circ \psi_{,u}^0 - (\partial^\circ d_1) \partial_z \psi_{,u}^0 = L \left[ \partial_{zz} U^{(2)} - \kappa \partial_z U^{(1)} + \partial_{ss} U^{(0)} \right] \quad (3.55)$$

### 3.3. SECOND ORDER ASYMPTOTICS IN THE TWO-PHASE CASE

where the independence of  $U^{(0)}$  on  $z$  was used. Integrating once with respect to  $z$  leads to

$$\begin{aligned}
 -L\partial_z U^{(2)} &= \underbrace{v\partial_z(\psi_{,uu}^0 U^{(1)} + \psi_{,u\varphi}^0 \Phi^{(1)}) - B}_{=:(s1)} \\
 &\quad + \underbrace{\int_0^z ((\partial^\circ d_1)\partial_z \psi_{,u}^0 - \partial^\circ \psi_{,u}^0) dz'}_{=:(s2)} - \underbrace{\kappa L U^{(1)}}_{=:(s3)} + L\partial_{ss} U^{(0)} z \quad (3.56)
 \end{aligned}$$

where  $B \in Y^N$  is an integration constant. The aim is now to derive a correction to the jump condition (3.53), i.e., a jump condition for  $u^{(1)}$ . Therefore only the terms contributing to  $\nabla u^{(1)} \cdot \nu$  in (3.13d) are of interest. Terms which are linear in  $z$  are abbreviated in the following as they are not needed. Applying (3.13b) to  $\Phi^{(1)}, U^{(1)}$  and using  $\tilde{h}'(0) = \tilde{h}'(1) = 0$  it is clear that

$$\begin{aligned}
 (s1) &\sim v(\psi_l)_{,uu}(u^{(0)})u^{(1)} - B + (\dots)z && \text{as } z \rightarrow \infty, \\
 &\sim v(\psi_s)_{,uu}(u^{(0)})u^{(1)} - B + (\dots)z && \text{as } z \rightarrow -\infty.
 \end{aligned}$$

Furthermore it holds that

$$\begin{aligned}
 (s2) &= (\partial^\circ d_1)(\psi_{,u}^0|_0^z) - \int_0^z [\partial^\circ((\psi_s)_{,u}^0) + (\partial^\circ \Psi_{,u}^0)(\tilde{h} \circ \Phi^{(0)})(z')] dz' \\
 &\sim \frac{1}{2}(\partial^\circ d_1)[\psi_{,u}(u^{(0)})]_s^l - (\partial^\circ(\psi_l)_{,u}(u^{(0)}))z + \partial^\circ[\psi_{,u}(u^{(0)})]_s^l \tilde{H} && \text{as } z \rightarrow \infty, \\
 &\sim -\frac{1}{2}(\partial^\circ d_1)[\psi_{,u}(u^{(0)})]_s^l - (\partial^\circ(\psi_s)_{,u}(u^{(0)}))z + \partial^\circ[\psi_{,u}(u^{(0)})]_s^l \tilde{H} && \text{as } z \rightarrow -\infty
 \end{aligned}$$

where for the first term the symmetry of  $\tilde{h}$  is used again. In (s3) identity (3.51) yields

$$(s3) = \kappa L u^{(1)}(t, s, 0) + (\dots)z \quad \text{as } z \rightarrow \pm\infty.$$

Finally the first order correction of the jump condition (3.53) on the phase boundary reads

$$[-L\nabla u^{(1)}]_s^l \cdot \nu = v[\psi_{,uu}(u^{(0)})]_s^l \cdot u^{(1)} + (\partial^\circ d_1)[\psi_{,u}(u^{(0)})]_s^l. \quad (3.57)$$

#### 3.3.4 Summary of the leading order problem and the correction problem

The problem to leading order consists of the bulk equation (3.40) which is coupled to the conditions (3.45), (3.53) and (3.48) (taking now the constants  $\sigma$  and  $\omega_0$  into account) on  $\Gamma(t; 0)$ :

(LOP) Find a function  $u^{(0)} : I \times D \rightarrow Y^N$  and a family of curves  $\{\Gamma(t; 0)\}_{t \in I}$  separating  $D$  into two domains  $D^l(t; 0)$  and  $D^s(t; 0)$  such that

$$\partial_t((\psi_l)_{,u}(u^{(0)})) = L\Delta u^{(0)}, \quad \text{in } D^l(t; 0), t \in I, \quad (3.58a)$$

$$\partial_t((\psi_s)_{,u}(u^{(0)})) = L\Delta u^{(0)}, \quad \text{in } D^s(t; 0), t \in I, \quad (3.58b)$$

such that

$$(L\nabla u^{(0)}) \cdot \nu_{ext} = 0 \quad \text{on } \partial D, t \in I, \quad (3.58c)$$

with the external unit normal  $\nu_{ext}$  of  $D$ , and such that on  $\Gamma(t; 0)$

$$u^{(0)} \text{ is continuous,} \quad (3.58d)$$

$$[-L\nabla u^{(0)}]_s^l \cdot \nu = v[\psi_{,u}(u^{(0)})]_s^l, \quad (3.58e)$$

$$\omega_0 v = \sigma \kappa - \frac{1}{2I}[\psi(u^{(0)})]_s^l \quad (3.58f)$$

for all  $t \in I$ , where  $\nu$  is the unit normal to  $\Gamma(t; 0)$  pointing into  $D^l(t; 0)$ .

If it holds that

$$\omega_1 = \omega_1(u^{(0)}) := [\psi_{,u}(u^{(0)})]_s^l \cdot L^{-1}[\psi_{,u}(u^{(0)})]_s^l \frac{H + \tilde{H} - 2J}{2I} \quad (3.59)$$

then the correction problem consisting of (3.41), (3.52), (3.57) and (3.54) reads as follows:

(CP) Let  $(u^{(0)}, \{\Gamma(t; 0)\}_t)$  be a solution to (LOP) and let  $l(t)$  be the length of  $\Gamma(t; 0)$  and set  $S_I = \{(t, s) : t \in I, s \in [0, l(t)]\}$ .

Then find functions  $u^{(1)} : I \times D \rightarrow Y^N$  and  $d_1 : S_I \rightarrow \mathbb{R}$  such that

$$\partial_t((\psi_l)_{,uu}(u^{(0)})u^{(1)}) = L\Delta u^{(1)}, \quad \text{in } D^l(t; 0), t \in I, \quad (3.60a)$$

$$\partial_t((\psi_s)_{,uu}(u^{(0)})u^{(1)}) = L\Delta u^{(1)}, \quad \text{in } D^s(t; 0), t \in I, \quad (3.60b)$$

such that

$$(L\nabla u^{(1)}) \cdot \nu_{ext} = 0 \quad \text{on } \partial D, t \in I, \quad (3.60c)$$

with the external unit normal  $\nu_{ext}$  of  $D$ , and such that on  $\Gamma(t; 0)$

$$u^{(1)} \text{ is continuous,} \quad (3.60d)$$

$$[-L\nabla u^{(1)}]_s^l \cdot \nu = v[\psi_{,uu}(u^{(0)})]_s^l u^{(1)} + (\partial^\circ d_1)[\psi_{,u}(u^{(0)})]_s^l, \quad (3.60e)$$

$$\omega_0(\partial^\circ d_1) = \sigma(\partial_{ss} + \kappa^2)d_1 - \frac{1}{2I}[\psi_{,u}(u^{(0)})]_s^l \cdot u^{(1)} \quad (3.60f)$$

for all  $t \in I$ .

Obviously,  $(u^{(1)}, d_1) \equiv 0$  is a solution given appropriate initial data. If this solution is unique then the leading order problem is approximated to second order in  $\varepsilon$  by the phase field model. The expansions (3.7a) and (3.7b) of curvature and normal velocity show that (CP) is in fact the linearisation of (LOP). It should be stated again that the choice (3.59) is crucial in order to guarantee that undesired terms in (3.54) vanish.

**3.5 Remark** If the diffusivity matrix  $L$  depends on  $u$  then equation (3.55) becomes

$$\begin{aligned} -v\partial_z(\psi_{,uu}^0 U^{(1)} + \psi_{,u\varphi}^0 \Phi^{(1)}) + \partial^\circ \psi_{,u}^0 - (\partial^\circ d_1)\partial_z \psi_{,u}^0 &= L(U^{(0)})\partial_{zz}U^{(2)} \\ + \partial_z(L_{,u}(U^{(0)})U^{(1)})\partial_z U^{(1)} + L_{,u}(U^{(0)})(\partial_s U^{(0)})^2 &+ L(U^{(0)})\partial_{ss}U^{(0)} - \kappa L(U^{(0)})\partial_z U^{(1)} \end{aligned}$$

resulting in

$$\begin{aligned} -L\partial_z U^{(2)} &= (s1) + (s2) \\ &\quad - \underbrace{\kappa L(U^{(0)})U^{(1)}}_{=(s3)} + \underbrace{L_{,u}(U^{(0)}) \cdot U^{(1)}\partial_z U^{(1)}}_{=:(s4)} + (L_{,u}(U^{(0)})(\partial_s U^{(0)})^2 + L(U^{(0)})\partial_{ss}U^{(0)})z \end{aligned}$$

instead of (3.56). The matching conditions (3.13a), (3.13b) and (3.13c) yield

$$(s4) = L_{,u}(u^{(0)}) \cdot u^{(1)}\nabla u^{(0)}(0^\pm) \cdot \nu + (\dots)z \quad \text{as } z \rightarrow \pm\infty.$$

This leads to an additional term in the jump condition of the correction problem. The condition (3.60e) now reads

$$[-L(u^{(0)})\nabla u^{(1)} - L_{,u}(u^{(0)}) \cdot u^{(1)}\nabla u^{(0)}]_s^l \cdot \nu = v[\psi_{,uu}(u^{(0)})]_s^l u^{(1)} + (\partial^\circ d_1)[\psi_{,u}(u^{(0)})]_s^l,$$

but this is still consistent with the above statement that (CP) is the linearisation of (LOP) as the additional term results from expanding  $L$  in a straightforward way.

### 3.4 Numerical simulations of test problems

Numerical simulations were performed in order to show that convergence to second order indicated by the analysis in the previous section can really be obtained. For this purpose, the  $\varepsilon$ -dependence of numerical solutions to the phase field system were analysed and, whenever available, compared with analytical solutions to the sharp interface problem.

The differential equations of the phase field system were discretised in space and time using finite differences on uniform grids with spatial mesh size  $\Delta x$  and time step  $\Delta t$ . The update in time was explicit, and to guarantee stability a time step  $\Delta t \lesssim \Delta x^2$  was chosen. If not otherwise stated, the mesh size  $\Delta x$  was decreased until being sure that the error due to the discretisation was negligible (cf. the example in Subsection 3.4.4).

The order of convergence in  $\varepsilon$  is always estimated by the following procedure: Assume that the  $\varepsilon$ -dependence of the error is approximately given by

$$Err(\varepsilon) = c_{err} \varepsilon^k + \text{higher order terms}$$

with a constant  $c_{err}$  and the exponent  $k > 0$  that is of interest. Given some  $m > 1$  (often,  $m = \sqrt{2}$  was chosen) it holds, up to higher terms, that

$$\frac{Err(\varepsilon) - Err(\frac{\varepsilon}{m})}{Err(\frac{\varepsilon}{m}) - Err(\frac{\varepsilon}{m^2})} = (\frac{1}{m})^{-k} = m^k,$$

from which  $k$  can be computed by inserting the measured values for  $Err(\varepsilon)$ .

#### 3.4.1 Scalar case in 1D

Let  $d = 1$  and  $N = 1$ . Setting  $u = u_0$  the following reduced grand canonical potential is postulated according to assumption B4:

$$\psi(u, \varphi) = \frac{1}{2}c_v u^2 + \lambda(u^m - u)(1 - \tilde{h}(\varphi)), \quad \text{i.e., } \Psi(u) = \lambda(u - u^m),$$

with constants  $\lambda$ ,  $u^m$  and  $c_v$ . Choosing  $w(\varphi) = \frac{9}{2}\varphi^2(1 - \varphi)^2$  as double-well potential the differential equations (3.37a) and (3.37b) read

$$\varepsilon(\omega_0 + \varepsilon\omega_1)\partial_t\varphi = \varepsilon\sigma\partial_{xx}\varphi - \frac{9\sigma}{\varepsilon}\varphi(1 - \varphi)(1 - 2\varphi) + \frac{1}{2}\lambda(u - u^m)h'(\varphi), \quad (3.61)$$

$$\partial_t\psi_{,u} = \partial_t(c_v u - \lambda(1 - \tilde{h}(\varphi))) = K\partial_{xx}u. \quad (3.62)$$

With these equations the following sharp interface problem ((LOP) of Subsection 3.3.4) for a single phase transition is approximated:

$$\begin{aligned} c_v\partial_t u &= K\partial_{xx}u, & \text{for } x \neq p(t), \\ u &\text{ is continuous} & \text{in } x = p(t), \\ \lambda p'(t) &= [-K\partial_x u]_s^l, & \text{in } x = p(t), \\ \omega_0 p'(t) &= \lambda(u^m - u), & \text{in } x = p(t), \end{aligned}$$

where  $p(t)$  denotes the position of the interface at time  $t$ . Imposing the boundary condition  $u \rightarrow u^\infty$  as  $x \rightarrow \infty$  there is the following travelling wave solution: Setting  $u^I := \frac{\lambda}{c_v} + u^\infty$  let

$$p(t) = vt = \frac{\lambda}{\omega_0}(u^m - u^I)t, \quad (3.63)$$

$$u = u^I, \quad x \leq vt, \quad (3.64)$$

$$u = u^\infty + (u^I - u^\infty) \exp(-K^{-1}c_v v(x - vt)), \quad x > vt. \quad (3.65)$$

### CHAPTER 3. ASYMPTOTIC ANALYSIS

For the interpolation functions  $\tilde{h}(\varphi) = h(\varphi) = \varphi^2(3-2\varphi)$  the constants can be computed explicitly:

$$I = \frac{1}{2}, \quad H + \tilde{H} - 2J = \frac{19}{90}.$$

Furthermore, if

$$\lambda = 0.5, \quad u^m = -1.0, \quad u^\infty = -2.0, \quad c_v = 1.0, \quad \omega_0 = 0.25, \quad K = 1.0, \quad \sigma = 1.0,$$

then the velocity  $v = 1.0$ , the value  $u^I = -1.5$  on the interface and, by (3.59), the correction term  $\omega_1 \approx 0.013194444$  are obtained.

The differential equations were solved on the time interval  $I = [0, 0.1]$  for several values for  $\varepsilon$  subject to Dirichlet boundary conditions for  $u$  given by the travelling wave solution (3.64), (3.65) to the sharp interface model and homogeneous Neumann boundary conditions for  $\varphi$ . To initialise  $\varphi$  the profile

$$\varphi(0, x) := \frac{1}{2} \left( 1 + \tanh \left( \frac{3}{2} z \right) \right) = \Phi^{(0)}(z), \quad z = \frac{x - x_0}{\varepsilon}, \quad (3.66)$$

was taken with some suitable initial transition point  $x_0$  such that the transition region (the set  $\{\varphi \in (\delta, 1-\delta)\}$  for some small  $\delta$ , e.g.,  $\delta = 10^{-3}$ ) remained away from the outer boundary during the evolution. The function  $\Phi^{(0)}$  is the solution to (3.42) with the boundary conditions  $\Phi^{(0)}(z) \rightarrow 1, 0$  as  $z \rightarrow \infty, -\infty$ . Initial values for  $u$  were obtained by matching outer and inner solution to leading and first order gained from the asymptotic expansions (cf. [LP88] for this technique),

$$u(0, x) = u^{(0)}(0, x) + \varepsilon u^{(1)}(0, x) + U^{(0)}(0, z) + \varepsilon U^{(1)}(0, z) - \text{common part}. \quad (3.67)$$

The function  $u^{(0)}(0, x)$ , the leading order solution to the energy equation (3.62), corresponds to the profile of the travelling wave solution:

$$u^{(0)}(0, x) = \begin{cases} u^\infty + (u^I - u^\infty) \exp\left(-\frac{c_v}{K} v(x - x_0)\right), & x > x_0, \\ u^I, & x \leq x_0. \end{cases} \quad (3.68)$$

As  $u^{(1)} \equiv 0$  is demanded to be a solution to the correction problem,  $u^{(1)}(0, x) = 0$  was chosen. Following equations (3.44) and (3.45) and the paragraph in between,  $U^{(0)} \equiv u^I$  is the constant interface value. Equation (3.13c) implies  $\partial_z U^{(1)}(z) \rightarrow \nabla \cdot u^{(0)}(x_0^-) = 0$  as  $z \rightarrow -\infty$ . Since  $u^{(1)}(0, x) = 0$ , equation (3.51) implies  $\bar{u} = -vL^{-1}[\psi_{,u}(u^{(0)})]_s^l \tilde{H} = -\frac{v}{K} \lambda \tilde{H}$ . From (3.50c) it then follows that, as  $z \rightarrow -\infty$ ,

$$\begin{aligned} 0 &\sim -L^{-1}(v(\psi_s)_{,u}(U^{(0)})z - Az) + vL^{-1}[\psi_{,u}(u^{(0)})]_s^l \tilde{H} + \bar{u} \\ &= L^{-1}(v(\psi_s)_{,u}(U^{(0)}) - A)z. \end{aligned}$$

Hence  $A = v(\psi_s)_{,u}(U^{(0)})$ , and (3.50a) yields

$$U^{(1)}(0, z) = \frac{v}{K} \begin{cases} \lambda - z + \int_0^z (1 - \tilde{h} \circ \varphi^{(0)})(z') dz' - \tilde{H}, & z > 0, \\ \lambda \int_z^0 (\tilde{h} \circ \varphi^{(0)})(z') dz' - \tilde{H}, & z < 0. \end{cases}$$

The common part is  $u^I - \frac{v\lambda}{K}z$  if  $z > 0$  and  $u^I$  if  $z < 0$  (cf. [LP88] on how to compute this term).

The phase boundaries  $\{\varphi = \frac{1}{2}\}$  were determined by linearly interpolating the values at the grid points. Subtracting from the computed transition point the exact position given by (3.63) yielded, up to the sign, the values in Fig. 3.1 on the left. It turns out that, when considering the correction term, the interface is too slow, but quadratic convergence is observed. Without the correction term  $\omega_1$  the interface is too fast, and larger errors occur indicating only linear convergence in  $\varepsilon$ . Similar results concerning the order of convergence hold true if

$$u(0, x) = u^{(0)}(0, x) \text{ or } \varphi = \chi_{[x_0, \infty]}$$



### 3.4. NUMERICAL SIMULATIONS OF TEST PROBLEMS

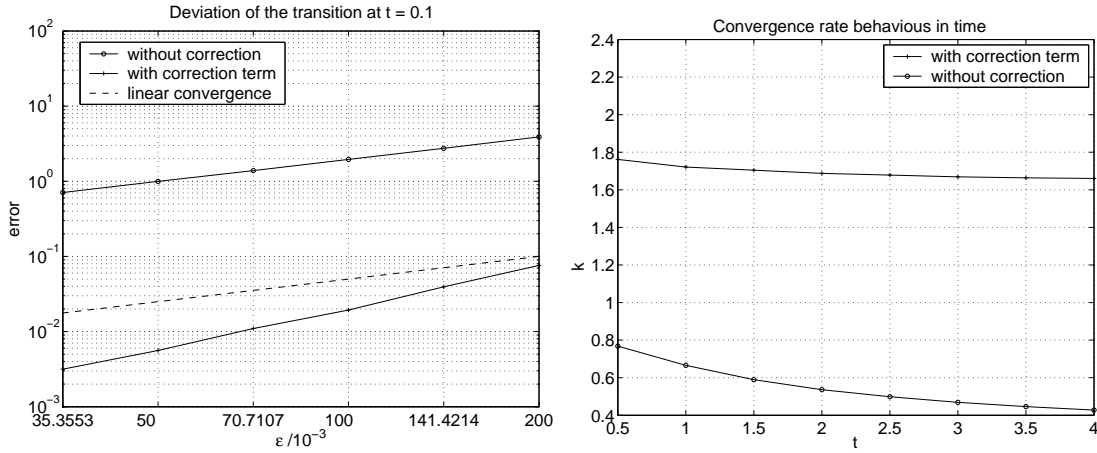


Figure 3.1: On the left: deviations of the phase boundaries measured from the exact interface position given by (3.63) over  $\varepsilon$ ; the resolution of the transition region is very fine such that the error caused by the discretisation is negligible; the dashed line indicates linear convergence in  $\varepsilon$ . On the right: behaviour of the numerically computed convergence rates in time for the angle  $\beta = 15^\circ$  (see Subsection 3.4.2).

was chosen as initial data instead of the above smooth functions. The only difference is that the errors are larger then.

In the above simulations, the transition regions were resolved by more than 100 grid points to determine the error and the convergence behaviour exactly. In applications, such resolutions of the interface are much too costly. Therefore, the same problem was simulated over the larger time interval  $I = [0, 8.0]$  with much less grid points in the interface. It was found that the  $\varepsilon/\Delta x$  ratio should be at least  $10/\sqrt{2}$ . The deviations at  $t = 8.0$  are:

With correction term				
$\Delta x \setminus \varepsilon$	0.4	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$
0.04	-0.06011	-0.05724	-0.08194	-0.14941
0.025	-0.04921	-0.03539	-0.03785	-0.05933
0.02	-0.04680	-0.03051	-0.02804	-0.03943

Without correction term							
$\Delta x \setminus \varepsilon$	0.4	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$	0.1	$\frac{0.1}{\sqrt{2}}$	0.05
0.04	0.58669	0.39191	0.22991	0.06608			
0.025	0.59902	0.41554	0.27636	0.15980			
0.02	0.60177	0.42083	0.28670	0.18033	0.08222		
0.0125				0.20204	0.12573	0.05428	
0.01					0.13548	0.07393	0.00792
0.00625						0.09479	0.05016

Again, the errors are much larger without correction term. To get an error as obtained with correction term,  $\varepsilon$  and  $\Delta x$  must be set eight times smaller. When using explicit methods the expenditure becomes 8 times larger if the grid constant is halved due to the stability constraint  $\Delta t \lesssim \Delta x^2$  for the time step. Hence, in the above example, the costs without the correction term are  $8^3 = 512$  times larger to obtain the same size of the error.

### 3.4.2 Scalar case in 2D

Now let  $N = 1$  and  $d = 2$  and consider the same reduced grand canonical potential as in Subsection 3.4.1. Instead of the smooth double-well potential an obstacle potential with two wells was used:

$$w_{ob}(\varphi) = \begin{cases} \frac{8}{\pi^2}\varphi(1-\varphi), & 0 \leq \varphi \leq 1, \\ \infty & \text{elsewhere.} \end{cases}$$

Then (3.61) has to be replaced by the variational inequality

$$0 \leq \int_{-\infty}^{\infty} \left( (\varepsilon(\omega_0 + \varepsilon\omega_1)\partial_t\varphi + \frac{\sigma}{\varepsilon}(w_{ob})_{,\varphi}(\varphi) - \frac{1}{2}\Psi(u)h'(\varphi))(\eta - \varphi) + \varepsilon\sigma\partial_x\varphi\partial_x(\eta - \varphi) \right) dx$$

for test functions  $\eta \in C_0^\infty(\mathbb{R}, [0, 1])$ , but the asymptotic analysis can be done in a similar way (cf. [BE93]). The main advantage of such a potential is that the stable minima 0 and 1 of  $w$  are attained outside of the interfacial region, and the phase field equations only have to be solved in the thin interfacial layer around the approximated phase boundary. The equation (3.62) for  $u$  remains the same except that  $\partial_{xx}$  is replaced by the Laplacian  $\Delta$ .

With the constants

$$\lambda = 0.5, u^m = 2.0, c_v = 1.0, \omega_0 = 0.25, K = 0.1, \sigma = 0.1$$

the evolution of a radial interface was simulated. Initially, for  $\varphi$  the profile

$$\varphi(0, x) = \begin{cases} 0, & -\infty < z \leq -\frac{\pi^2}{8}, \\ \frac{1}{2}(1 + \sin(\frac{4z}{\pi})), & -\frac{\pi^2}{8} \leq z \leq \frac{\pi^2}{8}, \\ 1, & \frac{\pi^2}{8} \leq z < \infty, \end{cases} \quad z = \frac{r - r_0}{\varepsilon},$$

was used which is the solution to the variational inequality corresponding to (3.42) when restricted to a radial direction. Here,  $r = \sqrt{x^2 + y^2}$  is the radius, and the initial radius  $r_0 = 0.8$  was chosen. With  $\tilde{h}(\varphi) = h(\varphi) = \varphi^2(3 - 2\varphi)$  the constants are  $I = \frac{1}{2}$ ,  $H + \tilde{H} - 2J = \frac{23\pi^2}{1024}$ , and hence

$$\omega_1 = \frac{\lambda^2 H + \tilde{H} - 2J}{K} \approx 0.554201419.$$

For  $u$  initially the 1D profile (3.68) of the travelling wave solution in Subsection 3.4.1 in radial direction was taken. As in the 1D case  $u^I = -1.5$ ,  $v = \frac{\omega_0}{\lambda}(u^m - u^I) = 0.25$  and  $u^\infty = -2.0$ .

For a first set of simulations the domain  $D = [0, 2]^2$  was considered. The grid constant was fixed and set to  $\Delta x = 0.004$ , but  $\varepsilon$  was changed. At different times the distance of the level set  $\varphi = \frac{1}{2}$  from the origin depending on the angle  $\beta$  with the  $x$ -direction was measured. Again, the values at the grid points were linearly interpolated. This procedure resulted in the following values at  $t = 0.5$ :

	without correction			with correction		
	$\beta = 20^\circ$	$\beta = 15^\circ$	$\beta = 0^\circ$	$\beta = 20^\circ$	$\beta = 15^\circ$	$\beta = 0^\circ$
$\varepsilon = 0.2$	1.276891	1.277098	1.277356	1.122416	1.122630	1.122895
$\varepsilon = 0.141421356$	1.239878	1.240082	1.240335	1.131427	1.131635	1.131896
$\varepsilon = 0.1$	1.212321	1.212519	1.212761	1.137193	1.137395	1.137644
$k$	0.851281	0.850897	0.850106	1.287845	1.289176	1.293952

The distances as well as the order of convergence do not essentially depend on the angle. The order of convergence is much better if the correction term is taken into account. Besides the change in the radius when changing  $\varepsilon$  is much smaller if a correction  $\omega_1$  is considered.

For a second set of simulations the larger domain  $D = [0, 8]^2$  with the fixed grid constant  $\Delta x = 0.02$  allowing for larger time intervals in acceptable computation time was considered. The same measurements as above were done at  $t = 1.5$ :

### 3.4. NUMERICAL SIMULATIONS OF TEST PROBLEMS

	without correction			with correction		
	$\beta = 20^\circ$	$\beta = 15^\circ$	$\beta = 0^\circ$	$\beta = 20^\circ$	$\beta = 15^\circ$	$\beta = 0^\circ$
$\varepsilon = 0.2$	2.398226	2.398924	2.399661	1.851693	1.852492	1.853469
$\varepsilon = 0.141421356$	2.277925	2.278367	2.278668	1.889131	1.889779	1.890377
$\varepsilon = 0.1$	2.180093	2.180095	2.179580	1.910175	1.910433	1.910311
k	0.596551	0.589719	0.576271	1.662103	1.704448	1.777240

The results are qualitatively the same as before. Fig. 3.1 shows that, in both cases, the convergence rates decrease in time. At  $t = 0.05$ , convergence rates of about 1.76 (with correction term) and 0.79 (without) on the coarsen grid are obtained while before, on the finer grid, the values are about 1.29 and 0.85. This demonstrates that the numerical computation of the order of convergence must be considered with care. In particular, it is indispensable to assess the measured values for the phase transitions itself.

#### 3.4.3 Binary isothermal systems

To model phase transformations in systems with non-trivial, non-linearised phase diagrams (see, for example, Fig. (3.2)) a  $u$ -dependent correction term has to be introduced. In this subsection it is demonstrated that the approach with the correction term in fact enables to obtain a superior approximation behaviour in this case as well.

Since  $(u_1, u_2) \in T\Sigma^2$  it is sufficient to consider  $u_1$ . The following reduced grand canonical potential is postulated:

$$\psi(u_0, u_1, \varphi) = \frac{1}{2}((u_0)^2 + (u_1)^2) + (\lambda(u_0 - u_{ref}) + G(u_1)^2(3 - 2u_1))(1 - \tilde{h}(\varphi))$$

with constants  $u_{ref} = -1.0$ ,  $\lambda = G = 0.1$ . The two phases  $l$  and  $s$  are in equilibrium if  $[\psi(u)]_s^l = 0$  by (2.26). Here the equilibrium condition reads

$$u_0 = u_{ref} - \frac{G}{\lambda}(u_1)^2(3 - 2u_1). \quad (3.69)$$

From this condition the phase diagram in Fig. 3.2 can be constructed using the relations  $T = \frac{-1}{u_0}$  and  $c_1 = \psi_{,u_1} = u_1 - 6Gh_s(\varphi)u_1(1 - u_1)$  where  $h_s(\varphi) := 1 - \tilde{h}(\varphi)$ . Besides it holds that

$$[c_1(u_1)]_s^l = 6Gu_1(1 - u_1).$$

For the isothermal case, i.e.,  $u_0$  is constant, equation (3.37a) and

$$\partial_t c_1(u_1) = \partial_t \psi_{,u_1}(u_1) = D_{mass} \partial_{xx} u_1$$

were numerically solved in the domain  $D = [0, 28]$  for  $t \in [0, 40]$ . The mass diffusivity  $D_{mass} = 0.4$  was taken. Homogeneous Neumann boundary conditions were imposed. Initially, for  $u_1$  a profile as in (3.68) for  $u_0$  was chosen,

$$u_1(0, x) = \begin{cases} u_{1,\infty} + (u_1^I - u_{1,\infty}) \exp(-\frac{1}{D_{mass}}v(x - x_0)), & x > x_0, \\ u_1^I, & x \leq x_0. \end{cases} \quad (3.70)$$

By

$$u_1 = \begin{cases} c_1, & h_s(\varphi) = 0, \\ \frac{1}{12Gh_s(\varphi)} (6Gh_s(\varphi) - 1 + \sqrt{(6Gh_s(\varphi) - 1)^2 + 24Gh_s(\varphi)c_1}), & h_s(\varphi) > 0, \end{cases}$$

the potential is expressed as a function in  $(c_1, \varphi)$ . Because of the fraction, this is numerically unstable as  $h_s(\varphi) \rightarrow 0$ . The value  $u_1 = c_1$  was taken if  $6Gh_s(\varphi) \leq 10^{-4}$ , but checks were done with different cut off values. The following results do not essentially depend on the cut off value.

Choosing  $u_1^I = 0.6$  for the interface value, the equilibrium concentrations are  $c_1^{(l)} = 0.6$  and  $c_1^{(s)} = 0.456$ . To model the solidification of an alloy of concentration 0.456,  $c_1^{(l)}$  and  $u_1$  decayed exponentially to this value by setting  $u_{1,\infty} = 0.456$ . For  $u_1 = u_1^I = 0.6$  the equilibrium value for  $u_0$  is  $u_{0,eq} \approx -1.648$  which corresponds to a temperature of  $T_{eq} \approx 0.6067$ . To make the front move the system was undercooled with a temperature of  $T = 0.55$ , i.e.,  $u_0 \equiv \frac{-1}{0.55}$ . Formula (3.63) yields an estimation of the initial velocity of the front: with  $\omega_0 = 0.08$  it holds that  $v \approx \frac{\lambda}{\omega_0}(u_{0,eq} - u_0) \approx 0.2$ . The initial position of the front  $x_0 = 8.0$  was appropriately chosen such that there was no interaction with the external boundary. Initial values for  $\varphi$  again were defined as in (3.66). By (3.59), the correction term is ( $h$  and  $\tilde{h}$  are chosen as before)

$$\omega_1(u_1) = \frac{([c_1(u_1)]_s^l)^2}{D_{mass}} \frac{H + \tilde{H} + J}{2I}.$$

Equation (3.70) does not describe the profile of a travelling wave solution, but a nearly travelling wave solution is observed (see Fig. 3.2). The following transition points of  $\varphi$  were computed: At  $t = 10.0$

$\Delta x \backslash \varepsilon$	without correction				with correction			
	0.4	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$	0.4	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$
0.04	10.1909	10.1605	10.1332	10.1019	10.0922	10.0917	10.0851	10.0682
0.025	10.1938	10.1661	10.1440	10.1240	10.0949	10.0970	10.0957	10.0901
0.02	10.1945	10.1674	10.1465	10.1289	10.0955	10.0982	10.0981	10.0950

and at  $t = 20.0$

$\Delta x \backslash \varepsilon$	without correction				with correction			
	0.4	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$	0.4	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$
0.04	12.3851	12.3232	12.2675	12.2049	12.1859	12.1843	12.1709	12.1375
0.025	12.3910	12.3344	12.2896	12.2491	12.1915	12.1952	12.1922	12.1811
0.02	12.3923	12.3369	12.2945	12.2589	12.1928	12.1976	12.1971	12.1907

In view of the positions with correction term it is remarkable that the behaviour in  $\varepsilon$  is not monotone, but comparing the values for the different grids it seems that this behaviour can be explained by numerical errors. If the correction term is considered and if the ratio  $\varepsilon/\Delta x$  is small enough (as was already mentioned in Subsection (3.4.1), a ratio of  $5\sqrt{2}$  is sufficient which means that for  $\varepsilon = 0.2/\sqrt{2}$  a grid spacing of  $\Delta x = 0.02$  is necessary) then the changes in the interface position are of order  $10^{-3}$  when changing  $\varepsilon$ . If the correction term is not considered deviations of several grid points are possible. This behaviour in  $\varepsilon$  indicates that the approximation of the sharp interface solution (an explicit solution to the corresponding sharp interface model to compare with is not known) is improved thanks to the correction term.

### 3.4.4 Binary non-isothermal case

A better convergence behaviour can also be observed if multiple conserved quantities are considered. The following reduced grand canonical potential is postulated:

$$\psi(u_0, u_1) = \frac{1}{2}((u_0)^2 + (u_1)^2) + (\lambda(u_0 - u_{ref}) + G(u_1 - u_e))(1 - \tilde{h}(\varphi))$$

with constants  $u_{ref} = -1.0$ ,  $u_e = 0.6$ ,  $\lambda = G = 0.2$ . For the energy  $e = \psi_{,u_0}$  the flux  $K\nabla u_0$  with  $K = 4.0$  and for the concentration  $c_1 = \psi_{,u_1}$  the flux  $D_{mass}\nabla u_1$  with  $D_{mass} = 0.1$  is postulated, i.e., there are no cross effects between mass and energy diffusion. Since  $[c_1(u)]_s^l = G$  and  $[e(u)]_s^l = \lambda$  are independent of  $u$  the correction term ( $h$  and  $\tilde{h}$  are chosen as above)

$$\omega_1 = \left( \frac{\lambda^2}{K} + \frac{G^2}{D_{mass}} \right) \frac{H + \tilde{H} - 2J}{2I} \approx 0.8655555$$

### 3.4. NUMERICAL SIMULATIONS OF TEST PROBLEMS

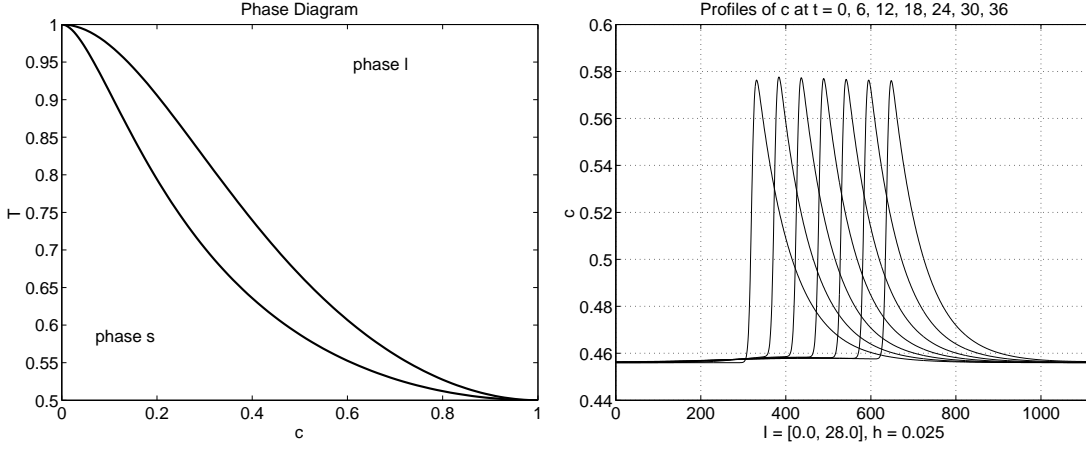


Figure 3.2: On the left: phase diagram for a binary mixture computed from (3.69);  $c = c_1$ . On the right: profiles of the solution  $c = c_1$  for the binary system in Subsection 3.4.3 during the evolution,  $\varepsilon = 0.4$ ; the figure indicates already that there is only a negligible influence of the boundary conditions on the evolution as gradients of  $c_1$  don't vanish only in the transition region. But simulations on domains with different lengths were performed to verify this conjecture.

is constant. Usually temperature diffusivity is much faster than mass diffusivity so that the influence of the concentration part on the correction term is much larger.

In equilibrium (cf. (2.26) in Subsection 2.4.1 for the conditions) the linear relation  $u_{1,eq} - u_e = u_{0,eq} - u_{ref}$  holds. For  $u_1 = u_e = 0.6$  and  $u_0 = u_{ref} = -1.0$  ( $\rightsquigarrow T^{(0)} = T_{ref} = 1.0$ ) the equilibrium concentrations are  $c_1^{(l)} = u_1 = 0.6$  and  $c_1^{(s)} = u_1 - G = 0.4$ .

The differential equations were solved for  $x \in D = [0.0, 1.4]$  and  $t \in I = [0.0, 0.5]$ . Initial values for  $\varphi$  again were defined as in (3.66) with an interface located at  $x_0 = 0.6$  away from the boundaries. Setting  $u_1(t = 0) \equiv 0.6$  and  $u_0(t = 0) \equiv -1.0$ , initial values for  $c_1$  and  $e$  were obtained from  $\psi$ . For  $\varphi$  and  $u_1$  homogeneous Neumann boundary conditions were imposed. The same boundary condition was imposed for  $u_0$  in  $x = 1.4$ , but on the other boundary point the Dirichlet boundary condition  $u_0(x = 0.0) = -1.25$  was imposed which corresponds to an undercooling of  $\frac{1}{5}$  and made the transition point move. Setting  $\omega_0 = 0.08$  and  $\sigma = 1.0$  and, at  $t = 0.4$ , measuring the interface position the following results were obtained:

	$\Delta x \setminus \varepsilon$	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$	0.1	$\frac{0.1}{\sqrt{2}}$
with correction	0.002	0.704470	0.708335	0.710319		
	0.001			0.710339	0.711441	0.712032
without correction	0.002	0.730570	0.726796	0.723258		
	0.001			0.723281	0.720480	0.718347

The computations for  $\varepsilon = \frac{0.2}{\sqrt{2}}$  reveal that the error due to the grid is small compared to the deviation due to the different values for  $\varepsilon$ . Computing numerically the order of convergence yielded the values  $k \approx 1.8$  with correction term and  $k \approx 0.6$  without correction term when comparing the runs for  $\varepsilon \in \{\frac{0.4}{\sqrt{2}}, \frac{0.2}{\sqrt{2}}, \frac{0.1}{\sqrt{2}}\}$ . Similar results were obtained at  $t = 0.5$ :

	$\Delta x \setminus \varepsilon$	$\frac{0.4}{\sqrt{2}}$	0.2	$\frac{0.2}{\sqrt{2}}$	0.1	$\frac{0.1}{\sqrt{2}}$
with correction	0.002	0.738533	0.743021	0.745364		
	0.001			0.745390	0.746678	0.747364
without correction	0.002	0.772149	0.766629	0.761871		
	0.001			0.761900	0.758197	0.755408



## Chapter 4

# Existence of Weak Solutions

The goal of this chapter is to show that weak solutions  $(u, \phi)$  exist to the system of parabolic differential equations

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

where  $0 \leq i \leq N$  and  $1 \leq \alpha \leq M$  with  $\lambda$  given by

$$\lambda = \frac{1}{M} \sum_{\alpha=1}^M (\nabla \cdot a_{,\nabla \phi_\alpha}(\phi, \nabla \phi) - a_{,\phi_\alpha}(\phi, \nabla \phi) - w_{,\phi_\alpha}(\phi) + \psi_{,\phi_\alpha}(u, \phi))$$

as stated in Definition 2.5 in Subsection 2.4.3 (the  $\varepsilon$  is dropped since it is not essential any more for the following analysis). In view of reduced grand canonical potentials as in Subsection 2.4.2 difficulties arise from the growth properties of such potentials  $\psi$ . First, the fact that  $\psi \rightarrow \infty$  if the temperature tends to infinity, i.e., if  $u_0 \nearrow 0$ , must be handled. Second, a linear growth of  $\psi$  in  $\tilde{u} = (u_1, \dots, u_N)$  means that a control of terms involving  $\psi_{,u}$  in general do not provide much information or a control of  $u$  itself any more, in contrast to the case of a quadratically growing  $\psi$ .

To precise these problems, suppose that the existence of solutions to approximating problems can be shown as, for example, a Galerkin approximation or solutions to a time discrete problem (here, a perturbation method will be used). In order to obtain a solution to the original problem from the approximations, often, convergence in certain  $L^p$  spaces is necessary. In view of the Riesz theorem, estimates of differences of the form  $f(x+h) - f(x)$  for small  $h$  are needed which are usually obtained from a priori estimates. In the case of parabolic differential equations the term with the time derivative yields a control of terms involving time differences, but in the present case only for  $\psi_{,u}$ , and the above stated growth properties make it difficult to deduce a control of time differences for  $u$ .

Not only the time differences impose difficulties. Standard a priori estimates gained by testing the first equation with  $u_i$  and the second one with  $\partial_t \phi_\alpha$  yield a bound for  $\nabla u$  in  $L^2$  from the diffusion term. But the weak growth of  $\psi$  in  $u$  provides no estimate of  $u$ , whence the mass of  $u$  is not under control. In order to overcome this problem, suitable boundary conditions differing from the conditions in Definition 2.5, i.e., (2.32e) and (2.32g), are imposed, namely Robin boundary conditions of the form

$$-\sum_{j=0}^N L_{ij}(\psi_{,u}(u, \phi), \phi) \nabla u_j \cdot \nu_{ext} = \sum_{j=0}^N \beta_{ij}(u_j - u_{bc,j})$$

where  $0 \leq i \leq N$ . The function  $u_{bc} = (u_{bc,0}, \dots, u_{bc,N}) : I \times \partial\Omega \rightarrow Y^N$  and the coefficient matrix  $\beta = (\beta_{ij})_{i,j}$  have to fulfil certain consistence conditions which will later be stated precisely. Then

these boundary conditions provide a control of  $u$  on the boundary of the domain under consideration, hence the Poincaré inequality gives the desired control.

The procedure applied in the present work is as follows: First, a reduced grand canonical potential of quadratic growth in  $u$  is considered. The terms of strongest growth are not multiplicatively coupled to the phase field variables which means that there are restrictions on how to interpolate given potentials  $\psi^{(\alpha)}$  for the possible phases in the sense of (2.28). Existence of weak solutions is shown using the Galerkin method. Thanks to the quadratic growth, the above stated difficulties do not arise, and generically derived estimates are sufficient for the limiting procedure.

The idea to solve the alloy problem is then to approximate a potential  $\psi$  of linear growth in  $u$  by potentials  $\psi^{(\nu)} = \psi + \nu|\tilde{u}|^2$  of quadratic growth and let  $\nu \searrow 0$ . Applying methods of Alt and Luckhaus [AL83], this procedure successfully generates a weak solution to the limiting problem.

Under a strong assumption on the diffusion matrix, namely, the exclusion of cross effects in mass and energy diffusion, it is also possible to manage the terms of the structure  $g^{(0)}(u_0) := -\ln(-u_0)$  in the example in Subsection 2.4.2 for  $\psi$ . Here, an approximation  $g^{(\eta)}(u_0)$  of quadratic growth is used and ideas of Alt and Pawlow [AP93] are applied when letting  $\eta \searrow 0$ . Unfortunately, the last limiting procedure is only possible for potentials  $\psi^{(\eta)}$  of quadratic growth in  $\tilde{u}$ , whence the problem corresponding to the example in Subsection 2.4.2 still remains open. This is because mixed terms of the form  $|u_0(t+h) - u_0(t)||\tilde{u}(t+h) - \tilde{u}(t)|$  appear and cannot be appropriately estimated. It should be remarked that Luckhaus and Visintin [LV83] can show existence of a weak solution in this case, but without coupling to phase field equations. Their work is based on [AL83], and they use an approximation of  $g^{(0)}$  with function of linear growth. They need a strong assumption on the energy flux to obtain  $u_0 < 0$  in the limit. Eck [Eck04] proved existence and uniqueness of weak solutions to a model for a binary mixture involving two conserved quantities (internal energy and concentration of one of the components). Allowing for a free energy density as in Subsection 2.4.2 the problem is formulated in terms of the temperature and the concentration. The energy equation is linearised in the temperature by appropriate choice of the temperature diffusion coefficient similarly as in Subsection 2.3.2. But a degenerate mass diffusivity of the form  $Dc(1-c)$ ,  $D$  being a material constant and  $c$  the concentration, is considered. Some additional difficulties arise from anisotropic surface energies.

A remark on the phase field equations: Since the focus lies on handling  $u$  and  $\psi$ , the functions for the phase field variables  $a$  and  $w$  are 'nice' in the sense that the managing of the order parameters is kept simple throughout this chapter. In particular, the same boundary conditions as in (2.32f), namely

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

are imposed. Special difficulties do not appear except perhaps in the coupling term to the thermodynamic potentials  $\psi, \phi$ . In works of Colli, Gajewski, Horn, Krejčí, Rocca, Sprekels, Zheng et al. (for instance cf. [SZ03, KRS05], but see also the references therein), non-local models for the phase field variables and the temperature are considered where again the difficulties due to the logarithmic term in the free energy density (corresponding to the term  $g^{(0)}$  in the reduced grand canonical potential) appear. Multiple conserved quantities are not considered there. Concerning the Penrose-Fife model in Subsection 2.3.2, which is the simplest model involving the above stated difficulties, the articles of Horn et al. and Klein [HLS96, Kle02] should be mentioned.

Necessary for a well-posed problem are initial conditions

$$u(t=0) = u_{ic}, \quad \phi(t=0) = \phi_{ic}$$

as in (2.32d). It is clear that they must fulfil certain consistence conditions. For example, when considering the problem involving  $g^{(0)} = -\ln(-u_0)$  the initial value for  $u_0$  should satisfy  $u_{0,ic} < 0$ .

In this chapter, numerous estimates appear involving constants independent of the variables but only from given data as the considered domain  $\Omega$ , the time interval  $I = [0, T]$  etc. In spite of the fact that they may change from line to line they remain denoted by  $C$ .



When applying compactness methods, convergence results in general only hold for subsequences. For shorter presentation, throughout this chapter this is usually not explicitly stated, and it was abstained from an indication on the indices. Moreover, the isometric isomorphisms  $L^p(I \times \Omega) \cong L^p(I; L^p(\Omega))$  often are implicitly applied.

Several theorems and results used in this chapter are listed in Appendix D (without proof but references), namely, results on Dirac sequences, the Picard-Lindelöf theorem, the Lebesgue dominated convergence theorem, Rellich and Sobolev embeddings, the Poincaré inequality, a trace theorem, the Riesz theorem, and the Gronwall lemma. In the following, precise references to these facts are therefore sometimes omitted.

## 4.1 Quadratic reduced grand canonical potentials

### 4.1.1 Assumptions and existence result

Let  $\Omega \subset \mathbb{R}^d$  be an open bounded domain with Lipschitz boundary,  $d \in \{1, 2, 3\}$ , and  $I = (0, T) \subset \mathbb{R}$  a time interval. Definition 1.1 motivates the following definition involving functions mapping to  $\Sigma^K$ :

**4.1 Definition** *Let  $D \subset \mathbb{R}^k$  together with the Lebesgue measure. The space  $H^1(D; \mathbb{H}\Sigma^M)$  consists of all measurable functions  $\phi : D \rightarrow \mathbb{H}\Sigma^M$  such that the square of  $\phi$  and the square of its weak derivative  $\nabla\phi : D \rightarrow (\mathbb{T}\Sigma^M)^d$  are integrable. The space  $H^1(D; \mathbb{T}\Sigma^M)$  is defined analogously.*

Let  $Y^N := \mathbb{R} \times \mathbb{T}\Sigma^N$ . The tangent space of  $Y^N$  in some point  $y \in Y^N$  can naturally be identified with  $Y^N$  again so that also the space  $H^1(D; Y^N)$  becomes well defined. The set  $D$  stands for  $\Omega$  or  $I \times \Omega$ .

Assume the following:

E1 The reduced canonical potential satisfies

$$\psi \in C^{2,1}(Y^N \times \mathbb{H}\Sigma^M), \quad (4.1a)$$

$$v \cdot \psi_{,uu}(u, \phi)v \geq k_0|v|^2 \quad \forall v \in Y^N, \quad (4.1b)$$

$$|w \cdot \psi_{,uu}(u, \phi)v| \leq k_1|w||v| \quad \forall w, v \in Y^N, \quad (4.1c)$$

$$|\psi_{,\phi}(u, \phi) \cdot \zeta| \leq k_2(1 + |u|) \quad \forall \zeta \in \mathbb{T}\Sigma^M, \quad (4.1d)$$

$$|v \cdot \psi_{,u\phi}(u, \phi)\zeta| \leq k_3|v||\zeta| \quad \forall v \in Y^N, \zeta \in \mathbb{T}\Sigma^M, \quad (4.1e)$$

$$|\psi(0, \phi)| \leq k_4, \quad (4.1f)$$

$$|\psi_{,u}(u, \phi) \cdot v| \leq k_5(1 + |u|)|v| \quad \forall v \in Y^N, \quad (4.1g)$$

$$|\psi(u, \phi)| \leq k_6(1 + |u|^2), \quad (4.1h)$$

$$(\psi_{,uu}(\cdot))^{-1} \in C^{0,1}(Y^N \times \mathbb{H}\Sigma^M, \text{Lin}(Y^N, Y^N)), \quad (4.1i)$$

for all  $(u, \phi) \in Y^N \times \mathbb{H}\Sigma^M$  where the  $k_i$  are positive constants. It should be remarked that the assumption (4.1i) indeed is redundant but follows already from (4.1a)–(4.1c). This is shown in Lemma 4.7 in Subsection 4.2.2. For completeness, it has been listed again.

E2 For the Onsager coefficients it holds that

$$L_{ij} \in C^{0,1}(Y^N \times \mathbb{H}\Sigma^M) \cap L^\infty(Y^N \times \mathbb{H}\Sigma^M). \quad (4.2a)$$

Uniformly in its arguments the coefficient matrix fulfils

$$L = (L_{ij})_{i,j=0}^N \text{ is symmetric and positive semi-definite,} \quad (4.2b)$$

$$\ker(L) = \text{span}\{(0, 1, \dots, 1) \in \mathbb{R}^{N+1}\} = (Y^N)^\perp. \quad (4.2c)$$

## CHAPTER 4. EXISTENCE OF WEAK SOLUTIONS

---

Moreover, when restricting the matrix  $L$  on  $Y^N$ , the smallest eigenvalue is uniformly bounded away from zero, and the largest eigenvalue is uniformly bounded away from infinity,

$$v \cdot L(y, \phi)v \geq l_0|v|^2 \quad \forall v \in Y^N, (y, \phi) \in Y^N \times \mathbf{H}\Sigma^M \quad (4.2d)$$

$$w \cdot L(y, \phi)v \leq L_0|w||v| \quad \forall w, v \in Y^N, (y, \phi) \in Y^N \times \mathbf{H}\Sigma^M \quad (4.2e)$$

where  $0 < l_0 \leq L_0$  are constants and  $|\cdot|$  is the Euclidian norm on  $Y^N$  induced from  $\mathbb{R}^{N+1}$ .

E3 The multi-well potential  $w(\phi)$  satisfies for all  $\phi \in \mathbf{H}\Sigma^M$

$$w \in C^1(\mathbf{H}\Sigma^M), \quad (4.3a)$$

$$|w(\phi)| \leq w_0(1 + |\phi|^p), \quad (4.3b)$$

$$|w_{,\phi}(\phi)| \leq w_1(1 + |\phi|^{p-1}), \quad (4.3c)$$

$$w(\phi) \geq w_2|\phi|^p - w_3, \quad (4.3d)$$

where the  $w_i$  are positive constants. Here,  $p > 2$  is such that  $1 - \frac{d}{2} > -\frac{d}{p}$  or, equivalently,  $p < 6$  if  $d = 3$  and  $p < \infty$  if  $d \leq 2$ . Observe that by Theorem D.4  $H^1(\Omega) \hookrightarrow L^p(\Omega)$  is compact, and if  $\phi \in L^p(I \times \Omega; \mathbf{H}\Sigma^M)$  then  $w_{,\phi}(\phi) \in L^{p^*}(I \times \Omega; \mathbf{T}\Sigma^M)$  with  $p^* = \frac{p}{p-1}$  the dual exponent to  $p$ .

E4 The gradient term  $a(\phi, \nabla\phi)$  fulfils

$$a \in C^{1,1}(\mathbf{H}\Sigma^M \times (\mathbf{T}\Sigma^M)^d), \quad (4.4a)$$

$$a(\phi, X) \geq a_0|X|^2, \quad (4.4b)$$

$$a(\phi, X) \leq a_1(|\phi|^2 + |X|^2), \quad (4.4c)$$

$$a_{,\phi}(\phi, X) \leq a_2(|\phi| + |X|), \quad (4.4d)$$

$$a_{,\nabla\phi}(\phi, X) \leq a_3(|\phi| + |X|), \quad (4.4e)$$

$$(a_{,\nabla\phi}(\phi, X) - a_{,\nabla\phi}(\phi, \hat{X})) : (X - \hat{X}) \geq a_4|X - \hat{X}|^2, \quad (4.4f)$$

for all  $\phi \in \mathbf{H}\Sigma^M$  and  $X, \hat{X} \in (\mathbf{T}\Sigma^M)^d$  where the  $a_i$  are positive constants.

E5 The kinetic coefficient satisfies

$$\omega \in C^{0,1}(\mathbf{H}\Sigma^M \times (\mathbf{T}\Sigma^M)^d), \quad (4.5a)$$

$$\omega(\phi, X) \geq \omega_0, \quad (4.5b)$$

$$\omega(\phi, X) \leq \omega_1, \quad (4.5c)$$

$$(\omega(\cdot))^{-1} \in C^{0,1}(\mathbf{H}\Sigma^M \times (\mathbf{T}\Sigma^M)^d), \quad (4.5d)$$

for all  $\phi \in \mathbf{H}\Sigma^M$  and  $X \in (\mathbf{T}\Sigma^M)^d$  where the  $\omega_i$  are positive constants. Condition (4.5d) follows from (4.5a)–(4.5c) (see Lemma 4.7) and has only been stated for completeness. In general, assumption (4.5a) is in conflict with (2.8b) since the homogeneity of degree zero can cause  $\omega$  to jump in  $X = 0$ . In a small ball around  $X = 0$  it may therefore be necessary to smooth out the kinetic coefficient for the (4.5a) is fulfilled.

E6 The initial data fulfil

$$u_{ic} \in L^2(\Omega; Y^N), \quad \phi_{ic} \in H^1(\Omega; \Sigma^M) \cap L^\infty(\Omega; \Sigma^M). \quad (4.6a)$$

and are such that

$$\int_{\Omega} \left[ \psi_{,u}(u_{ic}, \phi_{ic}) \cdot u_{ic} - \psi(u_{ic}, \phi_{ic}) + w(\phi_{ic}) + |\nabla\phi_{ic}|^2 \right] dx \leq C. \quad (4.6b)$$

Observe that it follows already from (4.3b) and (4.6a) that  $w(\phi_{ic}) \in L^1(\Omega)$  and  $|\nabla\phi_{ic}|^2 \in L^1(\Omega)$  whence the two last terms could be dropped.

## 4.1. QUADRATIC REDUCED GRAND CANONICAL POTENTIALS

---

E7 For the boundary data it holds that

$$u_{bc} \in C^0(\overline{I \times \partial\Omega}; Y^N) \cap L^2(I; L^2(\partial\Omega; Y^N)), \quad (4.7a)$$

$$\beta = (\beta_{ij})_{i,j=0}^N \in C^0(\overline{I \times \partial\Omega}, \text{Lin}(Y^N, Y^N)). \quad (4.7b)$$

Moreover, the matrix of coefficients  $\beta$  is symmetric and satisfies

$$\ker(\beta) \supset \text{span}\{(0, 1, \dots, 1) \in \mathbb{R}^{N+1}\} = (Y^N)^\perp, \quad (4.7c)$$

$$|w \cdot \beta(t, x)v| \leq \beta_1 |w||v| \quad \forall w, v \in Y^N, \quad (4.7d)$$

$$v \cdot \beta(t, x)v \geq \beta_0 |v|^2 \quad \forall v \in Y^N. \quad (4.7e)$$

for all  $(t, x) \in \overline{I \times \partial\Omega}$  where  $0 \leq \beta_0 \leq \beta_1$  are constants.

**4.2 Remark** Some additional comments on the above assumptions:

- The assumptions E2 on the Onsager coefficients imply that the diffusion is not degenerate.
- If  $d = 3$  then  $p < 6$  in the growth assumption in E3. But this restriction is necessary in order to obtain the strong convergence of the gradients of the phase field variables in Subsection 4.1.5. There, a difference of test functions is chosen which only in  $L^p(I \times \Omega)$  converges to zero so that (4.3c) is necessary.  
The growth assumptions are only needed if the phase field variables become big which means that one of them is far away from the Gibbs simplex  $\Sigma^M$ . But for the asymptotic analysis in the previous chapter only the behaviour around  $\Sigma^M$  is of interest, and the growth of  $w$  far away is not involved. Thus,  $w$  could be replaced by a function of smaller growth away from  $\Sigma^M$ .
- Assumption (4.4f) is imposed to obtain strong convergence in the gradients of the phase field variables. For gradients terms with no explicit dependence on  $\phi$  as in (2.17a) this holds true if the coefficients matrix  $(\tilde{g}_{\alpha\beta})_{\alpha,\beta}$  is positive definite. For the more general type (2.17b) it is not clear when the growth assumptions (4.4d) and (4.4e) are satisfied. This problem is left for future research.
- Continuity of the boundary data  $u_{bc}$  and  $\beta$  with respect to  $t$  is necessary to obtain a solution to the ordinary differential equations resulting from the Galerkin approach. In applications, rapid changes on a smaller time scale than the evolution can be modelled by instantaneous changes, i.e., jumps in the conditions. It may be possible to allow for more general boundary data (in some  $L^p$  space for example) using some approximation arguments for the boundary data and, after, compactness arguments as presented below for the corresponding solutions.
- Assumption (4.7c) is due to (1.4) and reads

$$\sum_{i=1}^N \beta_{ij} = 0 \quad \forall j \in \{0, \dots, N\}.$$

**4.3 Theorem** *If the assumptions E2–E7 are fulfilled then there are functions*

$$u \in L^2(I; H^1(\Omega; Y^N)), \quad \phi \in H^1(I \times \Omega; \mathbb{H}\Sigma^M) \cap L^p(I \times \Omega; \mathbb{H}\Sigma^M) \quad (4.8a)$$

such that

$$\phi(t, \cdot) \rightarrow \phi_{ic} \quad \text{in } L^2(\Omega; \mathbb{H}\Sigma^M) \quad \text{as } t \searrow 0 \quad (4.8b)$$

and such that

$$\begin{aligned}
0 = & \int_I \int_{\Omega} \left[ -\partial_t v \cdot (\psi_{,u}(u, \phi) - \psi_{,u}(u_{ic}, \phi_{ic})) + \nabla v : L(\psi_{,u}(u, \phi), \phi) \nabla u \right] dx dt \\
& + \int_I \int_{\partial\Omega} v \cdot \beta(u - u_{bc}) d\mathcal{H}^{d-1} dt \\
& + \int_I \int_{\Omega} \left[ \omega(\phi, \nabla\phi) \partial_t \phi \cdot \zeta + a_{,\nabla\phi}(\phi, \nabla\phi) : \nabla\zeta \right] dx dt \\
& + \int_I \int_{\Omega} \left[ a_{,\phi}(\phi, \nabla\phi) \cdot \zeta + w_{,\phi}(\phi) \cdot \zeta - \psi_{,\phi}(u, \phi) \cdot \zeta \right] dx dt
\end{aligned} \tag{4.8c}$$

for all test functions  $v \in H^1(I \times \Omega; Y^N)$  with  $v(\mathcal{T}) = 0$  and  $\zeta \in H^1(I \times \Omega; \mathbb{T}\Sigma^M) \cap L^p(I \times \Omega; \mathbb{T}\Sigma^M)$ .

**Proof:** The proof will be given in several steps corresponding to the following subsections:

- For a Galerkin approximation, the existence of solutions  $(u^{(n)}, \phi^{(n)})$  mapping into finite dimensional subspaces  $Y^{(n)} \times X^{(n)}$  of  $H^1(\Omega; Y^N) \times H^1(\Omega; \mathbb{T}\Sigma^M)$  is shown. The set of admissible test functions is restricted, too.
- Uniform estimates in  $n$  are derived by testing with appropriate functions. It is shown that for  $m \leq n$

$$\begin{aligned}
\|u^{(n)}\|_{L^\infty(I; L^2(\Omega; Y^N))} + \|\nabla u^{(n)}\|_{L^2(I; L^2(\Omega; (Y^N)^d))} + \|\partial_t u^{(n)}\|_{L^2(I; (Y^{(m)})^*)} &\leq C, \\
\|\phi^{(n)}\|_{L^\infty(I; L^p(\Omega; \mathbb{H}\Sigma^M))} + \|\nabla \phi^{(n)}\|_{L^\infty(I; L^2(\Omega; (\mathbb{T}\Sigma^M)^d))} + \|\partial_t \phi^{(n)}\|_{L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))} &\leq C.
\end{aligned}$$

- Thanks to the imposed regularity and growth conditions in E1–E5, the above estimates are sufficient to go to the limit as  $n \rightarrow \infty$  in most of the terms in the weak formulation of the Galerkin problem.
- Strong convergence of  $\nabla \phi^{(n)}$  to some limiting function  $\nabla \phi$  in  $L^2$  has to be shown in order to handle the terms involving  $\omega$ ,  $a_{,\phi}$  and  $a_{,\nabla\phi}$ . The idea is to use  $\zeta^{(n)} = \phi^{(n)} - \phi$  as test function in the Galerkin system and to use (4.4f) to get  $|\nabla \phi^{(n)} - \nabla \phi|$  under control. The fact that  $\phi$  is no admissible test function for the Galerkin system makes it necessary to construct an approximation appropriately converging to  $\phi$ .
- To conclude the proof, assertion (4.8b) is shown.

### 4.1.2 Galerkin approximation

Let  $\{s_0, s_1, s_2, \dots\}$  be a set of functions in  $L^\infty(\Omega)$  constituting a Schauder basis of  $H^1(\Omega)$  such that the matrix  $((s_i, s_j)_{L^2(\Omega)})_{i,j=0}^m$  is regular for each  $m \in \mathbb{N}$ . Furthermore, let  $\{v_0, \dots, v_{N-1}\}$  be a basis of  $Y^N = \mathbb{R} \times \mathbb{T}\Sigma^N \subset \mathbb{R}^{N+1}$ . Then the functions  $v_K s_m =: e_{Nm+K}$ ,  $0 \leq K \leq N-1$ ,  $m = 0, 1, 2, \dots$ , are elements of  $L^\infty(\Omega; Y^N)$  and constitute a Schauder basis of  $H^1(\Omega; Y^N)$  such that  $((e_i, e_j)_{L^2(\Omega; Y^N)})_{i,j=0}^k$  is regular for each  $k \in \mathbb{N}$ . Analogously, let  $\{\zeta_0, \dots, \zeta_{M-2}\}$  be a basis of  $\mathbb{T}\Sigma^M \subset \mathbb{R}^M$ . Then the set of functions  $\zeta_J s_m =: b_{(M-1)m+J}$ ,  $0 \leq J \leq M-2$ ,  $m = 0, 1, 2, \dots$ , in  $L^\infty(\Omega; \mathbb{T}\Sigma^M)$  constitute a Schauder basis of  $H^1(\Omega; \mathbb{T}\Sigma^M) \subset L^p(\Omega; \mathbb{T}\Sigma^M)$  (with  $p$  from (4.3b)–(4.3d), cf. Theorem D.4 for the embedding) such that  $((b_i, b_j)_{L^2(\Omega; \mathbb{T}\Sigma^M)})_{i,j=0}^k$  is regular for each  $k \in \mathbb{N}$ .

Given some  $n \in \mathbb{N}$  define  $N_n := Nn + N - 1$ ,  $M_n := (M-1)n + M - 2$ , and the finite dimensional Galerkin spaces

$$Y^{(n)} := \text{span}\{e_m, 0 \leq m \leq N_n\} \subset H^1(\Omega; Y^N), \tag{4.9a}$$

$$X^{(n)} := \text{span}\{b_m, 0 \leq m \leq M_n\} \subset H^1(\Omega; \mathbb{T}\Sigma^M) \subset L^p(\Omega; \mathbb{T}\Sigma^M), \tag{4.9b}$$

---

#### 4.1. QUADRATIC REDUCED GRAND CANONICAL POTENTIALS

and consider the Galerkin ansatz

$$u^{(n)}(t, x) = \sum_{k=0}^{N_n} u^{(k,n)}(t) e_k(x) \in Y^N, \quad \phi^{(n)}(t, x) = \mathbf{1}^M + \sum_{l=0}^{M_n} \phi^{(l,n)}(t) b_l(x) \in \mathbf{H}\Sigma^M. \quad (4.10)$$

The aim is to solve the following problem:

Find  $(u^{(n)}, \phi^{(n)}) \in C^1(I; Y^N) \times C^1(I; X^{(n)})$  such that in  $t = 0$

$$u^{(n)}(0, x) = u_{ic}^{(n)}(x) := \sum_{k=0}^{N_n} (u_{ic}, e_k)_{L^2(\Omega; Y^N)} e_k(x), \quad (4.11a)$$

$$\phi^{(n)}(0, x) = \phi_{ic}^{(n)}(x) := \sum_{l=0}^{M_n} (\phi_{ic}, b_l)_{L^2(\Omega; \mathbf{T}\Sigma^M)} b_l(x), \quad (4.11b)$$

and such that for each  $t \in I$

$$\begin{aligned} 0 = & \int_{\Omega} \left[ v^{(n)} \cdot (\psi_{,uu}(u^{(n)}, \phi^{(n)}) \partial_t u^{(n)} + \psi_{,u\phi}(u^{(n)}, \phi^{(n)}) \partial_t \phi^{(n)}) \right] dx \\ & + \int_{\Omega} \left[ \nabla v^{(n)} : L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \right] dx + \int_{\partial\Omega} \left[ v^{(n)} \cdot \beta(u^{(n)} - u_{bc}) \right] d\mathcal{H}^{d-1} \\ & + \int_{\Omega} \left[ \omega(\phi^{(n)}, \nabla \phi^{(n)}) \zeta^{(n)} \cdot \partial_t \phi^{(n)} + \nabla \zeta^{(n)} : a_{,\nabla\phi}(\phi^{(n)}, \nabla \phi^{(n)}) \right] dx \\ & + \int_{\Omega} \left[ \zeta^{(n)} \cdot (a_{,\phi}(\phi^{(n)}, \nabla \phi^{(n)}) + w_{,\phi}(\phi^{(n)}) - \psi_{,\phi}(u^{(n)}, \phi^{(n)})) \right] dx \end{aligned} \quad (4.12)$$

for all test functions of the form

$$v^{(n)} = \sum_{k=0}^{N_n} v^{(k,n)} e_k \in H^1(\Omega; Y^N), \quad \zeta^{(n)} = \sum_{l=0}^{M_n} \zeta^{(l,n)} b_l \in H^1(\Omega; \mathbf{T}\Sigma^M) \subset L^p(\Omega; \mathbf{T}\Sigma^M) \quad (4.13)$$

with real coefficients  $v^{(k,n)}$  and  $\zeta^{(l,n)}$ .

The identity (4.12) is linear in  $(v^{(n)}, \zeta^{(n)})$ , therefore the problem reduces to find a solution to

$$\begin{aligned} 0 = & \sum_{k=0}^{N_n} \left( \int_{\Omega} e_{m_1}(x) \cdot (\psi_{,uu}(u^{(n)}(t, x), \phi^{(n)}(t, x)) \cdot e_k(x)) dx \right) \partial_t u^{(k,n)}(t) \\ & + \sum_{l=0}^{M_n} \left( \int_{\Omega} e_{m_1}(x) \cdot (\psi_{,u\phi}(u^{(n)}(t, x), \phi^{(n)}(t, x)) \cdot b_l(x)) dx \right) \partial_t \phi^{(l,n)}(t) \\ & + \int_{\Omega} \nabla e_{m_1}(x) : L(\psi_{,u}(u^{(n)}(t, x), \phi^{(n)}(t, x)), \phi^{(n)}(t, x)) \nabla u^{(n)}(t, x) dx \\ & + \int_{\partial\Omega} e_{m_1}(x) \cdot \beta(t, x)(u^{(n)}(t, x) - u_{bc}(t, x)) d\mathcal{H}^{d-1}, \end{aligned} \quad (4.14a)$$

$$\begin{aligned} 0 = & \sum_{l=0}^{M_n} \left( \int_{\Omega} \omega(\phi^{(n)}, \nabla \phi^{(n)}) b_{m_2}(x) \cdot b_l(x) dx \right) \partial_t \phi^{(l,n)}(t) \\ & + \int_{\Omega} \left( \nabla b_{m_2}(x) : a_{,\nabla\phi}(\phi^{(n)}(t, x), \nabla \phi^{(n)}(t, x)) + b_{m_2}(x) \cdot a_{,\phi}(\phi^{(n)}(t, x), \nabla \phi^{(n)}(t, x)) \right) dx \\ & + \int_{\Omega} b_{m_2}(x) \cdot \left( w_{,\phi}(\phi^{(n)}(t, x)) - \psi_{,\phi}(u^{(n)}(t, x), \phi^{(n)}(t, x)) \right) dx \end{aligned} \quad (4.14b)$$

for all  $m_1 \in \{0, \dots, N_n\}$  and  $m_2 \in \{0, \dots, M_n\}$ .

Using assumption (4.1b) and the properties of the basis functions  $\{e_k\}_k$  it holds that

$$\int_{\Omega} \sum_{m_1, k=0}^{N_n, N_n} e_{m_1} \cdot \psi_{,uu}(u^{(n)}, \phi^{(n)}) e_k \, dx \geq k_0 \int_{\Omega} \left| \sum_{k=0}^{N_n} e_k \right|^2 \, dx = k_0 \sum_{i,j=0}^{N_n} \int_{\Omega} e_i \cdot e_j \, dx > 0.$$

Therefore, the symmetric matrix before the vector  $\partial_t(u^{(k,n)})_k$  can be inverted. Similarly, assumption (4.5b) and the properties of the  $\{b_l\}_l$  imply

$$\int_{\Omega} \sum_{m_2, l=0}^{M_n, M_n} \omega(\phi^{(n)}, \nabla \phi^{(n)}) b_{m_2} \cdot b_l \, dx \geq \omega_0 \int_{\Omega} \left| \sum_{l=0}^{M_n} b_l \right|^2 \, dx > 0$$

whence the matrix before the vector  $\partial_t(\phi^{(l,n)})_l$  can be inverted. By the assumptions (4.1i), (4.1a), (4.2a), (4.3a), (4.4a), and (4.5d) on the regularity of the occurring functions all terms are Lipschitz continuous with respect to the coefficient functions  $u^{(k,n)}(t)$  and  $\phi^{(l,n)}(t)$ , and thanks to (4.7a) and (4.7b) continuous with respect to  $t$ . Applying the theorem of Picard-Lindelöf (Theorem D.1 in Appendix D), there is a unique solution

$$(u^{(n)}, \phi^{(n)}) \in C^1(I; Y^{(n)}) \times C^1(I; X^{(n)}). \quad (4.15)$$

to (4.12) or, equivalently, to (4.14a) and (4.14b) subject to the initial data  $(u_{ic}^{(n)}, \phi_{ic}^{(n)})$  given in (4.17a), (4.17b). In particular, the coefficients  $u^{(k,n)}$  and  $\phi^{(l,n)}$  are  $C^1$ -functions.

Using test functions  $(v^{(m)}, \zeta^{(m)})$  of the form (4.13) with  $n$  replaced by  $m$  and coefficient functions  $v^{(k,m)} \in C^1(I)$  fulfilling  $v^{(m)}(\mathcal{T}) = 0$  and  $\zeta^{(l,m)} \in C^0(I)$ , equation (4.12) becomes when partially integrating with respect to  $t$  over  $I$  for  $n \geq m$

$$0 = - \int_I \int_{\Omega} \partial_t v^{(m)} \cdot (\psi_{,u}(u^{(n)}, \phi^{(n)}) - \psi_{,u}(u_{ic}^{(n)}, \phi_{ic}^{(n)})) \, dx dt \quad (4.16a)$$

$$+ \int_I \int_{\Omega} \nabla v^{(m)} L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) : \nabla u^{(n)} \, dx dt \quad (4.16b)$$

$$+ \int_I \int_{\partial\Omega} v^{(m)} \cdot \beta(u^{(n)} - u_{bc}) \, d\mathcal{H}^{d-1} dt \quad (4.16c)$$

$$+ \int_I \int_{\Omega} \omega(\phi^{(n)}, \nabla \phi^{(n)}) \zeta^{(m)} \cdot \partial_t \phi^{(n)} \, dx dt \quad (4.16d)$$

$$+ \int_I \int_{\Omega} \left[ \nabla \zeta^{(m)} : a_{,\nabla \phi}(\phi^{(n)}, \nabla \phi^{(n)}) + \zeta^{(m)} \cdot a_{,\phi}(\phi^{(n)}, \nabla \phi^{(n)}) \right] \, dx dt \quad (4.16e)$$

$$+ \int_I \int_{\Omega} \left[ \zeta^{(m)} \cdot w_{,\phi}(\phi^{(n)}) - \zeta^{(m)} \cdot \psi_{,\phi}(u^{(n)}, \phi^{(n)}) \right] \, dx dt. \quad (4.16f)$$

### 4.1.3 Uniform estimates

The goal is now to derive appropriate estimates to let  $n \rightarrow \infty$  in (4.16a)–(4.16f). For this purpose, multiply (4.14a) by  $u^{(m_1,n)}(t)$ , sum up over  $m_1$ , and integrate with respect to  $t$  over some time interval  $\tilde{I} = (0, \tilde{t})$ ,  $\tilde{t} < \mathcal{T}$ . Analogously, multiply (4.14b) by  $\partial_t \phi^{(m_2,n)}$ , sum up over  $m_2$ , and integrate to find

$$\begin{aligned} 0 = & \int_{\tilde{I}} \int_{\Omega} \left[ u^{(n)} \cdot \partial_t \psi_{,u}(u^{(n)}, \phi^{(n)}) - \partial_t \phi^{(n)} \cdot \psi_{,\phi}(u^{(n)}, \phi^{(n)}) \right] \, dx dt \\ & + \int_{\tilde{I}} \int_{\Omega} \left[ \nabla u^{(n)} : L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \right] \, dx dt \\ & + \int_{\tilde{I}} \int_{\partial\Omega} \left[ u^{(n)} \cdot \beta(u^{(n)} - u_{bc}) \right] \, d\mathcal{H}^{d-1} dt \\ & + \int_{\tilde{I}} \int_{\Omega} \left[ \omega(\phi^{(n)}, \nabla \phi^{(n)}) |\partial_t \phi^{(n)}|^2 + \partial_t (a(\phi^{(n)}, \nabla \phi^{(n)}) + w(\phi^{(n)})) \right] \, dx dt \end{aligned}$$

---

#### 4.1. QUADRATIC REDUCED GRAND CANONICAL POTENTIALS

---

$$\begin{aligned}
&= \int_{\tilde{I}} \int_{\Omega} \left[ \partial_t (\psi_{,u}(u^{(n)}, \phi^{(n)}) \cdot u^{(n)} - \psi(u^{(n)}, \phi^{(n)})) + \partial_t (a(\phi^{(n)}, \nabla \phi^{(n)}) + w(\phi^{(n)})) \right] dx dt \\
&+ \int_{\tilde{I}} \int_{\Omega} \left[ \omega(\phi^{(n)}, \nabla \phi^{(n)}) |\partial_t \phi^{(n)}|^2 + \sum_{l=1}^d \partial_{x_l} u^{(n)} \cdot L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \partial_{x_l} u^{(n)} \right] dx dt \\
&+ \int_{\tilde{I}} \int_{\partial \Omega} \left[ u^{(n)} \cdot \beta(u^{(n)} - u_{bc}) \right] d\mathcal{H}^{d-1} dt.
\end{aligned}$$

Here, the regularity assumptions on  $w$ ,  $a$ , and  $\psi$  were used again.

Thanks to properties of the basis functions  $\{e_k\}_k$  and the  $\{b_l\}_l$  it is clear that, as  $n \rightarrow \infty$ ,

$$u_{ic}^{(n)} \rightarrow u_{ic} \quad \text{almost everywhere and in } L^2(\Omega; Y^N), \quad (4.17a)$$

$$\phi_{ic}^{(n)} \rightarrow \phi_{ic} \quad \text{almost everywhere and in } H^1(\Omega; \mathbf{H}\Sigma^M). \quad (4.17b)$$

Since the embedding  $H^1(\Omega; \mathbf{H}\Sigma^M) \hookrightarrow L^p(\Omega; \mathbf{H}\Sigma^M)$  is compact for  $p$  from assumption E3 it also holds for a subsequence as  $n \rightarrow \infty$  that

$$\phi_{ic}^{(n)} \rightarrow \phi_{ic} \quad \text{in } L^p(\Omega; \mathbf{H}\Sigma^M). \quad (4.17c)$$

Altogether, (4.17a)–(4.17c) yield, using the Lebesgue convergence theorem D.2 and the growth properties (4.1g), (4.1h), (4.3b), and (4.4c):

$$\begin{aligned}
\psi_{,u}(u_{ic}^{(n)}, \phi_{ic}^{(n)}) &\rightarrow \psi_{,u}(u_{ic}, \phi_{ic}) \quad \text{in } L^2(\Omega; Y^N) && \text{by (4.1g),} \\
\psi(u_{ic}^{(n)}, \phi_{ic}^{(n)}) &\rightarrow \psi(u_{ic}, \phi_{ic}) \quad \text{in } L^1(\Omega) && \text{by (4.1h),} \\
w(\phi_{ic}^{(n)}) &\rightarrow w(\phi_{ic}) \quad \text{in } L^1(\Omega) && \text{by (4.3b),} \\
a(\phi_{ic}^{(n)}, \nabla \phi_{ic}^{(n)}) &\rightarrow a(\phi_{ic}, \nabla \phi_{ic}) \quad \text{in } L^1(\Omega) && \text{by (4.4c).}
\end{aligned}$$

By (4.11a), (4.11b), and (4.6b) it follows that (the dependence on  $x$  is dropped)

$$\begin{aligned}
&\int_{\Omega} \left[ \psi_{,u}(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t})) \cdot u^{(n)}(\tilde{t}) - \psi(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t})) \right] dx \\
&+ \int_{\Omega} \left[ w(\phi^{(n)}(\tilde{t})) + a(\phi^{(n)}(\tilde{t}), \nabla \phi^{(n)}(\tilde{t})) \right] dx \\
&+ \int_{\tilde{I}} \int_{\Omega} \left[ \omega(\phi^{(n)}, \nabla \phi^{(n)}) |\partial_t \phi^{(n)}|^2 + \sum_{l=1}^d \partial_{x_l} u^{(n)} \cdot L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \partial_{x_l} u^{(n)} \right] dx dt \\
&+ \int_{\tilde{I}} \int_{\Omega} \left[ u^{(n)} \cdot \beta(u^{(n)} - u_{bc}) \right] d\mathcal{H}^{d-1} dt \\
&\leq \int_{\Omega} \left[ \psi_{,u}(u_{ic}^{(n)}, \phi_{ic}^{(n)}) \cdot u_{ic}^{(n)} - \psi(u_{ic}^{(n)}, \phi_{ic}^{(n)}) + w(\phi_{ic}^{(n)}) + a(\phi_{ic}^{(n)}, \nabla \phi_{ic}^{(n)}) \right] dx \\
&\rightarrow \int_{\Omega} \left[ \psi_{,u}(u_{ic}, \phi_{ic}) \cdot u_{ic} - \psi(u_{ic}, \phi_{ic}) + w(\phi_{ic}) + a(\phi_{ic}, \nabla \phi_{ic}) \right] dx \leq C. \quad (4.18)
\end{aligned}$$

Assumption (4.1b) gives

$$\begin{aligned}
&\psi_{,u}(u^{(n)}, \phi^{(n)}) \cdot u^{(n)} - \psi(u^{(n)}, \phi^{(n)}) \\
&= \int_0^1 \frac{d}{d\theta} (\psi_{,u}(\theta u^{(n)}, \phi^{(n)}) \cdot \theta u^{(n)} - \psi(\theta u^{(n)}, \phi^{(n)})) d\theta - \psi(0, \phi^{(n)}) \\
&= \int_0^1 (\theta u^{(n)} \cdot (\psi_{,uu}(\theta u^{(n)}, \phi^{(n)}) u^{(n)})) d\theta - \psi(0, \phi^{(n)}) \\
&\geq \frac{k_0}{2} |u^{(n)}|^2 - k_4.
\end{aligned}$$

By assumptions (4.7d) and (4.7e), using Young's inequality with some small  $\delta$  (which will later be determined)

$$\begin{aligned} & \int_{\bar{I}} \int_{\partial\Omega} \left[ u^{(n)} \cdot \beta u^{(n)} - u^{(n)} \cdot \beta u_{bc} \right] d\mathcal{H}^{d-1} dt \\ & \geq \beta_0 \int_{\bar{I}} \int_{\partial\Omega} |u^{(n)}|^2 d\mathcal{H}^{d-1} dt - \beta_1 \int_{\bar{I}} \int_{\partial\Omega} |u^{(n)}| |u_{bc}| d\mathcal{H}^{d-1} dt \\ & \geq (\beta_0 - \beta_1 \delta) \int_{\bar{I}} \|u^{(n)}\|_{L^2(\partial\Omega)}^2 dt - C(\beta_1, \delta) \int_{\bar{I}} \|u_{bc}\|_{L^2(\partial\Omega)}^2 dt. \end{aligned}$$

Now, the estimate (4.18) yields thanks to (4.2e), (4.3d), (4.4b), and (4.5b)

$$\begin{aligned} & \int_{\Omega} \left[ \frac{k_0}{2} |u^{(n)}(\tilde{t})|^2 + w_2 |\phi^{(n)}(\tilde{t})|^p + a_0 |\nabla \phi^{(n)}(\tilde{t})|^2 \right] dx \\ & + \int_{\bar{I}} \int_{\Omega} \left[ \omega_0 |\partial_t \phi^{(n)}|^2 + l_0 |\nabla u^{(n)}|^2 \right] dx dt - \int_{\bar{I}} \int_{\partial\Omega} \delta \beta_1 |u^{(n)}|^2 d\mathcal{H}^{d-1} dt \leq C. \end{aligned} \quad (4.19)$$

By the trace theorem D.6 there is a constant  $C_{Tr}$  such that

$$-\delta \beta_1 \int_{\bar{I}} \int_{\partial\Omega} |u^{(n)}|^2 d\mathcal{H}^{d-1} dt \geq -\delta \beta_1 C_{Tr} \int_{\bar{I}} \int_{\Omega} |u^{(n)}|^2 + |\nabla u^{(n)}|^2 dx dt.$$

Choose  $\delta > 0$  so small such that  $l_0 - \delta \beta_1 C_{Tr} > 0$ . Then (4.19) gives

$$\int_{\Omega} \frac{k_0}{2} |u^{(n)}(\tilde{t}, x)|^2 dx \leq C + \int_0^{\tilde{t}} \int_{\Omega} \delta \beta_1 C_{Tr} |u^{(n)}(t, x)|^2 dx dt.$$

Applying the Gronwall lemma D.7 on the continuous functions  $t \mapsto \int_{\Omega} |u^{(n)}(t, x)|^2 dx$  yields

$$\int_{\Omega} |u^{(n)}(t, x)|^2 dx \leq \frac{2C}{k_0} e^{\frac{2\delta \beta_1 C_{Tr} T}{k_0}} \leq C,$$

and hence with (4.19)

$$\begin{aligned} & \|u^{(n)}\|_{L^\infty(I; L^2(\Omega; Y^N))} + \|\phi^{(n)}\|_{L^\infty(I; L^p(\Omega; \mathbb{H}\Sigma^M))} + \|\nabla \phi^{(n)}\|_{L^\infty(I; L^2(\Omega; (\mathbb{T}\Sigma^M)^d))} \\ & + \|\partial_t \phi^{(n)}\|_{L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))} + \|\nabla u^{(n)}\|_{L^2(I; L^2(\Omega; (Y^N)^d))} \leq C. \end{aligned} \quad (4.20)$$

Multiply (4.14a) by continuous coefficient functions  $v^{(k,n)}(t)$  and integrate with respect to  $t$  over  $I$ . With (4.1a), (4.2e) and (4.7d), and (4.20) it follows that

$$\begin{aligned} & \left| \int_I \int_{\Omega} v^{(n)} \cdot \partial_t \psi_{,u}(u^{(n)}, \phi^{(n)}) \right| \\ & = \left| \int_I \int_{\Omega} \nabla v^{(n)} : L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} dx dt + \int_I \int_{\partial\Omega} v^{(n)} \cdot \beta(u^{(n)} - u_{bc}) d\mathcal{H}^{d-1} dt \right| \\ & \leq L_0 \|\nabla v^{(n)}\|_{L^2(I; L^2(\Omega; (Y^N)^d))} \|\nabla u^{(n)}\|_{L^2(I; L^2(\Omega; (Y^N)^d))} \\ & \quad + \beta_1 \|v^{(n)}\|_{L^2(I; L^2(\partial\Omega; Y^N))} (\|u^{(n)}\|_{L^2(I; L^2(\partial\Omega; Y^N))} + \|u_{bc}\|_{L^2(I; L^2(\partial\Omega; Y^N))}) \\ & \leq C \|v^{(n)}\|_{L^2(I; H^1(\Omega; Y^N))} \end{aligned}$$

so that for all natural numbers  $n \geq m$  with some constant  $C(m)$  independent of  $n$

$$\|\partial_t \psi_{,u}(u^{(n)}, \phi^{(n)})\|_{L^2(I; (Y^{(m)})^*)} \leq C(m). \quad (4.21)$$

By (4.1b) and (4.1e)  $|\partial_t \psi_{,u}(u^{(n)}, \phi^{(n)})| \geq k_0 |\partial_t u^{(n)}| - k_3 |\partial_t \phi^{(n)}|$ , hence from (4.20) and (4.21) for  $n \geq m$  with some  $C(m)$  independent of  $n$

$$\|\partial_t u^{(n)}\|_{L^2(I; (Y^{(m)})^*)} \leq C(m). \quad (4.22)$$



#### 4.1.4 First convergence results

Since the Hilbert spaces  $L^2(I; H^1(\Omega; Y^N))$ ,  $L^2(I; L^2(\partial\Omega; Y^N))$ , and  $H^1(I \times \Omega; \mathbf{H}\Sigma^M)$  are reflexive, in view of (4.20) there are functions  $u$  and  $\phi$  such that for a subsequence as  $n \rightarrow \infty$  (as mentioned in the introduction, whenever there are convergence statements in the following, in general, they are only valid for subsequences which are relabelled with  $n$  again)

$$\phi^{(n)} \rightharpoonup \phi \quad \text{in } H^1(I \times \Omega; \mathbf{H}\Sigma^M), \quad (4.23a)$$

$$u^{(n)} \rightharpoonup u \quad \text{in } L^2(I; H^1(\Omega; Y^N)). \quad (4.23b)$$

The continuous trace map  $S : H^1(\Omega) \rightarrow L^2(\partial\Omega)$  of Theorem D.6 has a dense image since the functions  $\{f|_{\partial\Omega} : f \in C^\infty(\mathbb{R}^d)\}$  are dense in  $L^2(\partial\Omega)$  (cf. [Alt99], Section A6.5). Therefore, (4.23b) provides

$$u^{(n)} \rightharpoonup u \text{ in } L^2(I; L^2(\partial\Omega; Y^N)). \quad (4.23c)$$

Since  $H^1(\Omega; \mathbf{H}\Sigma^M) \hookrightarrow L^p(\Omega; \mathbf{H}\Sigma^M)$  is compact,  $L^p(\Omega; \mathbf{H}\Sigma^M) \hookrightarrow L^2(\Omega; \mathbf{H}\Sigma^M)$  is continuous, and since  $H^1(\Omega; \mathbf{H}\Sigma^M)$  and  $L^2(\Omega; \mathbf{H}\Sigma^M)$  are reflexive, Theorem D.8 provides that the embedding

$$\left\{ \zeta \in L^p(I; H^1(\Omega; \mathbf{H}\Sigma^M)) : \partial_t \zeta \in L^2(I; L^2(\Omega; \mathbf{H}\Sigma^M)) \right\} \hookrightarrow L^p(I; L^p(\Omega; \mathbf{H}\Sigma^M))$$

exists and is compact. Therefore from (4.20) and (4.23a) (in this context observe that clearly  $L^\infty(I; H^1(\Omega; \mathbf{H}\Sigma^M)) \subset L^p(I; H^1(\Omega; \mathbf{H}\Sigma^M))$ )

$$\phi^{(n)} \rightarrow \phi \quad \text{in } L^q(I \times \Omega; \mathbf{H}\Sigma^M), \quad (4.23d)$$

$$\phi^{(n)} \rightarrow \phi \quad \text{almost everywhere} \quad (4.23e)$$

for  $q = 2$  and  $q = p$  the value in (4.3b)–(4.3d).

As  $Y^{(m)} \subset H^1(\Omega; Y^N) \subset L^2(\Omega; Y^N) \Rightarrow L^2(\Omega; Y^N) \cong (L^2(\Omega; Y^N))^* \subset (Y^{(m)})^*$  there are the embeddings  $H^1(\Omega; Y^N) \hookrightarrow L^2(\Omega; Y^N) \hookrightarrow (Y^{(m)})^*$  where the first one is compact. Moreover,  $H^1(\Omega; Y^N)$  and  $(Y^{(m)})^*$  are reflexive. Using again Theorem D.8

$$\left\{ \xi \in L^2(I; H^1(\Omega; Y^N)), \partial_t \xi \in L^2(I; (Y^{(m)})^*) \right\} \hookrightarrow L^2(I; L^2(\Omega; Y^N)) \quad (4.24)$$

exists and is compact. By (4.1c), (4.1e), and using (4.20)

$$|\nabla \psi_{,u}(u^{(n)}, \phi^{(n)})| \leq k_1 |\nabla u^{(n)}| + k_3 |\nabla \phi^{(n)}| \in L^2(I; L^2(\Omega)),$$

and by (4.1g)  $\psi_{,u}(u^{(n)}, \phi^{(n)}) \in L^2(I; L^2(\Omega; Y^N))$ . Using the estimate (4.21) and applying (4.24) there is a function  $B \in L^2(I; L^2(\Omega; Y^N))$  such that

$$\psi_{,u}(u^{(n)}, \phi^{(n)}) \rightarrow B \text{ in } L^2(I; L^2(\Omega; Y^N)) \text{ and almost everywhere.} \quad (4.25)$$

Similarly, the estimates (4.20) and (4.22) together with (4.24) imply that there is some  $\hat{u} \in L^2(I; L^2(\Omega; Y^N))$  such that  $u^{(n)} \rightarrow \hat{u}$  almost everywhere and in  $L^2(I; L^2(\Omega; Y^N))$ . By (4.23b) (the weak limit is unique)  $\hat{u} = u$ , hence

$$u^{(n)} \rightarrow u \text{ almost everywhere and in } L^2(I; L^2(\Omega; Y^N)). \quad (4.26)$$

Together with (4.23e) this furnishes  $\psi_{,u}(u^{(n)}, \phi^{(n)}) \rightarrow \psi_{,u}(u, \phi)$  almost everywhere. With (4.25) it follows that  $B = \psi_{,u}(u, \phi)$ , whence

$$\psi_{,u}(u^{(n)}, \phi^{(n)}) \rightarrow \psi_{,u}(u, \phi) \text{ almost everywhere and in } L^2(I; L^2(\Omega; Y^N)). \quad (4.27)$$

In the preceding Subsection it was already demonstrated that

$$\psi_{,u}(u_{ic}^{(n)}, \phi_{ic}^{(n)}) \rightarrow \psi_{,u}(u_{ic}, \phi_{ic}) \text{ almost everywhere and in } L^2(\Omega; Y^N). \quad (4.28)$$

## CHAPTER 4. EXISTENCE OF WEAK SOLUTIONS

From (4.2a) it follows that  $L(\psi, u(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \rightarrow L(\psi, u(u, \phi), \phi)$  almost everywhere. By (4.2e) and again the Lebesgue convergence theorem

$$L(\psi, u(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla v^{(m)} \rightarrow L(\psi, u(u, \phi), \phi) \nabla v^{(m)} \text{ a.e. and in } L^2(I; L^2(\Omega; (Y^N)^d))$$

With (4.23b) this implies

$$\nabla v^{(m)} : L(\psi, u(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \rightarrow \nabla v^{(m)} : L(\psi, u(u, \phi), \phi) \nabla u \text{ in } L^1(I; L^1(\Omega)). \quad (4.29)$$

By (4.23e) and (4.26)  $\psi, \phi(u^{(n)}, \phi^{(n)}) \rightarrow \psi, \phi(u, \phi)$  almost everywhere. Using (4.1d), (4.20) and the theorem of dominated convergence

$$\psi, \phi(u^{(n)}, \phi^{(n)}) \rightarrow \psi, \phi(u, \phi) \text{ a.e. and in } L^2(I; L^2(\Omega; Y^N)). \quad (4.30)$$

Similarly, by (4.23e)  $w, \phi(\phi^{(n)}) \rightarrow w, \phi(\phi)$  almost everywhere. By (4.3c)  $|w, \phi(\phi^{(n)})|^{p^*} \leq C(w_1)(1 + |\phi^{(n)}|^p)$ . With (4.23d) and the theorem of dominated convergence

$$w, \phi(\phi^{(n)}) \rightarrow w, \phi(\phi) \text{ a.e. and in } L^{p^*}(I \times \Omega; \mathbb{T}\Sigma^M). \quad (4.31)$$

### 4.1.5 Strong convergence of the gradients of the phase fields

The first goal is to construct functions strongly converging to  $\phi$  in  $H^1(I \times \Omega; \mathbb{H}\Sigma^M)$  and in  $L^p(I \times \Omega; \mathbb{H}\Sigma^M)$  which are admissible test functions in (4.16a)–(4.16f).

Let  $\mathcal{P}(\bar{I}; H^1(\Omega; \mathbb{H}\Sigma^M))$  be the set of polynomials  $f : [0, T] \rightarrow H^1(\Omega; \mathbb{H}\Sigma^M)$ . Using standard density results (for example, cf. [Zei90], Proposition 23.2) these polynomials are dense in  $H^1(I; H^1(\Omega; \mathbb{H}\Sigma^M))$  whence in  $H^1(I \times \Omega; \mathbb{H}\Sigma^M)$ . Since  $H^1(\Omega; \mathbb{H}\Sigma^M) \subset L^p(\Omega; \mathbb{H}\Sigma^M)$  is dense the set  $\mathcal{P}(\bar{I}; H^1(\Omega; \mathbb{H}\Sigma^M))$  is even dense in  $L^p(I; L^p(\Omega; \mathbb{H}\Sigma^M)) \cong L^p(I \times \Omega; \mathbb{H}\Sigma^M)$ . Let  $\{f_n\}_{n \in \mathbb{N}}$  be a sequence of polynomials in  $\mathcal{P}(\bar{I}; H^1(\Omega; \mathbb{H}\Sigma^M))$  with

$$f_n \rightarrow \phi \text{ in } H^1(I \times \Omega; \mathbb{H}\Sigma^M) \text{ and } L^p(I \times \Omega; \mathbb{H}\Sigma^M) \text{ as } n \rightarrow \infty.$$

The union of the Galerkin spaces  $X^{(\infty)} := \bigcup_{m \in \mathbb{N}} X^{(m)}$  is dense in  $H^1(\Omega; \mathbb{H}\Sigma^M)$  and  $L^p(\Omega; \mathbb{H}\Sigma^M)$ . By appropriate projection of the coefficients of the polynomials  $f_k$  onto the spaces  $X^{(m)}$ , for each  $n \in \mathbb{N}$  there are polynomials  $\{f_n^{(m)}\}_{m \in \mathbb{N}} \subset \mathcal{P}(\bar{I}; X^{(m)})$  with

$$f_n^{(m)} \rightarrow f_n \text{ in } \mathcal{P}(\bar{I}; H^1(\Omega; \mathbb{H}\Sigma^M)) \text{ and } \mathcal{P}(\bar{I}; L^p(\Omega; \mathbb{H}\Sigma^M)) \text{ as } m \rightarrow \infty.$$

Taking an appropriate diagonal sequence

$$\{\hat{\phi}^{(n)}\}_{n \in \mathbb{N}} := \{f_n^{(m_n)}\}_{n \in \mathbb{N}}$$

this means that there are functions  $\hat{\phi}^{(n)} \in C^0(I; X^{(n)})$  with

$$\hat{\phi}^{(n)} \rightarrow \phi \text{ a. e. and in } H^1(I \times \Omega; \mathbb{H}\Sigma^M) \text{ and } L^p(I \times \Omega; \mathbb{H}\Sigma^M) \text{ as } n \rightarrow \infty \quad (4.32)$$

and, in addition, thanks to (4.23d), for  $q = 2$  and  $q = p$

$$\|\phi^{(n)} - \hat{\phi}^{(n)}\|_{L^q(I \times \Omega; \mathbb{T}\Sigma^M)} \rightarrow 0 \text{ as } n \rightarrow \infty. \quad (4.33)$$

Now, let  $m = n$  in (4.16a)–(4.16f) and take  $v^{(n)} = 0$  and  $\zeta^{(n)} = (\phi^{(n)} - \hat{\phi}^{(n)})$  as testfunction. By (4.23d) for  $q = p$ , the functions  $w, \phi(\phi^{(n)})$  are bounded in  $L^{p^*}(I \times \Omega; \mathbb{T}\Sigma^M)$  (cf. the remark in assumption E3). Then by (4.20) and using the growth assumptions (4.1d), (4.4d), and (4.5c), the

## 4.1. QUADRATIC REDUCED GRAND CANONICAL POTENTIALS

convergence in (4.33) implies

$$\begin{aligned}
& \left| \int_I \int_{\Omega} a_{,\nabla\phi}(\phi^{(n)}, \nabla\phi^{(n)}) : (\nabla\phi^{(n)} - \nabla\hat{\phi}^{(n)}) \, dxdt \right| \\
& \leq \left| \int_I \int_{\Omega} (\omega(\phi^{(n)}, \nabla\phi^{(n)}) \partial_t \phi^{(n)} + a_{,\phi}(\phi^{(n)}, \nabla\phi^{(n)}) \cdot \zeta^{(n)}) \, dxdt \right| \\
& \quad + \left| \int_I \int_{\Omega} (w_{,\phi}(\phi^{(n)}) - \psi_{,\phi}(u^{(n)}, \phi^{(n)})) \cdot \zeta^{(n)} \, dxdt \right| \\
& \leq \omega_1 \|\partial_t \phi^{(n)}\|_{L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))} \|\zeta^{(n)}\|_{L^2(I \times \Omega; \mathbb{T}\Sigma^M)} \\
& \quad + a_2 (\|\phi^{(n)}\|_{L^2(I; L^2(\Omega; \mathbb{H}\Sigma^M))} + \|\nabla\phi^{(n)}\|_{L^2(I; L^2(\Omega; (\mathbb{T}\Sigma^M)^d))}) \|\zeta^{(n)}\|_{L^2(I \times \Omega; \mathbb{T}\Sigma^M)} \\
& \quad + \|w_{,\phi}(\phi^{(n)})\|_{L^{p^*}(I \times \Omega; \mathbb{T}\Sigma^M)} \|\zeta^{(n)}\|_{L^p(I \times \Omega; \mathbb{T}\Sigma^M)} \\
& \quad + k_2 C (1 + \|u^{(n)}\|_{L^2(I; L^2(\Omega; Y^N))}) \|\zeta^{(n)}\|_{L^2(I \times \Omega; \mathbb{T}\Sigma^M)} \\
& \leq C (\|\zeta^{(n)}\|_{L^p(I \times \Omega; \mathbb{T}\Sigma^M)} + \|\zeta^{(n)}\|_{L^2(I \times \Omega; \mathbb{T}\Sigma^M)}) \rightarrow 0 \quad \text{as } n \rightarrow \infty. \tag{4.34}
\end{aligned}$$

By (4.32), (4.23d) for  $q = 2$ , and by assumption (4.4e) the Lebesgue convergence theorem yields

$$a_{,\nabla\phi}(\phi^{(n)}, \nabla\hat{\phi}^{(n)}) \rightarrow a_{,\nabla\phi}(\phi, \nabla\phi) \text{ in } L^2(I; L^2(\Omega; (\mathbb{T}\Sigma^M)^d)).$$

Since in addition  $\nabla\zeta^{(n)} = \nabla\phi^{(n)} - \nabla\hat{\phi}^{(n)} \rightarrow 0$  in  $L^2(I; L^2(\Omega; (\mathbb{T}\Sigma^M)^d))$  by (4.32) and (4.23a) is follows that

$$\int_I \int_{\Omega} a_{,\nabla\phi}(\phi^{(n)}, \nabla\hat{\phi}^{(n)}) : \nabla\zeta^{(n)} \, dxdt \rightarrow 0 \quad \text{as } n \rightarrow \infty. \tag{4.35}$$

The left hand side of (4.34) can be computed to

$$\begin{aligned}
& \int_I \int_{\Omega} a_{,\nabla\phi}(\phi^{(n)}, \nabla\phi^{(n)}) : (\nabla\phi^{(n)} - \nabla\hat{\phi}^{(n)}) \, dxdt \\
& = \int_I \int_{\Omega} (a_{,\nabla\phi}(\phi^{(n)}, \nabla\phi^{(n)}) - a_{,\nabla\phi}(\phi^{(n)}, \nabla\hat{\phi}^{(n)})) : (\nabla\phi^{(n)} - \nabla\hat{\phi}^{(n)}) \, dxdt \\
& \quad + \int_I \int_{\Omega} a_{,\nabla\phi}(\phi^{(n)}, \nabla\hat{\phi}^{(n)}) : (\nabla\phi^{(n)} - \nabla\hat{\phi}^{(n)}) \, dxdt.
\end{aligned}$$

Assumption (4.4f) applied on the first term on the right hand side now furnishes together with the convergence results in (4.34) and (4.35) that

$$\int_I \int_{\Omega} |\nabla\phi^{(n)} - \nabla\hat{\phi}^{(n)}|^2 \, dxdt \rightarrow 0 \text{ as } n \rightarrow \infty$$

which, in view of (4.23a) and (4.32), means that

$$\phi^{(n)} \rightarrow \phi \text{ in } L^2(I; H^1(\Omega; \mathbb{H}\Sigma^M)), \quad \nabla\phi^{(n)} \rightarrow \nabla\phi \text{ a.e.} \tag{4.36}$$

Using the growth and regularity assumptions in E4, The Lebesgue convergence theorem gives

$$a_{,\nabla\phi}(\phi^{(n)}, \nabla\phi^{(n)}) \rightarrow a_{,\nabla\phi}(\phi, \nabla\phi) \quad \text{in } L^2(I; L^2(\Omega; (\mathbb{T}\Sigma^M)^d)), \tag{4.37a}$$

$$a_{,\phi}(\phi^{(n)}, \nabla\phi^{(n)}) \rightarrow a_{,\phi}(\phi, \nabla\phi) \quad \text{in } L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M)). \tag{4.37b}$$

Moreover, for arbitrary test functions  $\zeta^{(m)}$ , by (4.5a) and (4.5c)

$$\omega(\phi^{(n)}, \nabla\phi^{(n)})\zeta^{(m)} \rightarrow \omega(\phi, \nabla\phi)\zeta^{(m)} \text{ a.e. and in } L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))$$

whence, since  $\partial_t \phi^{(n)} \rightarrow \partial_t \phi$  in  $L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))$  by (4.23a),

$$\omega(\phi^{(n)}, \nabla\phi^{(n)})\zeta^{(m)} \cdot \partial_t \phi^{(n)} \rightarrow \omega(\phi, \nabla\phi)\zeta^{(m)} \cdot \partial_t \phi \text{ in } L^1(I; L^1(\Omega)). \tag{4.38}$$

Finally, letting  $n$  converge to infinity in (4.16a)–(4.16f), the convergence results (4.27), (4.28), (4.29), (4.23c), (4.38), (4.37a), (4.37b), (4.31), and (4.30) yield that  $(u^{(n)}, \phi^{(n)})$  can be replaced by  $(u, \phi)$ . Altogether it holds for every  $m \in \mathbb{N}$  that

$$\begin{aligned}
 0 = & - \int_I \int_{\Omega} \left[ \partial_t v^{(m)} \cdot (\psi_{,u}(u, \phi) - \psi_{,u}(u_{ic}, \phi_{ic})) \right] dx dt \\
 & + \int_I \int_{\Omega} \left[ \nabla v^{(m)} : L(\psi_{,u}(u, \phi), \phi) \nabla u \right] dx dt + \int_I \int_{\partial\Omega} \left[ v^{(m)} \cdot \beta(u - u_{bc}) \right] d\mathcal{H}^{d-1} dt \\
 & + \int_I \int_{\Omega} \left[ \zeta^{(m)} \cdot \omega(\phi, \nabla\phi) \partial_t \phi + \nabla \zeta^{(m)} : a_{,\nabla\phi}(\phi, \nabla\phi) \right] dx dt \\
 & + \int_I \int_{\Omega} \left[ \zeta^{(m)} \cdot (a_{,\phi}(\phi, \nabla\phi) + w_{,\phi}(\phi) - \psi_{,\phi}(u, \phi)) \right] dx dt.
 \end{aligned} \tag{4.39}$$

By appropriate approximation, this is valid for testfunctions

$$v^{(m)} \in L^2(I; Y^{(m)}) \cap H^1(I; L^2(\Omega; Y^N)), \quad \zeta^{(m)} \in L^p(I; X^{(m)}) \cap H^1(I; L^2(\Omega; T\Sigma^M))$$

satisfying  $v^{(m)}(\mathcal{T}) = 0$ . Given arbitrary test functions  $v \in H^1(I \times \Omega; Y^N)$  with  $v(\mathcal{T}) = 0$  and  $\zeta \in H^1(I \times \Omega; T\Sigma^M) \cap L^p(I \times \Omega; T\Sigma^M)$  there are functions  $(v^{(m)}, \zeta^{(m)})$  of the above form with

$$\begin{aligned}
 v^{(m)} & \rightarrow v \text{ in } H^1(I \times \Omega; Y^N), \\
 \zeta^{(m)} & \rightarrow \zeta \text{ in } H^1(I \times \Omega; T\Sigma^M) \cap L^p(I \times \Omega; T\Sigma^M).
 \end{aligned}$$

Consider for example the procedure of defining  $\hat{\phi}^{(n)}$  for finding the  $\zeta^{(m)}$  and similar operations for finding the  $v^{(m)}$ . From (4.39) it then follows that  $(u, \phi)$  is a solution to (4.8c). To conclude the proof of Theorem 4.3, (4.8b) must be proven.

#### 4.1.6 Initial values for the phase fields

Consider the set

$$W := \left\{ \zeta \in L^2(I; H^{1,2}(\Omega)) : \partial_t \zeta \in L^2(I; L^2(\Omega)) \right\} \cong H^{1,2}(I \times \Omega).$$

Theorem D.8 provides that the embedding  $W \hookrightarrow C^0(\bar{I}; L^2(\Omega))$  exists and is continuous. Since the smooth functions  $C^\infty(\bar{I} \times \bar{\Omega})$  are dense in  $H^{1,2}(I \times \Omega)$  the functions  $C^1(\bar{I}; H^{1,2}(\Omega))$  are dense in  $W$ .

#### 4.4 Lemma The embedding

$$E : C^1(\bar{I}; H^{1,2}(\Omega)) \hookrightarrow C^0(\bar{I}; L^2(\Omega))$$

is compact.

**Proof:** It must be shown that, given a bounded series  $\{\zeta_n\}_{n \in \mathbb{N}} \subset C^1(\bar{I}; H^{1,2}(\Omega))$ , i.e.,

$$\sup_{n \in \mathbb{N}} \left( \max_{t \in \bar{I}} \|\zeta_n\|_{H^{1,2}(\Omega)} + \max_{t \in \bar{I}} \|\partial_t \zeta_n\|_{H^{1,2}(\Omega)} \right) \leq C, \tag{4.40}$$

the series  $\{E(\zeta_n)\}_n \subset C^0(\bar{I}; L^2(\Omega))$  is precompact.

For this purpose, let  $\delta > 0$  and  $t_j \in \bar{I}$ ,  $j = 1, \dots, l$ , such that

$$\bar{I} \subset \bigcup_{j=1}^l B_\delta(t_j) \subset \mathbb{R}$$

## 4.1. QUADRATIC REDUCED GRAND CANONICAL POTENTIALS

where  $B_\delta$  denotes the ball of radius  $\delta$ . The set of functions  $\zeta_n(t_j, \cdot) \in H^{1,2}(\Omega)$ ,  $n \in \mathbb{N}$ ,  $j \in \{1, \dots, l\}$ , is precompact in  $L^2(\Omega)$  since by Theorem D.3 the embedding  $H^{1,2}(\Omega) \hookrightarrow L^2(\Omega)$  is compact. Therefore there is a finite number of functions  $\xi_i \in L^2(\Omega)$ ,  $i \in \{1, \dots, k\}$ , such that

$$\{\zeta_n(t_j, \cdot)\}_{n,j} \subset \bigcup_{i=1}^k B_\delta(\xi_i) \subset L^2(\Omega). \quad (4.41)$$

Considering mappings  $\pi : \{1, \dots, l\} \rightarrow \{1, \dots, k\}$  define the sets

$$S_\pi := \{\zeta_n : \zeta_n(t_j, \cdot) \in B_\delta(\xi_{\pi(j)}), \forall j \in \{1, \dots, l\}\}.$$

For every map  $\pi$  such that  $S_\pi$  is not empty choose some function  $\zeta_\pi \in S_\pi$ .

Let  $n \in \mathbb{N}$  and  $t \in \bar{T}$ . It is clear from (4.41) that there is a mapping  $\pi$  such that  $\zeta_n \in S_\pi$ . With  $j \in \{1, \dots, l\}$  such that  $t \in B_\delta(t_j)$  is holds that

$$\|\zeta_n(t) - \zeta_\pi(t)\|_{L^2(\Omega)} \leq \|\zeta_n(t) - \zeta_n(t_j)\|_{L^2(\Omega)} \quad (4.42a)$$

$$+ \|\zeta_n(t_j) - \xi_{\pi(j)}\|_{L^2(\Omega)} \quad (4.42b)$$

$$+ \|\xi_{\pi(j)} - \zeta_\pi(t_j)\|_{L^2(\Omega)} \quad (4.42c)$$

$$+ \|\zeta_\pi(t_j) - \zeta_\pi(t)\|_{L^2(\Omega)}. \quad (4.42d)$$

The difference (4.42a) is estimated using (4.40) as follows:

$$\|\zeta_n(t) - \zeta_n(t_j)\|_{L^2(\Omega)} \leq \|\zeta_n(t) - \zeta_n(t_j)\|_{H^{1,2}(\Omega)} \leq \max_{\tau \in \bar{T}} \|\partial_t \zeta_n(\tau)\|_{H^{1,2}(\Omega)} |t - t_j| \leq C\delta.$$

Similarly, (4.42d) can be estimated, i.e.,  $\|\zeta_\pi(t_j) - \zeta_\pi(t)\|_{L^2(\Omega)} \leq C\delta$ . By the definition of the sets  $S_\pi$  (4.42b) and (4.42c) are smaller than  $\delta$  respectively. Altogether

$$\max_{t \in \bar{T}} \|\zeta_n(t) - \zeta_\pi(t)\|_{L^2(\Omega)} \leq 2(C+1)\delta.$$

Since  $\delta$  is arbitrary this provides the desired result: For every  $\varepsilon > 0$  (let  $\delta = \varepsilon/2(C+1)$  in the above calculations) there is a finite number  $\{\zeta_\pi\}_\pi$  of functions in the set  $\{\zeta_n\}_n$  such that the whole set  $\{\zeta_n\}_n$  is covered by  $\varepsilon$ -balls around the functions  $\{\zeta_\pi\}_\pi$ ,

$$\{\zeta_n\}_{n \in \mathbb{N}} \subset \bigcup_{\pi} B_\varepsilon(\zeta_\pi) \subset C^0(\bar{T}; L^2(\Omega)).$$

□

This lemma together with the extension principle for operators (cf. [Zei90], Section 18.12, Proposition 18.29) yields that the embedding

$$W \hookrightarrow C^0(\bar{T}; L^2(\Omega)) \quad \text{is compact.}$$

Observe that this result also holds when considering functions mapping into finite dimensional vector spaces as the  $\phi^{(n)}$ . Indeed, since  $\{\phi^{(n)}\}_n \subset H^{1,2}(I \times \Omega; \mathbb{H}\Sigma^M)$  the convergence result (4.23a) implies that (for a subsequence as  $n \rightarrow \infty$ )

$$\phi^{(n)} \rightarrow \phi \quad \text{in } C^0(\bar{T}; L^2(\Omega; \mathbb{H}\Sigma^M)).$$

In particular, at  $t = 0$  using (4.11b) and (4.17b)

$$\begin{aligned} \|\phi(0, \cdot) - \phi_{ic}\|_{L^2(\Omega; \mathbb{T}\Sigma^M)} &\leq \|\phi(0, \cdot) - \phi^{(n)}(0, \cdot)\|_{L^2(\Omega; \mathbb{T}\Sigma^M)} + \|\phi^{(n)}(0, \cdot) - \phi_{ic}\|_{L^2(\Omega; \mathbb{T}\Sigma^M)} \\ &\leq \|\phi - \phi^{(n)}\|_{C^0(\bar{T}; L^2(\Omega; \mathbb{T}\Sigma^M))} + \|\phi_{ic}^{(n)} - \phi_{ic}\|_{L^2(\Omega; \mathbb{T}\Sigma^M)} \\ &\rightarrow 0 \quad \text{as } n \rightarrow \infty. \end{aligned}$$

This proves assertion (4.8b) and, hence, Theorem 4.3. □

## 4.1.7 Additional a priori estimates

In addition to proving Theorem 4.3, the convergence results in the previous subsections allow to deduce estimates for the solution  $(u, \phi)$  which will turn out to be useful in the coming sections. It is assumed that  $\beta_0 > 0$  in this subsection.

Replacing  $\tilde{I}$  by  $I$  in (4.18) there is already the estimate

$$\begin{aligned}
 & \text{esssup}_{\tilde{t} \in I} \left( \int_{\Omega} \left[ \psi_{,u}(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t})) \cdot u^{(n)}(\tilde{t}) - \psi(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t})) \right] dx \right. \\
 & \quad \left. + \int_{\Omega} \left[ w(\phi^{(n)}(\tilde{t})) + a(\phi^{(n)}(\tilde{t}), \nabla \phi^{(n)}(\tilde{t})) \right] dx \right) \\
 & + \int_I \int_{\Omega} \left[ \omega(\phi^{(n)}, \nabla \phi^{(n)}) |\partial_t \phi^{(n)}|^2 + \sum_{l=1}^d \partial_{x_l} u^{(n)} \cdot L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \partial_{x_l} u^{(n)} \right] dx dt \\
 & + \int_I \int_{\partial \Omega} \left[ u^{(n)} \cdot \beta(u^{(n)} - u_{bc}) \right] d\mathcal{H}^{d-1} dt \leq C. \tag{4.43}
 \end{aligned}$$

By (4.26) and (4.27)

$$\int_{\Omega} \psi_{,u}(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t})) \cdot u^{(n)}(\tilde{t}) dx \rightarrow \int_{\Omega} \psi_{,u}(u(\tilde{t}), \phi(\tilde{t})) \cdot u(\tilde{t}) dx \tag{4.44a}$$

for almost every  $\tilde{t} \in I$ . By assumption (4.1a), (4.23e) and (4.26) imply  $\psi(u^{(n)}, \phi^{(n)}) \rightarrow \psi(u, \phi)$  almost everywhere. Using assumption (4.1h) and the Lebesgue convergence theorem it holds for almost every  $\tilde{t} \in I$  that

$$\int_{\Omega} \psi(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t})) dx \rightarrow \int_{\Omega} \psi(u(\tilde{t}), \phi(\tilde{t})) dx. \tag{4.44b}$$

By (4.23d) for  $q = p$  it holds for almost every  $\tilde{t} \in I$  that

$$\liminf_{n \rightarrow \infty} \int_{\Omega} w(\phi^{(n)}(\tilde{t})) dx \geq \liminf_{n \rightarrow \infty} \int_{\Omega} w_2 |\phi^{(n)}(\tilde{t})|^p dx - C \geq \int_{\Omega} w_2 |\phi(\tilde{t})|^p dx - C. \tag{4.44c}$$

Since by (4.36)  $\nabla \phi^{(n)}(\tilde{t}) \rightarrow \nabla \phi(\tilde{t})$  in  $L^2(\Omega; (\mathbb{T}\Sigma^M)^d)$  for almost every  $\tilde{t}$  and since the  $L^2$  norm is weakly lower semi-continuous it follows with assumption (4.4b) that

$$\begin{aligned}
 & \liminf_{n \rightarrow \infty} \int_{\Omega} a(\phi^{(n)}(\tilde{t}), \nabla \phi^{(n)}(\tilde{t})) dx \\
 & \geq \liminf_{n \rightarrow \infty} \int_I \int_{\Omega} a_0 |\nabla \phi^{(n)}(\tilde{t})|^2 dx \geq \int_I \int_{\Omega} a_0 |\nabla \phi(\tilde{t})|^2 dx. \tag{4.44d}
 \end{aligned}$$

Analogously, since by (4.23a)  $\partial_t \phi^{(n)} \rightharpoonup \partial_t \phi$  in  $L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))$

$$\liminf_{n \rightarrow \infty} \int_I \int_{\Omega} \omega(\phi^{(n)}, \nabla \phi^{(n)}) |\partial_t \phi^{(n)}|^2 dx dt \geq \int_I \int_{\Omega} \omega_0 |\partial_t \phi|^2 dx dt, \tag{4.44e}$$

and since by (4.23b)  $\nabla u^{(n)} \rightharpoonup \nabla u$  in  $L^2(I; L^2(\Omega; (Y^N)^d))$ , assumption (4.2d) yields

$$\begin{aligned}
 & \liminf_{n \rightarrow \infty} \int_I \int_{\Omega} \nabla u^{(n)} : L(\psi_{,u}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} dx dt \\
 & \geq \liminf_{n \rightarrow \infty} \int_I \int_{\Omega} l_0 |\nabla u^{(n)}|^2 dx dt \geq \int_I \int_{\Omega} l_0 |\nabla u|^2 dx dt. \tag{4.44f}
 \end{aligned}$$

---

#### 4.1. QUADRATIC REDUCED GRAND CANONICAL POTENTIALS

---

Finally for the boundary terms by (4.23c) and for  $\delta$  small enough (such that  $\beta_2 := \beta_0 - \delta\beta_1 > 0$ , remember that  $\beta_0 > 0$  was assumed for this subsection)

$$\begin{aligned}
& \liminf_{n \rightarrow \infty} \int_I \int_{\partial\Omega} u^{(n)} \cdot \beta(u^{(n)} - u_{bc}) \, d\mathcal{H}^{d-1} dt \\
& \geq \liminf_{n \rightarrow \infty} (\beta_0 - \delta\beta_1) \int_I \int_{\partial\Omega} |u^{(n)}|^2 \, d\mathcal{H}^{d-1} dt - \beta_1 \int_I \int_{\partial\Omega} |u_{bc}|^2 \, d\mathcal{H}^{d-1} dt \\
& \geq \beta_2 \int_I \int_{\partial\Omega} |u|^2 \, d\mathcal{H}^{d-1} dt - C.
\end{aligned} \tag{4.44g}$$

Due to (4.44a)–(4.44g), in the limit as  $n \rightarrow \infty$  the estimate (4.43) yields the following entropy estimate:

$$\begin{aligned}
& \text{esssup}_{\tilde{t} \in I} \int_{\Omega} \left[ \psi_{,u}(u(\tilde{t}), \phi(\tilde{t})) \cdot u(\tilde{t}) - \psi(u(\tilde{t}), \phi(\tilde{t})) + w_2 |\phi(\tilde{t})|^p + a_0 |\nabla \phi(\tilde{t})|^2 \right] dx \\
& \quad + \int_I \int_{\Omega} \left[ \omega_0 |\partial_t \phi|^2 + l_0 |\nabla u|^2 \right] dx dt + \beta_2 \int_I \int_{\partial\Omega} |u|^2 \, d\mathcal{H}^{d-1} dt \leq C.
\end{aligned} \tag{4.45}$$

Now, define for times  $0 < t_1 < t_2 < \mathcal{T} - \delta$  and small  $\delta > 0$  the functions

$$\chi_{\delta}(t) = \begin{cases} 0, & t \notin [t_1, t_2 + \delta], \\ \frac{1}{\delta}(t - t_1), & t \in [t_1, t_1 + \delta], \\ 1, & t \in (t_1 + \delta, t_2), \\ -\frac{1}{\delta}(t - (t_2 + \delta)), & t \in [t_2, t_2 + \delta]. \end{cases}$$

Since  $u \in L^2(H^{1,2}(\Omega; Y^N))$  and

$$\chi'_{\delta}(t) = \begin{cases} \frac{1}{\delta}, & t \in [t_1, t_1 + \delta], \\ -\frac{1}{\delta}, & t \in [t_2, t_2 + \delta], \\ 0, & \text{elsewhere} \end{cases}$$

it is clear that  $v(t, x) = \chi_{\delta}(t)(u(t_2, x) - u(t_1, x)) \in H^{1,2}(I \times \Omega; Y^N)$  for almost every  $t_1, t_2$ . The properties of the convolution (see Theorem D.11 in Appendix D, the functions  $\zeta_{\delta}(t) = \frac{1}{\delta} \chi_{(\tilde{t}, \tilde{t} + \delta)}(t)$  where  $\chi_{(\tilde{t}, \tilde{t} + \delta)}$  is the characteristic function of the interval  $(\tilde{t}, \tilde{t} + \delta)$  constitute a Dirac sequence) and the fact that  $\psi_{,u}(u, \phi) \in L^2(I; L^2(\Omega; Y^N))$  by (4.27) give

$$\int_{\tilde{t}}^{\tilde{t} + \delta} \int_{\Omega} \psi_{,u}(u(t), \phi(t)) \, dx dt \rightarrow \int_{\Omega} \psi_{,u}(u(\tilde{t}), \phi(\tilde{t})) \, dx$$

for almost every  $\tilde{t} \in I$ . Inserting the function  $v$  and  $\zeta = 0$  in (4.8c) yields for almost every  $t_1, t_2$  in the limit as  $\delta \searrow 0$  (the dependence on  $x$  is dropped and  $L(t) := L(\psi_{,u}(u(t), \phi(t)), \phi(t))$  was set for shorter presentation)

$$\begin{aligned}
0 &= \int_{t_1}^{t_1 + \delta} \int_{\Omega} -\frac{1}{\delta}(u(t_2) - u(t_1)) \cdot (\psi_{,u}(u(t), \phi(t)) - \psi_{,u}(u_{ic}, \phi_{ic})) \, dx dt \\
& \quad + \int_{t_2}^{t_2 + \delta} \int_{\Omega} \frac{1}{\delta}(u(t_2) - u(t_1)) \cdot (\psi_{,u}(u(t), \phi(t)) - \psi_{,u}(u_{ic}, \phi_{ic})) \, dx dt \\
& \quad + \int_{t_1}^{t_2 + \delta} \int_{\Omega} \chi_{\delta}(t) \nabla(u(t_2) - u(t_1)) \cdot L(t) \nabla u(t) \, dx dt \\
& \quad + \int_{t_1}^{t_2 + \delta} \int_{\partial\Omega} \chi_{\delta}(t)(u(t_2) - u(t_1)) \cdot \beta(t)(u(t) - u_{bc}(t)) \, d\mathcal{H}^{d-1} dt
\end{aligned}$$

$$\begin{aligned}
 & \rightarrow \int_{\Omega} (u(t_2) - u(t_1)) \cdot (\psi_{,u}(u(t_2), \phi(t_2)) - \psi_{,u}(u(t_1), \phi(t_1))) \, dx \\
 & + \int_{t_1}^{t_2} \int_{\Omega} \nabla(u(t_2) - u(t_1)) \cdot L(t) \nabla u(t) \, dx dt \\
 & + \int_{t_1}^{t_2} \int_{\partial\Omega} (u(t_2) - u(t_1)) \cdot \beta(t)(u(t) - u_{bc}(t)) \, d\mathcal{H}^{d-1} dt.
 \end{aligned}$$

For a small  $s > 0$  such that  $\mathcal{T} - s > 0$  let  $t_2 = t_1 + s$  and integrate the above identity with respect to  $t_1$  from  $t_1 = 0$  to  $t_1 = \mathcal{T} - s$ . The convolution estimate (inequality (D.2) in Theorem D.9, extend the functions  $t \mapsto \|L(t)\nabla u(t)\|_{L^2(\Omega; (Y^N)^d)}$  and  $t \mapsto \|\beta(t)(u(t) - u_{bc}(t))\|_{L^2(\partial\Omega; Y^N)}$  by zero on  $\mathbb{R} - I$ ) furthermore implies that

$$\begin{aligned}
 & \int_0^{\mathcal{T}-s} \int_{t_1}^{t_1+s} \|L(t)\nabla u(t)\|_{L^2(\Omega; (Y^N)^d)} \, dt dt_1 \leq \int_I \|L\nabla u(t_1)\|_{L^2(\Omega; (Y^N)^d)} \, dt_1, \\
 & \int_0^{\mathcal{T}-s} \int_{t_1}^{t_1+s} \|\beta(t)(u(t) - u_{bc}(t))\|_{L^2(\partial\Omega; Y^N)} \, dt dt_1 \leq \int_I \|\beta(t_1)(u(t_1) - u_{bc}(t_1))\|_{L^2(\partial\Omega; Y^N)} \, dt_1.
 \end{aligned}$$

It follows from (4.45) that

$$\begin{aligned}
 0 & \leq \left| \int_0^{\mathcal{T}-s} \int_{\Omega} (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1 + s)) - \psi_{,u}(u(t_1), \phi(t_1))) \, dx dt_1 \right| \\
 & \leq s \int_0^{\mathcal{T}-s} \left( \|\nabla u(t_1 + s)\|_{L^2(\Omega)} + \|\nabla u(t_1)\|_{L^2(\Omega)} \right) \int_{t_1}^{t_1+s} \|L(t)\nabla u(t)\|_{L^2(\Omega)} \, dt dt_1 \\
 & \quad + s \int_0^{\mathcal{T}-s} \left( \|u(t_1 + s)\|_{L^2(\partial\Omega)} + \|u(t_1)\|_{L^2(\partial\Omega)} \right) \int_{t_1}^{t_1+s} \|\beta(t)(u(t) - u_{bc}(t))\|_{L^2(\partial\Omega)} \, dt dt_1 \\
 & \leq s \int_I 2L_0 \|\nabla u(t_1)\|_{L^2(\Omega; (Y^N)^d)}^2 + 2\beta_1 \|u(t_1)\|_{L^2(\partial\Omega; Y^N)} \|u(t_1) - u_{bc}(t_1)\|_{L^2(\partial\Omega; Y^N)} \, dt_1 \quad (4.46)
 \end{aligned}$$

where the last inequality holds due to assumptions (4.2e) and (4.7d). Obviously

$$\begin{aligned}
 & (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1 + s)) - \psi_{,u}(u(t_1), \phi(t_1))) \\
 & = (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1 + s)) - \psi_{,u}(u(t_1 + s), \phi(t_1))) \\
 & \quad + (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1)) - \psi_{,u}(u(t_1), \phi(t_1))). \quad (4.47)
 \end{aligned}$$

Using (4.1e), the first term on the right hand side can be estimated by

$$\begin{aligned}
 & \left| (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1 + s)) - \psi_{,u}(u(t_1 + s), \phi(t_1))) \right| \\
 & = \left| (u(t_1 + s) - u(t_1)) \cdot \int_0^1 \frac{d}{d\theta} \psi_{,u}(u(t_1 + s), \theta\phi(t_1 + s) + (1 - \theta)\phi(t_1)) d\theta \right| \\
 & = \left| (u(t_1 + s) - u(t_1)) \cdot \int_0^1 \psi_{,u\phi}(u(t_1 + s), \theta\phi(t_1 + s) + (1 - \theta)\phi(t_1)) d\theta \cdot (\phi(t_1 + s) - \phi(t_1)) \right| \\
 & \leq \frac{1}{2} k_3 |u(t_1 + s) - u(t_1)| |\phi(t_1 + s) - \phi(t_1)|.
 \end{aligned}$$

Assumption (4.1b) implies that  $\psi_{,u}$  is monotone in  $u$  uniformly in  $\phi$ , hence from (4.46) and (4.47) the following estimation is obtained:

$$\begin{aligned}
 0 & \leq \int_0^{\mathcal{T}-s} \int_{\Omega} (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1)) - \psi_{,u}(u(t_1), \phi(t_1))) \, dx dt_1 \\
 & = \int_0^{\mathcal{T}-s} \int_{\Omega} (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1 + s)) - \psi_{,u}(u(t_1 + s), \phi(t_1))) \, dx dt_1 \\
 & \quad - \int_0^{\mathcal{T}-s} \int_{\Omega} (u(t_1 + s) - u(t_1)) \cdot (\psi_{,u}(u(t_1 + s), \phi(t_1 + s)) - \psi_{,u}(u(t_1), \phi(t_1))) \, dx dt_1
 \end{aligned}$$



$$\begin{aligned}
 &\leq \left| \int_0^{\mathcal{T}-s} \int_{\Omega} (u(t_1+s) - u(t_1)) \cdot (\psi_{,u}(u(t_1+s), \phi(t_1+s)) - \psi_{,u}(u(t_1), \phi(t_1))) \, dx dt_1 \right| \\
 &\quad + \left| \int_0^{\mathcal{T}-s} \int_{\Omega} (u(t_1+s) - u(t_1)) \cdot (\psi_{,u}(u(t_1+s), \phi(t_1+s)) - \psi_{,u}(u(t_1+s), \phi(t_1))) \, dx dt_1 \right| \\
 &\leq s \left( \int_I 2L_0 \|\nabla u(t_1)\|_{L^2(\Omega; (Y^N)^d)}^2 \, dt_1 \right) \\
 &\quad + s \left( \int_I 2\beta_1 \|u(t_1)\|_{L^2(\partial\Omega; Y^N)} \|u(t_1) - u_{bc}(t_1)\|_{L^2(\partial\Omega; Y^N)} \, dt_1 \right) \\
 &\quad + s \int_0^{\mathcal{T}-s} \int_{\Omega} \frac{1}{2} k_3 |u(t_1+s) - u(t_1)| \frac{1}{s} |\phi(t_1+s) - \phi(t_1)| \, dx dt_1 \\
 &\leq s \left( 2L_0 \|\nabla u\|_{L^2(I; L^2(\Omega; (Y^N)^d))}^2 + 2\beta_1 \|u\|_{L^2(I; L^2(\partial\Omega; Y^N))} \|u - u_{bc}\|_{L^2(I; L^2(\partial\Omega; Y^N))} \right) \\
 &\quad + s \left( k_3 \|u\|_{L^2(I; L^2(\Omega; Y^N))} \|\partial_t \phi\|_{L^2(I; L^2(\Omega; Y^N))} \right) \\
 &\leq s C(\|u\|_{L^2(I; H^{1,2}(\Omega; Y^N))}, \|u\|_{L^2(I; L^2(\partial\Omega; Y^N))}, \|\partial_t \phi\|_{L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))}). \tag{4.48}
 \end{aligned}$$

For the second last estimate it was used that

$$\begin{aligned}
 \int_{\Omega} \int_0^{\mathcal{T}-s} \left| \frac{\phi(t+s) - \phi(t)}{s} \right|^2 \, dt dx &= \int_{\Omega} \int_0^{\mathcal{T}-s} \left| \partial_t \int_t^{t+s} \phi(\tau) \, d\tau \right|^2 \, dt dx \\
 &= \int_{\Omega} \int_0^{\mathcal{T}-s} |\partial_t (\frac{1}{s} \chi_{(-s,0)} * \phi)(t)|^2 \, dt dx \\
 &= \int_{\Omega} \int_0^{\mathcal{T}-s} |(\frac{1}{s} \chi_{(-s,0)} * \partial_t \phi)(t)|^2 \, dt dx \\
 &\leq \mathcal{T} \|\partial_t \phi\|_{L^2(I \times \Omega; \mathbb{T}\Sigma^M)}^2 \tag{4.49}
 \end{aligned}$$

where  $\partial_t \phi$  was extended by zero on  $\mathbb{R} \setminus I$  and properties of the convolution in Theorem D.9 were applied.

## 4.2 Linear growth in the chemical potentials

In this section, existence of weak solutions to the problem in Definition 2.5 is shown for a reduced grand canonical potential of the form

$$\begin{aligned}
 \psi &: \mathbb{R} \times \mathbb{T}\Sigma^N \times \mathbb{H}\Sigma^M \rightarrow \mathbb{R}, \\
 \psi(u, \phi) &= g(u_0) + \sum_{\alpha=1}^M h(\phi_{\alpha}) \lambda^{(\alpha)}(u)
 \end{aligned}$$

where  $h : \mathbb{R} \rightarrow [0, 1]$  is a monotone smooth interpolation function, the functions  $\lambda^{(\alpha)}$  are convex but only of linear growth in  $u$ , and  $g$  is of quadratic growth replacing the logarithmic term of  $\psi$  in the example in Subsection 2.4.2. Because of the special structure of  $\psi$  it makes sense to split the variable  $u$  defining

$$u =: (u_0, \tilde{u}), \quad u_0 \in \mathbb{R}, \quad \tilde{u} \in \mathbb{T}\Sigma^N.$$

The idea of solving this problem is to approximate  $\psi$  with potentials satisfying the conditions in assumption E1. After, compactness arguments are applied to the solutions in order to deduce a limiting function which solves the differential equations with the original  $\psi$ . The arguments follow the lines of [AL83] for the potentials  $u$ . The challenge is to tackle the problems due to the coupling to the phase field variables  $\phi$ .

### 4.2.1 Assumptions and existence result

Let  $\Omega$  and  $I$  be as in Subsection 4.1.1 and define

$$\psi^{(\nu)}(u, \phi) := \nu|\tilde{u}|^2 + \psi(u, \phi). \quad (4.50)$$

Assume the following:

- N1 The functions  $g$  and  $\lambda^{(\alpha)}$  are of the class  $C^{2,1}$  in their arguments.  
 Moreover it holds for all  $(u, \phi) \in Y^N \times \mathbf{H}\Sigma^M$  that

$$|g(u_0)| \leq g_0(1 + u_0^2), \quad (4.51a)$$

$$|g'(u_0)| \leq g_1(1 + |u_0|), \quad (4.51b)$$

$$|g''(u_0)| \leq g_2, \quad (4.51c)$$

$$v \cdot \psi_{,uu}(u, \phi)v \geq k_0|v_0|^2 \quad \forall v \in Y^N, \quad (4.51d)$$

$$|\lambda^{(\alpha)}(u)| \leq \hat{k}_2(1 + |u|) \quad \forall \alpha, \quad (4.51e)$$

$$|\lambda_{,u}^{(\alpha)}(u) \cdot v| \leq \hat{k}_3|v| \quad \forall \alpha, \forall v \in Y^N, \quad (4.51f)$$

$$|w \cdot \lambda_{,uu}^{(\alpha)}(u)v| \leq \hat{k}_1|w||v| \quad \forall \alpha, \forall w, v \in Y^N, \quad (4.51g)$$

$$|\lambda^{(\alpha)}(0)| \leq \hat{k}_4, \quad (4.51h)$$

$$h \in W^{3,\infty}(\mathbb{R}; [0, 1]), \quad (4.51i)$$

$$h(r) = 0 \quad \text{if } r \leq 0, \quad (4.51j)$$

$$h(r) = 1 \quad \text{if } r \geq 1, \quad (4.51k)$$

$$|h'(r)| \leq k_7 \quad \forall r \in \mathbb{R}, \quad (4.51l)$$

where the  $g_i$ , the  $\hat{k}_i$  and the  $k_i$  are positive constants.

- N2 For initial data  $(u_{ic}, \phi_{ic})$  as in (4.6a) there is some  $\bar{\nu} > 0$  such that the inequality (4.6b) holds with a constant independent of  $\nu$  as long as  $\nu \in [0, \bar{\nu}]$ .

- N3 In addition to assumption E7, it holds that

$$\beta_0 > 0, \quad (4.52a)$$

and the boundary data  $u_{bc}$  are such that

$$\|\psi_{,u}^{(\nu)}(u_{bc}, \phi)\|_{L^2(I; L^2(\partial\Omega; Y^N))} \leq C \quad \text{for all } \nu \in [0, \bar{\nu}], \phi \in H^{1,2}(I \times \Omega; \mathbf{H}\Sigma^M). \quad (4.52b)$$

for some constant  $C > 0$ .

- N4 The assumptions in E2–E5 remain fulfilled.

**4.5 Remark** In the previous section, a control of  $u^{(n)}$  in  $L^2$  was obtained from the quadratic growth of  $\psi$  (see the estimate after (4.18)). Together with the estimate on the gradient  $\nabla u^{(n)}$  in (4.20) the convergence (4.23c) was obtained using the trace theorem D.6 in Appendix D. In particular, one can allow for  $\beta \equiv 0$  which corresponds to homogeneous Neumann boundary conditions for  $u$  in consistence with (2.32e) and (2.32g). But an estimate of  $u^{(n)}$  is not available any more in the case  $\nu = 0$  whence the above stated Robin boundary conditions with  $\beta_0 > 0$  are essential for  $\tilde{u}$  in the following. For  $u_0$  one could have applied the same procedure as in the previous section since by the assumption (4.51d) the situation has not changed.

The special choice of  $q(\nu) = \nu|\tilde{u}|^2$  is not essential. Another function of quadratic growth of  $C^{2,1}$ -regularity which converges to zero as  $\nu \rightarrow 0$  would do as well.

**4.6 Theorem** *If the assumptions N1–N4 are fulfilled then there are functions*

$$u \in L^2(I; H^1(\Omega; Y^N)), \quad \phi \in H^1(I \times \Omega; \mathbf{H}\Sigma^M) \cap L^p(I \times \Omega; \mathbf{H}\Sigma^M) \quad (4.53a)$$

such that

$$\phi(t, \cdot) \rightarrow \phi_{ic} \quad \text{in } L^2(\Omega; \mathbf{H}\Sigma^M) \quad \text{as } t \searrow 0 \quad (4.53b)$$

and such that

$$\begin{aligned} 0 = & \int_I \int_{\Omega} \left[ -\partial_t v \cdot (\psi_{,u}(u, \phi) - \psi_{,u}(u_{ic}, \phi_{ic})) + \nabla v : L(\psi_{,u}(u, \phi), \phi) \nabla u \right] dx dt \\ & + \int_I \int_{\partial\Omega} v \cdot \beta(u - u_{bc}) d\mathcal{H}^{d-1} dt \\ & + \int_I \int_{\Omega} \left[ \omega(\phi, \nabla\phi) \partial_t \phi \cdot \zeta + a_{,\nabla\phi}(\phi, \nabla\phi) : \nabla\zeta \right] dx dt \\ & + \int_I \int_{\Omega} \left[ a_{,\phi}(\phi, \nabla\phi) \cdot \zeta + w_{,\phi}(\phi) \cdot \zeta - \psi_{,\phi}(u, \phi) \cdot \zeta \right] dx dt \end{aligned} \quad (4.53c)$$

for all test functions  $v \in H^1(I; L^\infty(\Omega; Y^N)) \cap L^2(I; H^1(\Omega; Y^N))$  with  $v(T) = 0$  and  $\zeta \in H^1(I \times \Omega; \mathbf{T}\Sigma^M) \cap L^p(I \times \Omega; \mathbf{T}\Sigma^M)$ .

**Proof:** Again the proof will be given in steps corresponding to the following subsections:

- The reduced grand canonical potential  $\psi^{(\nu)}$  fulfils the assumptions of Theorem 4.3 yielding a solution  $(u^{(\nu)}, \phi^{(\nu)})$  and providing a useful set of a priori estimates from (4.45), (4.46), and (4.48). By functional analytical facts on the considered spaces candidates  $(u, \phi)$  for a solution of the weak problem are obtained. It remains to handle the nonlinearities in the  $\nu$  formulation of (4.8c).
- Several preparatory facts on  $\psi^{(\nu)}$  and its Legendre transform are shown. In particular, it holds that  $\psi_{,\phi} = -\psi_{,\phi}^*$ .
- The core of the proof is to show that the set of functions  $\{\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})\}_\nu$  is precompact in  $L^1$ .
- The results are sufficient to go to the limit in the weak formulation of the  $\nu$  problem as  $\nu \rightarrow 0$ . Strong convergence of  $\nabla\phi^{(\nu)}$  in  $L^2$  can be shown with arguments as in Subsection 4.1.5.

### 4.2.2 Solution to the perturbed problem

By the assumptions on the functions  $g, h$ , and the  $\lambda^{(\alpha)}$  the perturbed potential  $\psi^{(\nu)}$  is of the class  $C^{2,1}$  (for the dependence on  $\phi$  Theorem D.5 in Appendix D was applied on  $W^{3,\infty}(\mathbb{R})$  in which  $h$  lies). The following estimates imply that the perturbed potential  $\psi^{(\nu)}$  fulfils the assumptions (4.1b)–(4.1h): For all  $u, v, w \in Y^N$ ,  $\phi \in \mathbf{H}\Sigma^M$ , and  $\zeta \in \mathbf{T}\Sigma^M$

$$v \cdot \psi_{,uu}^{(\nu)}(u, \phi) v \geq k_0 v_0^2 + 2\nu |\tilde{v}|^2, \quad (4.54a)$$

$$|w \cdot \psi_{,uu}^{(\nu)}(u, \phi) v| \leq g_2 |w_0| |v_0| + 2\nu |\tilde{w}| |\tilde{v}| + M \hat{k}_1 |w| |v|, \quad (4.54b)$$

$$|\psi_{,\phi}^{(\nu)}(u, \phi) \cdot \zeta| \leq \hat{k}_2 (1 + |u|) M k_7 |\zeta|, \quad (4.54c)$$

$$|v \cdot \psi_{,u\phi}^{(\nu)}(u, \phi) \zeta| \leq |v| \hat{k}_3 M k_7 |\zeta|, \quad (4.54d)$$

$$|\psi^{(\nu)}(0, \phi)| \leq M \hat{k}_4, \quad (4.54e)$$

$$|\psi_{,u}^{(\nu)}(u, \phi) \cdot v| \leq g_1 (1 + |u_0|) |v_0| + 2\nu |\tilde{u}| |\tilde{v}| + M \hat{k}_3 |\tilde{v}|, \quad (4.54f)$$

$$|\psi^{(\nu)}(u, \phi)| \leq g_0 (1 + u_0^2) + \nu |\tilde{u}|^2 + M \hat{k}_2 C (1 + |u|^2). \quad (4.54f)$$

Assumption (4.1i) follows from (4.54a), (4.54b) and the following lemma (indeed, this assumption is redundant and has only been listed for completeness):

## CHAPTER 4. EXISTENCE OF WEAK SOLUTIONS

---

**4.7 Lemma** *Let  $L, K \in \mathbb{N}$  and  $Q \in C^{0,1}(\mathbb{R}^L; \mathbb{R}^{K \times K})$  be a function such that  $Q(x)$  is symmetric. Assume that there are constants  $q_1 > q_0 > 0$  so that  $q_0|v|^2 \leq v \cdot Q(x)v \leq q_1|v|^2$  for all  $x \in \mathbb{R}^L$  and  $v \in \mathbb{R}^K$ . Then the function  $x \mapsto Q^{-1}(x)$  is Lipschitz continuous.*

**Proof:** Clearly, the matrices  $Q(x)$  are invertible since they are positive definite, and it holds that  $v \cdot Q^{-1}(x)v \leq \frac{1}{q_0}|v|^2$  for all  $x \in \mathbb{R}^L$  and  $v \in \mathbb{R}^K$ . Let  $x \neq y \in \mathbb{R}^L$  and denote the Lipschitz constant of  $Q$  by  $\bar{q}$ . By  $|\cdot|$  some norms on  $\mathbb{R}^L$  and  $\mathbb{R}^{K \times K}$  are denoted.

From  $Q^{-1}(z)Q(z) = \text{Id}_K$  for all  $z \in \mathbb{R}^L$  it follows that

$$\frac{Q^{-1}(x)Q(x) - Q^{-1}(y)Q(y)}{|x - y|} = 0.$$

Subtracting and adding  $Q^{-1}(y)Q(x)$  gives

$$\frac{(Q^{-1}(x) - Q^{-1}(y))Q(x)}{|x - y|} + \frac{Q^{-1}(y)(Q(x) - Q(y))}{|x - y|} = 0.$$

From this the estimate

$$\frac{|Q^{-1}(x) - Q^{-1}(y)|}{|x - y|} \leq |Q^{-1}(y)| \frac{|Q(x) - Q(y)|}{|x - y|} |Q^{-1}(x)| \leq C \frac{\bar{q}}{q_0^2}.$$

is obtained showing the desired result. □

Assuming N2–N4, Theorem 4.3 furnishes functions

$$u^{(\nu)} \in L^2(I; H^1(\Omega; Y^N)), \quad \phi^{(\nu)} \in H^1(I \times \Omega; \mathbf{H}\Sigma^M) \quad (4.55a)$$

such that

$$\phi^{(\nu)}(t, \cdot) \rightarrow \phi_{ic} \quad \text{in } L^2(\Omega; \mathbf{H}\Sigma^M) \text{ as } t \searrow 0 \quad (4.55b)$$

and such that

$$\begin{aligned} 0 = & \int_I \int_{\Omega} \left[ -\partial_t v \cdot (\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) - \psi_{,u}^{(\nu)}(u_{ic}, \phi_{ic})) + \nabla v : L(\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}), \phi^{(\nu)}) \nabla u^{(\nu)} \right] dx dt \\ & + \int_I \int_{\partial\Omega} v \cdot \beta(u^{(\nu)} - u_{bc}) d\mathcal{H}^{d-1} dt \\ & + \int_I \int_{\Omega} \left[ \omega(\phi^{(\nu)}, \nabla \phi^{(\nu)}) \partial_t \phi^{(\nu)} \cdot \zeta + a_{\nabla \phi}(\phi^{(\nu)}, \nabla \phi^{(\nu)}) : \nabla \zeta \right] dx dt \\ & + \int_I \int_{\Omega} \left[ a_{,\phi}(\phi^{(\nu)}, \nabla \phi^{(\nu)}) \cdot \zeta + w_{,\phi}(\phi^{(\nu)}) \cdot \zeta - \psi_{,\phi}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \cdot \zeta \right] dx dt \end{aligned} \quad (4.55c)$$

for all test functions  $v \in H^1(I \times \Omega; Y^N)$  with  $v(\mathcal{T}) = 0$  and  $\zeta \in H^1(I \times \Omega; \mathbf{T}\Sigma^M) \cap L^p(I \times \Omega; \mathbf{T}\Sigma^M)$ . Furthermore, the following estimates resulting from (4.45) and (4.48) are fulfilled (remember that  $\beta_0 > 0$  in consistence with the additional assumption in Subsection 4.1.7):

$$\begin{aligned} \text{esssup}_{\tilde{t} \in I} \int_{\Omega} & \left[ \psi_{,u}^{(\nu)}(u^{(\nu)}(\tilde{t}), \phi^{(\nu)}(\tilde{t})) \cdot u^{(\nu)}(\tilde{t}) - \psi^{(\nu)}(u^{(\nu)}(\tilde{t}), \phi^{(\nu)}(\tilde{t})) \right. \\ & \left. + w_2 |\phi^{(\nu)}(\tilde{t})|^p + a_0 |\nabla \phi^{(\nu)}(\tilde{t})|^2 \right] dx \\ & + \int_I \int_{\Omega} \left[ \omega_0 |\partial_t \phi^{(\nu)}|^2 + l_0 |\nabla u^{(\nu)}|^2 \right] dx dt + \beta_2 \int_I \int_{\partial\Omega} |u^{(\nu)}|^2 d\mathcal{H}^{d-1} dt \leq C, \end{aligned} \quad (4.56a)$$

$$\begin{aligned} \int_0^{\mathcal{T}-s} \int_{\Omega} & (u^{(\nu)}(t+s) - u^{(\nu)}(t)) \\ & \cdot (\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))) dx dt \leq C s. \end{aligned} \quad (4.56b)$$

### 4.2.3 Properties of the Legendre transform

For shorter presentation define the function

$$B^{(\nu)} : Y^N \times \mathbb{H}\Sigma^M \rightarrow \mathbb{R}, \quad B^{(\nu)}(u, \phi) := \psi_{,u}^{(\nu)}(u, \phi) \cdot u - \psi^{(\nu)}(u, \phi) \quad (4.57)$$

for every  $\nu \in [0, \bar{\nu}]$ . The following two lemmata were proven in [AL83] for functions  $\psi^{(\nu)}$  not depending on  $\phi \in \mathbb{H}\Sigma^M$ .

**4.8 Lemma** *For every  $\tilde{\delta} > 0$  there is a constant  $C_{\tilde{\delta}} > 0$  independent of  $\nu$  such that*

$$|\psi_{,u}^{(\nu)}(z, \xi)| \leq \tilde{\delta} B^{(\nu)}(z, \xi) + C_{\tilde{\delta}} \quad (4.58)$$

for all  $(z, \xi) \in Y^N \times \mathbb{H}\Sigma^M$ .

**Proof:** For arbitrary points  $z, \tilde{z} \in Y^N$  and  $\xi \in \mathbb{H}\Sigma^M$  the convexity of  $\psi^{(\nu)}$  implies

$$\psi^{(\nu)}(\tilde{z}, \xi) \geq \psi_{,u}^{(\nu)}(z, \xi) \cdot (\tilde{z} - z) + \psi^{(\nu)}(z, \xi).$$

Therefore by the definition of  $B^{(\nu)}$

$$\begin{aligned} B^{(\nu)}(z, \xi) - B^{(\nu)}(\tilde{z}, \xi) &= (\psi_{,u}^{(\nu)}(z, \xi) - \psi_{,u}^{(\nu)}(\tilde{z}, \xi)) \cdot \tilde{z} \\ &\quad + \underbrace{\psi^{(\nu)}(\tilde{z}, \xi) - \psi_{,u}^{(\nu)}(z, \xi) \cdot (\tilde{z} - z) - \psi^{(\nu)}(z, \xi)}_{\geq 0}. \end{aligned}$$

Let  $e = \psi_{,u}^{(\nu)}(z, \xi) / |\psi_{,u}^{(\nu)}(z, \xi)| \in Y^N$ . Then

$$\begin{aligned} |\psi_{,u}^{(\nu)}(z, \xi)| &= \tilde{\delta} \psi_{,u}^{(\nu)}(z, \xi) \cdot \frac{e}{\tilde{\delta}} \\ &= \tilde{\delta} \psi_{,u}^{(\nu)}\left(\frac{e}{\tilde{\delta}}, \xi\right) \cdot \frac{e}{\tilde{\delta}} + \tilde{\delta} (\psi_{,u}^{(\nu)}(z, \xi) - \psi_{,u}^{(\nu)}\left(\frac{e}{\tilde{\delta}}, \xi\right)) \cdot \frac{e}{\tilde{\delta}} \\ &\leq \tilde{\delta} \psi_{,u}^{(\nu)}\left(\frac{e}{\tilde{\delta}}, \xi\right) \cdot \frac{e}{\tilde{\delta}} + \tilde{\delta} (B^{(\nu)}(z, \xi) - B^{(\nu)}\left(\frac{e}{\tilde{\delta}}, \xi\right)) \\ &\leq \tilde{\delta} B^{(\nu)}(z, \xi) + \tilde{\delta} \max_{|\tilde{z}|=\frac{1}{\tilde{\delta}}} \psi^{(\nu)}(\tilde{z}, \xi). \end{aligned}$$

In view of (4.54f), the assertion of the lemma holds for  $C_{\tilde{\delta}} = C \max\{g_0, M\hat{k}_2, \bar{\nu}\}(1 + \frac{1}{\tilde{\delta}^2})$ .  $\square$

**4.9 Lemma** *For all  $\Xi > 0$  there is a function  $\omega_{\Xi} : [0, \infty) \rightarrow [0, \infty)$  continuous in zero with  $\omega_{\Xi}(0) = 0$  so that for all  $\nu \in [0, \bar{\nu}]$  and all functions  $z_1, z_2, \xi \in H^1(\Omega)$  with  $\|z_1\|_{H^1}, \|z_2\|_{H^1}, \|\xi\|_{H^1} \leq \Xi$ ,  $\|B^{(\nu)}(z_i, \xi)\|_{L^1(\Omega)} \leq \Xi$ ,  $i = 1, 2$ , and*

$$\int_{\Omega} (\psi_{,u}^{(\nu)}(z_1, \xi) - \psi_{,u}^{(\nu)}(z_2, \xi)) \cdot (z_1 - z_2) \, dx \leq \delta$$

it holds that

$$\int_{\Omega} |\psi_{,u}^{(\nu)}(z_1, \xi) - \psi_{,u}^{(\nu)}(z_2, \xi)| \, dx \leq \omega_{\Xi}(\delta).$$

**Proof:** Suppose the contrary, i.e., there are  $\Xi, \varepsilon > 0$  such that for all  $\delta > 0$  there are functions  $z_i^{(\delta)}, \xi^{(\delta)} \in H^1(\Omega)$  and values  $\nu_{\delta} \in [0, \bar{\nu}]$  such that

$$\begin{aligned} \|z_i^{(\delta)}\|_{H^1} &\leq \Xi, \quad \|\xi^{(\delta)}\|_{H^1} \leq \Xi, \quad \|B^{(\nu_{\delta})}(z_i^{(\delta)}, \xi^{(\delta)})\|_{L^1(\Omega)} \leq \Xi, \quad i = 1, 2, \\ \int_{\Omega} (\psi_{,u}^{(\nu_{\delta})}(z_1^{(\delta)}, \xi^{(\delta)}) - \psi_{,u}^{(\nu_{\delta})}(z_2^{(\delta)}, \xi^{(\delta)})) \cdot (z_1^{(\delta)} - z_2^{(\delta)}) \, dx &\leq \delta \end{aligned}$$

but

$$\int_{\Omega} |\psi_{,u}^{(\nu_\delta)}(z_1^{(\delta)}, \xi^{(\delta)}) - \psi_{,u}^{(\nu_\delta)}(z_2^{(\delta)}, \xi^{(\delta)})| dx > \varepsilon.$$

There are functions  $z_i, \xi \in H^1(\Omega)$  and there is  $\nu \in [0, \bar{\nu}]$  such that, for a subsequence as  $\delta \rightarrow 0$  (still denoted by  $\nu$ ), it holds that  $\nu_\delta \rightarrow \nu$ ,  $z_i^{(\delta)} \rightharpoonup z_i$  in  $H^1(\Omega)$ , and  $\xi^{(\delta)} \rightharpoonup \xi$  in  $H^1(\Omega)$ . By the theorem of Rellich (cf. Appendix D, Theorem D.3), after eventually restricting again on a subsequence, it follows that  $(z_i^{(\delta)}, \xi^{(\delta)}) \rightarrow (z_i, \xi)$  in  $(L^2(\Omega))^2$  and almost everywhere. Hence  $\psi_{,u}^{(\nu_\delta)}(z_i^{(\delta)}, \xi^{(\delta)}) \rightarrow \psi_{,u}^{(\nu)}(z_i, \xi)$  almost everywhere. By the preceding lemma

$$\begin{aligned} \int_E |\psi_{,u}^{(\nu_\delta)}(z_i^{(\delta)}, \xi^{(\delta)})| dx &\leq \tilde{\delta} \int_E B^{(\nu_\delta)}(z_i^{(\delta)}, \xi^{(\delta)}) dx + \int_E C_{\tilde{\delta}} dx \\ &\leq \tilde{\delta} \Xi + C_{\tilde{\delta}} \mathcal{L}^d(E) \end{aligned}$$

for every  $\tilde{\delta} > 0$  and every Borel set  $E \subset \Omega$ . Choosing first  $\tilde{\delta}$  small and then  $E$  such that  $\mathcal{L}^d(E)$  becomes sufficiently small the Vitali convergence theorem D.12 yields  $\psi_{,u}^{(\nu_\delta)}(z_i^{(\delta)}, \xi^{(\delta)}) \rightarrow \psi_{,u}^{(\nu)}(z_i, \xi)$  in  $L^1(\Omega)$  whence

$$\int_{\Omega} |\psi_{,u}^{(\nu)}(z_1, \xi) - \psi_{,u}^{(\nu)}(z_2, \xi)| dx \geq \varepsilon. \quad (4.59)$$

Using the Fatou lemma (see Lemma D.13 in Appendix D) and the monotonicity of  $\psi_{,u}^{(\nu_\delta)}$  in  $u$  one first obtains

$$\begin{aligned} 0 &= \liminf_{\delta \rightarrow 0} \int_{\Omega} (\psi_{,u}^{(\nu_\delta)}(z_1^{(\delta)}, \xi^{(\delta)}) - \psi_{,u}^{(\nu_\delta)}(z_2^{(\delta)}, \xi^{(\delta)})) \cdot (z_1^{(\delta)} - z_2^{(\delta)}) dx \\ &\geq \int_{\Omega} \underbrace{\liminf_{\delta \rightarrow 0} (\psi_{,u}^{(\nu_\delta)}(z_1^{(\delta)}, \xi^{(\delta)}) - \psi_{,u}^{(\nu_\delta)}(z_2^{(\delta)}, \xi^{(\delta)})) \cdot (z_1^{(\delta)} - z_2^{(\delta)})}_{= (\psi_{,u}^{(\nu)}(z_1, \xi) - \psi_{,u}^{(\nu)}(z_2, \xi)) \cdot (z_1 - z_2)} dx \end{aligned}$$

and from this  $\psi_{,u}^{(\nu)}(z_1, \xi) = \psi_{,u}^{(\nu)}(z_2, \xi)$  almost everywhere which is a contradiction to (4.59).  $\square$

The following lemma precises the relation (2.31). Observe that, for a given  $\phi \in \mathbf{H}\Sigma^M$ , in the case  $\nu = 0$  the derivative  $\psi_{,u}(\cdot, \phi)$  is bounded in  $u$  so that  $\psi^*(\cdot, \phi)$  is defined on a real open subset  $C_\phi$  of  $\mathbb{R} \times \mathbf{H}\Sigma^N$  (cf. also Subsection 2.4.1 for the assumptions in order to obtain a well-defined potential  $\psi$ ).

**4.10 Lemma** *Let  $\nu \in [0, \bar{\nu}]$  and let*

$$(\psi^{(\nu)})^*(\psi_{,u}^{(\nu)}(u, \phi), \phi) := u \cdot \psi_{,u}^{(\nu)}(u, \phi) - \psi^{(\nu)}(u, \phi) = B^{(\nu)}(u, \phi)$$

*be the Legendre transform of  $\psi^{(\nu)}$  with respect to  $u$ . Then*

$$(\psi^{(\nu)})^*_{,\phi}(c, \phi) = -\psi_{,\phi}^{(\nu)}(u, \phi) \quad \text{where } c = \psi_{,u}^{(\nu)}(u, \phi). \quad (4.60)$$

**Proof:** Standard results of convex analysis give as a property of the Legendre transform (cf. [ET99])

$$(\psi^{(\nu)})^*_{,c} \Big|_{(c=\psi_{,u}^{(\nu)}(u, \phi), \phi)} = u.$$

The assertion follows since for every  $v \in \mathbf{T}\Sigma^M$

$$\begin{aligned} &\sum_{\alpha=1}^M \frac{d}{d\phi_\alpha} \left( (\psi^{(\nu)})^*(\psi_{,u}^{(\nu)}(u, \cdot), \cdot) \Big|_{\phi} \cdot v_\alpha \right. \\ &= (\psi^{(\nu)})^*_{,c} \Big|_{(c=\psi_{,u}^{(\nu)}(u, \phi), \phi)} \cdot \psi_{,u\phi}^{(\nu)}(u, \phi)v + (\psi^{(\nu)})^*_{,\phi}(\psi_{,u}^{(\nu)}(u, \phi), \phi) \\ &= u \cdot \psi_{,u\phi}^{(\nu)}(u, \phi)v + (\psi^{(\nu)})^*_{,\phi}(\psi_{,u}^{(\nu)}(u, \phi), \phi) \end{aligned}$$

---

## 4.2. LINEAR GROWTH IN THE CHEMICAL POTENTIALS

---

and on the other hand

$$\sum_{\alpha=1}^M \frac{d}{d\phi_\alpha} (\psi^{(\nu)})^* (\psi_{,u}^{(\nu)}(u, \phi), \phi) \cdot v_\alpha = B_{,\phi}^{(\nu)}(u, \phi) \cdot v = u \cdot \psi_{,u\phi}^{(\nu)}(u, \phi)v - \psi_{,\phi}^{(\nu)}(u, \phi).$$

□

The following lemma concerns the dependence of the  $\psi^{(\nu)}$  on  $\phi$  which has already been discussed in Subsection (2.4.3).

**4.11 Lemma** Consider series  $\{u^{(m)}\}_{m \in \mathbb{N}} \subset Y^N$ ,  $\{\phi^{(m)}\}_{m \in \mathbb{N}} \subset \mathbb{H}\Sigma^M$ , and  $\{\nu_m\}_{m \in \mathbb{N}} \subset [0, \bar{\nu}]$  such that  $\phi^{(m)} \rightarrow \phi$  in  $\mathbb{H}\Sigma^M$ ,  $\nu_m \searrow 0$ , and there is  $u \in Y^N$  such that

$$\psi_{,u}^{(\nu_m)}(u^{(m)}, \phi^{(m)}) \rightarrow \psi_{,u}(u, \phi)$$

as  $m \rightarrow \infty$ . Then

$$\psi_{,\phi}^{(\nu_m)}(u^{(m)}, \phi^{(m)}) \rightarrow \psi_{,\phi}(u, \phi) \quad \text{as } m \rightarrow \infty.$$

**Proof:** By (4.60) it must be demonstrated that

$$(\psi^{(\nu_m)})_{,\phi}^* (\psi_{,u}^{(\nu_m)}(u^{(m)}, \phi^{(m)}), \phi^{(m)}) \rightarrow \psi_{,\phi}^* (\psi_{,u}(u, \phi), \phi) \quad \text{as } m \rightarrow \infty. \quad (4.61)$$

The regularity assumptions on  $\psi$  in N1 provide that, for a given  $\phi \in \mathbb{H}\Sigma^M$ , the function  $\psi_{,u}(\cdot, \phi)$  is a  $C^1$ -diffeomorphism mapping an open set  $U_\phi \subset Y^N$  onto an open set  $C_\phi \subset \mathbb{R} \times \mathbb{H}\Sigma^N$  (cf. the discussion in Subsection (2.4.3)). These sets may be real subsets in contrast to the situation with  $\psi_{,u}^{(\nu_m)}(\cdot, \phi)$  which, thanks to the quadratic growth in  $u$ , is defined on the total space  $Y^N$  and maps onto the total space  $\mathbb{R} \times \mathbb{H}\Sigma^N$ .

Let  $q^{(\nu_m)}(u) := \nu_m |\tilde{u}|^2$ . The special structure of  $\psi^{(\nu_m)}(u, \phi) = q^{(\nu_m)}(u) + \psi(u, \phi)$  yields for all  $c \in C_\phi$  that

$$(\psi^{(\nu_m)})^*(c, \phi) = q^{(\nu_m)}(c) + \psi^*(c, \phi).$$

Furthermore, the regularity of  $\psi$  in  $\phi$  implies that if  $c \in C_\phi$  then also  $c \in C_{\tilde{\phi}}$  for all  $\tilde{\phi}$  in a small ball around  $\phi$ . Hence, fixing  $c$ , variations with respect to  $\phi$  are possible and give

$$(\psi^{(\nu_m)})_{,\phi}^* (c, \phi) = \psi_{,\phi}^* (c, \phi).$$

Consider now  $c = \psi_{,u}(u, \phi)$ . Since  $\phi^{(m)} \rightarrow \phi$  and using the regularity assumptions on  $\psi$  again there are a small  $\varepsilon > 0$  and  $m_1 \in \mathbb{N}$  such that

$$B_\varepsilon(\psi_{,u}(u, \phi)) \subset C_{\phi^{(m)}} \subset \mathbb{R} \times \mathbb{H}\Sigma^N \quad \text{for all } m \geq m_1.$$

Therefore  $(\psi^{(\nu_m)})_{,\phi}^* (c, \phi^{(m)}) = \psi_{,\phi}^* (c, \phi^{(m)})$  for all  $c \in B_\varepsilon(\psi_{,u}(u, \phi))$  as long as  $m \geq m_1$ .

Since  $\psi_{,u}^{(\nu_m)}(u^{(m)}, \phi^{(m)}) \rightarrow \psi_{,u}(u, \phi) \in C_\phi$  there is some  $m_2 \in \mathbb{N}$ ,  $m_2 \geq m_1$ , with

$$\psi_{,u}^{(\nu_m)}(u^{(m)}, \phi^{(m)}) \in B_\varepsilon(\psi_{,u}(u, \phi)) \quad \text{for all } m \geq m_2$$

whence

$$(\psi^{(\nu_m)})_{,\phi}^* (\psi_{,u}^{(\nu_m)}(u^{(m)}, \phi^{(m)}), \phi^{(m)}) = \psi_{,\phi}^* (\psi_{,u}^{(\nu_m)}(u^{(m)}, \phi^{(m)}), \phi^{(m)}) \quad \text{for all } m \geq m_2.$$

Standard results of convex analysis (cf. [ET99]) and, again, the regularity assumption in N1 provide that  $\psi_{,\phi}^*$  is continuous which gives the desired result (4.61). □

## 4.2.4 Compactness of the conserved quantities

As a first step to show precompactness of the set  $\{\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})\}_{\nu \in [0, \overline{\nu}]}$  a convergence result involving time differences  $\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))$  will be proven. For this purpose, define the set

$$E_{s, \Xi}^{(\nu)} := \left\{ t \in [0, \mathcal{T} - s] : \tilde{e}_{s, \Xi}^{(\nu)}(t) \leq \Xi \right\} \quad (4.62)$$

where

$$\begin{aligned} \tilde{e}_{s, \Xi}^{(\nu)}(t) &:= \|u^{(\nu)}(t)\|_{H^1(\Omega; Y^N)} + \|u^{(\nu)}(t+s)\|_{H^1(\Omega; Y^N)} + \|\phi^{(\nu)}(t)\|_{H^1(\Omega; \mathbb{H}\Sigma^M)} \\ &+ \frac{1}{s} \int_{\Omega} (u^{(\nu)}(t+s) - u^{(\nu)}(t)) \cdot (\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))) \, dx \\ &+ \left\| \frac{\phi^{(\nu)}(t+s) - \phi^{(\nu)}(t)}{s} \right\|_{L^2(\Omega; \mathbb{T}\Sigma^M)} \\ &+ \|B^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s))\|_{L^1(\Omega)} + \|B^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))\|_{L^1(\Omega)}. \end{aligned}$$

By (4.56a) and (4.56b) and using (4.49) there is a constant  $C > 0$  such that

$$C \geq \int_0^{\mathcal{T}-s} \tilde{e}_{s, \Xi}^{(\nu)}(t) \, dt = \int_{E_{s, \Xi}^{(\nu)}} \tilde{e}_{s, \Xi}^{(\nu)}(t) \, dt + \int_{[0, \mathcal{T}] \setminus E_{s, \Xi}^{(\nu)}} \tilde{e}_{s, \Xi}^{(\nu)}(t) \, dt \geq \Xi \mathcal{L}^1(E_{s, \Xi}^{(\nu)})$$

whence  $\mathcal{L}^1(E_{s, \Xi}^{(\nu)})$  becomes arbitrarily small when choosing  $\Xi$  sufficiently large. Obviously

$$\begin{aligned} &\int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))| \, dx dt \\ &= \int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t))| \, dx dt \\ &+ \int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))| \, dx dt. \end{aligned}$$

Applying Lemma 4.9 of the previous subsection with  $\delta = s\Xi$  gives

$$\int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))| \, dx dt \leq \mathcal{T} \omega_{\Xi}(s\Xi).$$

for the second term on the right hand side. With (4.54d), the first term can be estimated as follows:

$$\begin{aligned} &\int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t))| \, dx dt \\ &= \int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} \left| \int_0^1 \frac{d}{d\theta} \psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \underbrace{\theta \phi^{(\nu)}(t+s) + (1-\theta) \phi^{(\nu)}(t)}_{=: \phi_{\theta}}) \, d\theta \right| \, dx dt \\ &= \int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} \left| \int_0^1 \psi_{,u\phi}^{(\nu)}(u^{(\nu)}(t+s), \phi_{\theta}) \, d\theta \cdot (\phi^{(\nu)}(t+s) - \phi^{(\nu)}(t)) \right| \, dx dt \\ &\leq s \int_{[0, \mathcal{T}-s] \setminus E_{s, \Xi}^{(\nu)}} \int_{\Omega} \hat{k}_3 M k_7 \left| \frac{\phi^{(\nu)}(t+s) - \phi^{(\nu)}(t)}{s} \right| \, dx dt \leq s C \Xi. \end{aligned}$$



## 4.2. LINEAR GROWTH IN THE CHEMICAL POTENTIALS

For the last inequality it was used that, on bounded domains, the  $L^1$  norm can be estimated by the  $L^2$  norm, and estimate (4.49) was applied. Altogether, using (4.56a) and Lemma 4.8 with  $\tilde{\delta} = 1$ :

$$\begin{aligned}
& \int_0^{T-s} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))| \, dx dt \\
& \leq \int_{E_{s,\Xi}^{(\nu)}} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))| \, dx dt \\
& \quad + \int_{[0, T-s] \setminus E_{s,\Xi}^{(\nu)}} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t+s), \phi^{(\nu)}(t+s)) - \psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))| \, dx dt \\
& \leq 2 \operatorname{esssup}_{t \in I} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t))| \, dx \mathcal{L}^1(E_{s,\Xi}^{(\nu)}) + s C \Xi + \mathcal{T} \omega_{\Xi}(s \Xi) \\
& \leq 2 \left( \operatorname{esssup}_{t \in I} \int_{\Omega} B^{(\nu)}(u^{(\nu)}(t), \phi^{(\nu)}(t)) \, dx + \mathcal{L}^d(\Omega) C_1 \right) \mathcal{L}^1(E_{s,\Xi}^{(\nu)}) + s C \Xi + \mathcal{T} \omega_{\Xi}(s \Xi) \\
& \leq C \mathcal{L}^1(E_{s,\Xi}^{(\nu)}) + s C \Xi + \mathcal{T} \omega_{\Xi}(s \Xi).
\end{aligned}$$

Choosing first  $\Xi$  sufficiently large and, after,  $s$  sufficiently small, the right hand side becomes arbitrarily small, independently of  $\nu \in [0, \bar{\nu}]$ , hence as  $\Xi \rightarrow \infty$ ,  $s \rightarrow 0$

$$\sup_{\nu \in [0, \bar{\nu}]} \int_0^{T-s} \int_{\Omega} |\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(t+s) - \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(t)| \, dx dt \rightarrow 0. \quad (4.63)$$

In order to show precompactness of the  $\psi_{,u}^{(\nu)}$  in  $L^1(I \times \Omega; Y^N)$ , to each  $\kappa > 0$  a finite number of functions  $\{f_k\}_k$  has to be found such that the  $\psi_{,u}^{(\nu)}$  lie in the union of the balls with radius  $\kappa$  around the  $f_k$ . Indeed, it is sufficient if the set  $\{\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})\}_{\nu \in [0, \bar{\nu}]}$  is precompact in  $L^1(D; Y^N)$  for every  $D \subset\subset I \times \Omega$ . To see this, let  $\kappa > 0$  be given. Observe that for each  $f \in L^1(D; Y^N)$  by Lemma 4.8

$$\begin{aligned}
& \|\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) - \chi_D f\|_{L^1(I \times \Omega; Y^N)} \\
& = \int_{(I \times \Omega) \setminus D} |\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})| \, dx dt + \int_D |\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) - f| \, dx dt \\
& \leq \tilde{\delta} \int_{I \times \Omega} B^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \, dx dt + C_{\tilde{\delta}} \mathcal{L}^d((I \times \Omega) \setminus D) + \int_D |\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) - f| \, dx dt. \quad (4.64)
\end{aligned}$$

Choosing  $\tilde{\delta}$  small, thanks to (4.56a) the first term becomes smaller than  $\kappa/3$ . After, choose  $D$  appropriately so that the second term becomes smaller than  $\kappa/3$ , i.e., choose  $D$  such that  $\mathcal{L}^d((I \times \Omega) \setminus D) < \kappa/(3C_{\tilde{\delta}})$ . Finally, use the assumption that there are functions  $f_1, \dots, f_{k(\kappa, D)} \in L^1(D; Y^N)$  such that

$$\left\{ \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \right\}_{\nu \in [0, \bar{\nu}]} \subset \bigcup_{i=1}^{k(\kappa, D)} B_{\kappa/3}(f_i)$$

where  $B_{\varepsilon}(f) = \{g \in L^1(D; Y^N) : \|g - f\|_{L^1(D; Y^N)} < \varepsilon\}$  to find a suitable  $f = f_i \in L^1(D; Y^N)$  such that the last term in (4.64) becomes smaller than  $\kappa/3$ , too.

To show precompactness of the  $\psi_{,u}^{(\nu)}$  in  $L^1(D; Y^N)$  for each  $D \subset\subset I \times \Omega$ , approximating step functions will be constructed. For this purpose, let  $K \in \mathbb{N}$  and  $s = T/K$ , and define the functions

$$\begin{aligned}
v^{(\nu)}(t, x) & := \begin{cases} u^{(\nu)}(t, x), & \text{if } t \notin E_{s,\Xi}^{(\nu)}, \\ 0, & \text{elsewhere,} \end{cases} \\
\zeta^{(\nu)}(t, x) & := \begin{cases} \phi^{(\nu)}(t, x), & \text{if } t \notin E_{s,\Xi}^{(\nu)}, \\ 0, & \text{elsewhere.} \end{cases}
\end{aligned}$$

## CHAPTER 4. EXISTENCE OF WEAK SOLUTIONS

---

The step functions (with steps in time, not in space) are defined by

$$T_{r,s,\Xi}^{(\nu)}(t, x) := \sum_{i=1}^K \psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})((i-1)s + r, x) \chi_{(i-1)s, is]}(t)$$

where  $r \in [0, s)$  will later be chosen appropriately. The following calculation is essential for a control of the error between the original function and the step function. For times  $t_1 = j_1 s$  and  $t_2 = j_2 s$  with  $j_1, j_2 \in \{0, \dots, K\}$

$$\begin{aligned} & \int_0^s \int_{t_1}^{t_2} \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(t) - T_{r,s,\Xi}^{(\nu)}(t) \right\|_{L^1(\Omega; Y^N)} dt dr \\ &= \frac{1}{s} \sum_{i=j_1+1}^{j_2} \int_0^s \int_{(i-1)s}^{is} \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(t) - \psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})((i-1)s + r) \right\|_{L^1(\Omega; Y^N)} dt dr \\ &= \frac{1}{s} \sum_{i=j_1+1}^{j_2} \int_0^s \int_0^s \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})((i-1)s + \tilde{r}) - \psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})((i-1)s + r) \right\|_{L^1(\Omega; Y^N)} d\tilde{r} dr \\ &= \frac{1}{s} \sum_{i=j_1+1}^{j_2} \int_0^s \int_{(i-1)s}^{is} \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})((i-1)s + \tilde{r}) - \psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})(\tilde{t}) \right\|_{L^1(\Omega; Y^N)} d\tilde{t} d\tilde{r} \\ &= \frac{1}{s} \int_{t_1}^{t_2} \int_0^s \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})((i-1)s + \tilde{r}) - \psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})(\tilde{t}) \right\|_{L^1(\Omega; Y^N)} d\tilde{r} d\tilde{t}; \end{aligned}$$

inserting  $q = \tilde{r} + (i-1)s - \tilde{t} \in ((i-1)s - \tilde{t}, is - \tilde{t})$  this is estimated by

$$\begin{aligned} & \leq \frac{1}{s} \int_{t_1}^{t_2} \int_{-s}^s \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(\tilde{t} + q) - \psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})(\tilde{t}) \right\|_{L^1(\Omega; Y^N)} dq d\tilde{t} \\ & \leq \frac{1}{s} \int_{t_1}^{t_2} \int_{-s}^s \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(\tilde{t} + q) - \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(\tilde{t}) \right\|_{L^1(\Omega; Y^N)} dq d\tilde{t} \\ & \quad + \frac{1}{s} \int_{t_1}^{t_2} \int_{-s}^s \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(\tilde{t}) - \psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})(\tilde{t}) \right\|_{L^1(\Omega; Y^N)} dq d\tilde{t} \\ & \leq 2 \sup_{|q| \leq s} \int_{t_1}^{t_2} \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(\tilde{t} + q) - \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(\tilde{t}) \right\|_{L^1(\Omega; Y^N)} d\tilde{t} \\ & \quad + 2 \int_{E_{s,\Xi}^{(\nu)}} \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(\tilde{t}) - \psi_{,u}^{(\nu)}(0, 0)(\tilde{t}) \right\|_{L^1(\Omega; Y^N)} d\tilde{t}. \end{aligned}$$

The result (4.63) states that the first term on the right hand side tends to zero as  $s \rightarrow 0$ . Using Lemma 4.8 with  $\tilde{\delta} = 1$ , (4.54e), and (4.56a), the second term is estimated by

$$2\mathcal{L}^1(E_{s,\Xi}^{(\nu)}) \left( \text{esssup}_{\tilde{t} \in I} \int_{\Omega} B^{(\nu)}(u^{(\nu)}(\tilde{t}, x), \phi^{(\nu)}(\tilde{t}, x)) dx + C \right) \leq C \mathcal{L}^1(E_{s,\Xi}^{(\nu)})$$

and becomes arbitrarily small when choosing  $\Xi$  sufficiently large. Therefore, if a small  $\kappa > 0$  is given then it is possible to choose some large  $\Xi$ , some small  $s$  (by choosing  $K$  big), and some  $r_\nu \in [0, s)$  for every  $\nu \in [0, \bar{\nu}]$  such that

$$\int_{t_1}^{t_2} \left\| \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})(t) - T_{r_\nu, s, \Xi}^{(\nu)}(t) \right\|_{L^1(\Omega; Y^N)} dt \leq \kappa.$$

Hence, if the set of step functions  $\{T_{r_\nu, s, \Xi}^{(\nu)}\}_{\nu \in [0, \bar{\nu}]}$  is precompact in  $L^1(D)$  for every  $D \subset\subset I \times \Omega$  and every  $s, \Xi$ , then choose  $s$  small enough such that  $D \subset\subset [0, \mathcal{T} - s] \times \Omega$  and apply the above result to get that the set  $\{\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})\}_{\nu \in [0, \bar{\nu}]}$  is precompact in  $L^1(D; Y^N)$ .

## 4.2. LINEAR GROWTH IN THE CHEMICAL POTENTIALS

Finally, consider the set  $\{T_{r_\nu, s, \Xi}^{(\nu)}\}_{\nu \in [0, \bar{\nu}]}$  as a subset of  $L^1(D; Y^N)$  for some  $D \subset\subset I \times \Omega$ . It remains to demonstrate that there is a function  $\tilde{T} \in L^1(D; Y^N)$  and a subsequence  $(\nu_k)_{k \in \mathbb{N}}$  such that  $T_{r_{\nu_k}, s, \Xi}^{(\nu_k)} \rightarrow \tilde{T}$  in  $L^1(D; Y^N)$ . Since  $K$ ,  $s$ , and  $\Xi$  are fixed now it remains to examine whether the sets  $\{\psi_{,u}^{(\nu)}(v^{(\nu)}, \zeta^{(\nu)})((i-1)s + r_\nu)\}_{\nu \in [0, \bar{\nu}]}$  are precompact in  $L^1(D_x; Y^N)$  for every  $D_x \subset\subset \Omega$ ,  $i = 1, \dots, K$ . It holds that

$$\begin{aligned} \bar{t}^{(\nu)} := (i-1)s + r_\nu \in E_{s, \Xi}^{(\nu)} &\Rightarrow v^{(\nu)}(\bar{t}^{(\nu)}) = 0, \\ \bar{t}^{(\nu)} \notin E_{s, \Xi}^{(\nu)} &\Rightarrow \|v^{(\nu)}(\bar{t}^{(\nu)})\|_{H^1(D_x; Y^N)} \leq \Xi, \end{aligned}$$

and analogously for  $\zeta^{(\nu)}$ . It follows that for every sequence  $(\nu_k)_{k \in \mathbb{N}} \subset [0, \bar{\nu}]$  there is a subsequence, still denoted by  $(\nu_k)_k$ , there is  $\bar{\nu} \in [0, \bar{\nu}]$ , and there are functions  $\bar{v} \in H^1(D_x; Y^N)$  and  $\bar{\zeta} \in H^1(D_x; \mathbb{H}\Sigma^M)$  such that  $\nu_k \rightarrow \bar{\nu}$  and

$$\begin{aligned} v^{(\nu_k)}(\bar{t}^{(\nu_k)}) &\rightarrow \bar{v} \text{ weakly in } H^1(D_x; Y^N), & \text{strongly in } L^2(D_x; Y^N), & \text{and a.e.}, \\ \zeta^{(\nu_k)}(\bar{t}^{(\nu_k)}) &\rightarrow \bar{\zeta} \text{ weakly in } H^1(D_x; \mathbb{H}\Sigma^M), & \text{strongly in } L^2(D_x; \mathbb{H}\Sigma^M), & \text{and a.e.} \end{aligned}$$

as  $k \rightarrow \infty$ . Here, the Rellich theorem D.3 was applied. The same arguments as in the proof of Lemma 4.9 in the previous subsection, namely Lemma 4.8 and the Vitali convergence theorem D.12, yield the assertion:

$$\psi_{,u}^{(\nu_k)}(v^{(\nu_k)}, \zeta^{(\nu_k)})(\bar{t}^{(\nu_k)}) \rightarrow \psi_{,u}^{(\bar{\nu})}(\bar{v}, \bar{\zeta}) \text{ in } L^1(D_x; Y^N).$$

Altogether, it was proven that

$$\left\{ \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \right\}_{\nu \in [0, \bar{\nu}]} \subset L^1(I \times \Omega; Y^N) \text{ is precompact.} \quad (4.65)$$

### 4.2.5 Convergence statements

The aim of this section is to let  $\nu \rightarrow 0$  in (4.55c) in order to obtain (4.53c).

Since the set of functions  $\{u^{(\nu)}\}_{\nu \in [0, \bar{\nu}]}$  is bounded with respect to the norm  $\|\cdot\|_{L^2(I; L^2(\partial\Omega; Y^N))}$  in view of (4.56a), the first point of the Poincaré inequality (see Lemma D.14, Appendix D) is fulfilled, thus

$$\|u^{(\nu)}\|_{L^2(I; L^2(\Omega; Y^N))} \leq C. \quad (4.66)$$

By this, by the other estimates in (4.56a) and by (4.65) there are functions  $u \in L^2(I; H^1(\Omega; Y^N))$ ,  $b \in L^1(I \times \Omega; Y^N)$ , and  $\phi \in H^1(I \times \Omega; \mathbb{H}\Sigma^M)$  so that for a subsequence as  $\nu \rightarrow 0$  (as in Subsection 4.1.4 such subsequences will again be indexed by  $\nu$ , and it won't be explicitly stated any more when restricting to a subsequence in the following convergence statements)

$$\phi^{(\nu)} \rightharpoonup \phi \quad \text{in } H^1(I \times \Omega; \mathbb{H}\Sigma^M), \quad (4.67a)$$

$$u^{(\nu)} \rightharpoonup u \quad \text{in } L^2(I; H^1(\Omega; Y^N)), \quad (4.67b)$$

$$u^{(\nu)} \rightharpoonup u \quad \text{in } L^2(I; L^2(\partial\Omega; Y^N)), \quad (4.67c)$$

$$\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \rightarrow b \quad \text{in } L^1(I \times \Omega; Y^N). \quad (4.67d)$$

Observe that the third convergence result is already sufficient to obtain the second line of (4.53c) from the second line of (4.55c) as long as the test function fulfils  $v \in L^2(I; L^2(\partial\Omega; Y^N))$ .

With the same arguments as in Subsection 4.1.4

$$\phi^{(\nu)} \rightarrow \phi \quad \text{in } L^q(I \times \Omega; \mathbb{H}\Sigma^M), \quad (4.67e)$$

$$\phi^{(\nu)} \rightarrow \phi \quad \text{almost everywhere} \quad (4.67f)$$

## CHAPTER 4. EXISTENCE OF WEAK SOLUTIONS

---

for  $q = 2$  and  $q = p$  the value in (4.3b)–(4.3d). Let for  $R > 0$

$$\mathcal{P}_R : Y^N \rightarrow B_R(0) \subset Y^N, \quad \mathcal{P}_R(v) := \begin{cases} v, & \text{if } |v| \leq R, \\ \frac{R}{|v|}v, & \text{if } |v| > R. \end{cases}$$

The convexity of  $\psi^{(\nu)}$  in  $u$  implies that  $\psi_{,u}^{(\nu)}$  is monotone in  $u$ , hence for all  $v \in L^2(I \times \Omega; Y^N)$

$$0 \leq \int_I \int_\Omega \mathcal{P}_R(\psi_{,u}^{(\nu)}(v, \phi^{(\nu)}) - \psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})) \cdot (v - u^{(\nu)}) \, dxdt. \quad (4.68)$$

The convergence in (4.67e) and (4.67f) yields, thanks to the smoothness assumptions in N1 and the Lebesgue convergence theorem D.2 in Appendix D,

$$\psi_{,u}^{(\nu)}(v, \phi^{(\nu)}) \rightarrow \psi_{,u}(v, \phi) \text{ almost everywhere and in } L^1(I \times \Omega; Y^N).$$

Applying (4.67b) and (4.67d) gives

$$0 \leq \int_I \int_\Omega \mathcal{P}_R(\psi_{,u}(v, \phi) - b) \cdot (v - u) \, dxdt$$

from (4.68). Insert  $v = u + \varepsilon \bar{v}$  with some  $\bar{v} \in L^2(I \times \Omega; Y^N)$  and multiply by  $\varepsilon$  to obtain

$$0 \leq \int_I \int_\Omega \mathcal{P}_R(\psi_{,u}(u + \varepsilon \bar{v}, \phi) - b) \cdot \bar{v} \, dxdt.$$

Let  $\varepsilon \rightarrow 0$  which, using the Lebesgue convergence theorem again, yields

$$0 \leq \int_I \int_\Omega \mathcal{P}_R(\psi_{,u}(u, \phi) - b) \cdot \bar{v} \, dxdt.$$

Since  $R > 0$  and  $\bar{v}$  are arbitrary one can conclude that  $b = \psi_{,u}(u, \phi)$  almost everywhere, whence from (4.67d)

$$\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \rightarrow \psi_{,u}(u, \phi) \text{ in } L^1(I \times \Omega; Y^N) \text{ and a.e.} \quad (4.69a)$$

Similar arguments furnish

$$\psi_{,u}^{(\nu)}(u_{ic}, \phi_{ic}) \rightarrow \psi_{,u}(u_{ic}, \phi_{ic}) \text{ in } L^1(\Omega; Y^N). \quad (4.69b)$$

Therefore, for every test function  $v : I \times \Omega \rightarrow Y^N$  such that  $\partial_t v \in L^\infty(I \times \Omega; Y^N)$

$$\partial_t v \cdot (\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) - \psi_{,u}^{(\nu)}(u_{ic}, \phi_{ic})) \rightarrow \partial_t v \cdot (\psi_{,u}(u, \phi) - \psi_{,u}(u_{ic}, \phi_{ic})) \text{ in } L^1(I \times \Omega). \quad (4.70)$$

With the assumptions in N4 implying E2 it holds that  $L_{ij}(\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}), \phi^{(\nu)}) \rightarrow L_{ij}(\psi_{,u}(u, \phi), \phi)$  almost everywhere, and the same arguments as in Subsection 4.1.4 around (4.29) give

$$\nabla v : L(\psi_{,u}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}), \phi^{(\nu)}) \nabla u^{(\nu)} \rightarrow \nabla v : L(\psi_{,u}(u, \phi), \phi) \nabla u \text{ in } L^1(I \times \Omega) \quad (4.71)$$

if the test function fulfils  $v \in L^2(I; H^1(\Omega; Y^N))$ . Taking (4.70) and (4.71) together, the limit as  $\nu \rightarrow 0$  of the first line of (4.55c) indeed is the first line of (4.53c).

Also the terms involving the functions  $\omega$ ,  $a$  and  $w$  in the third and the fourth line of (4.55c) can be handled as previously in Subsection 4.1.4 and 4.1.5. No projection  $\mathcal{P}^{(n)}$  as in Subsection 4.1.5 is necessary since  $\zeta = \phi^{(\nu)} - \phi$  is allowed as test function in (4.55c). The following arguments of that subsection can be applied again to show strong convergence of  $\nabla \phi^{(\nu)}$  to  $\nabla \phi$  in  $L^2(I; L^2(\Omega; (T\Sigma^M)^d))$  and, therefore, to let  $\nu \rightarrow 0$  in the terms involving  $\omega$  and  $a$ . For handling the  $w$  term, the arguments around the result (4.31) can be applied again in view of (4.67e) and (4.67f). In particular, the limiting terms are exactly those appearing in (4.53c).

### 4.3. LOGARITHMIC TEMPERATURE TERM

It remains to consider the last term in (4.55c). By (4.67f) and (4.69a) the assumption in Lemma 4.11 are fulfilled almost everywhere which means that

$$\psi_{,\phi}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \rightarrow \psi_{,\phi}(u, \phi) \quad \text{almost everywhere as } \nu \rightarrow 0. \quad (4.72)$$

The growth assumptions on  $\psi_{,\phi}^{(\nu)}$  in N1, more precisely (4.54c), give, thanks to (4.56a),

$$\|\psi_{,\phi}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)})\|_{L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))} \leq C(1 + \|u^{(\nu)}\|_{L^2(I; L^2(\Omega; Y^N))}) \leq C,$$

whence there is some  $\bar{\zeta} \in L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))$  such that

$$\psi_{,\phi}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \rightharpoonup \bar{\zeta} \text{ in } L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M)).$$

Taking this and (4.72) together

$$\psi_{,\phi}^{(\nu)}(u^{(\nu)}, \phi^{(\nu)}) \rightharpoonup \psi_{,\phi}(u, \phi) \text{ in } L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M)) \quad (4.73)$$

which is sufficient to go to the limit in the last term of (4.55c) as long as  $\zeta \in L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))$  and to obtain the last term of (4.53c).

Assertion (4.53b) can be derived with similar arguments as in Subsection 4.1.6 which concludes the proof of Theorem 4.6.  $\square$

## 4.3 Logarithmic temperature term

In this section, the aim is to show existence of a weak solution to the problem in Definition 2.5 in Subsection 2.4.3 for a reduced grand canonical potential of the form

$$\begin{aligned} \psi &: (-\infty, 1) \times \mathbb{T}\Sigma^N \times \mathbb{H}\Sigma^M \rightarrow \mathbb{R}, \\ \psi(u, \phi) &= \underbrace{-c_v(1 + \ln(\text{Tr}_{ef}(u_0 - 1)))}_{:=g(u_0)} + \nu|\tilde{u}|^2 + \sum_{\alpha=1}^M h(\phi_\alpha)\lambda^{(\alpha)}(u) \end{aligned} \quad (4.74)$$

with a monotone smooth interpolation function  $h : \mathbb{R} \rightarrow [0, 1]$  and convex functions  $\lambda^{(\alpha)}$  of linear growth in  $u$ . Observe that, in contrast to the potential in the example in Subsection 2.4.2, there is a shift by 1 in  $u_0$ . This is done only for technical reasons, namely, to have a well defined value at  $u = 0$ .

As in the preceding section, the idea is to approximate  $\psi$  with potentials satisfying the conditions in Assumption E1 in order to apply Theorem 4.3. After, apply compactness arguments on the solutions to deduce a limiting function. To obtain convergence in  $u_0$ , ideas of [AP93] are used.

For  $\eta \in [0, \bar{\eta}]$  let  $y_\eta$  and  $z_\eta$  be the points such that  $g'(y_\eta) = \frac{1}{\eta}$  and  $g'(z_\eta) = \eta$ . The points exist if  $\bar{\eta}$  is small enough since  $g'$  is continuous,  $g'(u_0) \rightarrow \infty$  as  $u_0 \rightarrow 1$  and  $g'(u_0) \rightarrow 0$  as  $u_0 \rightarrow -\infty$ . Clearly  $y_\eta \rightarrow 1$  and  $z_\eta \rightarrow \infty$  as  $\eta \rightarrow 0$ . Uniqueness follows from the fact that  $g$  is strictly convex, hence,  $g'$  is strictly monotone increasing.

Let  $g_\eta^+ : \mathbb{R} \rightarrow \mathbb{R}$  be the unique polynomial of degree 2 such that  $g_\eta^+(y_\eta) = g(y_\eta)$ ,  $(g_\eta^+)'(y_\eta) = g'(y_\eta)$  and  $(g_\eta^+)''(y_\eta) = g''(y_\eta)$ . An explicit expression of the polynomial can be obtained by integrating up the constant function  $x \mapsto g''(y_\eta)$  two times and adjusting the integration constants according to the other two conditions. Analogously, let  $g_\eta^- : \mathbb{R} \rightarrow \mathbb{R}$  be the unique quadratic polynomial such that  $g_\eta^-(z_\eta) = g(z_\eta)$ ,  $(g_\eta^-)'(z_\eta) = g'(z_\eta)$  and  $(g_\eta^-)''(z_\eta) = g''(z_\eta)$ . Define

$$g^{(\eta)}(u_0) = \begin{cases} g_\eta^+(u_0), & y_\eta \leq u_0, \\ g(u_0), & z_\eta \leq u_0 \leq y_\eta, \\ g_\eta^-(u_0), & u_0 \leq z_\eta, \end{cases} \quad (4.75)$$

and then  $\psi^{(\eta)} \in C^{2,1}(Y^N \times \mathbb{H}\Sigma^M)$  by

$$\psi^{(\eta)}(u, \phi) = g^{(\eta)}(u_0) + \nu|\tilde{u}|^2 + \sum_{\alpha=1}^M h(\phi_\alpha)\lambda^{(\alpha)}(u). \quad (4.76)$$

Observe that, in this section,  $\eta$  varies but  $\nu$  is a fixed positive constant. Letting  $\eta \rightarrow 0$  it must be shown that a solution  $u^{(\eta)}$  to the perturbed problem converges to a function  $u$  with  $u_0 < 1$  almost everywhere. For this purpose, an additional estimate for the conserved quantities of the form

$$\|\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})\|_{L^2} \leq C$$

is derived. Since  $g'(u_0) = -c_v \frac{1}{u_0-1}$  this enables to get the desired result. Unfortunately, in order to obtain that estimate, additional assumptions on the Onsager coefficients and the boundary conditions have to be imposed. Cross effects between mass and energy diffusion are neglected, and Robin boundary conditions are only imposed for the energy flux while it is assumed that there is no mass flux across the external boundary. The assumptions and the result are precisely stated in the following subsection.

### 4.3.1 Assumptions and existence result

Let  $\Omega$  and  $I$  be as in Subsection 4.1.1. Assume the following:

- G1 The functions  $\lambda^{(\alpha)}$  are of the class  $C^{2,1}$  in their arguments.  
 Moreover it holds for all  $(u, \phi) \in Y^N \times \mathbb{H}\Sigma^M$  that

$$v \cdot \psi_{,uu}^{(\eta)}(u, \phi)v \geq \hat{k}_0|\tilde{v}|^2 \quad \forall v \in Y^N, \quad (4.77a)$$

$$|\lambda^{(\alpha)}(u)| \leq \hat{k}_2(1 + |u|) \quad \forall \alpha, \quad (4.77b)$$

$$|\lambda_{,u}^{(\alpha)}(u) \cdot v| \leq \hat{k}_3|v| \quad \forall \alpha, \forall v \in Y^N, \quad (4.77c)$$

$$|w \cdot \lambda_{,uu}^{(\alpha)}(u)v| \leq \hat{k}_1|w||v| \quad \forall \alpha, \forall w, v \in Y^N, \quad (4.77d)$$

$$|\lambda^{(\alpha)}(0)| \leq \hat{k}_4, \quad (4.77e)$$

$$h \in W^{3,\infty}(\mathbb{R}; [0, 1]), \quad (4.77f)$$

$$h(r) = 0 \quad \text{if } r \leq 0, \quad (4.77g)$$

$$h(r) = 1 \quad \text{if } r \geq 1, \quad (4.77h)$$

$$|h'(r)| \leq k_7 \quad \forall r \in \mathbb{R}, \quad (4.77i)$$

where the  $\hat{k}_i$  and  $k_i$  are positive constants.

There is a small  $\delta_0 > 0$  and a constant  $k_8$  such that

$$\psi_{,u_0}^{(\eta)}(u, \phi) \geq k_\eta(u_0 - 1) - k_8 \quad \text{whenever } u_0 > 1 - \delta_0 \quad (4.77j)$$

with  $0 < k_\eta \rightarrow \infty$  as  $\eta \rightarrow 0$ .

- G2 The Onsager coefficients are as in assumption E2 but, in addition, fulfil

$$L_{i0} = L_{0i} = 0 \quad \forall i \in \{1, \dots, N\}. \quad (4.78)$$

- G3 For initial data  $(u_{ic}, \phi_{ic})$  as in assumption E6 there is some  $\bar{\eta} > 0$  such that

$$\psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic}) = \psi_{,u}(u_{ic}, \phi_{ic}) \quad \text{for all } \eta \leq \bar{\eta} \quad (4.79a)$$

Moreover,

$$\|\psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})\|_{L^2(\Omega)} \leq C \quad \text{for all } \eta \leq \bar{\eta}, \quad (4.79b)$$

and the inequality (4.6b) holds with a constant independent of  $\eta$ , too.

G4 For the energy flux the boundary condition

$$J_0 \cdot \nu_{ext} = \beta_{00}(u_0 - u_{bc,0})$$

is imposed with a continuous function  $\beta_{00} : I \times \Omega \rightarrow \mathbb{R}$  satisfying

$$0 < \beta_0 \leq \beta_{00}(t, x) < \beta_1 \tag{4.80a}$$

and a function  $u_{bc,0} \in C(\overline{I \times \partial\Omega}; Y^N) \cap L^2(I; L^2(\partial\Omega; Y^N))$  such that

$$\|\psi_{,u_0}^{(\eta)}(u_{bc,0}, \tilde{u}^{(\eta)}, \phi^{(\eta)})\|_{L^2(I; L^2(\partial\Omega))} \leq C \tag{4.80b}$$

for all sets  $\{\tilde{u}^{(\eta)}\}_{\eta \in [0, \bar{\eta}]} \subset \mathbf{T}\Sigma^N$ ,  $\{\phi^{(\eta)}\}_{\eta \in [0, \bar{\eta}]} \subset \mathbf{H}\Sigma^M$  with

$$\sup_{\eta \in [0, \bar{\eta}]} \left( \|\phi^{(\eta)}\|_{L^2(I; L^2(\partial\Omega; \mathbf{H}\Sigma^M))} + \|\tilde{u}^{(\eta)}\|_{L^2(I; L^2(\partial\Omega; \mathbf{H}\Sigma^N))} \right) \leq C. \tag{4.80c}$$

G5 The assumptions in E3–E5 are satisfied.

**4.12 Theorem** *If the assumptions G1–G5 are fulfilled then there are functions*

$$u \in L^2(I; H^1(\Omega; Y^N)), \quad \phi \in H^1(I \times \Omega; \mathbf{H}\Sigma^M) \cap L^p(I \times \Omega; \mathbf{H}\Sigma^M) \tag{4.81a}$$

such that

$$u_0 < 1 \text{ almost everywhere,} \tag{4.81b}$$

$$\phi(t, \cdot) \rightarrow \phi_{ic} \text{ in } L^2(\Omega; \mathbf{H}\Sigma^M) \text{ as } t \searrow 0, \tag{4.81c}$$

and such that

$$\begin{aligned} 0 = & \int_I \int_{\Omega} \left[ -\partial_t v \cdot (\psi_{,u}(u, \phi) - \psi_{,u}(u_{ic}, \phi_{ic})) + \nabla v : L(\psi_{,u}(u, \phi), \phi) \nabla u \right] dx dt \\ & + \int_I \int_{\partial\Omega} v_0 \cdot \beta_{00}(u_0 - u_{bc,0}) d\mathcal{H}^{d-1} dt \\ & + \int_I \int_{\Omega} \left[ \omega(\phi, \nabla\phi) \partial_t \phi \cdot \zeta + a_{\nabla\phi}(\phi, \nabla\phi) : \nabla\zeta \right] dx dt \\ & + \int_I \int_{\Omega} \left[ a_{,\phi}(\phi, \nabla\phi) \cdot \zeta + w_{,\phi}(\phi) \cdot \zeta - \psi_{,\phi}(u, \phi) \cdot \zeta \right] dx dt \end{aligned} \tag{4.81d}$$

for all test functions  $v \in H^1(I \times \Omega; Y^N)$  with  $v(T) = 0$  and  $\zeta \in H^1(I \times \Omega; \mathbf{T}\Sigma^M) \cap L^p(I \times \Omega; \mathbf{T}\Sigma^M)$ .

**Proof:** The proof of the theorem is given in several steps, each one corresponding to one of the following subsections:

- The perturbed reduced grand canonical potential  $\psi^{(\eta)}$  fulfils the assumptions of Theorem 4.3. Since the other assumptions are satisfied, too, there is a weak solution to the perturbed problem  $(u^{(\eta)}, \phi^{(\eta)})$  such that the estimates (4.45) and (4.48) with  $\psi$ ,  $u$ , and  $\phi$  replaced by  $\psi^{(\eta)}$ ,  $u^{(\eta)}$ , and  $\phi^{(\eta)}$  respectively hold true.
- An estimate for the conserved quantities  $\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})$  is derived. Together with the other estimates, candidates  $(u, \phi)$  for a solution to (4.81d) can be obtained, and it can be shown that the candidate satisfies  $u_0 \leq 1$ . A subsequence of the  $\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})$  converges weakly to some limiting function  $b$  in  $L^2$ .

- It remains to identify  $b$  with  $\psi_{,u}(u, \phi)$  and to go to the limit in the term with  $\psi_{,\phi}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})$ . For this purpose, strong convergence of the  $u^{(\eta)}$  to  $u$  will be shown. The main task is to get a control of time differences of the form  $|u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)|$ . The images of the functions  $u_0^{(\eta)}$  are projected onto a compact interval where the second derivatives of the  $\psi^{(\eta)}$  with respect to  $u_0$  are bounded from below by a positive constant independent of  $\eta$ . From estimate (4.48) a control of time differences of the truncated functions is obtained. Thanks to the other estimates, the error due to the truncation, measured in the norm of the space  $L^1(I \times \Omega)$ , becomes arbitrarily small which enables to conclude as desired.
- Collecting the obtained convergence results it is possible to let  $\eta \rightarrow 0$  in the weak formulation of the perturbed problem and to show that the candidate  $(u, \phi)$  in fact is a solution to (4.81d). In particular, it is shown that the solution fulfils  $u_0 < 1$  almost everywhere.

### 4.3.2 Solution to the perturbed problem

First observe that  $\psi^{(\eta)}$  is of the class  $C^{2,1}$ . Furthermore

$$\psi_{,u}^{(\eta)}(u, \phi) \cdot v = \left( g_{,u_0}^{(\eta)}(u_0)v_0 \right) + \sum_{\alpha=1}^M h(\phi_\alpha) \lambda_{,u}^{(\alpha)}(u), \quad (4.82a)$$

$$\psi_{,u_0 u_0}^{(\eta)}(u, \phi) = g_{,u_0 u_0}^{(\eta)}(u_0) + \sum_{\alpha=1}^M h(\phi_\alpha) \lambda_{,u_0 u_0}^{(\alpha)}(u), \quad (4.82b)$$

$$\psi_{,u_0 \tilde{u}}^{(\eta)}(u, \phi) \tilde{v} = \sum_{\alpha=1}^M h(\phi_\alpha) \lambda_{,u_0 \tilde{u}}^{(\alpha)}(u) \tilde{v}, \quad (4.82c)$$

$$\tilde{v} \cdot \psi_{,\tilde{u} \tilde{u}}^{(\eta)}(u, \phi) \tilde{v} = 2\nu |\tilde{v}|^2 + \sum_{\alpha=1}^M h(\phi_\alpha) \tilde{v} \cdot \lambda_{,\tilde{u} \tilde{u}}^{(\alpha)}(u) \tilde{v}, \quad (4.82d)$$

$$\psi_{,\phi}^{(\eta)}(u, \phi) \cdot \zeta = \sum_{\alpha=1}^M h'(\phi_\alpha) \zeta_\alpha \lambda^{(\alpha)}(u), \quad (4.82e)$$

$$\psi_{,u\phi}^{(\eta)}(u, \phi) \zeta = \sum_{\alpha=1}^M h'(\phi_\alpha) \zeta_\alpha \lambda_{,u}^{(\alpha)}(u), \quad (4.82f)$$

where  $\tilde{v} \in \mathbb{T}\Sigma^N$ ,  $v_0 \in \mathbb{R}$ , and  $\zeta \in \mathbb{T}\Sigma^M$ . Obviously there are coefficients functions  $\tilde{k}_1(\eta)$  and  $\tilde{k}_0(\eta)$  with

$$\tilde{k}_1(\eta) \geq g_{,u_0 u_0}^{(\eta)}(u_0) \geq \tilde{k}_0(\eta) > 0$$

for  $\eta > 0$  where  $\tilde{k}_1(\eta) \rightarrow \infty$  and  $\tilde{k}_0(\eta) \rightarrow 0$  as  $\eta \rightarrow 0$ .

By (4.77a) assumption (4.1b) is fulfilled with  $k_0 = \min\{\tilde{k}_0(\eta), \hat{k}_0\}$  for each  $\eta > 0$ . Similarly, by (4.77b)–(4.77d) the assumptions (4.1c), (4.1g), and (4.1h) are fulfilled for each  $\eta > 0$  with  $k_1 = \max\{\tilde{k}_1(\eta), 2\nu + M\hat{k}_1\}$ ,  $k_5 = \max\{\tilde{k}_1(\eta), 2\nu + M\hat{k}_3\}$ , and  $k_6 = \max\{\tilde{k}_1(\eta), 2\nu + M\hat{k}_2\}$ , respectively.

Assumption (4.1f) is fulfilled thanks to (4.77e), and the assumptions (4.1d) and (4.1e) follow from (4.77g)–(4.77i) and (4.77b)–(4.77c) in view of (4.82e) and (4.82f). Finally, assumption (4.1i) follows from Lemma 4.7 in Subsection 4.2.2.

Considering G2–G5, the assumptions of Theorem 4.3 are satisfied. Thus, there are functions

$$u^{(\eta)} \in L^2(I; H^1(\Omega; Y^N)), \quad \phi^{(\eta)} \in H^1(I \times \Omega; \mathbb{H}\Sigma^M) \quad (4.83a)$$

such that

$$\phi(t, \cdot) \rightarrow \phi_{ic} \quad \text{in } L^2(\Omega; \mathbb{H}\Sigma^M) \text{ as } t \searrow 0 \quad (4.83b)$$



and such that

$$\begin{aligned}
 0 = & \int_I \int_{\Omega} -\partial_t v \cdot (\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) \, dx dt \\
 & + \int_I \int_{\Omega} \nabla v : L(\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}), \phi^{(\eta)}) \nabla u \, dx dt \\
 & + \int_I \int_{\partial\Omega} v_0 \cdot \beta_{00}(u_0^{(\eta)} - u_{bc,0}) \, d\mathcal{H}^{d-1} dt \\
 & + \int_I \int_{\Omega} \left[ \omega(\phi^{(\eta)}, \nabla \phi^{(\eta)}) \partial_t \phi^{(\eta)} \cdot \zeta + a_{,\nabla\phi}(\phi^{(\eta)}, \nabla \phi^{(\eta)}) : \nabla \zeta \right] \, dx dt \\
 & + \int_I \int_{\Omega} \left[ a_{,\phi}(\phi^{(\eta)}, \nabla \phi^{(\eta)}) \cdot \zeta + w_{,\phi}(\phi^{(\eta)}) \cdot \zeta - \psi_{,\phi}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \cdot \zeta \right] \, dx dt \tag{4.83c}
 \end{aligned}$$

for all test functions  $v \in H^1(I \times \Omega; Y^N)$  with  $v(\mathcal{T}) = 0$  and  $\zeta \in H^1(I \times \Omega; \mathbb{T}\Sigma^M) \cap L^p(I \times \Omega; \mathbb{T}\Sigma^M)$ . Estimate (4.45) for the solution  $(u^{(\eta)}, \phi^{(\eta)})$  looks slightly different with respect to the boundary term, namely

$$\begin{aligned}
 \text{esssup}_{\tilde{t} \in I} \int_{\Omega} & \left[ \psi_{,u}^{(\eta)}(u^{(\eta)}(\tilde{t}), \phi^{(\eta)}(\tilde{t})) \cdot u^{(\eta)}(\tilde{t}) - \psi^{(\eta)}(u^{(\eta)}(\tilde{t}), \phi^{(\eta)}(\tilde{t})) \right. \\
 & \quad \left. + w_2 |\phi^{(\eta)}(\tilde{t})|^p + a_0 |\nabla \phi^{(\eta)}(\tilde{t})|^2 \right] \, dx \\
 & + \int_I \int_{\Omega} \left[ \omega_0 |\partial_t \phi^{(\eta)}|^2 + l_0 |\nabla u^{(\eta)}|^2 \right] \, dx dt + \beta_2 \int_I \int_{\partial\Omega} |u_0^{(\eta)}|^2 \, d\mathcal{H}^{d-1} dt \leq C. \tag{4.84}
 \end{aligned}$$

The change in the last term results from the fact that  $u^{(\eta)}$ ,  $\beta$ ,  $u_{bc}$ , and  $u$  have to be replaced by  $u_0^{(\eta)}$ ,  $\beta_0$ ,  $u_{bc,0}$ , and  $u_0$  in (4.43) and (4.44g). Thanks to assumption (4.77a)

$$\begin{aligned}
 & \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \cdot u^{(\eta)} - \psi^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \\
 = & \int_0^1 \frac{d}{d\theta} \left( \psi_{,u}^{(\eta)}(\theta u^{(\eta)}, \phi^{(\eta)}) \cdot \theta u^{(\eta)} - \psi^{(\eta)}(\theta u^{(\eta)}, \phi^{(\eta)}) \right) \, d\theta - \psi^{(\eta)}(0, \phi^{(\eta)}) \\
 \geq & \int_0^1 \theta u^{(\eta)} \cdot \psi_{,uu}^{(\eta)}(\theta u^{(\eta)}, \phi^{(\eta)}) u^{(\eta)} \, d\theta - k_4 \\
 \geq & \int_0^1 \theta \, d\theta \, \hat{k}_0 |\tilde{u}^{(\eta)}|^2 - k_4.
 \end{aligned}$$

Therefore for almost every  $\tilde{t} \in I$

$$\int_{\Omega} (\psi_{,u}^{(\eta)}(u^{(\eta)}(\tilde{t}), \phi^{(\eta)}(\tilde{t})) \cdot u^{(\eta)}(\tilde{t}) - \psi(u(\tilde{t})^{(\eta)}, \phi(\tilde{t})^{(\eta)})) \, dx \geq C \left( \int_{\Omega} |\tilde{u}^{(\eta)}(\tilde{t})|^2 \, dx - 1 \right).$$

In view of (4.84), applying the Poincaré inequality D.14 on  $u_0^{(\eta)}$  furnishes the estimate

$$\|u^{(\eta)}\|_{L^2(I; L^2(\Omega))} \leq C \quad \text{for all } \eta \in (0, \bar{\eta}]. \tag{4.85}$$

Estimate (4.48) provides

$$\begin{aligned}
 \int_0^{\mathcal{T}-s} \int_{\Omega} & (u^{(\eta)}(t+s) - u^{(\eta)}(t)) \\
 & \cdot (\psi_{,u}^{(\eta)}(u^{(\eta)}(t+s), \phi^{(\eta)}(t)) - \psi_{,u}^{(\eta)}(u^{(\eta)}(t), \phi^{(\eta)}(t))) \, dx dt \leq C s. \tag{4.86}
 \end{aligned}$$

### 4.3.3 Estimate of the conserved quantities

Let  $\chi(t) := \chi_{(0, \tilde{t})}(t)$  be the characteristic function of the interval  $\tilde{I} = (0, \tilde{t})$ , and define

$$v_\delta(t, x) := \int_t^{t+\delta} \chi(s) \psi_{,u}^{(\eta)}(u^{(\eta)}(s, x), \phi^{(\eta)}(s, x)) ds.$$

The functions  $\varphi_\delta(s) = \frac{1}{\delta} \chi_{(-\delta, 0)}(s)$  constitute a Dirac sequence (cf. Definition D.10). By the assumptions in G1 and (4.83a)

$$\nabla \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) = \psi_{,uu}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \nabla u^{(\eta)} + \psi_{,u\phi^{(\eta)}}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \nabla \phi^{(\eta)} \in L^2(I; L^2(\Omega; (Y^N)^d)),$$

and with the results on Dirac sequences in Theorem D.11

$$\varphi_\delta * \chi \nabla \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightarrow \chi \nabla \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \text{ in } L^2(I; L^2(\Omega; (Y^N)^d))$$

in the limit as  $\delta \searrow 0$ . Since

$$\begin{aligned} & (\varphi_\delta(\cdot) * \chi(\cdot) \nabla \psi_{,u}^{(\eta)}(u^{(\eta)}(\cdot, x), \phi^{(\eta)}(\cdot, x)))(t) \\ &= \int_{\mathbb{R}} \varphi_\delta(t-s) \chi(s) \nabla \psi_{,u}^{(\eta)}(u^{(\eta)}(s, x), \phi^{(\eta)}(s, x)) ds \\ &= \int_t^{t+\delta} \chi(s) \nabla \psi_{,u}^{(\eta)}(u^{(\eta)}(s, x), \phi^{(\eta)}(s, x)) ds = \nabla v_\delta \end{aligned}$$

it is clear that  $\nabla v_\delta \in L^2(I; L^2(\Omega; (Y^N)^d))$  and, hence,

$$\nabla v_\delta \rightarrow \chi \nabla \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \text{ in } L^2(I; L^2(\Omega; (Y^N)^d)).$$

Analogously  $v_\delta \rightarrow \chi \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})$  in  $L^2(I; L^2(\Omega; Y^N))$ , thus it holds that

$$v_\delta \rightarrow \chi \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \text{ in } L^2(I; H^1(\Omega; Y^N)). \quad (4.87)$$

Define

$$\partial_t^\delta f(t) := \frac{1}{\delta} (f(t+\delta) - f(t)), \quad \partial_t^{-\delta} f(t) := \frac{1}{\delta} (f(t) - f(t-\delta))$$

for a function  $f : \mathbb{R} \rightarrow Z$  mapping into some Banach space  $Z$ . Then

$$\partial_t v_\delta(t, x) = \partial_t^\delta (\chi(\cdot) \psi_{,u}^{(\eta)}(u^{(\eta)}(\cdot, x), \phi^{(\eta)}(\cdot, x)))(t),$$

hence  $v_\delta \in H^1(\tilde{I} \times \Omega; Y^N)$  if  $\delta < \mathcal{T} - \tilde{t}$ .

Let  $\zeta = 0$  and  $v = v_\delta$  in (4.83c) and suppose that  $\delta < \mathcal{T} - \tilde{t}$ . Then

$$\begin{aligned} 0 &= \int_I \int_\Omega -\partial_t v_\delta \cdot (\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) dx dt \\ &+ \int_I \int_\Omega \nabla v_\delta : L(\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}), \phi^{(\eta)}) \nabla u dx dt \\ &+ \int_I \int_{\partial\Omega} v_{\delta,0} \cdot \beta_{00}(u_0^{(\eta)} - u_{bc,0}) d\mathcal{H}^{d-1} dt. \end{aligned} \quad (4.88)$$

Extend  $(u^{(\eta)}, \phi^{(\eta)})$  for  $t \in (-\delta, 0)$  by  $(u_{ic}, \phi_{ic})$ . Using

$$y \cdot (y - z) = \frac{1}{2}((y+z) + (y-z)) \cdot (y-z) \geq \frac{1}{2}(y+z) \cdot (y-z) = \frac{1}{2}(|y|^2 - |z|^2) \quad \forall y, z \in Y^N$$

it holds that

$$\begin{aligned} & - \int_I \int_\Omega \partial_t v_\delta \cdot (\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) dx dt \\ &= - \int_0^{\mathcal{T}} \int_\Omega \partial_t^\delta \chi \psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \cdot (\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) dx dt \end{aligned}$$

$$\begin{aligned}
 &= - \int_0^{\tilde{t}-\delta} \int_{\Omega} \frac{1}{\delta} \psi_{,u}^{(\eta)}(u^{(n)}(t+\delta), \phi^{(n)}(t+\delta)) \cdot (\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t)) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) \, dx dt \\
 &\quad + \int_0^{\tilde{t}} \int_{\Omega} \frac{1}{\delta} \psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t)) \cdot (\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t)) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) \, dx dt \\
 &= - \int_0^{\tilde{t}} \int_{\Omega} \frac{1}{\delta} \psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t)) \cdot (\psi_{,u}^{(\eta)}(u^{(n)}(t-\delta), \phi^{(n)}(t-\delta)) \, dx dt - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) \, dx dt \\
 &\quad + \int_0^{\tilde{t}} \int_{\Omega} \frac{1}{\delta} \psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t)) \cdot (\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t)) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) \, dx dt \\
 &\geq \int_0^{\tilde{t}} \frac{1}{2\delta} \int_{\Omega} (|\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t))|^2 - |\psi_{,u}^{(\eta)}(u^{(n)}(t-\delta), \phi^{(n)}(t-\delta))|^2) \, dx dt \\
 &= \frac{1}{2} \int_{\tilde{t}-\delta}^{\tilde{t}} \|\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t))\|_{L^2(\Omega; Y^N)}^2 \, dt - \frac{1}{2} \int_{-\delta}^0 \|\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t))\|_{L^2(\Omega; Y^N)}^2 \, dt \\
 &= \frac{1}{2} \int_{\tilde{t}-\delta}^{\tilde{t}} \|\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t))\|_{L^2(\Omega; Y^N)}^2 \, dt - \frac{1}{2} \|\psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})\|_{L^2(\Omega; Y^N)}^2.
 \end{aligned}$$

Using again the properties of a convolution with a Dirac sequence it holds that

$$\begin{aligned}
 \int_{\tilde{t}-\delta}^{\tilde{t}} \|\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t))\|_{L^2(\Omega; Y^N)}^2 \, dt &= \left( \phi_{\delta}^{(\eta)} * \|\psi_{,u}^{(\eta)}(u^{(n)}, \phi^{(n)})\|_{L^2(\Omega; Y^N)}^2 \right)(\tilde{t}) \\
 &\rightarrow \|\psi_{,u}^{(\eta)}(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t}))\|_{L^2(\Omega; Y^N)}^2
 \end{aligned}$$

for almost every  $\tilde{t} \in I$ , whence for the first term on the right hand side of (4.88) thanks to (4.79b)

$$\begin{aligned}
 &- \int_I \int_{\Omega} \partial_t v_{\delta} \cdot (\psi_{,u}^{(\eta)}(u^{(n)}, \phi^{(n)}) - \psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})) \, dx dt \\
 &\geq \frac{1}{2} \int_{\tilde{t}-\delta}^{\tilde{t}} \|\psi_{,u}^{(\eta)}(u^{(n)}(t), \phi^{(n)}(t))\|_{L^2(\Omega; Y^N)}^2 \, dt - \frac{1}{2} \|\psi_{,u}^{(\eta)}(u_{ic}, \phi_{ic})\|_{L^2(\Omega; Y^N)}^2 \\
 &\rightarrow \frac{1}{2} \|\psi_{,u}^{(\eta)}(u^{(n)}(\tilde{t}), \phi^{(n)}(\tilde{t}))\|_{L^2(\Omega; Y^N)}^2 - C
 \end{aligned} \tag{4.89}$$

for almost every  $\tilde{t} \in I$  as  $\delta \rightarrow 0$ .

Now, consider the second term of (4.88). By (4.87) as  $\delta \rightarrow 0$

$$\begin{aligned}
 &\int_I \int_{\Omega} \nabla v_{\delta} : L(\psi_{,u}^{(\eta)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \, dx dt \\
 &\rightarrow \int_I \int_{\Omega} \chi \nabla \psi_{,u}^{(\eta)}(u^{(n)}, \phi^{(n)}) : L(\psi_{,u}^{(\eta)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \, dx dt \\
 &= \int_{\tilde{I}} \int_{\Omega} \left( \nabla u^{(n)} : \psi_{,uu}^{(\eta)}(u^{(n)}, \phi^{(n)}) L(\psi_{,u}^{(\eta)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \right) \, dx dt \\
 &\quad + \int_{\tilde{I}} \int_{\Omega} \left( \nabla \phi^{(n)} : \psi_{,\phi u}^{(\eta)}(u^{(n)}, \phi^{(n)}) L(\psi_{,u}^{(\eta)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \right) \, dx dt.
 \end{aligned} \tag{4.90}$$

Thanks to assumption (4.78)

$$\begin{aligned}
 & \nabla u^{(n)} : \psi_{,uu}^{(n)}(u^{(n)}, \phi^{(n)}) L(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \\
 = & |\nabla u_0^{(n)}|^2 g_{,u_0 u_0}^{(n)}(u_0^{(n)}) L_{00}(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \\
 & + 2\nu \sum_{i,j=1}^N \nabla u_i^{(n)} \cdot L_{ij}(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u_j^{(n)} \\
 & + \sum_{\alpha} h(\phi_{\alpha}) \nabla u^{(n)} : \lambda_{,uu}^{(\alpha)}(u^{(n)}) L(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)}.
 \end{aligned}$$

The integral of the second and the third term can be estimated using (4.77d), (4.2e), and (4.84):

$$\begin{aligned}
 & \left| \int_{\bar{I}} \int_{\Omega} 2\nu \sum_{i,j=1}^N \nabla u_i^{(n)} \cdot L_{ij}(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u_j^{(n)} \, dx dt \right| \\
 & + \left| \int_{\bar{I}} \int_{\Omega} \sum_{\alpha} h(\phi_{\alpha}) \nabla u^{(n)} : \lambda_{,uu}^{(\alpha)}(u^{(n)}) L(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \, dx dt \right| \\
 & \leq (2\nu + M\hat{k}_1) L_0 \int_{\bar{I}} \int_{\Omega} |\nabla u^{(n)}|^2 \, dx dt \leq C.
 \end{aligned}$$

The positivity of  $L$  (see assumption E2) implies  $L_{00} \geq 0$ , therefore for the integral of the first term

$$\int_{\bar{I}} \int_{\Omega} |\nabla u_0^{(n)}|^2 g_{,u_0 u_0}^{(n)}(u_0^{(n)}) L_{00}(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \, dx dt \geq 0.$$

In view of (4.82f), by the assumptions (4.1e) and (4.2e) and using the estimate (4.84)

$$\begin{aligned}
 & \left| \int_{\bar{I}} \int_{\Omega} \nabla \phi^{(n)} : \psi_{,\phi u}^{(n)}(u^{(n)}, \phi^{(n)}) L(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \, dx dt \right| \\
 & \leq k_3 \int_0^{\bar{t}} \int_{\Omega} |\nabla \phi^{(n)}| |L(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)}| \, dx dt \\
 & \leq k_3 L_0 \int_0^{\bar{t}} \int_{\Omega} |\nabla \phi^{(n)}| |\nabla u^{(n)}| \, dx dt \\
 & \leq k_3 L_0 \int_0^{\bar{t}} \int_{\Omega} \frac{1}{2} (|\nabla \phi^{(n)}|^2 + |\nabla u^{(n)}|^2) \, dx dt \leq C.
 \end{aligned}$$

Together, (4.90) gives for the second term of (4.88)

$$\begin{aligned}
 & \int_{\bar{I}} \int_{\Omega} \nabla v_{\delta} : L(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \, dx dt \\
 \rightarrow & \int_{\bar{I}} \int_{\Omega} \chi \nabla \psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}) : L(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \nabla u^{(n)} \, dx dt \\
 \geq & \int_{\bar{I}} \int_{\Omega} |\nabla u_0^{(n)}|^2 g_{,u_0 u_0}^{(n)}(u_0^{(n)}) L_{00}(\psi_{,u}^{(n)}(u^{(n)}, \phi^{(n)}), \phi^{(n)}) \, dx dt - C. \tag{4.91}
 \end{aligned}$$

Considering the third term of the right hand side of (4.88) observe first that by (4.87) and the trace theorem D.6 it holds for the first component of  $v_{\delta}$

$$v_{\delta,0} \rightarrow \chi \psi_{,u_0}^{(n)}(u^{(n)}, \phi^{(n)}) \text{ in } L^2(I; L^2(\partial\Omega)).$$

This yields with the assumptions in G4 and since it follows from (4.84) that (4.80c) is satisfied

$$\begin{aligned}
 & \int_{\bar{I}} \int_{\partial\Omega} v_{\delta,0} \beta_{00}(u_0^{(n)} - u_{bc,0}) \, d\mathcal{H}^{d-1} dt \\
 \rightarrow & \int_{\bar{I}} \int_{\partial\Omega} \chi \psi_{,u_0}^{(n)}(u^{(n)}, \phi^{(n)}) \beta_{00}(u_0^{(n)} - u_{bc,0}) \, d\mathcal{H}^{d-1} dt
 \end{aligned}$$

### 4.3. LOGARITHMIC TEMPERATURE TERM

$$\begin{aligned}
&= \int_0^{\tilde{t}} \int_{\partial\Omega} (\psi_{,u_0}^{(\eta)}(u_0^{(\eta)}, \tilde{u}^{(\eta)}, \phi^{(\eta)}) - \psi_{,u_0}^{(\eta)}(u_{bc,0}, \tilde{u}^{(\eta)}, \phi^{(\eta)})) \beta_{00}(u_0^{(\eta)} - u_{bc,0}) \, d\mathcal{H}^{d-1} \, dt \\
&\quad + \int_0^{\tilde{t}} \int_{\partial\Omega} \psi_{,u_0}^{(\eta)}(u_{bc,0}, \tilde{u}^{(\eta)}, \phi^{(\eta)}) \beta_{00}(u_0^{(\eta)} - u_{bc,0}) \, d\mathcal{H}^{d-1} \, dt \\
&\geq \int_0^{\tilde{t}} \int_{\partial\Omega} \int_0^1 \frac{d}{d\theta} \psi_{,u_0}^{(\eta)}(\underbrace{\theta u_0^{(\eta)} + (1-\theta)u_{bc,0}}_{=:v_{bc,\theta}}, \tilde{u}^{(\eta)}, \phi^{(\eta)}) \, d\theta \cdot \beta_{00}(u_0^{(\eta)} - u_{bc,0}) \, d\mathcal{H}^{d-1} \, dt \\
&\quad - \beta_1 \int_0^{\tilde{t}} \int_{\partial\Omega} |\psi_{,u_0}^{(\eta)}(u_{bc,0}, \tilde{u}^{(\eta)}, \phi^{(\eta)})| |u_0^{(\eta)} - u_{bc,0}| \, d\mathcal{H}^{d-1} \, dt \\
&\geq \int_0^{\tilde{t}} \int_{\partial\Omega} (u_0^{(\eta)} - u_{bc,0}) \cdot \left( \int_0^1 \psi_{,u_0 u_0}^{(\eta)}(v_{bc,\theta}, \tilde{u}^{(\eta)}, \phi^{(\eta)}) \, d\theta \right) \beta_{00}(u_0^{(\eta)} - u_{bc,0}) \, d\mathcal{H}^{d-1} \, dt \\
&\quad - \beta_1 \|\psi_{,u}^{(\eta)}(u_{bc,0}, \phi^{(\eta)})\|_{L^2(I; L^2(\partial\Omega; Y^N))} \left( \|u_0^{(\eta)}\|_{L^2(I; L^2(\partial\Omega; Y^N))} + \|u_{bc,0}\|_{L^2(I; L^2(\partial\Omega; Y^N))} \right) \\
&\geq -C. \tag{4.92}
\end{aligned}$$

Altogether, choosing  $(v, \zeta) = (v_\delta, 0)$  in (4.83c) yields as  $\delta \rightarrow 0$  with (4.89), (4.91) and (4.92)

$$\operatorname{esssup}_{\tilde{t} \in I} \|\psi_{,u}^{(\eta)}(u^{(\eta)}(\tilde{t}), \phi^{(\eta)}(\tilde{t}))\|_{L^2(\Omega; Y^N)}^2 \leq C \tag{4.93}$$

for all  $\eta \in (0, \bar{\eta}]$ .

As a conclusion from (4.84), (4.85), and (4.93) there are functions  $u \in L^2(I; H^1(\Omega; Y^N))$ ,  $b \in L^2(I; L^2(\Omega; Y^N))$  and  $\phi \in H^1(I \times \Omega; \mathbf{H}\Sigma^M) \cap L^p(I \times \Omega; \mathbf{H}\Sigma^M)$  such that for a subsequence as  $\eta \rightarrow 0$  (in the following, convergence in general holds only for subsequences without stating this explicitly)

$$u^{(\eta)} \rightharpoonup u \quad \text{in } L^2(I; H^1(\Omega; Y^N)), \tag{4.94a}$$

$$u^{(\eta)} \rightharpoonup u \quad \text{in } L^2(I; L^2(\partial\Omega; Y^N)), \tag{4.94b}$$

$$\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightharpoonup b \quad \text{in } L^2(I; L^2(\Omega; Y^N)), \tag{4.94c}$$

$$\phi^{(\eta)} \rightharpoonup \phi \quad \text{in } H^1(I \times \Omega; \mathbf{H}\Sigma^M), \tag{4.94d}$$

$$\phi^{(\eta)} \rightarrow \phi \quad \text{in } L^q(I \times \Omega; \mathbf{H}\Sigma^M) \text{ and almost everywhere, } q = 2, p. \tag{4.94e}$$

The goal is to show that  $(u, \phi)$  is a solution to (4.81d) by considering the limit of (4.83c) as  $\eta \rightarrow 0$ . Strong convergence of  $\nabla\phi(\eta)$  to  $\nabla\phi$  in  $L^2(I; L^2(\Omega; (\mathbf{T}\Sigma^M)^d))$  can be shown as in Subsection 4.1.5. As a consequence, (4.31), (4.37a), (4.37b), and (4.38) hold true with  $\phi^{(n)}$  replaced by  $\phi^{(\eta)}$  and  $\zeta^{(m)}$  by  $\zeta$ :

$$w_{,\phi}(\phi^{(\eta)}) \rightarrow w_{,\phi}(\phi) \quad \text{in } L^{p^*}(I \times \Omega; \mathbf{T}\Sigma^M), \tag{4.95a}$$

$$a_{,\nabla\phi}(\phi^{(\eta)}, \nabla\phi^{(\eta)}) \rightarrow a_{,\nabla\phi}(\phi, \nabla\phi) \quad \text{in } L^2(I; L^2(\Omega; (\mathbf{T}\Sigma^M)^d)), \tag{4.95b}$$

$$a_{,\phi}(\phi^{(\eta)}, \nabla\phi^{(\eta)}) \rightarrow a_{,\phi}(\phi, \nabla\phi) \quad \text{in } L^2(I; L^2(\Omega; \mathbf{T}\Sigma^M)), \tag{4.95c}$$

$$\omega(\phi^{(\eta)}, \nabla\phi^{(\eta)})\zeta \cdot \partial_t\phi^{(\eta)} \rightarrow \omega(\phi, \nabla\phi)\zeta \cdot \partial_t\phi \quad \text{in } L^1(I; L^1(\Omega)). \tag{4.95d}$$

It remains to identify  $b$  with  $\psi_{,u}(u, \phi)$  and to show  $\psi_{,\phi}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightharpoonup \psi_{,\phi}(u, \phi)$  in  $L^2(I; L^2(\Omega; \mathbf{T}\Sigma^M))$  and pointwise almost everywhere.

As a first step it is shown that the temperature is nonnegative. Define

$$W_1 := \{(t, x) \in I \times \Omega : u_0(t, x) > 1\}, \quad |W_1| := \mathcal{L}^{d+1}(W_1)$$

## CHAPTER 4. EXISTENCE OF WEAK SOLUTIONS

The set  $I \times \Omega \subset \mathbb{R}^{d+1}$  has finite measure, whence the norm on  $L^1(I \times \Omega)$  can be estimated by the norm on  $L^2(I \times \Omega)$ . It follows from (4.93) and assumption (4.77j) that

$$\begin{aligned}
 C &\geq \int_{I \times \Omega} |\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})| \, dxdt \\
 &\geq \int_{I \times \Omega} |\psi_{,u_0}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})| \, dxdt \\
 &\geq \int_{W_1} |\psi_{,u_0}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})| \, dxdt \\
 &\geq \int_{W_1} |k_\eta(u_0^{(\eta)} - 1) - k_8| \, dxdt \\
 &\geq k_\eta \int_{W_1} |u_0^{(\eta)} - 1| \, dxdt - k_8 |W_1|.
 \end{aligned}$$

The weak lower semi-continuity of norms implies

$$\int_{W_1} (u_0 - 1) \, dxdt \leq \liminf_{\eta \rightarrow 0} \int_{W_1} |u_0^{(\eta)} - 1| \, dxdt \leq \liminf_{\eta \rightarrow 0} \frac{C + k_8 |W_1|}{k_\eta} = 0,$$

hence  $|W_1| = 0$  and

$$u_0 \leq 1 \text{ almost everywhere.} \tag{4.96}$$

### 4.3.4 Strong convergence of temperature and chemical potentials

The goal of this subsection is to show strong convergence of the  $u^{(\eta)}$  to  $u$  in  $L^2$  (for a subsequence). Since the phase field variables are not of interest here, the value  $\phi^{(\eta)}(t, x)$  at which  $\psi^{(\eta)}$  and its derivatives are evaluated is dropped for shorter presentation.

Using (4.77a), it follows from (4.86) that

$$\begin{aligned}
 sC &\geq \int_0^{T-s} \int_\Omega (u^{(\eta)}(t+s) - u^{(\eta)}(t)) \cdot \int_0^1 \frac{d}{d\theta} \psi_{,u}^{(\eta)}(\underbrace{\theta u^{(\eta)}(t+s) + (1-\theta)u^{(\eta)}(t)}_{=:v_\theta}) \, d\theta \, dxdt \\
 &= \int_0^{T-s} \int_\Omega (u^{(\eta)}(t+s) - u^{(\eta)}(t)) \cdot \int_0^1 \psi_{,uu}^{(\eta)}(v_\theta) \, d\theta (u^{(\eta)}(t+s) - u^{(\eta)}(t)) \, dxdt \\
 &\geq \int_0^{T-s} \int_\Omega \hat{k}_0 |\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)|^2 \, dxdt.
 \end{aligned} \tag{4.97}$$

Extending  $\tilde{u}^{(\eta)}$  by zero if  $t \in \mathbb{R} \setminus (0, T)$  or if  $x \in \mathbb{R}^d \setminus \Omega$ , (4.97) and (4.85) yield

$$\begin{aligned}
 &\int_{\mathbb{R}} \int_{\mathbb{R}^d} |\tilde{u}^{(\eta)}(t+s, x) - \tilde{u}^{(\eta)}(t, x)|^2 \, dxdt \\
 &= \int_0^{T-s} \int_\Omega |\tilde{u}^{(\eta)}(t+s, x) - \tilde{u}^{(\eta)}(t, x)|^2 \, dxdt \\
 &\quad + \int_{-s}^0 \int_\Omega |\tilde{u}^{(\eta)}(t+s, x)|^2 \, dxdt + \int_{T-s}^T \int_\Omega |\tilde{u}^{(\eta)}(t, x)|^2 \, dxdt \\
 &\rightarrow 0 \quad \text{as } s \rightarrow 0.
 \end{aligned}$$

To obtain an analogous result for differences in space consider

$$\Omega_h := \left\{ x \in \mathbb{R}^d : x + \theta h \in \Omega \quad \forall \theta \in [0, 1] \right\}$$

### 4.3. LOGARITHMIC TEMPERATURE TERM

for some  $h \in \mathbb{R}^d$ . By the assumptions on  $\Omega$

$$\mathcal{L}^d(\Omega \setminus \Omega_h) \rightarrow 0 \text{ and } \mathcal{L}^d((\Omega - h) \setminus \Omega_h) \rightarrow 0 \quad \text{as } |h| \rightarrow 0$$

where  $\Omega - h = \{x - h : x \in \Omega\}$  and  $\mathcal{L}^d$  is the Lebesgue measure of dimension  $d$ . By (4.84) there is an upper bound for  $\{\|\nabla \tilde{u}^{(\eta)}\|_{L^2(I; L^2(\Omega; (\mathbb{H}\Sigma^N)^d))}\}_{\eta \in (0, \bar{\eta}]}$ , hence

$$\begin{aligned} & \int_{\mathbb{R}} \int_{\mathbb{R}^d} |\tilde{u}^{(\eta)}(t, x+h) - \tilde{u}^{(\eta)}(t, x)|^2 dx dt \\ = & \int_0^T \int_{\Omega_h} \left| \int_0^1 \frac{d}{d\theta} \tilde{u}^{(\eta)}(t, x+\theta h) d\theta \right|^2 dx dt \\ & + \int_0^T \int_{\mathbb{R}^d \setminus \Omega_h} |\tilde{u}^{(\eta)}(t, x+h) - \tilde{u}^{(\eta)}(t, x)|^2 dx dt \\ \leq & \int_0^T \int_{\Omega_h} \left| \int_0^1 \nabla \tilde{u}^{(\eta)}(t, x+\theta h) \cdot h d\theta \right|^2 dx dt \\ & + \int_0^T \int_{(\Omega-h) \setminus \Omega_h} |\tilde{u}^{(\eta)}(t, x+h)|^2 dx dt + \int_0^T \int_{\Omega \setminus \Omega_h} |\tilde{u}^{(\eta)}(t, x)|^2 dx dt \\ \leq & \int_0^T \int_{\Omega_h} \int_0^1 |\nabla \tilde{u}^{(\eta)}(t, x+\theta h)|^2 d\theta |h|^2 dx dt \\ & + C(\mathcal{L}^d((\Omega-h) \setminus \Omega_h) + \mathcal{L}^d(\Omega \setminus \Omega_h)) \\ \rightarrow & 0 \quad \text{as } |h| \rightarrow 0. \end{aligned}$$

The Riesz theorem D.15 furnishes that the set  $\{\tilde{u}^{(\eta)}\}_\eta$  is precompact in  $L^2(I; L^2(\Omega; \mathbb{T}\Sigma^N))$ . By (4.94a)

$$\tilde{u}^{(\eta)} \rightarrow \tilde{u} \quad \text{almost everywhere and in } L^2(I; L^2(\Omega; \mathbb{T}\Sigma^N)). \quad (4.98)$$

It holds that

$$\begin{aligned} & (u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)) (\psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{u}^{(\eta)}(t+s)) - \psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{u}^{(\eta)}(t))) \\ = & (u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)) \int_0^1 \frac{d}{d\theta} \psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t+s), \underbrace{\theta \tilde{u}^{(\eta)}(t+s) + (1-\theta)\tilde{u}^{(\eta)}(t)}_{=: \tilde{v}_\theta}) d\theta \\ = & (u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)) \int_0^1 \psi_{,u_0 \tilde{u}}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{v}_\theta) d\theta \cdot (\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)). \end{aligned} \quad (4.99a)$$

Analogously

$$\begin{aligned} & (\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)) \cdot (\psi_{,\tilde{u}}^{(\eta)}(u^{(\eta)}(t+s)) - \psi_{,\tilde{u}}^{(\eta)}(u^{(\eta)}(t))) \\ = & (\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)) \cdot \int_0^1 \psi_{,\tilde{u}u}^{(\eta)}(v_\theta) d\theta (u^{(\eta)}(t+s) - u^{(\eta)}(t)). \end{aligned} \quad (4.99b)$$

Estimate (4.86) means that

$$\begin{aligned} sC & \geq \int_0^{T-s} \int_{\Omega} (u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)) \cdot (\psi_{,u_0}^{(\eta)}(u^{(\eta)}(t+s)) - \psi_{,u_0}^{(\eta)}(u^{(\eta)}(t))) dx dt \\ & + \int_0^{T-s} \int_{\Omega} (\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)) \cdot (\psi_{,\tilde{u}}^{(\eta)}(u^{(\eta)}(t+s)) - \psi_{,\tilde{u}}^{(\eta)}(u^{(\eta)}(t))) dx dt \end{aligned}$$

$$\begin{aligned}
 &= \int_0^{T-s} \int_{\Omega} s \partial_t^s u_0^{(\eta)}(t) (\psi_{,u_0}^{(\eta)}(u^{(\eta)}(t+s)) - \psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{u}^{(\eta)}(t))) \, dx dt \\
 &+ \int_0^{T-s} \int_{\Omega} s \partial_t^s u_0^{(\eta)}(t) (\psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{u}^{(\eta)}(t)) - \psi_{,u_0}^{(\eta)}(u^{(\eta)}(t))) \, dx dt \\
 &+ \int_0^{T-s} \int_{\Omega} s \partial_t^s \tilde{u}^{(\eta)}(t) \cdot (\psi_{,\tilde{u}}^{(\eta)}(u^{(\eta)}(t+s)) - \psi_{,\tilde{u}}^{(\eta)}(u^{(\eta)}(t))) \, dx dt.
 \end{aligned}$$

Plugging the first and the last term of the right hand side to the other side yields thanks to (4.99a) and (4.99b), taking the assumptions (4.77d) and (4.77h) into account,

$$\begin{aligned}
 &\int_0^{T-s} \int_{\Omega} (u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)) (\psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{u}^{(\eta)}(t)) - \psi_{,u_0}^{(\eta)}(u^{(\eta)}(t))) \, dx dt \\
 \leq &\int_0^{T-s} \int_{\Omega} \left| s \partial_t^s u_0^{(\eta)}(t) \int_0^1 \psi_{,u_0 \tilde{u}}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{v}_{\theta}) \, d\theta \cdot s \partial_t^s \tilde{u}^{(\eta)}(t) \right| \, dx dt \\
 &+ \int_0^{T-s} \int_{\Omega} \left| s \partial_t^s \tilde{u}^{(\eta)}(t) \cdot \int_0^1 \psi_{,\tilde{u} u}^{(\eta)}(v_{\theta}) \, d\theta s \partial_t^s u^{(\eta)}(t) \right| \, dx dt \\
 &+ s C \\
 \leq &\int_0^{T-s} \int_{\Omega} \left| s \partial_t^s u_0^{(\eta)}(t) \int_0^1 \sum_{\alpha=1}^M h(\phi_{\alpha}) \lambda_{,u_0 \tilde{u}}^{(\alpha)}(u_0^{(\eta)}(t+s), \tilde{v}_{\theta}) \, d\theta \cdot s \partial_t^s \tilde{u}^{(\eta)}(t) \right| \, dx dt \\
 &+ \int_0^{T-s} \int_{\Omega} \left| s \partial_t^s u_0^{(\eta)}(t) \int_0^1 \sum_{\alpha=1}^M h(\phi_{\alpha}) \lambda_{,u_0 \tilde{u}}^{(\alpha)}(v_{\theta}) \, d\theta \cdot s \partial_t^s \tilde{u}^{(\eta)}(t) \right| \, dx dt \\
 &+ \int_0^{T-s} \int_{\Omega} \left| s \partial_t^s \tilde{u}^{(\eta)}(t) \cdot \int_0^1 2\nu \text{Id}_N + \sum_{\alpha=1}^M h(\phi_{\alpha}) \lambda_{,\tilde{u} \tilde{u}}^{(\alpha)}(v_{\theta}) \, d\theta s \partial_t^s \tilde{u}^{(\eta)}(t) \right| \, dx dt \\
 &+ s C \\
 \leq &2 \int_0^{T-s} \int_{\Omega} \frac{M}{2} \hat{k}_1 |u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)| |\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)| \, dx dt \\
 &+ \int_0^{T-s} \int_{\Omega} \frac{M}{2} \hat{k}_1 |\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)|^2 \, dx dt \\
 &+ s C.
 \end{aligned}$$

In view of (4.97) and (4.85) this is for  $s \leq 1$

$$\begin{aligned}
 &\leq C \left( \int_0^{T-s} \int_{\Omega} |u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)|^2 \, dx dt \right)^{1/2} \\
 &\quad \cdot \sqrt{s} \left( \frac{1}{s} \int_0^{T-s} \int_{\Omega} |\tilde{u}^{(\eta)}(t+s) - \tilde{u}^{(\eta)}(t)|^2 \, dx dt \right)^{1/2} + s C \\
 &\leq \sqrt{s} C (2 \|u_0^{(\eta)}\|_{L^2(I; L^2(\Omega))}) + s C \\
 &\leq \sqrt{s} C.
 \end{aligned} \tag{4.100}$$

For  $\delta \in (0, \delta_0)$  define

$$u_{0,\delta}^{(\eta)} := \max \left( -\frac{1}{\delta}, \min(1 - \delta, u_0^{(\eta)}) \right) = \kappa_{\delta} \circ u_0^{(\eta)}, \tag{4.101}$$

i.e.,  $u_0^{(\eta)}$  is projected onto the interval  $[-\frac{1}{\delta}, 1 - \delta]$  by the truncation function  $\kappa_{\delta}$ . Let

$$W^+(\delta, \eta) := \{(t, x) \in I \times \Omega : u_0^{(\eta)}(t, x) > 1 - \delta\}, \quad |W^+(\delta, \eta)| := \mathcal{L}^{d+1}(W^+(\delta, \eta)),$$



### 4.3. LOGARITHMIC TEMPERATURE TERM

which means that  $u_{0,\delta}^{(\eta)} = 1 - \delta$  on  $W^+(\delta, \eta)$ . With (4.93) and (4.77j)

$$\begin{aligned} C &\geq \int_{I \times \Omega} |\psi_{,u_0}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})| \, dx dt \\ &\geq \int_{W^+(\delta, \eta)} k_\eta (u_0^{(\eta)} - 1 + \delta - \delta) \, dx dt - k_7 |W^+(\delta, \eta)| \\ &= k_\eta \int_{W^+(\delta, \eta)} |u_0^{(\eta)} - u_{0,\delta}^{(\eta)}| \, dx dt - (k_\eta \delta + k_7) |W^+(\delta, \eta)|. \end{aligned}$$

Since  $k_\eta \rightarrow \infty$  as  $\eta \rightarrow 0$  and as  $|W^+(\delta, \eta)|$  is bounded by  $\mathcal{L}^{d+1}(I \times \Omega)$  for all  $\delta$  and  $\eta$  there exists  $\bar{\eta}(\delta)$  and  $C > 0$  independent of  $\delta$  such that for all  $\eta \leq \bar{\eta}(\delta)$

$$\int_{W^+(\delta, \eta)} |u_0^{(\eta)} - u_{0,\delta}^{(\eta)}| \, dx dt \leq \frac{C}{k_\eta} + \left( \delta + \frac{k_7}{k_\eta} \right) |W^+(\delta, \eta)| \leq C \delta.$$

On the set

$$W^-(\delta, \eta) := \left\{ (t, x) \in I \times \Omega : u_0^{(\eta)}(t, x) < -\frac{1}{\delta} \right\}$$

it holds almost everywhere that  $|u_0^{(\eta)} - u_{0,\delta}^{(\eta)}| \frac{1}{\delta} = (-u_0^{(\eta)} - \frac{1}{\delta}) \frac{1}{\delta} \leq (-u_0^{(\eta)}) \frac{1}{\delta} \leq (-u_0^{(\eta)})^2$ , therefore  $|u_0^{(\eta)} - u_{0,\delta}^{(\eta)}| \leq \delta |u_0^{(\eta)}|^2$ . As by (4.85)  $\|u_0^{(\eta)}\|_{L^2(I; L^2(\Omega))}$  is bounded by a constant independent of  $\eta$

$$\int_{W^-(\delta, \eta)} |u_0^{(\eta)} - u_{0,\delta}^{(\eta)}| \, dx dt \leq C \delta,$$

and since  $u_0^{(\eta)}$  and  $u_{0,\delta}^{(\eta)}$  agree on  $I \times \Omega \setminus (W^+(\delta, \eta) \cup W^-(\delta, \eta))$ , altogether the following convergence result is obtained (for an appropriate diagonal sequence):

$$\int_I \int_\Omega |u_0^{(\eta)} - u_{0,\delta}^{(\eta)}| \, dx dt \rightarrow 0 \quad \text{as } \eta, \delta \rightarrow 0. \quad (4.102)$$

Observe that

$$\begin{aligned} &\psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t+s), \tilde{u}^{(\eta)}(t), \phi^{(\eta)}(t)) - \psi_{,u_0}^{(\eta)}(u_0^{(\eta)}(t), \tilde{u}^{(\eta)}(t), \phi^{(\eta)}(t)) \\ &= \int_0^1 \frac{d}{d\theta} \psi_{,u_0}^{(\eta)}(\underbrace{\theta u_0^{(\eta)}(t+s) + (1-\theta)u_0^{(\eta)}(t)}_{=: v_{0,\theta}}, \tilde{u}^{(\eta)}(t), \phi^{(\eta)}(t)) \, d\theta \\ &= \int_0^1 \psi_{,u_0 u_0}^{(\eta)}(v_{0,\theta}, \tilde{u}^{(\eta)}(t), \phi^{(\eta)}(t)) \cdot (u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)) \, d\theta \\ &= \int_{u_0^{(\eta)}(t)}^{u_0^{(\eta)}(t+s)} \psi_{,u_0 u_0}^{(\eta)}(v_{0,\theta}, \tilde{u}^{(\eta)}(t), \phi^{(\eta)}(t)) \, dv_{0,\theta}. \end{aligned}$$

Thus the estimate (4.100) reads

$$C \sqrt{s} \geq \int_0^{T-s} \int_\Omega \int_{u_0^{(\eta)}(t)}^{u_0^{(\eta)}(t+s)} \psi_{,u_0 u_0}^{(\eta)}(v_{0,\theta}, \tilde{u}^{(\eta)}(t), \phi^{(\eta)}(t)) \, dv_{0,\theta} \cdot (u_0^{(\eta)}(t+s) - u_0^{(\eta)}(t)) \, dx dt.$$

By the convexity of  $\psi$  clearly  $\psi_{,u_0 u_0}^{(\eta)} \geq 0$ . Replacing  $u_0^{(\eta)}$  by  $u_{0,\delta}^{(\eta)}$  can therefore only lower the right side of the above inequality leading to

$$C \sqrt{s} \geq \int_0^{T-s} \int_\Omega \int_{u_{0,\delta}^{(\eta)}(t)}^{u_{0,\delta}^{(\eta)}(t+s)} \psi_{,u_0 u_0}^{(\eta)}(v_{0,\theta}, \tilde{u}^{(\eta)}(t), \phi^{(\eta)}(t)) \, dv_{0,\theta} \cdot (u_{0,\delta}^{(\eta)}(t+s) - u_{0,\delta}^{(\eta)}(t)) \, dx dt.$$

## CHAPTER 4. EXISTENCE OF WEAK SOLUTIONS

---

But then  $v_{0,\theta} \in [-\frac{1}{\delta}, 1 - \delta]$  where, for  $\eta$  small enough,  $\psi^{(\eta)}$  coincides with  $\psi$ . In particular, there is a constant  $c_0(\delta) > 0$  such that  $\psi_{,u_0 u_0}^{(\eta)}(v, \phi^{(\eta)}(t)) \geq c_0(\delta)$ . Therefore

$$C\sqrt{s} \geq \int_0^{T-s} \int_{\Omega} c_0(\delta) |u_{0,\delta}^{(\eta)}(t+s) - u_{0,\delta}^{(\eta)}(t)|^2 dx dt.$$

Since  $|u_{0,\delta}^{(\eta)}| \leq |u_0^{(\eta)}|$ , by (4.85) there is an upper bound for  $\|u_{0,\delta}^{(\eta)}\|_{L^2(I; L^2(\Omega))}$  independent of  $\eta$  and  $\delta$ . Since by (4.101)  $u_{0,\delta}^{(\eta)} = \kappa_\delta \circ u_0^{(\eta)}$  where  $\kappa_\delta \in W^{1,\infty}(\mathbb{R})$ , the chain rule for Sobolev functions and (4.84) gives that there is also an upper bound for the set  $\{\|\nabla u_{0,\delta}^{(\eta)}\|_{L^2(I; L^2(\Omega; \mathbb{R}^d))}\}_{\eta, \delta}$ . Applying analogous arguments as above for  $\tilde{u}^{(\eta)}$ , for a given  $\delta$ , the set  $\{u_{0,\delta}^{(\eta)}\}_\eta$  is precompact in  $L^2(I; L^2(\Omega))$ , whence in  $L^1(I; L^1(\Omega))$ , too.

The convergence result (4.102) together with an argument involving diagonal sequences (choose first  $\delta$  sufficient small and after choose an appropriate  $\eta$ ) implies with (4.94a)

$$u_0^{(\eta)} \rightarrow u_0 \quad \text{almost everywhere and in } L^1(I; L^1(\Omega)). \quad (4.103)$$

### 4.3.5 Convergence statements

Consider the set

$$W_0 := \{(t, x) \in I \times \Omega : u_0(t, x) = 1\}, \quad |W_0| := \mathcal{L}^{d+1}(W_0).$$

By (4.98), (4.103), and (4.94e)

$$\psi_{,u_0}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightarrow \psi_{,u_0}(u, \phi) = \infty \quad \text{almost everywhere in } W_0.$$

But the estimate (4.93) gives in view of (4.94c)

$$\|\psi_{,u_0}(u, \phi)\|_{L^2(W_0; Y^N)} \leq \liminf_{\eta \rightarrow 0} \|\psi_{,u_0}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})\|_{L^2(W_0; Y^N)} \leq C,$$

therefore  $|W_0| = 0$ . As a conclusion, taking (4.96) into account,  $u_0^{(\eta)} \rightarrow u_0 < 1$  almost everywhere which proves the first assertion in (4.81b).

If  $u_0 < 1$  the kind of way as  $\psi^{(\eta)}$  approximates  $\psi = \psi^{(0)}$  implies that  $\psi_{,u}^{(\eta)}(u, \phi) = \psi_{,u}(u, \phi)$  as long as  $\eta$  is big enough. Therefore by (4.98), (4.103), and (4.94e)  $\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightarrow \psi_{,u}(u, \phi)$  almost everywhere. In view of (4.94c)  $b = \psi_{,u}(u, \phi)$ , i.e.,

$$\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightarrow \psi_{,u}(u, \phi) \quad \text{in } L^2(I; L^2(\Omega)). \quad (4.104a)$$

Analogously as done in Subsection 4.1.5 for  $u^{(\eta)}$  (cf. the result (4.29)) it can be derived that

$$\nabla v : L(\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}), \phi^{(\eta)}) \nabla u^{(\eta)} \rightarrow \nabla v : L(\psi_{,u}(u, \phi), \phi) \nabla u \quad \text{in } L^1(I; L^1(\Omega)). \quad (4.104b)$$

The assumptions (4.77b) and (4.77i) together with estimate (4.85) yield that the functions  $\|\psi_{,\phi}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)})\|_{L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))}$  are bounded by a constant independent of  $\eta$  so that there is  $f \in L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M))$  with

$$\psi_{,\phi}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightharpoonup f \quad \text{in } L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M)).$$

Since  $\phi^{(\eta)} \rightarrow \phi$  and  $\psi_{,u}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightarrow \psi_{,u}(u, \phi)$  almost everywhere it holds that (see Lemma 4.11 in Subsection 4.2.3)  $\psi_{,\phi}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightarrow \psi_{,\phi}(u, \phi)$  almost everywhere, therefore  $f = \psi_{,\phi}(u, \phi)$  and

$$\psi_{,\phi}^{(\eta)}(u^{(\eta)}, \phi^{(\eta)}) \rightharpoonup \psi_{,\phi}(u, \phi) \quad \text{in } L^2(I; L^2(\Omega; \mathbb{T}\Sigma^M)). \quad (4.104c)$$

The convergence results (4.95a)–(4.95d) and (4.79a) together with (4.104a)–(4.104c) complete the list necessary to let  $\eta \rightarrow 0$  in (4.83c), i.e.,  $(u, \phi)$  indeed solves (4.81d). Since assertion (4.81c) can be derived as in Subsection 4.1.6 the proof of Theorem 4.12 is complete.  $\square$

# Appendix A

## Notation

$a(\phi, \nabla\phi)$	gradient entropy term (2.6a)
$\mathcal{A}$	index set (1.17b)
$A, B$	Chapter 3: integration constants
$B^{(\nu)}$	$= \psi_{,u}^{(\nu)}(u, \phi) \cdot u - \psi^{(\nu)}(u, \phi)$ (4.57)
$B_\varepsilon$	ball with radius $\varepsilon$
$c_i$	concentration of component $i \in \{1, \dots, N\}$
$c$	$= (e, c_1, \dots, c_N) \in Y^N$ vector of the conserved quantities (2.3a)
$\hat{c}$	$= (c_1, \dots, c_N) \in \Sigma^N$ vector of the concentrations (2.3b)
$C$	estimation constant, may change from line to line
$C^{m,\alpha}$	space of $m \in \mathbb{N}$ times differentiable functions, the $m^{\text{th}}$ derivative being Hölder continuous with coefficient $\alpha \in [0, 1]$
$d$	$\in \{1, 2, 3\}$ , spatial dimension
$D_{ij}, D_{ik}^N, D_i$	diffusion constants, see Section 1.4.2
$e$	internal energy density
$f$	(Helmholtz) free energy density
$g$	Chapter 1: (Gibbs) free energy density Chapter 4: convex function in $u_0$
$\mathcal{G}$	Greens operator (1.8)
$h$	interpolation function (2.29), see also assumption A2
$\mathcal{H}^d$	$d$ -dimensional Hausdorff measure
$H^1$	$= W^{1,2}$ Sobolev space
$I = [0, T]$	time interval
$J_i$	flux of the conserved quantity $c_i$
$L_{ij}$	Onsager coefficients for the fluxes (1.5)
$L^p$	Lebesgue space, $p \in [1, \infty]$
$m_{\alpha\beta}(\nu)$	mobility coefficient (1.14)
$M$	number of phases
$N$	number of components
$\mathcal{P}^K$	projection onto $\text{T}\Sigma^K$ , Definition 1.1, Section 1.1.1
$Q_{\alpha,\beta,\delta,\eta}, Q_{\alpha,\beta,\eta,ext}$	sets of quadruple junctions, see Subsection 1.1.2
$R_g$	gas constant
$\tilde{R}$	$= \frac{R_g}{v_m}$ scaled gas constant
$s$	Chapter 1: bulk entropy density Chapter 3: arc-length
$t$	time
$T$	temperature
$T_{\alpha,\beta,\delta}, T_{\alpha,\beta,ext}$	sets of triple junctions, see Subsection 1.1.2

## APPENDIX A. NOTATION

---

$u$	$= (\frac{-1}{T}, \frac{\bar{\mu}_1}{T}, \dots, \frac{\bar{\mu}_N}{T})$ thermodynamic potentials
$u^{(k)}$	outer expansion of $u$ (3.17)
$U^{(k)}$	inner expansion of $u$ (3.24)
$v$	Chapter 4: test function
$v_{\alpha\beta}$	normal velocity of interface $\Gamma_{\alpha\beta}$
$v_m$	molar volume (allover assumed to be constant)
$w(\phi)$	multi-well potential (2.6b)
$W^{m,p}$	Sobolev space, $m \in \mathbb{N}$ , $p \in [1, \infty]$
$X^{(n)}$	Galerkin space (4.9b)
$Y^{(n)}$	Galerkin space (4.9a)
$Y^N$	$= \mathbb{R} \times \mathbb{H}\Sigma^N$
$z$	Chapter 3: scaled distance, $= \frac{z}{\varepsilon}$
$\gamma_{\alpha\beta}(\nu)$	surface entropy on $\Gamma_{\alpha\beta}$
$\Gamma, \Gamma_{\alpha\beta}(\nu)$	phase boundary between phases $\Omega_\alpha$ and $\Omega_\beta$
$\Gamma_{\alpha,ext}$	external boundary of phase $\Omega_\alpha$
$\varepsilon$	small length scale related to the diffuse interface thickness
$\zeta$	Chapter 4: test function
$\eta$	Chapter 4: limit parameter
$\theta$	angle between interface normal vector and the first axis of a given coordinate system
$\theta^\varepsilon$	local deformation (1.20)
$\kappa_{\alpha\beta}$	scalar curvature of $\Gamma_{\alpha\beta}$
$\lambda$	Lagrange multiplier (2.11)
$\mu_i,$	chemical potential of component $i \in \{1, \dots, N\}$
$\bar{\mu}_i$	chemical potential projected onto $\mathbb{T}\Sigma^N$ , $\bar{\mu} = \mathcal{P}\mu$
$\nu$	unit normal vector, Chapter 4: limit parameter
$\nu_{\alpha\beta}$	normal vector on $\Gamma_{\alpha\beta}$
$\nu_{ext}$	outer unit normal vector on $\partial\Omega$
$\xi_{\alpha\beta}(\nu)$	(rotated) capillary forces acting on $\Gamma_{\alpha\beta}$ (1.15)
$\sigma_{\alpha\beta}(\nu)$	surface tension on $\Gamma_{\alpha\beta}$
$\Sigma^K$	Gibbs simplex (1.1b)
$\mathbb{H}\Sigma^K$	plane in which $\Sigma^K$ lies (1.1a)
$\mathbb{T}\Sigma^K$	tangent space onto $\Sigma^K$ (1.1c)
$\tau$	unit tangent vector
$\phi_\alpha$	phase field variable of phase $\alpha$
$\phi$	$= (\phi_1, \dots, \phi_M) \in \Sigma^M$ phase field variables
$\phi^{(k)}$	outer expansion of $\phi$ (3.17)
$\Phi^{(k)}$	inner expansion of $\phi$ (3.24)
$\chi$	characteristic function of some subset of $I$ or $\subset \Omega$
$\psi$	reduced grand canonical potential, cf. Definition 2.4 in Subsection 2.4
$\omega(\phi, \nabla\phi)$	mobility coefficient in the phase field model (2.8b)
$\Omega, \partial\Omega$	open, bounded domain, $\subset \mathbb{R}^d$ , with Lipschitz boundary
$\Omega_\alpha$	region occupied by phase $\alpha$
$\partial^\circ$	(intrinsic) normal time derivative (C.1)
$\nabla_\Gamma, \nabla_\Sigma$	surface gradient (C.2)
$\nabla_{\Gamma^\cdot}, \nabla_{\Sigma^\cdot}$	surface divergence (C.3)
$\Delta x, \Delta t$	grid constant and time step in the numerical algorithms

## Appendix B

# Equilibrium thermodynamics

The following facts are based on [Haa94], Chapter 5, and [Mül01], Chapter 7.

Consider a thermodynamic system with  $K$  components. The extensive quantities are

- $V$  : volume,
- $S$  : entropy,
- $F$  : (Helmholtz) free energy,
- $G$  : (Gibbs) free energy or free enthalpy,
- $N_i$  : mass of component  $i$ ,  $1 \leq i \leq K$ ,

and the intensive quantities are

- $M_i$  : chemical potential (per unit mass) of component  $i$ ,  $1 \leq i \leq K$ ,
- $P$  : pressure,
- $T$  : temperature.

Additional quantities and densities are defined as follows:

- $b$  : grand canonical potential density,
- $c_i$  : concentration of component  $i$ ,  $1 \leq i \leq K$ ,
- $e$  : internal energy density,
- $f$  : (Helmholtz) free energy density,
- $g$  : (Gibbs) free energy density,
- $\mu_i$  : chemical potential (per unit volume) of component  $i$ ,  $1 \leq i \leq K$ ,
- $s$  : entropy density.

Fix the temperature  $T$  and the pressure  $P$ , and consider  $(N_1, \dots, N_K)$  as variables. Then

$$G = G(N_1, \dots, N_K), \quad M_i = \partial_{N_i} G_i(N_1, \dots, N_K).$$

The total mass and the concentrations of the components are defined by

$$N := \sum_{i=1}^K N_i, \quad c_i := \frac{N_i}{N}, \quad 1 \leq i \leq K.$$

The chemical potential  $M_i$  being intensive quantity implies

$$M_i(\lambda N_1, \dots, \lambda N_K) = M_i(N_1, \dots, N_K) \quad \forall \lambda > 0.$$

## APPENDIX B. EQUILIBRIUM THERMODYNAMICS

---

Therefore  $M_i$  can be written as a function in the concentrations,

$$M_i = M_i(c_1, \dots, c_K) = M_i(\hat{c})$$

where  $\hat{c} := (c_1, \dots, c_K)$ . Since  $G$  is extensive it holds that

$$G(\lambda N_1, \dots, \lambda N_K) = \lambda G(N_1, \dots, N_K) \quad \forall \lambda > 0.$$

Derivation with respect to  $\lambda$  yields at  $\lambda = 1$

$$G(N_1, \dots, N_K) = \sum_i \partial_{N_i} G(N_1, \dots, N_K) N_i = \sum_i M_i(c_1, \dots, c_K) c_i N.$$

Let

$$\tilde{g} := \frac{G}{N} = \sum_i M_i(c_1, \dots, c_K) c_i.$$

**B.1 Lemma** *In the above situation the following identity holds:*

$$\overline{M}_i := (\mathcal{P}^K M) \cdot e_i = \nabla_{\hat{c}} \tilde{g} \cdot \mathcal{P}^K e_i, \quad e_i = (\delta_{ij})_{j=1}^K.$$

**Proof:** For some small  $\delta \in \mathbb{R}$  set

$$\hat{c}_\delta := \hat{c} + \delta \mathcal{P}^K e_i, \quad N_\delta := N \hat{c}_\delta = N \hat{c} + \delta N \mathcal{P}^K e_i = (N_1, \dots, N_K) + \delta N \mathcal{P}^K e_i.$$

It holds that  $\hat{c}_\delta \in \text{HS}^K$  and  $N = \sum_{j=1}^K (N_\delta)_j$ ,  $(N_\delta)_j$  being the components of the vector  $N_\delta$ . A change of the mass fractions into the direction  $\mathcal{P}^K e_i$  does obviously not change the whole mass in the system. Therefore  $G(N_\delta) = N \tilde{g}(\hat{c}_\delta)$  for all  $\delta$ . Using the symmetry of  $\mathcal{P}^K$  the identities

$$\partial_\delta G(N_\delta) \Big|_{\delta=0} = \nabla_N G(N \hat{c}) \cdot N \mathcal{P}^K e_i = N M(\hat{c}) \cdot \mathcal{P}^K e_i = N (\mathcal{P}^K M) \cdot e_i = N \overline{M}_i$$

and, on the other hand,

$$\partial_\delta (N \tilde{g}(\hat{c}_\delta)) \Big|_{\delta=0} = N \nabla_{\hat{c}} \tilde{g}(\hat{c}) \cdot \mathcal{P}^K e_i$$

yield the desired identity.  $\square$

When relaxing into equilibrium the system may perform work against the pressure. If the volume changes by  $dV$  then the work performed is given by  $P dV$ . Following [Haa94], Section 5.1, the term  $P dV$  is small under usual solidification conditions. Therefore, the volume  $V$  is kept fix (cf. the assumptions in Subsection 1.1.1). Since  $F = G - PV$  the free energy and the free enthalpy only distinguish by a constant. Moreover, by Assumption S4 in Subsection 1.1.1, the mass density  $\rho = \frac{N}{V}$  is constant so that the total mass  $N$  is constant, too.

In the following the temperature is taken into account and not fixed any more, i.e.,

$$M_i = M_i(T, c_1, \dots, c_K), \quad G = G(T, N_1, \dots, N_K).$$

Defining

$$\tilde{f} := \frac{F}{N} = \frac{G - PV}{N} = \tilde{g} - P \frac{V}{N} = \sum_i M_i(T, c_1, \dots, c_K) c_i - \frac{P}{\rho}$$

and using that  $\rho$  is fixed it is clear that  $\tilde{f}$  is a function in  $(T, c_1, \dots, c_K)$ .

**B.2 Lemma** *Under the assumptions in Subsection 1.1.1 the following identity holds:*

$$\overline{M}_i := (\mathcal{P}^K M) \cdot e_i = \nabla_{\hat{c}} \tilde{f} \cdot \mathcal{P}^K e_i, \quad e_i = (\delta_{ij})_{j=1}^K.$$

---

**Proof:** The proof can be done analogously to the proof of the previous Lemma B.1. Observe that  $\tilde{f} = \tilde{g} - P\frac{V}{N}$  and the last term is independent of  $\delta$  when considering variations of  $\hat{c}$  as in the proof there. This is why the free enthalpy can be replaced by the free energy.  $\square$

Let

$$\mu_i(T, \hat{c}) := \rho M_i(T, \hat{c}), \quad (\text{B.1})$$

$$f(T, \hat{c}) := \rho \tilde{f}(T, \hat{c}) = \sum_i \mu_i(T, \hat{c}) c_i - P. \quad (\text{B.2})$$

The entropy density is given by  $s = -\partial_T f$ . By Lemma B.2

$$df = -s dT + \bar{\mu} \cdot d\hat{c}.$$

If  $f$  is concave in  $T$  then the Legendre transform (cf. [ET99])  $e$  of  $-f$  with respect to  $T$ , the internal energy density, is a well-defined real function, and there are the identities

$$e = T\partial_T(-f) - (-f) = f + Ts, \quad de = Tds + \bar{\mu} \cdot d\hat{c}. \quad (\text{B.3})$$

As a consequence, for the entropy density it holds that

$$s = s(e, \hat{c}), \quad ds = \frac{1}{T} de - \frac{\bar{\mu}}{T} \cdot d\hat{c}. \quad (\text{B.4})$$

If  $f$  is convex in  $\hat{c}$  then, analogously to the definition of  $\psi$  in Section 2.4, the Legendre transform  $b$  of  $f$  with respect to  $\hat{c}$ , the grand canonical potential, is a well-defined real function, and the following identities hold:

$$b = \hat{c} \cdot \nabla_{\hat{c}} f - f = \hat{c} \cdot \bar{\mu} - f, \quad db = sdT + \hat{c} \cdot d\bar{\mu}. \quad (\text{B.5})$$

During the above computations always a system in equilibrium was assumed. In thermodynamics of irreversible processes local equilibrium is assumed so that the above results still hold. This fact is used during the derivation of the model with moving boundaries in Chapter 1.

Now, let  $\alpha, \beta$  be two phases present in the system. At fixed temperature (and, as before, fixed volume, pressure and mass density) there is the equilibrium condition.

$$M_i^\alpha = M_i^\beta, \quad 1 \leq i \leq K.$$

This can be derived from the equilibrium condition  $dG = dG^\alpha + dG^\beta = 0$ . Equivalently, by (B.1) at constant mass density  $\rho$

$$\mu_i^\alpha = \mu_i^\beta, \quad 1 \leq i \leq K. \quad (\text{B.6})$$

There is another equivalent expression involving the free energy densities:

**B.3 Lemma** *In the above situation two phases are in equilibrium if and only if*

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta \quad \forall i \quad \text{and} \quad f^\beta - \bar{\mu}^\beta \cdot \hat{c}^\beta = f^\alpha - \bar{\mu}^\alpha \cdot \hat{c}^\alpha. \quad (\text{B.7})$$

**Proof:** By (B.2)  $f + P = \sum_i \mu_i c_i = \mu \cdot \hat{c}$ , hence

$$P + f - \bar{\mu} \cdot \hat{c} = ((\text{Id}_K - \mathcal{P}^K)\mu) \cdot \hat{c} = \left(\frac{1}{K} \mathbf{1}(\cdot \mu)\right) \cdot \hat{c} = \frac{1}{K} (\mathbf{1} \cdot \mu) \underbrace{(\mathbf{1} \cdot \hat{c})}_{=1} = \frac{1}{K} \sum_i \mu_i.$$

Now, it is easy to see that

$$\mu_i^\alpha = \mu_i^\beta \quad \forall i \quad \iff \quad \bar{\mu}_i^\alpha = \bar{\mu}_i^\beta \quad \forall i \quad \text{and} \quad \sum_i \mu_i^\alpha = \sum_i \mu_i^\beta$$

from which the equivalence of (B.6) and (B.7) can be concluded.  $\square$

As a last remark observe that by (B.5) the condition (B.7) is equivalent to

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta \quad \forall i \quad \text{and} \quad b^\beta = b^\alpha. \quad (\text{B.8})$$





## Appendix C

# Facts on evolving surfaces and transport identities

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

**C.1 Definition**  $(\Sigma_t)_{t \in I}$  is an evolving  $m$ -dimensional surface in  $\mathbb{R}^d$  if

1. for each  $t \in I$ , the surface  $\Sigma_t$  can be parameterised over a fixed smooth orientable submanifold  $U \subset \mathbb{R}^{m+1}$ ,
2. the set  $\Sigma' := \{x' = (t, x) : t \in I, x \in \Sigma_t\} \subset \mathbb{R} \times \mathbb{R}^d$  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  $V \cong \mathbb{R}^{m+1}$ .

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  $\vec{v}_\Sigma : \Sigma' \rightarrow \mathbb{R}^{d+1}$  such that  $(1, \vec{v}_\Sigma(t, x)) \in \mathbb{T}_{x'}\Sigma'$  and  $\vec{v}_\Sigma(t, x) \in \mathbb{N}_x\Sigma_t$ ;  $\vec{v}_\Sigma(t, x)$  is the vectorial normal velocity of the evolving surface. It can be verified that

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

Let  $\varphi$  be a smooth scalar field on  $\Sigma'$ . The derivative

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

is the normal time derivative of  $\varphi$  in  $x'$  and describes the variation of  $\varphi$  when following the curve  $\delta \mapsto c(\delta) \in \Sigma_{t+\delta}$  defined by  $c(0) = x$  and  $\partial_\delta c(\delta) = \vec{v}_\Sigma(t + \delta, c(\delta))$ ,  $\delta \in (t - \delta_0, t + \delta_0)$  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  $\varphi$  into direction  $(0, \tau_k) \in \mathbb{T}_{x'}\Sigma'$  is denoted. The surface gradient of  $\varphi$  in  $x'$  is defined by

$$\nabla_\Sigma \varphi(x') := \sum_{k=1}^m \partial_{\tau_k} \varphi(x') \tau_k \in \mathbb{T}_x\Sigma_t \quad (\text{C.2})$$

Let  $\vec{\varphi}$  be a smooth vector field on  $\Sigma'$ . The surface divergence of  $\vec{\varphi}$  in  $x'$  is defined by

$$\nabla_\Sigma \cdot \vec{\varphi}(x') := \sum_{k=1}^m \partial_{\tau_k} \vec{\varphi}(x') \cdot \tau_k. \quad (\text{C.3})$$

## APPENDIX C. FACTS ON EVOLVING SURFACES AND TRANSPORT IDENTITIES

---

If  $m = d - 1$  the normal space  $N_x \Sigma_t$  has dimension one, and  $\Sigma'$  is orientable. Then there is a smooth vector field  $\nu_\Sigma$  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

$$\kappa_\Sigma := -\nabla_\Sigma \cdot \nu_\Sigma, \quad \vec{\kappa}_\Sigma := \kappa_\Sigma \nu_\Sigma. \quad (\text{C.4})$$

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

$$v_\Sigma = \vec{v}_\Sigma \cdot \nu_\Sigma, \quad (\text{C.5})$$

and the following relation, derived in [Gur00], Chapter 15b, holds:

$$\partial^\circ \nu_\Sigma = -\nabla_\Sigma v_\Sigma. \quad (\text{C.6})$$

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

1. the set  $\Gamma_t$  is a relatively open connected subset of  $\Sigma_t$  for each  $t \in I$ ,
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  $t \in I$ ,  $\partial\Gamma_t$  is the graph of a Lipschitz continuous map.

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

In some point  $x \in \partial\Gamma_t$  the tangent cone on  $\Gamma_t$  is denoted by  $T_x \Gamma_t$ . If  $x$  is in the interior of one of the pieces the cone is a half-space of  $T_x \Sigma_t$ . Besides then the boundary of  $T_x \Gamma_t$  in  $T_x \Sigma_t$  coincides with the tangent space of the boundary  $\partial\Gamma_t$ , i.e.,  $\partial T_x \Gamma_t = T_x \partial\Gamma_t$ . In such points  $x$  there is a unique unit vector  $\tau_\Gamma \in T_x \Sigma_t \cap N_x \partial\Gamma_t$  with

$$\tau_\Gamma \cdot \tilde{\tau} \leq 0 \quad \text{for all } \tilde{\tau} \in T_x \Gamma_t. \quad (\text{C.7})$$

This vector  $\tau_\Gamma$  is said to be the external unit normal of  $\Gamma_t$  with respect to  $\Sigma_t$ . For example, in Figure 1.1 where  $d = 2$  and  $m = 1$ , the external unit normal of  $\Gamma_{\alpha\beta}$  in the triple junction is  $\tau_{\alpha\beta}$ . A set corresponding to  $\Sigma_t$  can be obtained by smoothly extending  $\Gamma_{\alpha\beta}$  over the triple junction.

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

**C.3 Theorem** ([Bet86], Corollary 4 ) *In the above described situation there is the following identity:*

$$\int_{\Gamma_t} (\nabla_\Sigma \cdot \vec{\varphi} + \vec{\kappa}_\Sigma \cdot \vec{\varphi}) \, d\mathcal{H}^m(x) = \int_{\partial\Gamma_t} \vec{\varphi} \cdot \tau_\Gamma \, d\mathcal{H}^{m-1}. \quad (\text{C.8})$$

If  $\vec{\varphi}$  is a tangent vector field then  $\vec{\kappa}_\Sigma \cdot \vec{\varphi} = 0$  so that one gets the usual divergence theorem on surfaces. It should be remarked that the proof in [Bet86] 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). Next, a transport identity is stated:

**C.4 Theorem** ([Bet86], Theorem 1) *In the above described situation it holds for every  $t \in I$  that*

$$\left. \frac{d}{dt} \left( \int_{\Gamma_t} \varphi \, d\mathcal{H}^m \right) \right|_t = \int_{\Gamma_t} (\partial^\circ \varphi - \varphi \vec{v}_\Sigma \cdot \vec{\kappa}_\Sigma) \, d\mathcal{H}^m + \int_{\partial\Gamma_t} (\varphi \vec{v}_{\partial\Gamma} \cdot \tau_\Gamma) \, d\mathcal{H}^{m-1}. \quad (\text{C.9})$$

**C.5 Remark** If  $\vec{v}_\Sigma = 0$  and  $\vec{\kappa}_\Sigma = 0$  then  $\Gamma_t$  is flat,  $\partial^\circ$  reduces to  $\partial_t$  and  $\vec{v}_{\partial\Gamma}$  is tangential. Altogether, the Reynold's transport theorem is obtained.

## Appendix D

# Several functional analytical results

This chapter contains a list of important facts for chap. 4 including references.

**D.1 Theorem (Picard-Lindelöf, cf. [Wal96], Theorem II.§10.VI.)** Let  $0 \in (-\delta, a) \subset \mathbb{R}$  be an open interval and  $D \subset \mathbb{R}^n$  an open domain. Let  $f \in C^0((-\delta, a) \times D)$  be Lipschitz continuous with respect to the second variable, i.e., there is a constant  $L > 0$  such that  $|f(t, y) - f(t, \hat{y})| \leq L|y - \hat{y}|$  or all  $y, \hat{y} \in D, t \in (-\delta, a)$ .

Let  $y_0 \in D$ . Then the initial value problem

$$y'(t) = f(t, y(t)), \quad y(0) = y_0$$

has a unique solution which can be extended to both sides of  $t = 0$  until reaching the boundary.

**D.2 Theorem (Lebesgue, cf. [Alt99], Theorem 1.21)** Consider a set  $D \subset \mathbb{R}^d$  and  $p \in [1, \infty)$ . For  $k \in \mathbb{N}$ , let  $g_k \rightarrow g$  in  $L^1(D; \mathbb{R})$  as  $k \rightarrow \infty$  and let  $f_k, f : D \rightarrow Y$  be measurable functions mapping into some Banach space  $Y$  such that

- (i)  $f_k \rightarrow f$  almost everywhere as  $k \rightarrow \infty$ ,
- (ii)  $|f_k|^p \leq g_k$  almost everywhere for all  $k$ .

Then  $f_k, f \in L^p(D; Y)$  and

$$f_k \rightarrow f \text{ in } L^p(D; Y) \text{ as } k \rightarrow \infty.$$

**D.3 Theorem (Rellich, cf. [Alt99], Theorem A6.4)** Let  $D \subset \mathbb{R}^d$  be an open, bounded domain with Lipschitz boundary,  $1 \leq p < \infty$  and  $m \geq 1$ . For  $k \in \mathbb{N}$ , let  $f_k, f \in W^{m,p}(D)$ . Then, as  $k \rightarrow \infty$ ,

$$f_k \rightarrow f \text{ in } W^{m,p}(D) \quad \Rightarrow \quad f_k \rightarrow f \text{ in } W^{m-1,p}(D).$$

**D.4 Theorem (Sobolev, cf. [Alt99], Theorem 8.9)** Let  $D \subset \mathbb{R}^d$  be an open, bounded domain with Lipschitz boundary,  $1 \leq p_1, p_2 < \infty$  and  $m_1, m_2 \geq 0$ .

1. If  $m_1 - \frac{d}{p_1} \geq m_2 - \frac{d}{p_2}$  and  $m_1 \geq m_2$  then there is the continuous embedding

$$H^{m_1, p_1}(D) \hookrightarrow H^{m_2, p_2}(D).$$

2. If  $m_1 - \frac{d}{p_1} > m_2 - \frac{d}{p_2}$  and  $m_1 > m_2$  then the above embedding is compact.

**APPENDIX D. SEVERAL FUNCTIONAL ANALYTICAL RESULTS**

---

**D.5 Theorem (Cf. [Alt99], Theorem 8.5)** *Let  $D \subset \mathbb{R}^d$  be an open, bounded domain with Lipschitz boundary. Then the embedding*

$$C^{k,1}(\overline{D}) \rightarrow W^{k+1,\infty}(D)$$

*exists and is an isomorphism (in the sense that to each  $f \in W^{k+1,\infty}(D)$  there is a function  $\tilde{f} \in C^{k,1}(\overline{D})$  with  $f = \tilde{f}$  almost everywhere). In particular, it holds that*

$$W^{k+1,\infty}(\mathbb{R}) \hookrightarrow C^{k,1}(\mathbb{R}).$$

**D.6 Theorem (Trace theorem, cf. [Alt99], Theorem A6.6 and A6.13)** *Let the set  $\Omega \subset \mathbb{R}^d$  be an open, bounded domain with Lipschitz boundary and  $1 \leq p \leq \infty$ . There is a unique linear continuous map*

$$S : W^{1,p}(\Omega) \rightarrow L^p(\partial\Omega)$$

*such that*

$$S(f) = f|_{\partial\Omega} \text{ for all } f \in W^{1,p}(\Omega) \cap C^0(\overline{\Omega}).$$

*Let now  $p < \infty$ . For  $k \in \mathbb{N}$ , let  $f_k, f \in W^{1,p}(D)$ . Then, as  $k \rightarrow \infty$ ,*

$$f_k \rightharpoonup f \text{ in } W^{1,p}(D) \quad \Rightarrow \quad f_k \rightarrow f \text{ in } L^p(\partial D).$$

**D.7 Lemma (Gronwall lemma, cf. [Wal96], V.§29.X.)** *Let  $f \in C^0([0, \beta]; \mathbb{R})$  satisfying*

$$f(t) \leq \alpha + \int_0^t h(r)f(r)dr$$

*where  $\alpha \in \mathbb{R}$  and  $h \in L^1([0, \beta])$  is nonnegative (almost everywhere). Then*

$$f(t) \leq \alpha e^{H(t)} \quad \text{where } H(t) = \int_0^t h(r)dr.$$

**D.8 Theorem (Cf. [Zei90], Ex. 23.13)** *Let  $I = (0, T) \subset \mathbb{R}$  be an open interval and let  $X, Y, Z$  be real Banach spaces. Consider the set*

$$W := \{u \in L^p(I; X), u' \in L^q(I; Z)\}.$$

1. *The embedding  $W \hookrightarrow C^0(\overline{I}; Z)$  exists and is continuous provided*
  - (i) *the embedding  $X \hookrightarrow Z$  is continuous,*
  - (ii) *it holds that  $1 \leq p, q \leq \infty$ .*
2. *The embedding  $W \hookrightarrow L^p(I; Y)$  exists, is continuous, and is compact provided*
  - (i) *there are continuous embeddings  $X \hookrightarrow Y \hookrightarrow Z$ ,*
  - (ii) *the embedding  $X \hookrightarrow Y$  is compact,*
  - (iii) *the spaces  $X$  and  $Z$  are reflexive,*
  - (iv) *it holds that  $1 < p, q < \infty$ .*

**D.9 Theorem (Convolution estimate, cf. [Alt99], Theorem 2.12)** *Let  $\zeta \in L^1(\mathbb{R}^d)$  and  $f \in L^p(\mathbb{R}^d; Y)$  with some Banach space  $Y$ , and let  $p \in [1, \infty]$ . Then by*

$$(\zeta * f)(x) := \int_{\mathbb{R}^d} \zeta(x-y)f(y)dy = \int_{\mathbb{R}^d} \zeta(y)f(x-y)dy \tag{D.1}$$

a function  $\zeta * f \in L^p(\mathbb{R}^d; Y)$  is defined satisfying

$$\|\zeta * f\|_{L^p(\mathbb{R}^d; Y)} \leq \|\zeta\|_{L^1(\mathbb{R}^d)} \|f\|_{L^p(\mathbb{R}^d; Y)}. \quad (\text{D.2})$$

If  $f$  has weak derivatives then the weak derivatives of  $\zeta * f$  are the convolutions of the weak derivatives of  $f$  with  $\zeta$ , i.e.

$$\partial^\alpha(\zeta * f) = \zeta * \partial^\alpha f \quad (\text{D.3})$$

where  $\alpha = (\alpha_1, \dots, \alpha_d)$  is some multi-index indicating the derivatives with respect to the variables corresponding to  $(x_1, \dots, x_d)$ .

**D.10 Definition (Dirac sequences)** A sequence  $(\zeta_k)_{k \in \mathbb{N}}$  in  $L^1(\mathbb{R}^d)$  is a Dirac sequence if

$$\zeta_k \geq 0, \quad \int_{\mathbb{R}^d} \zeta_k = 1, \quad \int_{\mathbb{R}^d \setminus B_\rho(0)} \zeta_k \rightarrow 0 \text{ as } k \rightarrow \infty \text{ for all } \rho > 0. \quad (\text{D.4})$$

If  $\zeta \in L^1(\mathbb{R}^d)$  fulfils  $\zeta \geq 0$  and  $\int_{\mathbb{R}^d} \zeta = 1$  then the sequence  $(\zeta_\varepsilon)_{\varepsilon > 0}$  defined by

$$\zeta_\varepsilon(x) := \varepsilon^{-d} \zeta\left(\frac{x}{\varepsilon}\right) \quad (\text{D.5})$$

is the Dirac sequence associated to  $\zeta$ .

**D.11 Theorem (Cf. [Alt99], Theorem 2.14)** Let  $(\zeta_k)_k$  be a Dirac sequence,  $Y$  be a Banach space,  $p \in [1, \infty)$ , and let  $f \in L^p(\mathbb{R}^d; Y)$ . Then

$$\zeta_k * f \rightarrow f \text{ in } L^p(\mathbb{R}^d; Y) \text{ as } k \rightarrow \infty. \quad (\text{D.6})$$

**D.12 Theorem (Vitali, cf. [Alt99], Theorem 1.19)** Consider a bounded domain  $D \subset \mathbb{R}^d$  and  $p \in [1, \infty)$ . For  $k \in \mathbb{N}$ , let  $f_k, f : D \rightarrow Y$  be measurable functions mapping into some Banach space  $Y$  such that  $f_k \rightarrow f$  as  $k \rightarrow \infty$  almost everywhere, and assume  $f_k \in L^p(D; Y)$ .

Then  $f_k \rightarrow f$  in  $L^p(D; Y)$  if and only if

$$\sup_k \int_E |f_k|^p dx \rightarrow 0 \text{ as } \mathcal{L}^d(E) \rightarrow 0.$$

**D.13 Lemma (Fatou, cf. [Alt99], Lemma A1.19)** Consider a domain  $D \subset \mathbb{R}^d$  and let  $\{f_k\}_k$  be a set of non-negative integrable functions on  $D$ . Then

$$\int_D \liminf_{k \rightarrow \infty} f_k(x) dx \leq \liminf_{k \rightarrow \infty} \int_D f_k(x) dx.$$

**D.14 Lemma (Poincaré inequality, cf. [Alt99], Theorem 6.15)** Let the set  $D \subset \mathbb{R}^d$  be an open bounded domain with Lipschitz boundary  $\partial D$ . Let  $J \subset W^{1,p}(D; \mathbb{R}^k)$  be a nonempty, convex, and closed subset with some  $p \in (1, \infty)$ . The following points are equivalent:

1. There is some  $f_0 \in J$  and some  $C_0 > 0$  such that for all  $v \in \mathbb{R}^k$  with  $f_0 + v \in J$  it follows that  $|v| \leq C_0$ .
2. A constant  $C > 0$  exists so that for all  $f \in J$

$$\|f\|_{L^p(D; \mathbb{R}^k)} \leq C(\|\nabla f\|_{L^p(D; (\mathbb{R}^k)^d)} + 1). \quad (\text{D.7})$$

**D.15 Theorem (Riesz, cf. [Alt99], Theorem 2.15)** Let  $p \in [1, \infty)$ . A set  $\mathcal{A} \subset L^p(\mathbb{R}^d)$  is precompact if and only if there is a constant  $C > 0$  such that

- (i)  $\sup_{f \in \mathcal{A}} \|f\|_{L^p} \leq C$ ,
- (ii)  $\sup_{f \in \mathcal{A}} \|f(\cdot - h) - f\|_{L^p} \rightarrow 0$  as  $|h| \rightarrow 0$ ,
- (iii)  $\sup_{f \in \mathcal{A}} \|f\|_{L^p(\mathbb{R}^d \setminus B_R(0))} \rightarrow 0$  as  $R \rightarrow \infty$ .



# Bibliography

- [AB98] G. Alberti and G. Bellettini. *A non-local anisotropic model for phase transitions: asymptotic behaviour of rescaled energies*. *Europ. J. Appl. Math.* 9, pp. 261-284, 1998.
- [ABC94] N. D. Alikakos, P. Bates, and X. Chen. *Convergence of the Cahn-Hilliard equation to the Hele-Shaw model*. *Arch. Rat. Mech. Anal.* 128, pp. 165-205, 1994.
- [AL83] H. W. Alt and S. Luckhaus. *Quasilinear elliptic-parabolic differential equations*. *Math. Z.* 183, pp. 311-341, 1983.
- [Alm99] R. F. Almgren. *Second-order phase field asymptotics for unequal conductivities*. *SIAM J. Appl. Math.* 59, pp. 2086-2107, 1999.
- [Alt99] H. W. Alt. *Lineare Funktionalanalysis*. 3. ed., Springer, ISBN 3-540-65421-6, 1999.
- [And02] C. Andersson. *Third order asymptotics of a phase-field model*. TRITA-NA-0217, Dep. of Num. Anal. and Comp. Sc., Royal Inst. of Technology, Stockholm, 2002.
- [AP92] H. W. Alt and I. Pawlow. *A mathematical model of dynamics of non-isothermal phase separation*. *Phys. D* 59, pp. 389-416, 1992.
- [AP93] H. W. Alt and I. Pawlow. *Solutions for a model of nonisothermal phase separation*. Free boundary problems involving solids (Montreal, PQ, 1990), pp. 214-219, Pitman Res. Notes Math. Ser., 281, Longman Sci. Tech., Harlow, 1993.
- [BBR05] G. Bellettini, A. Braides, and G. Riey. *Variational approximation of anisotropic functionals on partitions*. *Annali di matematica* 184, pp. 75-93, 2005.
- [BE93] J.F. Blowey and C.M. Elliott. *Curvature dependent phase boundary motion and parabolic double obstacle problems*. *Degenerate diffusions (Minneapolis, MN, 1991)*. IMA Vol. Math. Appl. 47, Springer, pp. 19-60, 1993.
- [Bet86] D. E. Betounes. *Kinematics of submanifolds and the mean curvature normal*. *Arch. Rat. Mech. Anal.* 96, pp. 1-27, 1986.
- [BGS98] L. Bronsard, H. Garcke, and B. Stoth. *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, pp. 481-506, 1998.
- [Cag89] G. Caginalp. *Stefan and Hele Shaw type models as asymptotic limits of the phase field equations*. *Phys. Rev. A* 39, pp. 5887-5896, 1989.
- [CC98] G. Caginalp and X. Chen. *Convergence of the phase field model to its sharp interface limits*. *European J. Appl. Math.* 9, pp. 417-445, 1998.
- [CF88] G. Caginalp and P. C. Fife. *Dynamics of layered interfaces arising from phase boundaries*. *SIAM J. Appl. Math.* 48, pp. 506-518, 1988.

- [CH58] J. W. Cahn and J. E. Hilliard. *Free Energy of a Nonuniform System. I. Interfacial Free Energy*. J. Chem. Phys. 28, pp. 258-267, 1958.
- [CH74] J. W. Cahn and D. W. Hoffmann. *A vector thermodynamics for anisotropic surfaces II. Curved and faceted surfaces*. Acta Metall. Mater. 22, pp. 1205-1214, 1974.
- [Che02] L. Q. Chen. *Phase-field models for microstructural evolution*. Ann. Rev. Mater. Res. 32, pp. 113-140, 2002.
- [Dar49] L. Darken. *Diffusion of carbon in austenite with a discontinuity in composition*. Trans AIME 180, pp. 430-438, 1949.
- [Dav01] S. H. Davis. *Theory of solidification*. Cambridge University Press, ISBN 0-521-65080-1, 2001.
- [Eck04] C. Eck. *A Two-Scale Phase Field Model for Liquid-Solid Phase Transitions of Binary Mixtures with Dendritic Microstructure*. Habilitationsschrift, Universität Erlangen, 2004.
- [ET99] I. Ekeland and R. Temam. *Convex analysis and variational problems*. Unabridged, corr. republ. of the work 1. publ. in English Amsterdam and New York, 1976, Classics in applied mathematics 28, Philadelphia Soc. for Industrial and A, ISBN 0-89871-450-8, 1999.
- [FP95] P.C. Fife and O. Penrose. *Interfacial dynamics for thermodynamically consistent phase-field models with nonconserved order parameter*. EJDE 1995, No. 16, pp. 1-49, 1995.
- [Gar02] H. Garcke. *Einführung in die mathematische Modellierung*. Lecture notes, NWF I - Mathematik, University of Regensburg, summer term 2002.
- [GHS05] H. Garcke, R. Haas, and B. Stinner. *On Ginzburg-Landau type free energies for multi-phase systems*. In preparation, 2005.
- [Giu77] E. Giusti. *Minimal surfaces and functions of bounded variation*. Notes on Pure Mathematics 10, Australian National Univ., Canberra, ISBN = 0-7081-1294-3, 1977.
- [GN00] H. Garcke and B. Nestler. *A mathematical model for grain growth in thin metallic films*. Math. Models and Methods in Applied Sciences, Vol. 10, pp. 895-921, 2000.
- [GNC00] H. Garcke and A. Novick-Cohen. *A singular limit for a system of degenerate Cahn-Hilliard equations*. Adv. Differential Equations 5, pp. 401-434, 2000.
- [GNS98] H. Garcke, B. Nestler, and B. Stoth. *On anisotropic order parameter models for multi-phase systems and their sharp interface limits*. Phys. D 115, pp. 87-108, 1998.
- [GNS99a] H. Garcke, B. Nestler, and B. Stoth. *Anisotropy in multi-phase systems: A phase field approach*. Interfaces Free Bound. 1, pp. 175-198, 1999.
- [GNS99b] H. Garcke, B. Nestler, and B. Stoth. *A multiphase field concept: Numerical simulations of moving phase boundaries and multiple junctions*. SIAM J. Appl. Math. 60, pp. 295-315, 1999.
- [Gur93] M. E. Gurtin. *Thermomechanics of evolving phase boundaries in the plane*. Clarendon Press, Oxford, ISBN 0-19-853694-1, 1993.
- [Gur00] M. E. Gurtin. *Configurational forces as basic concepts of continuum physics*. Appl. Math. Sc. 137, Springer, ISBN 0-387-98667-7, 2000.
- [Haa94] P. Haasen. *Physikalische Metallkunde*. 3. ed., Springer, ISBN 3-540-57210-4, 1994.



- [HLS96] W. Horn, P. Laurençot, and J. Sprekels. *Global solutions to a Penrose-Fife phase-field model under flux boundary conditions for the inverse temperature*. Math. Methods Appl. Sci. 19, pp. 1053–1072, 1996.
- [JH66] K. A. Jackson and J. D. Hunt. *Lamellar and rod eutectic growth*. Trans. Metall. Soc. AIME 236, p. 1129-1142, 1966.
- [Kar01] A. Karma. *Phase-field formulation for quantitative modeling of alloy solidification*. Phys. Rev. Lett. 87, pp. 115701-1-4, 2001.
- [KKS99] S.-G. Kim, W.-T. Kim, and T. Suzuki. *Phase-field model for binary alloys*. Phys. Rev. E, Vol. 60, No. 6, pp. 7186-7197, 1999.
- [Kle02] O. Klein. *Existence and approximation of solutions to an anisotropic phase field system for the kinetics of phase transitions*. Interfaces Free Bound. 4, pp. 47–70, 2002.
- [KR98] A. Karma and J.-W. Rappel. *Quantitative phase-field modeling of dendritic growth in two and three dimensions*. Phys. Rev. E 57, pp. 4323-4349, 1998.
- [KRS05] P. Krejčí, E. Rocca, and J. Sprekels. *Nonlocal temperature-dependent phase-field models for non-isothermal phase transitions*. WIAS Preprint No. 1006, 2005.
- [KY87] J. S. Kirkaldy and D. J. Young. *Diffusion in the condensed state*. The Institute of Metals, London, ISBN 0-904357-87-2, 1987.
- [Lan86] J.S. Langer. *Models of pattern formation in first-order phase transitions*. Directions in Condensed Matter Physics, World Scientific, Singapore, pp. 165-186, 1986.
- [LG50] L. D. Landau and V. I. Ginzburg. *K teorii sverkhrovodimosti*. Zh. Eksp. Teor. Fiz 20, pp. 1064-1082 (english translation: On the theory of superconductivity, Collected Papers of L.D. Landau, D. ter Haar, ed., Pergamon, Oxford, UK, pp. 626-633 (1965)), 1950.
- [LP88] P.-A. Lagerstrom and A. Paco. *Matched asymptotic expansions : ideas and techniques*. Appl. Math. Sc. 76, Springer, ISBN 0-387-96811-3, 1988.
- [Luc91] S. Luckhaus. *The Stefan problem with the Gibbs Thompson law*. Report univ. Pisa 591, 1991.
- [LV83] S. Luckhaus and A. Visintin. *Phase transition in multicomponent systems*. Man. Math. 43, pp. 261-288, 1983.
- [Mod87] L. Modica. *The gradient theory of phase transitions and the minimal interface criterion*. Arch. Rat. Mech. Anal. 98, pp. 123-142, 1987.
- [MS95] P. De Mottoni and M. Schatzman. *Geometrical evolution of developed interfaces*. Trans. Amer. Math. Soc. Vol. 347, pp. 1533-1589, 1995.
- [Mül01] I. Müller. *Grundzüge der Thermodynamik*. 3. ed., Springer, ISBN = 3-540-42210-2, 2001.
- [MWA00] G.B. McFadden, A.A. Wheeler, and D.M. Anderson. *Thin interface asymptotics for an energy/entropy approach to phase-field models with unequal conductivities*. Phys. D 144, pp. 154-168, 2000.
- [NGS05] B. Nestler, H. Garcke, and B. Stinner. *Multicomponent alloy solidification: Phase-field modelling and simulations*. Phys. Rev. E 71, pp. 041609-1-6, 2005.

- [OKS01] M. Ode, S.-G. Kim, and T. Suzuki. *Recent advances in the phase-field model for solidification*. ISIJ International 41, pp. 1076-1082, 2001.
- [Ons31] L. Onsager. *Reciprocal relations in irreversible processes I*. Phys. Rev. 37, pp. 405-426, 1931.
- [PF90] O. Penrose and P. C. Fife. *Thermodynamically consistent models of phase field type for the kinetics of phase transition*. Phys. D 43, pp. 44-62, 1990.
- [RBKD04] J. C. Ramirez, C. Beckermann, A. Karma, and H.-J. Diepers. *Phase-field modeling of binary alloy solidification with coupled heat and solute diffusion*. Phys. Rev. E 69, pp. 51607-1-16, 2004.
- [RK48] O. Redlich and A. T. Kister. *Algebraic Representation of Thermodynamic Properties and the Classification of Solutions*. Indust. Eng. Chem. 40, pp. 345-348, 1948.
- [Sch98] A. Schmidt. *Approximation of crystalline dendrite growth in two space dimensions*. Acta Math. Univ. Com. 86, pp. 57-68, 1998.
- [Smo94] J. Smoller. *Shock Waves and Reaction-Diffusion Equations*. 2. ed., Grundlehren der Math. Wissenschaften 258, Springer, ISBN 3-540-94259-9, 1994.
- [SPN<sup>+</sup>96] I. Steinbach, F. Pezolla, B. Nestler, M. Seeßelberg, R. Prieler, G. J. Schmitz, and J. L. L. Rezende. *A phase field concept for multi phase systems*. Phys. D 94, pp. 35-147, 1996.
- [Ste91] P. Sternberg. *Vector-valued local minimizers of nonconvex variational problems*. Rocky Mountain J. Math. 21, pp. 799-807, 1991.
- [Sto96] B. Stoth. *A sharp interface limit of the phase field equations, one-dimensional and axisymmetric*. Europ. J. Appl. Math. 7, pp. 603-633, 1996.
- [SZ03] J. Sprekels and S. Zheng. *Global existence and asymptotic behaviour for a nonlocal phase-field model for non-isothermal phase transitions*. J. Math. Anal. Appl. 279, pp. 97-110, 2003.
- [TÅV03] K. Thornton, J. Ågren, and P. W. Voorhees. *Modelling the evolution of phase boundaries in solids at the meso- and nano-scales*. Acta Mat. 51, pp. 5675-5710, 2003.
- [TC94] J. E. Taylor and J. W. Cahn. *Linking anisotropic sharp and diffuse motion laws via gradient flows*. J. Stat. Phys. 77, pp. 183-197, 1994.
- [vdW83] J. D. van der Waals. *The thermodynamic theory of capillarity under the hypothesis of a continuous variation of density*. Konink. Nederl. Akad. Wetensch. Afd. Natuurk. Eerste Reeks, 1 (english translation with commentary: J. S. Rowlinson, J. Statist. Phys. 20 , pp. 197-244 (1979)), 1983.
- [Wal96] W. Walter. *Gewöhnliche Differentialgleichungen*. 6. ed., Springer, ISBN 3-540-59038-2, 1996.
- [WM97] A. A. Wheeler and G. B. McFadden. *On the notion of a  $\xi$ -vector and a stress tensor for a general class of anisotropic diffuse interface models*. Proc. Roy. Soc. London Ser. A 453, pp. 1611-1630, 1997.
- [WMB92] A.A. Wheeler, G. B. McFadden, and W. J. Boettinger. *Phase-field model for isothermal phase transitions in binary alloys*. Phys. Rev. A 45, pp. 7424-7439, 1992.

- [WSW<sup>+</sup>93] S.-L. Wang, R. F. Sekerka, A. A. Wheeler, B. T. Murray, S. R. Coriell, R. J. Braun, and G. B. McFadden. *Thermodynamically-consistent phase-field models for solidification*. Physica D 69, pp. 189-200, 1993.
- [Zei90] E. Zeidler. *Nonlinear functional analysis and its applications II/A, linear monotone operators*. Springer, ISBN 0-387-96802-4, 1990.