MODELING AND ANALYSIS FOR GENERAL NON-ISOTHERMAL CONVECTIVE PHASE FIELD SYSTEMS.

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Contents.

Thanks.

The Lord is my shepherd
I shall no want.
Psalm 23,1

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Introduction.

Phase transition phenomena in theory and practice.

Today technical alloys are widely used in a large variety of applications. The development of such alloys strongly depends on the intended purpose and one aims to optimize the material properties in this sense. In fact this has led to many different technical alloys that hopefully fulfill the required material properties. A prominent example is provided by the development of different steel alloys. Steel as an alloy of iron and carbon is a classical prototype of a technical metal whose material properties have facilitated a widespread use for many different purposes. The amount of further admixtures like chrome, cobalt, molybdenum or vanadium depends on the usage of the actual steel product. In this context a lot of attention has been paid to the replacement of steel by aluminium where weight, stiffness, elasticity and production costs are important variables and have important influence on the material choice. In general, one aims to achieve appropriate material properties for the actual purpose of application. Therefore there is a natural interest in many technical and physical disciplines to get more insight into melting and solidification phenomena. Typically the structure of any solidificated metallic alloy has important influence on its material properties like its mechanical strength, corrosion resistance and magnetizability.

Beyond the experimental development of alloys, the theoretical and numerical treatment of constructing reliable materials has gained more and more importance since it can lead to a reduction of time and cost. Besides some experimental constructions are based on a theoretical and numerical feasability analysis.

The process of (alloy) solidification is embedded in the more general framework of *phase transitions*, where the term *phase* may describe different aggregate states as well as different orientations of the crystal lattice or different species. A first thermodynamic model of phase transitions has been presented in the 19th century by Lamé and Clapeyron in [57]. Some years later Stefan devoted several papers [77, 78, 79, 80] to phase transition phenomena in connection with heat and material diffusion. As a result, a straightforward generalization of the heat conduction equation led to a class of *moving boundary problems* also known as *Stefan problems*. Here the time-dependent phase interface is represented by a moving boundary. Nevertheless such moving boundary problems entail a lot of difficulties:

On the one hand, solutions of moving boundary problems suffer from jump discontinuities

in general and, on the other hand, the front-tracking of the moving boundary leads to enormous difficulties in several space dimensions, where phases may develop or vanish.

Since moving boundary problems have non-smooth solutions the classical framework of function spaces fails in order to state a well-posed problem in the sense of Hadamard (cf. [49]). Although explicit solutions exist in some special cases cf. [56], the theory of generalized solutions developed in the 1930s has opened a way for a more general analytical treatment. In this framework one can expect very weak solutions.

Furthermore, resolving the free boundary reveals the strong nonlinearity of the Stefan problem. Here the mathematical tools of nonlinear functional analysis and nonlinear semigroups have been developed after 1950. So in the following decades one observes a significant increase of publications devoted to moving boundary problems of phase transitions (cf. [84, p. 7]).

A new point of view has been provided by the class of *diffuse interface models*. In their principal ideas these models replace the sharp phase interface by a diffuse interface layer. Originally proposed by van der Waals in [85], the further development has been split up into Allen-Cahn theory by Ginzburg and Landau in [43] and Cahn-Hilliard theory by Cahn and Hilliard in [16].

In [59] Langer proposed a phase field model for solidification of a pure melt, based on Model C of Halperin, Hohenberg and Ma, cf. [50]. Step by step phase field models had been extended to alloys of two (cf. [86]) and more (cf. [69]) species as well as to multiple phases as in [30] and [37]. In view of the theory in [37] phase field models apply to describe thermodynamic systems of an arbitrary number of components and phases for isotropic as well as for anisotropic and crystalline materials. In addition the solidification of monotectic, peritectic and eutectic alloys as well as metallic glasses can described by sufficiently general phase field models as in [37].

Besides, phase field models have been related to *continuum mechanics* by incorporating convection and elastic effects. These extensions contribute to the fact that particle flow or mechanical effects in the material have significant consequences for the microscopic structure and the material properties. During the recent ten years convective phase field models have been widely studied both for systems of pure [6] and multi-component [29, 68] materials in solidification. In addition Lowengrub and Truskinovsky developed a Cahn-Hilliard-theory for binary fluids in [64]. Moreover, elastic effects in Cahn-Hilliard theory have been extensively studied in the recent decade, cf. [33, 34, 36].

The question of well-posedness and the relation to sharp-interface models arise as fields of further interest. Here many types of phase field models turned out to be well-posed. In particular, existence and stability of solutions could be shown. A central problem here and in further analytic treatment is the non-linearity of all phase field models.

The relation to sharp interface models is a quite interesting problem since phase field models can be considered as an approximation, especially for interesting quantities in the phase transition layer, which is assumed to be thicker than the real transition layer. Usually the relation to sharp interface models is tackled by a formal limit procedure via an expansion as power series

of the interface thickness as proposed first by Prandtl in [71]. In their papers [14, 15] Caginalp and Fife showed by use of these methods that a certain class of phase field models leads to a sharp interface model by this formal limit procedure. In addition such formal methods could be rigorously justified in many cases, cf. [1, 25, 76, 83]. Karma and Rappel were the first to propose an asymptotic analysis in the so-called thin-interface regime in [54].

Beyond applications in solidification phenomena phase field models were used to describe magnetism, melting, coarsening, and microbiology. For a comprehensive and widespread treatment of phase transition we refer to [70] as well as to [20].

Overview.

In Chapter 1 a kinematic and thermodynamic framework will be introduced for use in the following chapters. First we introduce in a standard manner a kinematic theory for the motion of particles and frame changes and their principal laws. This framework will be used in Chapter 3 where a phase field model with convection is constructed. In the second part of Chapter 1 there we will introduce conservation laws in multi-phase systems under the principal postulates that the considered thermodynamical system is closed and that the thermodynamics of this system is irreversible. As a consequence the mass of this system is conserved and the internal entropy production is non-negative. Further balance laws are stated for the energy and the mass of each component. From the stated conservation laws there we will construct a system of differential equations supplemented by equations for the phase fields. In a non-convective system this phase field equations are postulated as a gradient flow of an energy functional where in the convective case the phase field equations are a consequence of an entropy principle.

In Chapter 2 we discuss the modeling of interfacial free energies via a Ginzburg-Landau functional. As two central tasks for modeling such Ginzburg-Landau energies we state that first in a two-phase transition layer no other phase is present and second that the surface energies can be recovered from an appropriate reparametrization of an one-dimensional energy functional. To fulfill these two tasks an abstract framework is developed and applied to smooth Ginzburg-Landau energies. Precisely the considered Ginzburg-Landau energies consist of a gradient term and a multi-stable potential. The gradient term is supposed to depend only on the gradients of the phase fields where the multi-stable potential is supposed to be a polynomial of the phase fields. The construction of the gradient energies allows for different surface energies as well as for some classes of equal anisotropies.

In Chapter 3 we will construct a thermodynamic consistent model of phase transitions in multi-phase systems of multi-component convective fluids. We will derive our differential relations from thermodynamic balance and imbalance relations in integral form. We will exploit the entropy principle proposed by Müller, cf. [65] by use of Lagrange multipliers as done in [61] by Liu. This method is different from the method of Coleman and Noll, cf. [23] since there will be made no explicit assumptions on the fluxes of energy and entropy. Although their standard

a-priori assumptions on entropy and energy flux is reliable in many cases there are some examples where these assumptions are not justified. This has been discussed for example in [53] and references therein. We will construct a phase field model and a related sharp interface model. The phase field model is a generalization of the non-convective model in [37]. In particular it allows for an arbitrary number of phases and components as well as for isotropic, anisotropic and crystalline materials. Our convective regime prevents us from using standard variational calculus, i.e. to use variational derivatives to postulate the gradient flows. Thus we start with balance laws and an entropy inequality. Hence thermodynamic consistency in the sense of the first and second thermodynamic law is a-priori fulfilled. The exploitation of the entropy principle will reduce our variable list we have initially postulated. Besides we obtain the phase field equation and restrictions to the fluxes and the stress tensor. In a similar way we derive the sharp interface model in the second part of Chapter 3, which is again thermodynamically consistent. As the phase field model it allows for an arbitrary number of phases and components and different types of materials. The exploitation of the entropy principle leads to further restrictions to the interfacial fluxes and tensors beyond the bulk quantities. Besides the analysis of the entropy principle relates interfacial and bulk quantities by the laws of Young-Laplace and Gibbs-Thomson. While the first relates interfacial curvature to the pressure jump at the interface the second one will replace the phase field equation and relates interfacial velocity to surface tension, curvature and the energy jump at the interface. Besides, we will discuss relations to other models of sharp interface type as well as of phase field type.

In the last chapter we will consider a non-convective model problem that is reduced to the system of phase field equations and prove an existence result. Thus it is a single-component isothermal model. These assumptions will lead to a system of non-linear parabolic equations. In addition this system will be supplemented by initial conditions, no-flux boundary conditions and an algebraic condition that will assure that all phase fields sum up to one and are non-negative. Nevertheless the principal difficulty is not this differential-algebraic structure rather than its non-convex nature that results in a non-monotone time-space differential operator. Our starting point will be a variational functional for the free energy which we assume to depend on the phase field as well as on its derivatives. Usually one will prove existence of solutions by constructing a sequence of approximate solutions and veryfing its convergence to a solution. In our case that means the following. We will construct a sequence of approximate problems by a Galerkin ansatz. To prove convergence of these approximate solutions one proves first weak convergence. For linear problems this is already sufficient but in our nonlinear case we need weak convergence in a space with better topology. Precisely we need weak convergence in a compactly embedded space then we obtain strong convergence in the initial space which will be sufficient for many nonlinear problems. Thus we need deep uniform estimates which which are difficult to obtain. Then we obtain estimates which allow for compactness arguments in order to obtain a convergent subsequence. Then it remains to verify that the limit it is a solution. In our case this will work in one spatial dimension.

The Appendices provide some auxiliary material which is used in the chapters before.

Chapter 1

Phase Transitions – From the Phenomenon to Mathematical Models.

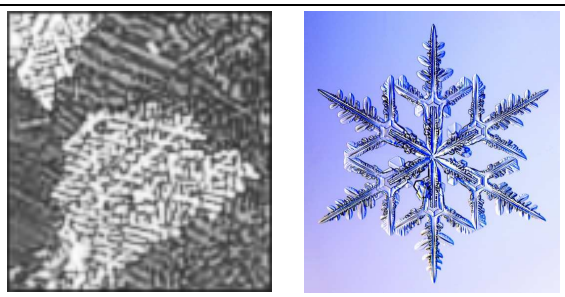
1.1 Phase transitions as a complex transformation process.

Phase transitions from a phenomenological point of view.

Solidification phenomena arise in a wide range of transformation processes as casting, rolling and welding. In case of the first two processes the complete matter undergoes a transition from melted to solid matter, while in the latter case the relevant transition processes arise locally. Nevertheless in all cases these transition processes deeply influence the mesoscopic and microscopic solidification structure of the considered material. Especially the welding process involves heat and material diffusion processes as well as transport processes by moving mass particles. As implicitly mentioned solidification processes involve *different length scales* that range from the visible level to microscopic units as nanometer or Ångström. The solidification structure reflects this multiscale nature as follows. During the solidification the material develops several domains (grains) that may change their size or orientation until they are completely solidified. Usually different grains carry a different orientation of their atomic or molecular lattice and different phases may have different concentration of their constituent materials like a copper-rich phase neighboring a nickel-rich phase. At a much smaller length scale the boundary between two such grains may develop finger-like structures, facetted-like fronts or dendritic branches. But this structures itself may devlop substructures that arise again at a much smaller length scale, for example these finger-like structures may carry lamellar structures.

The Figure 1.1 gives a slight impression of the numerous variety of solidification structures in materials: The left picture shows a grain-like one with some grain boundaries whose roughness is due to the described substructures. The right figure shows a snow crystal and its dendritic crystal structure. In fact snow crystals show a various range of structures, beyond star-like also plate-like crystals. Besides this example exhibits a certain center-symmetric structure that has also influence on the solidification process.

Figure 1.1 Various solidification structures: Grain growth (left picture, from http://www.fak-i.hs-karlsruhe.de/lab/studies/pace/index.php) and star-shaped solidification (right picture, from http://www.its.caltech.edu/ ˜atomic/ snowcrystals/).



The interplay of diffusion and transport processes.

To understand these various range of material and structural properties it is essential to understand the process where these structures and properties develop. As already mentioned grains and their boundary structures develop due to the enrichment or migration of one or more substances and thus a single grain may change its size, its orientation or its shape. Enrichment or thinning out processes are effects of diffusing mass particles of a species. Usually such mass diffusion arises at phase interfaces at a small length scale and is driven by differences of temperature and chemical potentials. For example diffusion mechanisms are important during the formation of lamellar and dendritic structures.

On the other hand stress and external forces like gravity or buoyancy forces lead to particle fluctuations on large length scales. These mass transport processes influence the material properties in a essential way: Phase boundaries may be also deformed or carried by mass transport or convection, for example. Thus the impact of convection to the solidification structure is evident.

To be more precise let us consider the casting process of a metallic alloy, for example steel. During the solidification process a lot of thermodynamical processes interact with each other. There are at least two regions: one occupied by the solid, the other one by the melt. Both phases are separated by an interface that moves along the time range into the liquid phase. In fact this interface is a thin layer of a thickness of some Ångström. This transition layer will develop a various range of structures: typically one can find lamellae and dendrites. Usually the interdendritic regions are solute-rich areas of liquid whereas the dendritic regions are solute-poor areas of solid. As a consequence, species conservation implies that solute is rejected into the liquid area during solidification. These highly enriched areas can be washed out in the presence of fluid flow and, consequently solute can be carried away into liquid regions far away from the solid-liquid-interface. Since conservation of matter must hold other regions of the material are highly enriched with the species. Precisely, solute-rich areas are these which solidify at last while solute-poor are these which solidify at first. But such a material is no longer reliable. This described phase transition-fluid flow phenomenon is known as *macrosegregation*.

Another complicated phenomenon is fluid flow in welding processes. During this process there arises a liquid phase, the weld pool. This weld pool carries extremely high temperature gradients on its surface and since surface tension is a temperature-dependent material parameter there are high surface tension differences. As a result one faces very fast surface flow velocities usually called *thermal Marangoni flow*. Inside the weld pool bouyancy, Lorentz forces and shear stresses cause a fluid flow. This transport mechanism determines the heat transfer as well as the melting process in a significant way. As a consequence the final shape of the weld pool is a result of these transport and diffusion phenomena. But the quality of the welded joint strongly depends on the pool shape. Without considering these thermal and convective effects such a weld pool may become too flat or too deep.

1.2 Kinematics and thermodynamics in multi-component systems.

Kinematic and mechanical laws.

Deformation and motion.

Assume that motion and deformation phenomena are embedded in the Newtonian time-space $\mathcal{W}$. We can identify $\mathcal{W}$ with the cartesian product of $\mathbb{R}$ and the d-dimensional Euclidean space $\mathcal{E}$ via an one-to-one mapping

$$\mathbf{\Phi} : \mathcal{W} \to \mathbb{R} \times \mathcal{E},$$

which is called *frame of reference*. Usually a body $\mathcal{B}$ can be identified with a region of the Euclidean space $\mathcal{E}$ relative to a frame of reference. An one-to-one mapping from $\mathcal{B}$ into $\mathcal{E}$ is referred to as *configuration*. If a particular configuration

$$\boldsymbol{\kappa} : \mathcal{B} \to \mathcal{E} \text{ and } \boldsymbol{\kappa} : \boldsymbol{X} \mapsto \boldsymbol{x} \in \mathcal{E} \text{ for every point } \boldsymbol{X} \in \mathcal{B},$$

is chosen, it is called *reference configuration*.

Let $\{\boldsymbol{\chi}_t : \mathcal{B} \to \mathcal{E}\}_{t\in\mathbb{R}}$ a family of configurations which are continuous with respect to t. Then $\{\boldsymbol{\chi}_t\}_{t\in\mathbb{R}}$ is referred to as *motion*. For a reference configuration $\boldsymbol{\kappa}$ and a material point $\boldsymbol{x}_0 \in \mathcal{E}$ we define $\boldsymbol{s}(., \boldsymbol{x}_0) : \mathbb{R} \to \mathcal{E}$ via

$$\boldsymbol{s}(t, \boldsymbol{x}_0) = \boldsymbol{\chi}_t \circ \boldsymbol{\kappa}^{-1}(\boldsymbol{x}_0),$$

and $\boldsymbol{s}(., \boldsymbol{x}_0)$ is called *path* of $\boldsymbol{X_0} = \boldsymbol{\kappa}^{-1}(\boldsymbol{x}_0)$. If $\boldsymbol{s}(., \boldsymbol{x}_0)$ is differentiable for $\boldsymbol{x}_0$ we define

$$\boldsymbol{v}(t, \boldsymbol{x}_0) = \frac{\partial \boldsymbol{s}(t, \boldsymbol{x}_0)}{\partial t},$$

as the velocity of $\boldsymbol{X_0}$.

Change of observer.

For two frames of reference, say $\mathbf{\Phi}$ and $\mathbf{\Phi}^\star$ we call

$$\mathbf{\Phi}^\star \circ \mathbf{\Phi}^{-1} : \mathbb{R} \times \mathcal{E} \to \mathbb{R} \times \mathcal{E}, \quad \mathbf{\Phi}^\star \circ \mathbf{\Phi}^{-1} : (t, \boldsymbol{x}) \to (t^\star, \boldsymbol{x}^\star)$$

a *change of frame* from $\mathbf{\Phi}$ to $\mathbf{\Phi}^\star$. We assume that these frame changes admit the representation

$$t^\star = t \text{ and } \boldsymbol{x}^\star = \boldsymbol{\alpha}(t) + \boldsymbol{Q}(t)(\boldsymbol{x} - \boldsymbol{x}_0),$$

with a vector $\boldsymbol{\alpha}$ and an orthogonal matrix $\boldsymbol{Q}$ with positive determinant. Note that $t^\star = t + a$ leads to a more general change of frame. Clearly the mapping $\boldsymbol{x} \mapsto \boldsymbol{x}^\star$ is invertible and we have

$$\boldsymbol{x} = \boldsymbol{Q}^\top(\boldsymbol{x}^\star - \boldsymbol{\alpha}) + \boldsymbol{x}_0 \text{ and } \mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{x} = \boldsymbol{Q}^\top. \tag{1.1}$$

As already mentioned the rotation is represented by an orthogonal matrix $\boldsymbol{Q}$ and we briefly remark that $\boldsymbol{Q}^\top$ is just the backward rotation. Let us now introduce some notation. For a scalar field $f : \mathcal{E} \to \mathbb{R}$ as it appears to the observer in the frame $\mathbf{\Phi}$ we denote by $f^\star$ the same field in the frame $\mathbf{\Phi}^\star$. Analogously we define $\boldsymbol{q}^\star$ and $\boldsymbol{T}^\star$ for vector fields $\boldsymbol{q} : \mathcal{E} \to \mathcal{E}$ or tensor fields $\boldsymbol{T} : \mathcal{E} \to \mathcal{L}(\mathcal{E}, \mathcal{E})$. In this manner $\boldsymbol{v}^\star$ denotes the velocity in the frame of $\boldsymbol{x}^\star$-coordinates and $\mathrm{D}_{\boldsymbol{x}^\star}$ the transformed Fréchet differential. Hence we obtain

$$\mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{v} \;=\; \mathrm{D}_{\boldsymbol{x}}\, \boldsymbol{v}\, \mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{x} = \mathrm{D}_{\boldsymbol{x}}\, \boldsymbol{v} \boldsymbol{Q}^\top, \tag{1.2}$$

by use of (1.1) and the chain rule. The velocity $\boldsymbol{v}^\star$ as well as its Frèchet differential $\mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{v}^\star$ admit an expression in terms of $\boldsymbol{v}$ and $\boldsymbol{Q}$ as follows. Since the velocity is always the time derivative of the spatial position that means $\boldsymbol{v}^\star = \partial_t \boldsymbol{x}^\star$ we obtain

$$\begin{aligned} \boldsymbol{v}^\star &= \partial_t \left(\boldsymbol{\alpha}(t) + \boldsymbol{Q}(t)(\boldsymbol{x} - \boldsymbol{x}_0)\right) \\ &= \dot{\boldsymbol{\alpha}} + \dot{\boldsymbol{Q}}(\boldsymbol{x} - \boldsymbol{x}_0) + \boldsymbol{Q}\boldsymbol{v} \\ &= \dot{\boldsymbol{\alpha}} + \dot{\boldsymbol{Q}}(\boldsymbol{Q}^\top(\boldsymbol{x}^\star - \boldsymbol{\alpha})) + \boldsymbol{Q}\boldsymbol{v}. \end{aligned}$$

In addition $\mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{v}^\star$ turns into

$$\begin{aligned} \mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{v}^\star &= \dot{\boldsymbol{Q}}\, \mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{x} + \boldsymbol{Q}\, \mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{v} \\ &= \dot{\boldsymbol{Q}}\boldsymbol{Q}^\top + \boldsymbol{Q}\, \mathrm{D}_{\boldsymbol{x}}\, \boldsymbol{v} \boldsymbol{Q}^\top, \end{aligned}$$

by use of (1.2).

Now we discuss the behaviour of f, $\boldsymbol{q}$ and $\boldsymbol{T}$ under frame changes $\boldsymbol{x} \mapsto \boldsymbol{x}^\star = \boldsymbol{\alpha} + \boldsymbol{Q}(\boldsymbol{x} - \boldsymbol{x}_0)$. Our aim is to define objective quantities that are in some sense independent of the observer frame and consistent with the transformed differential $\mathrm{D}_{\boldsymbol{x}^\star}$. Especially the balance laws we will postulate later should be invariant under Euclidean transformations. For example, let two observers with distinct frames of reference consider the absolute temperature. Of course one measured temperature should equal each other. Hence for such a scalar field $f : \mathcal{E} \to \mathbb{R}$ we assume $f(t, \boldsymbol{x}) = f^\star(t, \boldsymbol{x}^\star)$. For the fields $\boldsymbol{q}$ and $\boldsymbol{T}$ a similar duscussion can be done. Let us summarize these considerations by the following definition.

Definition 1.2.1 (Objective field). We call a scalar field $f : \mathcal{E} \to \mathbb{R}$, a vector field $\boldsymbol{q} : \mathcal{E} \to \mathcal{E}$ or a tensor field $\boldsymbol{T} : \mathcal{E} \to \mathcal{L}(\mathcal{E}, \mathcal{E})$ an *objective field*, if

$$\begin{aligned} f(t, \boldsymbol{x}) &= f^\star(t, \boldsymbol{x}^\star), \\ \boldsymbol{q}(t, \boldsymbol{x}) &= \boldsymbol{Q}^\top \boldsymbol{q}^\star(t, \boldsymbol{x}^\star), \text{ or} \\ \boldsymbol{T}(t, \boldsymbol{x}) &= \boldsymbol{Q}^\top \boldsymbol{T}^\star(t, \boldsymbol{x}^\star)\boldsymbol{Q} \end{aligned}$$

holds.

Hence it is clear that in general neither $\boldsymbol{v}$ nor $\mathrm{D}_{\boldsymbol{x}}\, \boldsymbol{v}$ is an objective field. For further reading we refer to Chapter 1 of [62].

Conservation laws for multi-component systems.

Definitions and principal postulates.

We consider a thermodynamical system that is represented by a spatial domain $R \subset \mathbb{R}^d$ imbedded into the time space $\mathbb{R}_+ \times \mathbb{R}^d$ where $d \in \mathbb{N}$ is the spatial dimension. The volume $R = R(t)$ is allowed to depend on time $t \in \mathbb{R}_+$ and supposed to contain an appropriate number of mass particles. For this thermodynamical system we state our principal postulates:

(A1) The thermodynamical system represented by R is *closed*: For all times $t \geq 0$ no mass particles migrate or penetrate across the boundary of $R(t)$. As a consequence the volume $R = R(t)$ consists of the same mass particles at all times $t \geq 0$. Paraphrasing, all mass particles of $R(t_0)$ at a referential time $t_0 \geq 0$ belong to $R(t)$ for all times $t \geq 0$.

(A2) The thermodynamical processes are assumed to be *irreversible*: Once reached the final state it is not warranted that it is posssible to reach the initial state again. This holds true for all thermodynamical processes which go ahead spontaneously, i.e. without external forces or energy sources. Then during such a transformation the *entropy* can only decrease by fluctations across the boundary ∂R, the internal rate of entropy production is non-negative (cf. [89], [66]). This postulate is known as *Second Law of Thermodynamics* and usually stated in form of an entropy inequality.

As a consequence of postulate (A1) the volume $R = R(t)$ cannot be chosen arbitrarily rather it is transported with the particle velocity. Besides the mass $\mathscr{M} = \mathscr{M}(R(t))$ of all particles in $R(t)$ is constant for all $t \geq 0$, i.e.

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathscr{M}\left(R(t)\right) = 0, \tag{1.3}$$

which is another consequence of postulate (A1). The mass of the system that occupies $R = R(t)$ is given by

$$\mathscr{M} = \mathscr{M}\left(R(t)\right) = \int_R \varrho(t, \boldsymbol{x})\ \mathrm{d}\boldsymbol{x},$$

where $\varrho : \mathbb{R}_+ \times \mathbb{R}^d \to \mathbb{R}$ denotes the mass density. As usual we postulate further conservation laws for the energy $\mathscr{E} = \mathscr{E}(R)$, the mass of the i-th component $\mathscr{M}_i = \mathscr{M}_i(R)$ and the linear momentum $\mathscr{P} = \mathscr{P}(R)$ in R. In terms of specific densities these quantities admit the following integral repesentations:

$$\begin{aligned}
\mathscr{E} &= \int_R \varrho E \, \mathrm{d}\boldsymbol{x} + \mathscr{E}_{\mathrm{kin}}, \text{ where } \mathscr{E}_{\mathrm{kin}} = \frac{1}{2}\int_R \varrho |\boldsymbol{v}|^2 \, \mathrm{d}\boldsymbol{x}, \\
\mathscr{M}_i &= \int_R \varrho c_i \, \mathrm{d}\boldsymbol{x}, \text{ for all } i \in \{1, \dots M\}, \\
\mathscr{P} &= \int_R \varrho \boldsymbol{v} \, \mathrm{d}\boldsymbol{x},
\end{aligned}$$

where E denotes the specific density of internal energy, $\mathscr{E}_{\mathrm{kin}}$ the kinetic energy, c_i the mass concentration of component i and $\boldsymbol{v}$ the (macroscopic) particle velocity. In general let $u : \mathbb{R}_+ \times \mathbb{R}^d \to \mathbb{R}$ the (specific) density of any conserved quantity, $\boldsymbol{J}_u : \mathbb{R}_+ \times \mathbb{R}^d \to \mathbb{R}^d$ its flux and $k_u : \mathbb{R}_+ \times \mathbb{R}^d \to \mathbb{R}$ the density of sinks and sources of u inside R. Then the general conservation law on R reads as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_R \varrho u \, \mathrm{d}\boldsymbol{x} = -\int_{\partial R} \boldsymbol{J}_u \cdot \boldsymbol{\nu}_R \, \mathrm{d}\mathcal{H}^{d-1} + \int_R \varrho k_u \, \mathrm{d}\boldsymbol{x}, \tag{1.4}$$

where $\boldsymbol{\nu}_R$ denotes the outer unit normal at ∂R. Since ∂R is sufficiently smooth we obtain by the divergence theorem (cf. Appendix B, Theorem 1)

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_R \varrho u \, \mathrm{d}\boldsymbol{x} = \int_R \left(-\nabla \cdot \boldsymbol{J}_u + \varrho k_u\right) \mathrm{d}\boldsymbol{x}.$$

In the sequel we distinguish between two cases:

Spatially fixed particles and constant density.

In the first case we consider a bounded domain $\Omega \subset \mathbb{R}^d$ and for given $T > 0$ the time-space cylinder $\Omega_T = (0, T) \times \Omega$. Inside of Ω_T the density ϱ is assumed to be a constant, without loss of generality let $\varrho(t, \boldsymbol{x}) = 1$ for all $(t, \boldsymbol{x}) \in \Omega_T$. Besides we assume that all mass particles have a macroscopically fixed spatial position as time proceeds forward, i.e. for every time-independent measurable subset $R \subset \Omega$ no mass particles can migrate across the boundary ∂R. Hence in such a subset R the mass conservation is fulfilled and obviously the macroscopic particle velocity $\boldsymbol{v}(t, \boldsymbol{x})$ equals zero for all $(t, \boldsymbol{x}) \in \Omega_T$. As a consequence (1.3) is trivially fulfilled, hence we can omit this balance law in case of $\boldsymbol{v} = 0$ and $\varrho = 1$. Since R is independent of time t we are allowed to interchange differentiation and integration in (1.4), which consequently gives

$$\int_R \frac{\partial u}{\partial t} \, \mathrm{d}\boldsymbol{x} = -\int_R \nabla \cdot \boldsymbol{J}_u \, \mathrm{d}\boldsymbol{x} + \int_R k_u \, \mathrm{d}\boldsymbol{x} \tag{1.5}$$

for all measurable subsets $R \subset \Omega$. Thus we arrive at a local version given by

$$\frac{\partial u}{\partial t}(t, \boldsymbol{x}) = -\nabla \cdot \boldsymbol{J}_u(t, \boldsymbol{x}) + k_u(t, \boldsymbol{x}), \tag{1.6}$$

for all $(t, \boldsymbol{x}) \in \Omega_T$. We then infer the balance laws

$$\frac{\partial E}{\partial t} = -\nabla \cdot \boldsymbol{J}_E,$$

for internal energy and

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \boldsymbol{J}_i,$$

for the concentrations of each component where we have tacitly assumed that the bulk sources k_E and k_{c_i} for all $i \in \{1, \dots, M\}$ are not present. Besides, to warrant $\sum_{i=1}^{M} c_i = 1$ we assume $\sum_{i=1}^{M} \boldsymbol{J}_i = 0$. Since $\boldsymbol{v}$ is supposed to be zero the linear momentum is zero, thus we omit its balance law. If this thermodynamical system consists of several phases, the time evolution of the defining order parameters ϕ_α is usually postulated to be the L^2 gradient flow of an entropy functional $\mathscr{S}$ that is

$$\omega\varepsilon \frac{\partial \phi_\alpha}{\partial t} = \frac{\delta \mathscr{S}}{\delta \phi_\alpha} - \tilde{\lambda}, \tag{1.7}$$

for all $\alpha \in \{1, \dots, N\}$ and a Lagrange multiplier $\tilde{\lambda}$ that guarantees $\sum_{\alpha=1}^{N} \phi_\alpha = 1$. In addition $\omega > 0$ is a kinetic multiplier and $\varepsilon > 0$ is a thickness parameter that determines how strong the interface is blurred. Following [37] equation (1.7) can be rewritten as an L^2 gradient flow of a free energy $\mathscr{F}$, i.e.

$$\omega\varepsilon \frac{\partial \phi_\alpha}{\partial t} = -\frac{\delta \mathscr{F}}{\delta \phi_\alpha} + \lambda, \text{ with } \lambda = -\tilde{\lambda}, \tag{1.8}$$

if an isothermal and one-component system is considered. In this case we will model the free energy $\mathscr{F}$ via a Ginzburg-Landau functional, given by

$$\mathscr{F}(\boldsymbol{\phi}) = \int_\Omega \left(F(\boldsymbol{\phi}) + \left(\varepsilon a(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) + \frac{1}{\varepsilon} w(\boldsymbol{\phi}) \right) \right) \, \mathrm{d}\boldsymbol{x}, \tag{1.9}$$

where $F(\boldsymbol{\phi})$ is the free energy density in each pure phase, $a(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi})$ models surface contributions of the free energy that may depend on the interface orientation and finally $w(\boldsymbol{\phi})$ is a multistable potential with N minima that correspond to each pure phase. This model has been derived and anlyzed in [37] and [82].

Multi-component systems with particle flow.

The second case involves a non-constant mass density ϱ as well as particle flow with non-trivial velocity $\boldsymbol{v} : \Omega \to \mathbb{R}^d$. We then say that $R = R(t)$ is a *material volume*. As a consequence it is not posssible to interchange differentiation and integration in (1.4) in the way as before. By Reynold's Transport Theorem (cf. Theorem 3.2.2 of Section 3.2) one has

$$\int_R \left(\frac{\partial(\varrho u)}{\partial t} + \nabla \cdot (\varrho u \boldsymbol{v}) \right) \, \mathrm{d}\boldsymbol{x} = \int_R \left(\varrho k_u - \nabla \cdot \boldsymbol{J}_u \right) \, \mathrm{d}\boldsymbol{x}$$

for all material volumes R. Hence we arrive at a local version given by

$$\frac{\partial(\varrho u)}{\partial t} + \nabla \cdot (\varrho u \boldsymbol{v}) = \varrho k_u - \nabla \cdot \boldsymbol{J}_u.$$

For $u = 1$ we then have a local form of the mass conservation, i.e.

$$\frac{\partial \varrho}{\partial t} + \nabla \cdot (\varrho \boldsymbol{v}) = 0.$$

This and additional conservation laws for energy, mass of every component and linear momentum are precisely introduced in Chapter 3. If our multi-component system consists of several phases we cannot postulate a phase field equation via a gradient flow of an energy functional. The reason for that is the (macroscopic) motion of particles, so that the control volume R is time-dependent. Such a material volume prevents us to use variational methods. In view of this the phase field equation follows from an appropriate statement and treatment of the second law of irreversible thermodynamics, cf. [23], [61], [63] and [65]. The derivation and discussion of a multi-component multi-phase model that incorporates macroscopic particle flow (convection) is done in Chapter 3.

Chapter 2

Construction of Ginzburg-Landau-Energies for Multi-Phase Systems.

2.1 Introduction.

In this chapter we study systems with two or more distinct physical states in which the only energy contributions arise from the interfaces separating the phases. Let $\Omega \subset \mathbb{R}^d$ denote an open, bounded, and connected domain with Lipschitz boundary which is divided into N not necessarily connected sub-domains Ω_α, $1 \leq \alpha \leq N$. There are $\frac{N(N-1)}{2}$ possible types of two-phase interfaces, denoted by $\Gamma_{\alpha\beta} = \Gamma_{\beta\alpha} := \overline{\Omega}_\beta \cap \overline{\Omega}_\alpha$, $1 \leq \alpha, \beta \leq N$, and the total energy of the system is postulated to be of the form

$$\mathscr{F} = \sum_{\alpha<\beta} \int_{\Gamma_{\alpha\beta}} \gamma_{\alpha\beta}(\nu_{\alpha\beta}) \, \mathrm{d}\mathcal{H}^{d-1}. \tag{2.1}$$

Here, $\mathcal{H}^{d-1}$ is the $(d-1)$-dimensional surface measure ($d \in \{1,2,3\}$ being the spatial dimension). The interfacial energy densities $\gamma_{\alpha\beta}$ are positive fields defined on the interfaces $\Gamma_{\alpha\beta}$ and may depend on the local orientation of $\Gamma_{\alpha\beta}$ which is given in terms of the unit normal $\nu_{\alpha\beta}$ pointing into the adjacent domain Ω_β.

The goal is to model interfacial energy in such multi-phase systems with a diffuse interface model based on a Ginzburg-Landau type energy functional. Instead of hypersurfaces the interfaces then are smeared out and involve transition layers with a thickness scaling with a small length scale $\varepsilon > 0$. Given some interfacial energy densities $\gamma_{\alpha\beta}$ the task is to construct potentials for the Ginzburg-Landau energy in such a way that these interfacial energies are recovered as the diffuse interface thickness tends to zero. Let us motivate the problem more carefully.

In order to define the Ginzburg-Landau energy we introduce phase fields (or order parameters) $\boldsymbol{\phi} = (\phi_1, \ldots, \phi_N)$ standing for the local fractions of the phases labelled by the indices

$1, \ldots, N$. This means that the fields ϕ_α are nonnegative and sum up to give one,

$$\boldsymbol{\phi} : \Omega \to \mathscr{G} := \left\{ \boldsymbol{\phi} \in \mathbb{R}^N \;\middle|\; \sum_{\alpha=1}^{N} \phi_\alpha = 1,\ \phi_\alpha \geq 0,\ \forall \alpha \right\}. \tag{2.2}$$

For fields $\boldsymbol{\phi}$ whose components are not necessarily nonnegative but sum up to give one we consider a Ginzburg-Landau functional of the form

$$\mathscr{F}(\boldsymbol{\phi}) = \int_\Omega \left(\epsilon a(\boldsymbol{\phi}, \nabla \boldsymbol{\phi}) + \frac{1}{\epsilon} w(\boldsymbol{\phi}) \right) \mathrm{d}x. \tag{2.3}$$

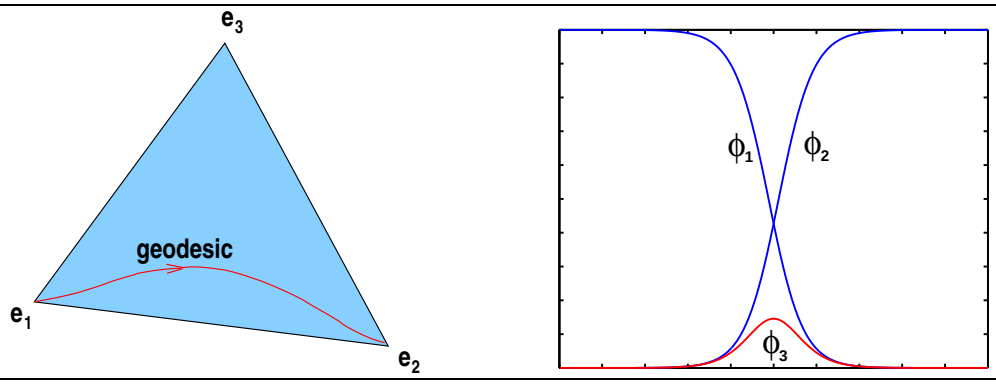
The multi-well potential w is assumed to be nonnegative and to vanish only in the corners of $\mathscr{G}$, i.e., in the points $e_\alpha = (\delta_{\alpha\beta})_{\beta=1,\ldots,N}$ where $\delta_{\alpha\beta}$ is the Kronecker symbol. According to the above statements on the phase fields, $\boldsymbol{\phi} = e_\alpha$ corresponds to the pure phase with index α. The gradient energy density a is assumed to be nonnegative and positively homogeneous of degree two in the variable corresponding to $\nabla \boldsymbol{\phi}$.

The Γ limit of (2.3) as $\varepsilon \to 0$ was carefully analyzed and derived in [10]. In particular, a relation between the surface energies $\gamma_{\alpha\beta}$ and the potentials a and w is stated there. Using matched asymptotic expansions the following simpler relation was found (cf. [81], [38], [67]):

$$\begin{aligned} \gamma_{\alpha\beta}(\nu) := \inf_p \Big\{ 2 \int_{-1}^{1} \sqrt{w(p) a(p, p' \otimes \nu)}\ \mathrm{d}y \;\Big| \\ p \in C^{0,1}\left([-1,1]; \left\{ \boldsymbol{\phi} \in R^N \,|\, \phi_1 + \ldots + \phi_N = 1 \right\}\right),\ p(-1) = e_\alpha,\ p(1) = e_\beta \Big\} \end{aligned} \tag{2.4}$$

This formula was shown to hold true in the case of isotropic surface energies (i.e., the $\gamma_{\alpha\beta}$ do not depend on ν). Numerical simulations (see [40]) furthermore indicate that the formula is even true for a large class of anisotropic functions a as well.

Figure 2.1 Geodesics and third phase (ϕ_3-) contribution.



In many applications, the interfacial energy densities $\gamma_{\alpha\beta}$ are known. Therefore, it is our goal that the potentials a and w in the Ginzburg-Landau energy can be adjusted such that, via (2.4), the given interfacial energies really are obtained. The solution p to (2.4) may be interpreted as a geodesic in a metric with a weight depending on p (see Fig. 2.1 on the left). In general, the geodesic lies in the interior of the Gibbs-Simplex $\mathscr{G}$ so that, in the interfacial region of, e.g.,

phase 1 and 2 the component of phase 3 appears (cf. Fig. 2.1). We demand the solution to (2.4) to be of the form

$$p(y) = h(y)e_\beta + (1 - h(y))e_\alpha \tag{2.5}$$

with a Lipschitz continuous monotone function $h : [-1, 1] \to [0, 1]$ fulfilling $h(-1) = 0$ and $h(1) = 1$. The reason why we want to avoid those third phase contributions is, first, that they have no physical meaning and are artificial. The second reason is that if the optimal p is of the form (2.5) then the right hand side of (2.4) reduces to the much simpler formula

$$\gamma_{\alpha\beta}(\nu) = 2 \int_0^1 \sqrt{w(se_\beta + (1 - s)e_\alpha)\, a(se_\beta + (1 - s)e_\alpha, (e_\beta - e_\alpha) \otimes \nu)}\, \mathrm{d}s. \tag{2.6}$$

Let us now summarize our goals.

Task 1. *Given surface energy densities $\gamma_{\alpha\beta}(\nu)$, $1 \le \alpha < \beta \le N$, construct potentials a and w with the following properties for each pair $\alpha \neq \beta$:*

I. The minimizer of (2.4) *is of the form* (2.5)*, i.e., in the interfacial layer between the domains occupied by the phases α and β only the phase fields ϕ_α and ϕ_β are present.*

II. Evaluation of the right hand side of (2.6) *gives $\gamma_{\alpha\beta}(\nu)$, i.e., the surface energy densities are recovered.*

The natural first step to solve the task is to discuss the Euler-Lagrange equation to (2.4). After an appropriate reparametrization it turns out to be the leading order inner equation arising when applying the method of matched asymptotic expansions to the problem (cf. [38]). Once a solution of the Euler-Lagrange equations with the desired structure (2.5) is found, i.e., a critical point of (2.4), we have to study whether it is indeed a minimizer. Since rigorous results could not always be obtained we made use of numerical simulations with suitable test problems. They are based on straightforward finite difference methods for the L^2 gradient flow of the energy (2.3).

In the next section we derive the equations that have to hold such that critical points of (2.4) are of the desired form. Moreover we impose some additional assumptions on the potentials a and w in order to simplify the computation of the right hand side of (2.6).

In Section 2.3 we consider a gradient potential $a = a(\nabla\boldsymbol{\phi})$ independent of $\boldsymbol{\phi}$ and derive necessary as well as sufficient conditions on polynomial multi-well potentials w. Unfortunately, it turns out that the quotients $\frac{\gamma_{\alpha\beta}(\nu)}{\gamma_{\alpha'\beta'}(\nu)}$ for different pairs $(\alpha, \beta) \neq (\alpha', \beta')$ need to be constant, hence, we can allow only for one form of anisotropic for all surface energy densities.

2.2 Preliminaries and definitions.

Let us first say a few words on the surface energies appearing in the sharp interface formulation of the system energy (2.1). Proceeding as in [51, 52], we consider functions $\gamma_{\alpha\beta}$ which are positive, smooth, and defined on the unit sphere S^{d-1}, and which are symmetric in the sense

that $\gamma_{\alpha\beta} = \gamma_{\beta\alpha}$. On may extend the functions one-homogeneously to the total space $\mathbb{R}^d$, i.e., given some vector $y \in \mathbb{R}^d \backslash \{0\}$ there is exactly one vector $\nu \in S^{d-1}$ and one real $r \in (0, \infty)$ such that $y = r\nu$, and we then set $\gamma_{\alpha\beta}(y) = \gamma_{\alpha\beta}(r\nu) := r\gamma_{\alpha\beta}(\nu)$. In order to avoid wetting effects we impose the following no-wetting condition:

$$\gamma_{\alpha\beta}(\nu) + \gamma_{\beta\delta}(\nu) > \gamma_{\alpha\delta}(\nu) \quad \text{for all triples } \alpha, \beta, \delta \in \{1, \dots, N\} \text{ and all } \nu \in S^{d-1}. \tag{2.7}$$

This avoids that in the transition region between phase α and δ a thin layer of phase β appears.

In the following we restrict our analytical considerations to smooth energies and potentials a. For later use we define the following spaces:

$$\Sigma := \Big\{ \boldsymbol{\phi} \in \mathbb{R}^N \;\Big|\; \sum_{\alpha=1}^{N} \phi_\alpha = 1 \Big\}, \quad T\Sigma := \Big\{ d \in \mathbb{R}^N \;\Big|\; \sum_{\alpha=1}^{N} d_\alpha = 0 \Big\}.$$

Definition 2.2.1. Let

$$\mathcal{A} := \big\{ (\alpha, \beta) \in \{1, \dots, N\}^2 \;\big|\; \alpha \neq \beta \big\}. \tag{2.8}$$

A gradient potential $a \in C^\infty(\Sigma \times (T\Sigma)^d) \to [0, \infty)$ is called admissible if

i. $a(\boldsymbol{\phi}, \eta X) = \eta^2 a(\boldsymbol{\phi}, X)$ for all $\eta \in \mathbb{R}$, $(\boldsymbol{\phi}, X) \in \Sigma \times (T\Sigma)^d$,

ii. $a(\boldsymbol{\phi}, X) > 0$ whenever $X \neq 0$,

iii. for all $(\alpha, \beta) \in \mathcal{A}$ and $\nu \in S^{d-1}$ the quantities $a_{\alpha\beta}(\nu) := a(se_\beta + (1-s)e_\alpha, (e_\beta - e_\alpha) \otimes \nu)$ do not depend on $s \in [0, 1]$.

A multi-well potential $w : \Sigma \to \mathbb{R}$ is called admissible if

i. it is a polynomial,

ii. the following condition is fulfilled for all $s \in [0, 1]$ and $(\alpha, \beta) \in \mathcal{A}$:

$$w(se_\beta + (1-s)e_\alpha) = 9 w_{\alpha\beta} s^2 (1-s)^2 \text{ with } w_{\alpha\beta} > 0. \tag{2.9}$$

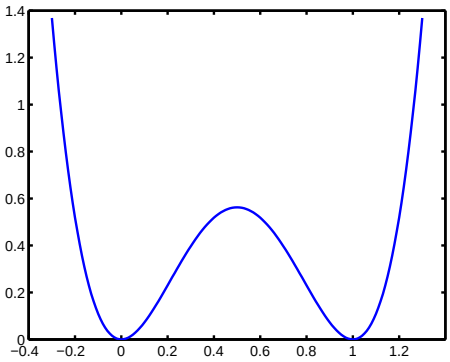
Remark 2.2.1. Condition ii. for the multi-well potential implies that w reduces to the classical double-well potential along the Gibbs simplex edge $se_\beta + (1-s)e_\alpha$, cp. Figure 2.2.

In the following, we will use the notation $w_{,\phi_\alpha}$ for the partial derivative of w with respect to ϕ_α. We implicitly extended w to the whole space $\mathbb{R}^N \supset \Sigma$. But since we will only consider derivatives of w in directions tangential to Σ, i.e., in directions belonging to $T\Sigma$, it does not matter how this extension precisely is defined. Similarly we will use the notations $a_{,\phi_\alpha}$ and a_{X_α} for partial derivatives of a.

The last assumptions on a and w respectively enable to compute the right hand side of (2.6) explicitly, namely we obtain

$$\gamma_{\alpha\beta}(\nu) = 2\sqrt{a_{\alpha\beta}(\nu)} \int_0^1 \sqrt{w(se_\beta + (1-s)e_\alpha)}\, \mathrm{d}s = \sqrt{a_{\alpha\beta}(\nu) w_{\alpha\beta}} \quad \forall (\alpha, \beta) \in \mathcal{A}. \tag{2.10}$$

Figure 2.2 Classical double-well potential.



Consider a smooth potential w as in (2.9) and some $(\alpha,\beta)\in\mathcal{A}$. A solution p to (2.4) then solves the Euler-Lagrange equation

$$\frac{\sqrt{a(p,p'\otimes\nu)}}{\sqrt{w(p)}}w_{,\boldsymbol{\phi}}(p)+\frac{\sqrt{w(p)}}{\sqrt{a(p,p'\otimes\nu)}}a_{,\boldsymbol{\phi}}(p,p'\otimes\nu) - \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\sqrt{w(p)}}{\sqrt{a(p,p'\otimes\nu)}}a_{,X}(p,p'\otimes\nu)\nu\right)=\boldsymbol{\mu}$$

where $\boldsymbol{\mu}=\mu(1,\dots,1)\in\mathbb{R}^N$ with some real valued Lagrange multiplier μ which is due to the fact that the phase fields sum up to give one. As in [38, 81] we now use the reparametrization

$$\boldsymbol{\phi}(z)=p(\beta(z)),\quad \text{where } \beta'(z)=\frac{\sqrt{w(p(\beta(z)))}}{\sqrt{a(p(\beta(z)),p'(\beta(z))\otimes\nu)}},\ \beta(\pm\infty)=\pm1. \tag{2.11}$$

Observe that the function β is defined only up to a translation in z. Together with the boundary conditions $p(-1)=e_\alpha$, $p(1)=e_\beta$ we get that $\boldsymbol{\phi}$ solves

$$w_{,\boldsymbol{\phi}}(\boldsymbol{\phi})+a_{,\boldsymbol{\phi}}(\boldsymbol{\phi},\partial_z\boldsymbol{\phi}\otimes\nu)-\tfrac{\mathrm{d}}{\mathrm{d}z}\Big(a_{,X}(\boldsymbol{\phi},\partial_z\boldsymbol{\phi}\otimes\nu)\nu\Big)=\boldsymbol{\lambda}, \tag{2.12}$$

$$\lim_{z\to\infty}\boldsymbol{\phi}(z)=e_\beta,\quad \lim_{z\to-\infty}\boldsymbol{\phi}(z)=e_\alpha \tag{2.13}$$

with $\boldsymbol{\lambda}=\lambda(1,\dots,1)\in\mathbb{R}^N$ and

$$\lambda=-\frac{1}{N}\sum_{i=1}^{N}\Big[w_{,\phi_i}(\boldsymbol{\phi})+a_{,\phi_i}(\boldsymbol{\phi},\partial_z\boldsymbol{\phi}\otimes\nu)-\frac{\mathrm{d}}{\mathrm{d}z}\Big(a_{,X_i}(\boldsymbol{\phi},\partial_z\boldsymbol{\phi}\otimes\nu)\nu\Big)\Big].$$

Moreover, from (2.4) the reparametrization yields

$$\gamma_{\alpha\beta}(\nu)=\int_{-1}^{1}\sqrt{w(p)a(p,p'\otimes\nu)}\,\mathrm{d}y=\int_{-\infty}^{\infty}\Big(a(\boldsymbol{\phi},\partial_z\boldsymbol{\phi}\otimes\nu)+w(\boldsymbol{\phi})\Big)\,\mathrm{d}z.$$

Therefore, after the reparametrization according to (2.11) we obtain the minimization problem

$$\gamma_{\alpha\beta}(\nu):=\inf_{\boldsymbol{\phi}}\Big\{\int_{-\infty}^{\infty}\big(a(\boldsymbol{\phi},\partial_z\boldsymbol{\phi}\otimes\nu)+w(\boldsymbol{\phi})\big)\,\mathrm{d}z\,\Big| \boldsymbol{\phi}\in C^{0,1}(\mathbb{R};\Sigma),\ \lim_{z\to-\infty}\boldsymbol{\phi}(z)=e_\alpha,\ \lim_{z\to\infty}\boldsymbol{\phi}(z)=e_\beta\Big\}. \tag{2.14}$$

Critical points then fulfill the Euler-Lagrange equation (2.12).

It is worth to mention that solutions to (2.12) determine the form of the interfacial layers to leading order in the following sense: In the neighborhood of a hypersurface Γ belonging to $\Gamma_{\alpha\beta}$ one can construct an asymptotic expansion $\boldsymbol{\phi}(x) = \boldsymbol{\phi}^0(z,s) + \epsilon\boldsymbol{\phi}^1(z,s) + \dots$ using the $\frac{1}{\varepsilon}$-scaled signed distance $z(x) = \operatorname{dist}(x,\Gamma)/\varepsilon$ and tangential coordinates $s(x)$, $x \in \Omega$. Plugging the expansion into the Euler-Lagrange equation of (2.3) gives that to leading order equation (2.12) has to hold for $\boldsymbol{\phi}^0$. For the details we refer to [38] where the above procedure has been performed for an L^2 gradient flow of (2.3).

Lemma 2.2.1 (Equipartition of Energy). *Let $\boldsymbol{\phi} : \mathbb{R} \to \Sigma$ be a function fulfilling* (2.13) *and solving* (2.12)*. Then in points where $\partial_z\boldsymbol{\phi}$ is defined it holds that*

$$a(\boldsymbol{\phi}, \partial_z\boldsymbol{\phi} \otimes \nu) = w(\boldsymbol{\phi}).$$

Proof. Multiplying (2.12) by $\partial_z\boldsymbol{\phi} : \mathbb{R} \to T\Sigma$ yields

$$\begin{aligned} 0 &= \frac{\mathrm{d}}{\mathrm{d}z} w(\boldsymbol{\phi}) + a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \partial_z\boldsymbol{\phi} \otimes \nu) \cdot \partial_z\boldsymbol{\phi} - \frac{\mathrm{d}}{\mathrm{d}z}\left(a_{,X}(\boldsymbol{\phi}, \partial_z\boldsymbol{\phi} \otimes \nu)\nu\right) \cdot \partial_z\boldsymbol{\phi} \\ &= \frac{\mathrm{d}}{\mathrm{d}z}\left(w(\boldsymbol{\phi}) + a(\boldsymbol{\phi}, \partial_z\boldsymbol{\phi} \otimes \nu) - a_{,X}(\boldsymbol{\phi}, \partial_z\boldsymbol{\phi} \otimes \nu) : \partial_z\boldsymbol{\phi} \otimes \nu\right) \\ &= \frac{\mathrm{d}}{\mathrm{d}z}\left(w(\boldsymbol{\phi}) - a(\boldsymbol{\phi}, \partial_z\boldsymbol{\phi} \otimes \nu)\right). \end{aligned}$$

To obtain the last identity we have used the two-homogeneity of a with respect to the second variable. Since the term $w(\boldsymbol{\phi}) - a(\boldsymbol{\phi}, \partial_z\boldsymbol{\phi} \otimes \nu)$ vanishes for $z \to \pm\infty$ we obtain the desired result. □

Let p be a solution to (2.4) of the form (2.5). By (2.11), the corresponding solution to (2.12) then has the form

$$\boldsymbol{\phi}(z) = \chi(z)e_\beta + (1 - \chi(z))e_\alpha. \tag{2.15}$$

with some sufficiently smooth monotone increasing function $\chi : \mathbb{R} \to [0,1]$. The boundary conditions imply

$$\lim_{z\to\infty} \chi(z) = 1, \quad \lim_{z\to-\infty} \chi(z) = 0. \tag{2.16}$$

Lemma 2.2.2. *Let a be an admissible gradient potential, let w be a smooth multi-well potential of the type* (2.9)*, and let $\boldsymbol{\phi}$ be a function of the form* (2.15)*.*

Then $\boldsymbol{\phi}$ is a critical point of (2.14)*, i.e., $\boldsymbol{\phi}$ solves* (2.12) *and* (2.13)*, if and only if the following conditions hold:*

$$\chi(z) = \frac{1}{2}\Big(1 + \tanh\Big(\sqrt{\tfrac{w_{\alpha\beta}}{a_{\alpha\beta}(\nu)}}\,\frac{3z}{2}\Big)\Big) \tag{2.17}$$

up to translation, and there is some function λ such that for all $i = 1, \dots, N$

$$\lambda = w_{,\phi_i} + |\chi'|^2 a_{,\phi_i} - \frac{\mathrm{d}}{\mathrm{d}z}\Big(a_{,X_i}\nu\chi'\Big) \tag{2.18}$$

or

$$\lambda = w_{,\phi_i} + \Big(a_{,\phi_i} - \big((a_{,X_i})_{,\boldsymbol{\phi}} \cdot (e_\beta - e_\alpha)\big)\nu\Big)\frac{w}{a_{\alpha\beta}(\nu)} - (a_{,X_i}\nu)\frac{1}{2a_{\alpha\beta}(\nu)}\big(w_{,\boldsymbol{\phi}} \cdot (e_\beta - e_\alpha)\big) \quad (2.19)$$

where w and its derivatives are evaluated at $\boldsymbol{\phi}(z)$ and a and its derivatives at $(\boldsymbol{\phi}(z), (e_\beta - e_\alpha) \otimes \nu)$.

Proof. Let us first assume that $\boldsymbol{\phi} = \chi e_\beta + (1-\chi)e_\alpha$ solves (2.12) and (2.13). Using the two-homogeneity of a we get

$$\begin{aligned} \boldsymbol{\lambda} &= w_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) + a_{,\boldsymbol{\phi}}(\chi e_\beta + (1-\chi)e_\alpha, \chi'(e_\beta - e_\alpha) \otimes \nu) \\ &\quad -\frac{\mathrm{d}}{\mathrm{d}z}\Big(a_{,X}(\chi e_\beta + (1-\chi)e_\alpha, \chi'(e_\beta - e_\alpha) \otimes \nu)\nu\Big) \\ &= w_{,\boldsymbol{\phi}} + |\chi'|^2 a_{,\boldsymbol{\phi}} - \frac{\mathrm{d}}{\mathrm{d}z}\Big(a_{,X}\nu\chi'\Big) \end{aligned} \quad (2.20)$$

which is the identity (2.18). Moreover, a being admissible implies that

$$\begin{aligned} &a_{,\boldsymbol{\phi}}(se_\beta + (1-s)e_\alpha, (e_\beta - e_\alpha) \otimes \nu) \cdot (e_\beta - e_\alpha) \\ &\qquad = \frac{\mathrm{d}}{\mathrm{d}s}a(se_\beta + (1-s)e_\alpha, (e_\beta - e_\alpha) \otimes \nu) = \frac{\mathrm{d}}{\mathrm{d}s}a_{\alpha\beta}(\nu) = 0. \end{aligned} \quad (2.21)$$

Multiplying (2.20) with $e_\beta - e_\alpha$ therefore yields

$$\begin{aligned} 0 &= w_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot (e_\beta - e_\alpha) + |\chi'|^2 a_{,\boldsymbol{\phi}}((\chi e_\beta + (1-\chi)e_\alpha, \chi'(e_\beta - e_\alpha) \otimes \nu) \cdot (e_\beta - e_\alpha) \\ &\quad -\frac{\mathrm{d}}{\mathrm{d}z}\Big(a_{,X}(\chi e_\beta + (1-\chi)e_\alpha, (e_\beta - e_\alpha) \otimes \nu) : (e_\beta - e_\alpha) \otimes \nu\chi'\Big) \\ &= w_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot (e_\beta - e_\alpha) + 0 - \frac{\mathrm{d}}{\mathrm{d}z}\Big(2a(\chi e_\beta + (1-\chi)e_\alpha, (e_\beta - e_\alpha) \otimes \nu)\chi'\Big) \\ &= w_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot (e_\beta - e_\alpha) - 2a_{\alpha\beta}(\nu)\chi''. \end{aligned} \quad (2.22)$$

The assumption (2.9) on w provides

$$w_{,\boldsymbol{\phi}}(se_\beta + (1-s)e_\alpha) \cdot (e_\beta - e_\alpha) = \frac{\mathrm{d}}{\mathrm{d}s}w(se_\beta + (1-s)e_\alpha) = 18w_{\alpha\beta}s(1-s)(1-2s).$$

The last identity in (2.22) then becomes

$$\chi'' = \frac{9w_{\alpha\beta}}{a_{\alpha\beta}(\nu)}\chi(1-\chi)(1-2\chi). \quad (2.23)$$

But, up to translation, the unique solution to (2.23) subject to the boundary conditions (2.16) is (2.17).

Using the previous Lemma 2.2.1 we see that

$$w(\boldsymbol{\phi}) = a(\boldsymbol{\phi}, \chi'(e_\beta - e_\alpha) \otimes \nu) = |\chi'|^2 a(\boldsymbol{\phi}, (e_\beta - e_\alpha) \otimes \nu) = |\chi'|^2 a_{\alpha\beta}(\nu)$$

whence

$$|\chi'|^2 = \frac{w(\boldsymbol{\phi})}{a_{\alpha\beta}(\nu)} = \frac{9w_{\alpha\beta}}{a_{\alpha\beta}(\nu)}\chi^2(1-\chi)^2. \quad (2.24)$$

Using this and (2.23) in (2.20) yields the remaining identity (2.19):

$$\begin{aligned}
\lambda &= w_{,\phi_i}(\boldsymbol{\phi}) + |\chi'|^2 a_{,\phi_i}(\boldsymbol{\phi}, (e_\beta - e_\alpha)\otimes\nu) - \frac{\mathrm{d}}{\mathrm{d}z}\Big(a_{,X_i}(\boldsymbol{\phi}, (e_\beta - e_\alpha)\otimes\nu)\nu\chi'\Big) \\
&= w_{,\phi_i} + \frac{w}{a_{\alpha\beta}(\nu)} a_{,\phi_i} - \big(a_{,X_i}\nu\big)\chi'' - \big((a_{,X_i})_{,\boldsymbol{\phi}}\cdot(e_\beta - e_\alpha)\chi'\big)\nu\chi' \\
&= w_{,\phi_i} + \frac{w}{a_{\alpha\beta}(\nu)} a_{,\phi_i} - \big((a_{,X_i})_{,\boldsymbol{\phi}}\cdot(e_\beta - e_\alpha)\big)\nu|\chi'|^2 - \big(a_{,X_i}\nu\big)\chi'' \\
&= w_{,\phi_i} + \Big(a_{,\phi_i} - \big((a_{,X_i})_{,\boldsymbol{\phi}}\cdot(e_\beta - e_\alpha)\big)\nu\Big)\frac{w}{a_{\alpha\beta}(\nu)} \qquad (2.25) \\
&- (a_{,X_i}\nu)\frac{1}{2a_{\alpha\beta}(\nu)}\big(w_{,\boldsymbol{\phi}}\cdot(e_\beta - e_\alpha)\big).
\end{aligned}$$

Vice versa, let us now assume that the function χ in (2.15) is given by (2.17). Obviously, the boundary conditions (2.13) then are satisfied. If in addition (2.18) holds the identity (2.12) follows immediately from (2.20). In the case that, instead, (2.19) holds true then we first need to see that χ fulfills (2.23) and (2.24). Inserting those identities into (2.19) shows as in (2.25) that (2.18) is satisfied, and we are in the previous situation. □

Thanks to the lemma we will only need to check whether (2.18) or (2.19) are fulfilled in order to find critical points of the minimization problem (2.14) provided the postulated potentials a and w are admissible.

The above stated lemmata help to find critical points of (2.14). Once such a point characterized by the problem (2.12) is found we must ascertain whether we really found a local minimizer. One possibility is to derive the second variation of (2.14) and to show that it is nonnegative. But not for all potentials a and w we could do so. Instead we applied numerical methods, see Section 2.4.

Let us consider the gradient flow dynamics

$$\epsilon\partial_t\boldsymbol{\phi} = -\frac{\delta\mathscr{F}}{\delta\boldsymbol{\phi}} + \boldsymbol{\lambda} = \epsilon\nabla\cdot a_{,\nabla\boldsymbol{\phi}} - \epsilon a_{,\boldsymbol{\phi}} - \frac{1}{\epsilon}w_{,\boldsymbol{\phi}} + \boldsymbol{\lambda}, \qquad (2.26)$$

where $\lambda = -\frac{1}{N}\sum_{\alpha=1}^{N}(\epsilon\nabla\cdot a_{,\nabla\phi_\alpha} - \epsilon a_{,\phi_\alpha} - \frac{1}{\epsilon}w_{,\phi_\alpha})$, of the Ginzburg-Landau energy (2.3) with respect to an ε-weighted L^2 scalar product. Given some initial data at time $t = 0$ one may let the system relax. In time, the energy (2.3) can only decrease. An asymptotic analysis as performed in [72] motivates that energetically favorable states are formed in the interfacial regions which we are mainly interested in, and those states appear on a faster time scale than the one on which the motion of the diffuse phase boundaries takes place.

Numerically, we solved (2.26) with finite difference methods as have been carefully described in [39]. Given a fixed mesh with grid constant Δx on a rectangular domain Ω spatial gradients are replaced by forward differences and divergence operators by backward differences. Denoting the discrete time step by Δt we used an explicit method, i.e., we replaced the time differentials by forward differences.

2.3 Suitable gradient and multi-well potentials.

2.3.1 Polynomial multi-well potentials

In this section we will study gradient energy densities which do not depend on ϕ but only on $\nabla\phi$ and smooth multi-well potentials of polynomial form on Σ. As a consequence (2.3) simplifies to

$$\mathscr{F}(\phi) = \int_\Omega \left(\epsilon a(\nabla\phi) + \frac{1}{\epsilon} w(\phi) \right) \mathrm{d}x \tag{2.27}$$

with a as a 2-homogeneous function in $\nabla\phi$. Let us note that then the gradient flow dynamics given by (2.26) reduces to

$$\epsilon\partial_t\phi = \epsilon\nabla \cdot a_{,\nabla\phi} - \frac{1}{\epsilon} w_{,\phi} + \boldsymbol{\lambda}.$$

Our goal is to find analytic expressions for a and w in (2.27) such that these potentials fulfill the properties I. and II. of the task stated in the Introduction. For this purpose we will apply the techniques introduced in Section 2.2, especially we have to validate the conditions given in Lemma 2.2.2. Our first result will only concern the multistable potential w independently of the special structure of a.

Proposition 2.3.1. *a) On Σ every polynomial w of degree lower or equal than four admits the representation*

$$\sum_{i\le j\le k\le l} \tilde{b}_{ijkl}\phi_i\phi_j\phi_k\phi_l. \tag{2.28}$$

b) There is no polynomial of degree lower than four which fulfills (2.9).

c) A polynomial w of degree four that fulfills (2.9) has the representation

$$w(\phi) = \frac{1}{2}\sum_{i\neq j} b_{ij}\phi_i^2\phi_j^2 + \frac{1}{2}\sum_{\substack{i,j,k \\ i\neq j, j\neq k, k\neq i}} b_{ijk}\phi_i\phi_j\phi_k^2 + \sum_{i<j<k<l} b_{ijkl}\phi_i\phi_j\phi_k\phi_l \text{ where } b_{ij} > 0. \tag{2.29}$$

Proof. To prove a) the constraint

$$\phi_1 + \phi_2 + \ldots + \phi_N = 1$$

can be used to increase the degree of lower order terms. Thus the polynomial admits the representation (2.28).

Secondly, assume that w has degree lower than four then $w(se_\beta + (1-s)e_\alpha)$ has degree lower than four in the variable s. This contradicts (2.9) and b) is valid.

Using a) we can assume that w has the representation (2.28). Now we consider w along $se_\beta + (1-s)e_\alpha$. Then

$$\begin{aligned} w(se_\beta + (1-s)e_\alpha) &= \tilde{b}_{\alpha\alpha\alpha\alpha}s^4 + \tilde{b}_{\alpha\alpha\alpha\beta}s^3(1-s) + \tilde{b}_{\alpha\alpha\beta\beta}s^2(1-s)^2 \\ &+ \tilde{b}_{\alpha\beta\beta\beta}s(1-s)^3 + \tilde{b}_{\beta\beta\beta\beta}(1-s)^4 \end{aligned}$$

holds. Since $\{s^4,\ s^3(1-s),\ s^2(1-s)^2,\ s(1-s)^3,\ (1-s)^4\}$ is a basis of the space of fourth-order polynomials condition (2.9) yields

$$\tilde{b}_{\alpha\alpha\alpha\alpha} = \tilde{b}_{\alpha\alpha\alpha\beta} = \tilde{b}_{\alpha\beta\beta\beta} = \tilde{b}_{\beta\beta\beta\beta} = 0.$$

Then $\tilde{b}_{\alpha\alpha\beta\beta} = 9w_{\alpha\beta} > 0$ follows from (2.9) and w has the representation

$$\sum_{\substack{i\le j\le k<l\\ i\neq k, j\neq l}} \tilde{b}_{ijkl}\phi_i\phi_j\phi_k\phi_l. \tag{2.30}$$

Now we set $b_{ij} = \tilde{b}_{iijj}$ for all $i \neq j$, $b_{ijkl} = \tilde{b}_{ijkl}$ for all $i < j < k < l$ and

$$b_{ijk} = \begin{cases} \tilde{b}_{ijkk} & \text{if } k > j, \\ \tilde{b}_{ikkj} & \text{if } i < k < j, \\ \tilde{b}_{kkij} & \text{if } k < i. \end{cases}$$

Then we arrive at the representation

$$w(\phi) = \sum_{i<j} b_{ij}\phi_i^2\phi_j^2 + \sum_{\substack{i<j\\ k\neq i,j}} b_{ijk}\phi_i\phi_j\phi_k^2 + \sum_{i<j<k<l} b_{ijkl}\phi_i\phi_j\phi_k\phi_l, \tag{2.31}$$

and by symmetrical extension of the coefficients, i.e.,

$$b_{ji} = b_{ij}, \quad b_{jik} = b_{ijk}, \tag{2.32}$$

we obtain the representation (2.29) where $b_{ij} > 0$. □

Throughout this Section we need the partial derivatives of w along a Gibbs simplex edge. Therefore setting $p = \chi e_\beta + (1-\chi)e_\alpha$ we are led to

$$w_{\phi_k}(p) = \begin{cases} 2b_{\alpha\beta}\chi^2(1-\chi) & \text{if } k = \alpha, \\ 2b_{\alpha\beta}\chi(1-\chi)^2 & \text{if } k = \beta, \\ b_{\beta k\alpha}\chi(1-\chi)^2 + b_{\alpha k\beta}(1-\chi)\chi^2 & \text{else.} \end{cases} \tag{2.33}$$

Proposition 2.3.2. *Assume that the Ginzburg-Landau energy is given by (2.27) with an admissible gradient potential $a = a(\nabla\phi)$ and an admissible multi-well potential w as in Proposition 2.3.1, i.e., w is of the form (2.29). For $\phi = \chi e_\beta + (1-\chi)e_\alpha$ and $X = (e_\beta - e_\alpha)\otimes\nu$ let λ_k given by*

$$\lambda_k = w_{,\phi_k}(\phi) - \frac{a_{,X_k}(X)\cdot\nu}{2a_{\alpha\beta}(\nu)}\left(w_{,\phi_\beta}(\phi) - w_{,\phi_\alpha}(\phi)\right). \tag{2.34}$$

Then we have $\lambda_\alpha = \lambda_\beta$.

Proof. We just consider the difference $\lambda_\beta - \lambda_\alpha$, that is

$$\begin{aligned}\lambda_\beta - \lambda_\alpha &= w_{,\phi_\beta} - w_{,\phi_\alpha} - \frac{\left(a_{,X_\beta} - a_{,X_\alpha}\right)\cdot\nu}{2a_{\alpha\beta}(\nu)}\left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right)\\ &= \left(1 - \frac{\left(a_{,X_\beta} - a_{,X_\alpha}\right)\cdot\nu}{2a_{\alpha\beta}(\nu)}\right)\left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right).\end{aligned}$$

Now by two-homgeneity of a we conclude that

$$\begin{aligned}\lambda_\beta - \lambda_\alpha &= \left(1 - \frac{a_{,X} : (e_\beta - e_\alpha)\otimes\nu}{2a_{\alpha\beta}(\nu)}\right)\left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right)\\ &= \left(1 - \frac{2a}{2a_{\alpha\beta}(\nu)}\right)\left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right)\\ &= \left(1 - \frac{a_{\alpha\beta}(\nu)}{a_{\alpha\beta}(\nu)}\right)\left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right) = 0,\end{aligned}$$

which proves our result. □

2.3.2 General results.

To construct Ginzburg-Landau energies that are suitable to fulfill the properties I. and II. of the task stated in the introduction of this chapter we have to validate that functions of the form (2.15) and (2.17) are in fact critical points of (2.14). For this purpose we employ the key condition (2.19) of Lemma 2.2.2. For Ginzburg-Landau energies of the form (2.27) we will now give abstract conditions, which follow from (2.19) for critical points of (2.14) and, conversely, from which condition (2.19) follows.

Proposition 2.3.3. *Assume that the Ginzburg-Landau energy is given by (2.27) with an admissible gradient potential $a = a(\nabla\phi)$ and the admissible multi-well potential w as in Proposition 2.3.1, i.e., w is of the form (2.29). In addition assume that condition (2.19) of Lemma 2.2 is fulfilled. Then we have*

$$2b_{\alpha\beta} = b_{\alpha k\beta} + b_{\beta k\alpha} \tag{2.35}$$

$$2(b_{\alpha k} - b_{\beta k}) = b_{\beta k\alpha} - b_{\alpha k\beta} \tag{2.36}$$

for all k.

Proof. First from (2.33) we obtain

$$w_{,\phi_\beta} - w_{,\phi_\alpha} = 2b_{\alpha\beta}\chi(1-\chi)(1-2\chi).$$

Then we consider (2.34) for $\chi = \frac{1}{2}$ where $w_{,\phi_\beta} - w_{,\phi_\alpha}$ vanishes. Using that is (2.19) fulfilled we derive

$$\begin{aligned}0 &= 2\lambda_k - \lambda_\alpha - \lambda_\beta\\ &= 2w_{,\phi_k} - w_{,\phi_\alpha} - w_{,\phi_\beta}\\ &= \frac{1}{4}\left(b_{\alpha k\beta} + b_{\beta k\alpha} - 2b_{\alpha\beta}\right),\end{aligned}$$

which proves the first result. The second one follows from the first:

$$\begin{aligned} 2b_{\alpha k} - 2b_{\beta k} &= b_{\alpha\beta k} + b_{k\beta\alpha} - b_{\beta\alpha k} - b_{k\alpha\beta} \\ &= b_{k\beta\alpha} - b_{k\alpha\beta} = b_{\beta k\alpha} - b_{\alpha k\beta}, \end{aligned}$$

by symmetry. □

Remark 2.3.1. As a consequence we infer an explicit representation for the coefficients b_{ijk} which is given by

$$b_{ijk} = b_{ik} + b_{jk} - b_{ij}, \tag{2.37}$$

provided condition (2.19) of Lemma 2.2 is fulfilled.

Remark 2.3.2. (i) Besides assume γ_{ij} independent of ν and $b_{ij} = 9\gamma_{ij}$ for all indices i and j. If (2.7) is filfilled for all surface energies γ_{ij} we obtain $b_{ijk} > 0$.

(ii) If, in addition, $b_{ijkl} \geq 0$ for all $i < j < k < l$, the potential w given by (2.29) has its minima in the corners of the Gibbs simplex $\mathscr{G}$.

Proposition 2.3.4. *Assume that the Ginzburg-Landau energy is given by (2.27) with an admissible gradient potential $a = a(\nabla\phi)$ and the admissible multi-well potential w as in Proposition 2.3.1, i.e., w is of the form (2.29). In addition assume that condition (2.19) of Lemma 2.2 is fulfilled and besides for the partial derivatives of a in $X = (e_\beta - e_\alpha) \otimes \nu$ the condition*

$$a_{,X_k}(X) \cdot \nu = \begin{cases} -a_{\alpha\beta}(\nu) & \text{if } k = \alpha, \\ a_{\alpha\beta}(\nu) & \text{if } k = \beta, \\ a_{\alpha k}(\nu) - a_{\beta k}(\nu) & \text{else.} \end{cases} \tag{2.38}$$

holds true. Then we have the following relation between $b_{\alpha\beta}$ and $a_{\alpha\beta}(\nu)$:

$$\frac{b_{\alpha k} - b_{\beta k}}{b_{\alpha\beta}} = \frac{a_{\alpha k}(\nu) - a_{\beta k}(\nu)}{a_{\alpha\beta}(\nu)}. \tag{2.39}$$

Remark 2.3.3. From (2.38) we have $\left(a_{,X_\alpha}(X) + a_{,X_\beta}(X)\right) \cdot \nu = 0$ and thus $2\lambda_\alpha = 2\lambda_\beta = w_{,\phi_\alpha} + w_{,\phi_\beta}$ holds.

Proof. As in Proposition 2.3.3 we consider the difference $2\lambda_k - \lambda_\alpha - \lambda_\beta$, i.e.

$$\begin{aligned} 0 &= 2\lambda_k - \lambda_\alpha - \lambda_\beta \\ &= 2w_{,\phi_k} - w_{,\phi_\alpha} - w_{,\phi_\beta} - \frac{\left(2a_{,X_k} - a_{,X_\alpha} - a_{,X_\beta}\right) \cdot \nu}{2a_{\alpha\beta}(\nu)} \left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right) \\ &= \chi(1-\chi)\left(2\left(b_{\alpha k\beta}\chi + (1-\chi)b_{\beta k\alpha}\right) - b_{\alpha k\beta} - b_{\beta k\alpha}\right) \\ &- \frac{1}{2a_{\alpha\beta}(\nu)}\left(2(a_{\alpha k}(\nu) - a_{\beta k}(\nu)) + a_{\alpha\beta}(\nu) - a_{\alpha\beta}(\nu)\right) \cdot \nu \left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right) \\ &= \chi(1-\chi)(1-2\chi)\left(\left(b_{\beta k\alpha} - b_{\alpha k\beta}\right) - \frac{1}{2a_{\alpha\beta}(\nu)} 2\left(a_{\alpha k}(\nu) - a_{\beta k}(\nu)\right) \cdot \nu 2b_{\alpha\beta}\right). \end{aligned}$$

By setting $\chi = \frac{1}{4}$ we obtain from Proposition 2.3.3

$$0 \;=\; 2\left(b_{\alpha k} - b_{\beta k}\right) - \frac{1}{a_{\alpha\beta}(\nu)} 2\left(a_{\alpha k}(\nu) - a_{\beta k}(\nu)\right) \cdot \nu b_{\alpha\beta}. \tag{2.40}$$

Moreover by (2.38) we see that $\left(a_{,X_\alpha} + a_{,X_\beta}\right)\cdot\nu$ vanishes, where $2a_{,X_k}\cdot\nu = 2\left(a_{\alpha k}(\nu) - a_{\beta k}(\nu)\right)$. Then (2.40) turns into

$$0 \;=\; 2\left(b_{\alpha k} - b_{\beta k}\right) - \frac{2\left(a_{\alpha k}(\nu) - a_{\beta k}(\nu)\right)}{a_{\alpha\beta}(\nu)} b_{\alpha\beta},$$

which is equivalent to

$$\frac{b_{\alpha k} - b_{\beta k}}{b_{\alpha\beta}} \;=\; \frac{a_{\alpha k}(\nu) - a_{\beta k}(\nu)}{a_{\alpha\beta}(\nu)},$$

our desired result. □

Proposition 2.3.5. *Assume that for a given pair (a, w) of admissible functions in (2.27) the consistency condition (2.39) is fulfilled. Then the quotient*

$$f(\nu) := \frac{a_{ij}(\nu)}{b_{ij}} \tag{2.41}$$

is independent of the actual choice of i and $j \neq i$.

Proof. We start with the consistency condition (2.39), i.e.

$$\frac{b_{ln} - b_{mn}}{b_{lm}} = \frac{a_{ln}(\nu) - a_{mn}(\nu)}{a_{lm}(\nu)},$$

which is equivalent to

$$\left(a_{ln}(\nu) - a_{mn}(\nu)\right) b_{lm} = \left(b_{ln} - b_{mn}\right) a_{lm}(\nu). \tag{2.42}$$

First we consider (2.42) for $(l, m, n) = (i, k, j)$ and $(l, m, n) = (i, j, k)$ and after summation of both equations we obtain

$$\left(a_{ik}(\nu) + a_{ij}(\nu)\right) b_{jk} = \left(b_{ik} + b_{ij}\right) a_{jk}(\nu). \tag{2.43}$$

Secondly (2.42) with $(l, m, n) = (k, j, i)$ gives

$$\left(a_{ik}(\nu) - a_{ij}(\nu)\right) b_{jk} = \left(b_{ik} - b_{ij}\right) a_{jk}(\nu). \tag{2.44}$$

Now the sum and difference of (2.43) and (2.44) yield

$$a_{ik}(\nu)b_{jk} = b_{ik}a_{jk}(\nu) \text{ and } a_{ij}(\nu)b_{jk} = b_{ij}a_{jk}(\nu),$$

that is for all indices i, j, k:

$$\frac{a_{ij}(\nu)}{b_{ij}} = \frac{a_{jk}(\nu)}{b_{jk}} = \frac{a_{ik}(\nu)}{b_{ik}},$$

our desired result. □

Remark 2.3.4. From (2.17) with $b_{ij} = 9w_{ij}$ we then observe that (2.41) is responsible for *equal interface thicknesses* at every transition.

Theorem 2.3.1. *Assume that we are given a Ginzburg-Landau energy of the form (2.27) with admissible potentials a and w. In addition let the conditions (2.35), (2.38) and (2.39) be fulfilled. Then λ_k as defined in (2.34) is independent of k; thus condition (2.19) of Lemma 2.2.2 is fulfilled. Thus (2.17) with $b_{ij} = 9w_{ij}$ is in fact a critical point of (2.14) and every transition region has equal interface thicknesses.*

Proof. Again we consider $2\lambda_k - \lambda_\alpha - \lambda_\beta$ for $k \neq \alpha,\ \beta$, i.e.

$$\begin{aligned} 2\lambda_k - \lambda_\alpha - \lambda_\beta &= 2w_{,\phi_k} - w_{,\phi_\alpha} - w_{,\phi_\beta} - \frac{a_{,X_k}\cdot\nu}{a_{\alpha\beta}}\left(w_{,\phi_\beta} - w_{,\phi_\alpha}\right) \\ &= \chi(1-\chi)\left(2\left(b_{\alpha k\beta}\chi + b_{\beta k\alpha}(1-\chi)\right) - 2b_{\alpha\beta}\right) \\ &- \frac{a_{,X_k}\cdot\nu}{a_{\alpha\beta}} 2b_{\alpha\beta}\chi(1-\chi)(1-2\chi) \\ &= (b_{\beta k\alpha} - b_{\alpha k\beta})\chi(1-\chi)(1-2\chi) \\ &- \frac{a_{\alpha k}(\nu) - a_{\beta k}(\nu)}{a_{\alpha\beta}} 2b_{\alpha\beta}\chi(1-\chi)(1-2\chi), \end{aligned}$$

by condition (2.38). By conditions (2.35) and (2.39) we arrive at

$$\begin{aligned} 2\lambda_k - \lambda_\alpha - \lambda_\beta &= 2(b_{\alpha k} - b_{\beta k})\chi(1-\chi)(1-2\chi) \\ &- 2\frac{b_{\alpha k} - b_{\beta k}}{b_{\alpha\beta}} b_{\alpha\beta}\chi(1-\chi)(1-2\chi) = 0, \end{aligned}$$

which proves the assertion. □

2.3.3 Isotropic gradient energies for different surface tensions.

We consider the Ginzburg-Landau energy given by (2.27), where we assume the gradient energy density to be

$$a(X) = \frac{1}{2}\sum_{i,j=1}^{N} -g_{ij} X_i \cdot X_j, \tag{2.45}$$

where $g_{ij} \in \mathbb{R}$ and $G = (-g_{ij})_{i,j=1}^N$ denotes the quadratic matrix that contains all numbers $-g_{ij}$. We fix our assumptions on (2.45) and (2.27) as follows:

Assumption 2.3.1. We assume that for our pair of isotropic functions (a, w) the following conditions are fulfilled:

(B1) The multi-well potential $w : \Sigma \to \mathbb{R}$ is given by (2.29).

(B2) The matrix $G = (-g_{ij})_{i,j=1}^N$ is *symmetric* and *positive definite* on the tangent space $T(\mathscr{G})$.

(B3) Exactly one of the conditions (i), (ii) is fulfilled:

(i) $g_{ij} = 0$ if and only if $i \neq j$.

(ii) $g_{ij} = 0$ if $i = j$.

(B4) The consistency conditions (2.35) and (2.39) are fulfilled.

Remark 2.3.5. Assume that in (B3) condition (i) is valid. Then by (B2) all $-g_{ii}$ are positive and assume that $g_{ii} = g_{jj} = -g$ for all i and j Then $a(X)$ reduces to the density of the classical Dirichlet energy, i.e.

$$a(\nabla\phi) = \frac{1}{2}g\sum_{i=1}^{N}|\nabla\phi_i|^2.$$

Remark 2.3.6. Note that $-2g_{ij}\nabla\phi_i \cdot \nabla\phi_j$ equals $g_{ij}|\nabla\phi_i|^2 + g_{ij}|\nabla\phi_j|^2 - g_{ij}|\nabla\phi_i + \nabla\phi_j|^2$ and thus (2.45) admits the representation (2.67) in Section 2.3.4.

Remark 2.3.7. Assume $X = (e_\beta - e_\alpha) \otimes \nu$. Then we have:

1. By symmetry, i.e. Assumption (B2) we have $a_{\alpha\beta}(\nu) = g_{\alpha\beta} \geq 0$.

2. The partial derivatives $a_{,X_k}$ in X are

$$a_{,X_k}(X) = \begin{cases} -g_{\alpha\beta}\nu & \text{if } k = \alpha, \\ g_{\alpha\beta}\nu & \text{if } k = \beta, \\ (g_{\alpha k} - g_{\beta k})\nu & \text{else.} \end{cases}$$

3. From 1. and 2. equation (2.38) follows by two-homogeneity. Then (2.45) leads to *equal interface thicknesses* along every phase transition by Proposition 2.3.5.

Theorem 2.3.2. *Let the function pair (a, w) given via (2.27) with (2.45) fulfill the conditions in Assumption 2.3.1. Then $\phi(z) = \chi(z)e_\beta + (1 - \chi(z)e_\alpha$ with $\chi(z)$ given by (2.17) is a critical point of (2.14). Hence this pair (a, w) is suitable to fulfill the properties I. and II. stated in the Task presented in the Introduction.*

This Theorem follows directly from Theorem 2.3.1 in view of the foregoing remarks of this paragraph.

Remark 2.3.8. By Proposition 2.3.5 all numbers $\frac{g_{ij}}{b_{ij}}$ are constant. This constant ratio can be adjusted by the choice of the thickness parameter ε, i.e. we can assume $\frac{9g_{ij}}{b_{ij}} = 1$. Then for given surface energies γ_{ij} we obtain b_{ij}, g_{ij} by

$$b_{ij} = 9\gamma_{ij} \text{ and } g_{ij} = \gamma_{ij}.$$

Besides, by Remark 2.3.1 we have $b_{ijk} = 9(\gamma_{ik} + \gamma_{jk} - \gamma_{ij})$.

Up to now we have developed conditions that assert that $\phi(z) = \chi(z)e_\beta + (1 - \chi(z)e_\alpha$ with $\chi(z)$ given by (2.17) is a critical point of (2.14). Moreover, one is interested in conditions that state optimality for a given critical point, precisely we ask under which conditions a critical point is in fact a minimum of (2.14).

Local optimality of critical points.

For a differentiable function $\rho : \mathbb{R} \to \mathscr{G}$ and $a(\rho') = \frac{1}{2}\rho' \cdot G\rho' = \frac{1}{2}\sum_{i,j=1}^{N} -g_{ij}\rho_i'\rho_j'$ we define a Ginzburg-Landau energy via

$$f(\rho) = \int_{\mathbb{R}} \left(\frac{1}{2}\rho' \cdot G\rho' + w(\rho) \right) \mathrm{d}x, \tag{2.46}$$

subject to the conditions (B1) - (B4) of Assumption 2.3.1. Then by Theorem 2.3.2 the function $\rho = \chi e_\beta + (1-\chi)e_\alpha$ with χ given by (2.17) is a critical point of (2.46), i.e. ρ solves the Euler-Lagrange equation

$$P\left(-G\rho'' + w_{,\boldsymbol{\phi}}(\rho)\right) = -G\rho'' + w_{,\boldsymbol{\phi}}(\rho) - \boldsymbol{\lambda} = 0 \tag{2.47}$$

for (2.46), where $P : \mathbb{R}^N \to T(\mathscr{G})$ denotes the orthogonal projection onto $T(\mathscr{G})$. For shorter presentation let $G^P = P^\top G P$ and $w^P_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho) = P^\top w_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho)P$.

Lemma 2.3.1. *Assume that $\rho = \chi e_\beta + (1-\chi)e_\alpha$ with χ given by (2.17) solves (2.47). Then $e_\beta - e_\alpha$ is an eigenvector of the generalized eigenvalue problem given by*

$$w^P_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho)v - \mu G^P v = 0, \tag{2.48}$$

and the corresponding eigenvalue is given by $\mu = 9(1 - 6\chi + 6\chi^2)$. All other eigenvectors (i.e. eigenvectors that belong to eigenvalues $\neq \mu$) are perpendicular to $e_\beta - e_\alpha$ with respect to to the inner product induced by G.

Proof. We just differentiate (2.47) with respect to z to get

$$P(-G\rho''' + w_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho)\rho') = -G^P\rho''' + w^P_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho)\rho' = 0. \tag{2.49}$$

Since for $\frac{\mathrm{d}^n\rho}{\mathrm{d}z^n} = (e_\beta - e_\alpha)\frac{\mathrm{d}^n\chi}{\mathrm{d}z^n}$ for $n \geq 1$ we obtain that $e_\beta - e_\alpha$ is an eigenvector of (2.48) and $\mu = \frac{\chi'''}{\chi'}$ the corresponding eigenvalue. For $c = \sqrt{\frac{9w_{\alpha\beta}}{4g_{\alpha\beta}}}$ and $\chi(z) = \frac{1}{2}(1 + \tanh(cz))$ one verifies

$$\chi''' = 4c^2\chi'(1 - 6\chi + 6\chi^2) = 9\chi'(1 - 6\chi + 6\chi^2),$$

since $9w_{\alpha\beta} = b_{\alpha\beta} = 9g_{\alpha\beta}$. Thus we infer $\mu = 9(1 - 6\chi + 6\chi^2)$.

For completeness, given an eigenvalue $\mu_2 \neq \mu_1 = 9(1 - 6\chi + 6\chi^2)$ with corresponding eigenvectors v_2 and $v_1 = e_\beta - e_\alpha$ respectively we obtain

$$v_2 \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}v_1 = \mu_1 v_2 \cdot Gv_1 = \mu_1 v_1 \cdot Gv_2,$$

by symmetry of G. Since w is smooth also $w_{,\boldsymbol{\phi}\boldsymbol{\phi}}$ is symmetric, thus we have

$$\mu_1 v_1 \cdot Gv_2 = v_1 \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}v_2 = \mu_2 v_1 \cdot Gv_2.$$

Since $\mu_1 \neq \mu_2$ we infer $v_2 \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}v_1 = v_2 \cdot Gv_1 = 0$. □

Theorem 2.3.3. *Assume $\rho : \mathbb{R} \to \mathscr{G}$, $\rho = \chi e_\beta + (1-\chi)e_\alpha$ is a critical point of (2.46), where χ is given by (2.17). In addition we assume $v \cdot w_{,\boldsymbol{\phi\phi}}(\rho)v \geq c|v|^2$ for a constant $c > 0$ and all $v \in T(\mathscr{G})$ with $v \cdot G(e_\beta - e_\alpha) = 0$. Then ρ is a local minimum of (2.46), i.e. there is some $\epsilon > 0$ such that*

$$f(\rho + \psi) \geq f(\rho),$$

for all $\psi \in H^1(\mathbb{R}; T(\mathscr{G}))$ with $\|\psi\|_{C^0(\mathbb{R};T(\mathscr{G}))} < \epsilon$.

Proof. Let $\psi \in H^1(\mathbb{R}; T(\mathscr{G}))$ a test function, then we define for some $z \in \mathbb{R}$ a new test function $\tilde{\psi} \in H^1(\mathbb{R}; T(\mathscr{G}))$ by

$$\tilde{\psi}(x) := \psi(x) + \rho(x) - \rho(x+z).$$

We consider a Taylor series expansion (cf. [88, Vol. I, p. 148]):

$$\begin{aligned} f(\rho+\psi) &= f(\rho(.+z) + \tilde{\psi}) \\ &= f(\rho(.+z)) + \frac{\delta f(\rho(.+z))}{\delta \rho}(\tilde{\psi}) + \frac{1}{2}\frac{\delta^2 f(\rho(.+z))}{\delta \rho^2}(\tilde{\psi},\tilde{\psi}) \\ &+ \int_0^1 \frac{(1-\tau)^2}{2}\frac{\delta^3 f(\rho(.+z)+\tau\tilde{\psi})}{\delta\rho^3}(\tilde{\psi},\tilde{\psi},\tilde{\psi})\,\mathrm{d}\tau \\ &= f(\rho) + \frac{1}{2}\int_{\mathbb{R}} \left(\tilde{\psi}' \cdot G\tilde{\psi}' + \tilde{\psi}\cdot w_{,\boldsymbol{\phi\phi}}(\rho(.+z))\tilde{\psi}\right)\mathrm{d}x \qquad (2.50) \\ &+ \int_0^1 \frac{(1-\tau)^2}{2}\int_{\mathbb{R}} \tilde{\psi}\cdot\left(w_{,\boldsymbol{\phi\phi\phi}}(\rho(.+z)+\tau\tilde{\psi})\tilde{\psi}\right)\tilde{\psi}\,\mathrm{d}x\,\mathrm{d}\tau. \end{aligned}$$

We want to adjust z and hence $\tilde{\psi}$ such that

$$\int_{\mathbb{R}} \tilde{\psi}(x)\cdot G\rho'(x+z)\,\mathrm{d}x = 0. \qquad (2.51)$$

For this purpose we consider a function $H : H^1(\mathbb{R}; T(\mathscr{G})) \times \mathbb{R} \to C^0(\mathbb{R})$ given by

$$H : (\psi, z) \mapsto \int_{\mathbb{R}} (\rho(x) - \rho(x+z) + \psi(x)) \cdot G\rho'(x+z)\,\mathrm{d}x,$$

and consider the partial derivative $\partial_z H$ in $(\psi, z) = (0,0)$, which is

$$\partial_z H\,|_{(\psi,z)=(0,0)} = -\int_{\mathbb{R}} \rho'(x)\cdot G\rho'(x)\,\mathrm{d}x \neq 0,$$

since $\rho' \neq 0$ and G is positive definite. Then the implicit function theorem (cf. [88, Vol. I, p. 149 f.]) asserts the existence of neighborhoods $U = U(0) \subset H^1(\mathbb{R}; T(\mathscr{G}))$ and $V = V(0) \subset \mathbb{R}$ and a function $g : U \to V$ such that the zero level set of H on $U \times V$ is given by the points $(\tilde{\psi}, g(\tilde{\psi}))$ with $\tilde{\psi} \in U$. That means

$$\int_{\mathbb{R}} \tilde{\psi}(x)\cdot G\rho'(x+z)\,\mathrm{d}x = 0 \text{ for all } \tilde{\psi} \in U, \text{ where } z = g(\tilde{\psi}).$$

In the next step we are going to estimate the second variation in (2.50). Since $\tilde{\psi}(x) \in T(\mathscr{G})$ we have

$$\int_{\mathbb{R}} \left(\tilde{\psi}' \cdot G\tilde{\psi}' + \tilde{\psi} \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho(.+z))\tilde{\psi} \right) \mathrm{d}x = \int_{\mathbb{R}} \left(\tilde{\psi}' \cdot G^P\tilde{\psi}' + \tilde{\psi} \cdot w^P_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho(.+z))\tilde{\psi} \right) \mathrm{d}x.$$

This observation will prepare the decomposition of $\tilde{\psi}(x)$ which will be done in the sequel. For this purpose let $v \in \operatorname{span}\{e_\beta - e_\alpha\} \in T(\mathscr{G})$ with $v \cdot Gv = v \cdot G^P v = 1$ and

$$\tilde{\psi}(x) = \tilde{\alpha}(x)v + \tilde{\theta}(x),$$

where $\tilde{\theta}(x)$ is in the G-orthogonal complement of $\operatorname{span}\{v\}$. Since $\tilde{\psi}(x) \in T(\mathscr{G})$ for all $x \in \mathbb{R}$ we then have $\tilde{\theta}(x) \in T(\mathscr{G})$ for all $x \in \mathbb{R}$. Then the second variation reads as

$$\begin{aligned} \int_{\mathbb{R}} \left(\tilde{\psi}' \cdot G\tilde{\psi}' + \tilde{\psi} \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho(.+z))\tilde{\psi} \right) \mathrm{d}x &= \int_{\mathbb{R}} \left(|\tilde{\alpha}'|^2 + 9|\tilde{\alpha}|^2(1 - 6\chi + 6\chi^2) \right) \mathrm{d}x \\ &+ \int_{\mathbb{R}} \left(\tilde{\theta}' \cdot G\tilde{\theta}' + \tilde{\theta} \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho(.+z))\tilde{\theta} \right) \mathrm{d}x. \end{aligned}$$

Now equation (2.51) turns into

$$0 = \int_{\mathbb{R}} \tilde{\alpha}(x)v \cdot G\rho'(x+z)\,\mathrm{d}x + \int_{\mathbb{R}} \tilde{\theta}(x) \cdot G\rho'(x+z)\,\mathrm{d}x. \tag{2.52}$$

Since $\rho'(x) \in \operatorname{span}\{v\}$ for all $x \in \mathbb{R}$ the last integral in (2.52) vanishes and we infer

$$0 = \int_{\mathbb{R}} \tilde{\alpha}(x)v \cdot G\rho'(x+z)\,\mathrm{d}x = \frac{\sqrt{2}}{|v|} \int_{\mathbb{R}} \tilde{\alpha}(x)\chi'(x+z)\,\mathrm{d}x.$$

Now we can apply a result of De Mottoni and Schatzman (cf. [25]) that asserts the existence of a constant $c_0 > 0$ such that

$$\int_{\mathbb{R}} \left(|\tilde{\alpha}'|^2 + 9|\tilde{\alpha}|^2(1 - 6\chi + 6\chi^2) \right) \mathrm{d}x \;\geq\; c_0 \|\tilde{\alpha}\|^2_{L^2(\mathbb{R})}.$$

Since $\tilde{\theta}$, $\tilde{\theta}'$ are G-orthogonal to v we obtain $\tilde{\theta} \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho(.+z))\tilde{\theta} \geq c|\tilde{\theta}|^2$, hence we have

$$\begin{aligned} \int_{\mathbb{R}} \left(\tilde{\psi}' \cdot G\tilde{\psi}' + \tilde{\psi} \cdot w_{,\boldsymbol{\phi}\boldsymbol{\phi}}(\rho(.+z))\tilde{\psi} \right) \mathrm{d}x &\geq c_0 \|\tilde{\alpha}\|^2_{L^2(\mathbb{R})} + c\|\tilde{\theta}\|^2_{L^2(\mathbb{R};T(\mathscr{G}))} \\ &\geq \frac{c_1}{2} \|\tilde{\psi}\|^2_{L^2(\mathbb{R};T(\mathscr{G}))}, \end{aligned}$$

where $c_1 = \min\{c, c_0\} > 0$.

It remains to estimate the remainder of (2.50). Since w is polynomial of degree four we see that its third derivative is linear, hence

$$\begin{aligned} &\left| \int_0^1 \frac{(1-\tau)^2}{2} \int_{\mathbb{R}} \tilde{\psi} \cdot \left(w_{,\boldsymbol{\phi}\boldsymbol{\phi}\boldsymbol{\phi}}(\rho(.+z) + \tau\tilde{\psi})\tilde{\psi} \right) \tilde{\psi}\,\mathrm{d}x\,\mathrm{d}\tau \right| \\ = \;& \left| \int_0^1 \frac{(1-\tau)^2}{2} \int_{\mathbb{R}} \tilde{\psi} \cdot \left(w_{,\boldsymbol{\phi}\boldsymbol{\phi}\boldsymbol{\phi}}(\tilde{\nu})\tilde{\psi} \right) \tilde{\psi}|\rho(.+z) + \tau\tilde{\psi}|\,\mathrm{d}x\,\mathrm{d}\tau \right|, \end{aligned}$$

where $\tilde{\nu} = \frac{\rho(.+z)+\tau\tilde{\psi}}{|\rho(.+z)+\tau\tilde{\psi}|}$. We then define $c_2 \in \mathbb{R}$ as $c_2 := \sup_{\nu\in S^{N-1}} \|w_{,\boldsymbol{\phi\phi\phi}}(\nu)\|$ and hence

$$\begin{aligned}
&\left|\int_0^1 \frac{(1-\tau)^2}{2}\int_{\mathbb{R}} \tilde{\psi}\cdot\left(w_{,\boldsymbol{\phi\phi\phi}}(\tilde{\nu})\tilde{\psi}\right)\tilde{\psi}|\rho(.+z)+\tau\tilde{\psi}|\,\mathrm{d}x\,\mathrm{d}\tau\right| \\
\leq\ & \int_0^1 \frac{(1-\tau)^2}{2}\int_{\mathbb{R}} c_2|\tilde{\psi}|^2|\tilde{\psi}||\rho(.+z)+\tau\tilde{\psi}|\,\mathrm{d}x\,\mathrm{d}\tau \\
\leq\ & \int_0^1 \frac{(1-\tau)^2}{2}\int_{\mathbb{R}} c_2|\tilde{\psi}|^2|\tilde{\psi}|\left(|\rho(.+z)|+|\tilde{\psi}|\right)\mathrm{d}x\,\mathrm{d}\tau \\
\leq\ & \frac{c_2}{6}\int_{\mathbb{R}} |\tilde{\psi}|^2|\tilde{\psi}|\left(1+|\tilde{\psi}|\right)\mathrm{d}x \\
\leq\ & \frac{c_2}{6}\|\tilde{\psi}\|^2_{L^2(\mathbb{R};T(\mathscr{G}))}\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\left(1+\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\right).
\end{aligned}$$

Thus we obtain

$$f(\rho+\psi) \ \geq\ f(\rho)+c_1\|\tilde{\psi}\|^2_{L^2(\mathbb{R};T(\mathscr{G}))}-\frac{c_2}{6}\|\tilde{\psi}\|^2_{L^2(\mathbb{R};T(\mathscr{G}))}\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\left(1+\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\right).$$

Now choose $0\neq\tilde{\psi}\in U$ such that

$$\frac{c_2}{6}\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\left(1+\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\right)<c_1. \tag{2.53}$$

In this case we have

$$f(\rho+\psi) \ \geq\ f(\rho). \tag{2.54}$$

Now we define

$$\epsilon=\frac{1}{4}\left(\sqrt{1+\tfrac{24c_1}{c_2}}-1\right),$$

and assume that $\|\psi\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}<\epsilon$. For sufficiently small z we then infer $\|\rho(.+z)-\rho\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}<\epsilon$ by continuity of ρ. Hence we derive

$$\begin{aligned}
\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\leq\|\psi\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}+\|\rho(.+z)-\rho\|_{L^\infty(\mathbb{R};T(\mathscr{G}))} &< 2\varepsilon \\
&= \frac{1}{2}\left(\sqrt{1+\tfrac{24c_1}{c_2}}-1\right).
\end{aligned}$$

In this case we arrive at

$$\begin{aligned}
&\frac{c_2}{6}\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\left(1+\|\tilde{\psi}\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}\right) \\
<\ & \frac{c_2}{12}\left(\sqrt{1+\tfrac{24c_1}{c_2}}-1\right)\left(1+\frac{1}{2}\left(\sqrt{1+\tfrac{24c_1}{c_2}}-1\right)\right) \\
=\ & \frac{c_2}{24}\left(\sqrt{1+\tfrac{24c_1}{c_2}}-1\right)\left(\sqrt{1+\tfrac{24c_1}{c_2}}+1\right)=c_1,
\end{aligned}$$

and (2.54) is fulfilled for all ψ with $\|\psi\|_{L^\infty(\mathbb{R};T(\mathscr{G}))}<\epsilon$. □

Remark 2.3.9. Assume w is given by (2.29) where G is given by $G=(-g_{ij})_{i,j=1}^N$ subject to conditions (B1)-(B4). For a system of $N=3$ phases there exist surface energies γ_{12}, γ_{13} and γ_{23} that fulfill the no-wet condition (2.7), but $v\cdot w_{,\boldsymbol{\phi\phi}}(\chi,1-\chi,0)v<0$ for some $v\in T(\mathscr{G})$ with $v\cdot G(e_1-e_2)=0$. For such surface energies Theorem 3.3 is not applicable.

Proof. As one verifies, the second derivatives of w evaluated at $(\chi, 1-\chi, 0)$ are given by

$$\begin{aligned} w_{,\phi_1\phi_1} &= 2b_{12}(1-\chi)^2, \\ w_{,\phi_1\phi_2} &= 4b_{12}\chi(1-\chi), \\ w_{,\phi_1\phi_3} &= \left(b_{132}(1-\chi) + 2b_{231}\chi\right)(1-\chi), \\ w_{,\phi_2\phi_2} &= 2b_{12}\chi^2, \\ w_{,\phi_2\phi_3} &= \left(b_{231}\chi + 2b_{132}(1-\chi)\right)\chi, \\ w_{,\phi_3\phi_3} &= 2b_{13}\chi^2 + 2b_{23}(1-\chi)^2 + 2b_{123}\chi(1-\chi). \end{aligned} \tag{2.55}$$

We consider a configuration of surface energies γ_{12} and $\gamma_{13} = \gamma_{23}$ In this case the matrix G multiplied with $e_1 - e_2$ gives

$$G(e_1 - e_2) = (\gamma_{12}, -\gamma_{12}, 0)^\top,$$

and an G-orthogonal vector to $e_1 - e_2$ is given by $v = (1, 1, -2)^\top$. Furthermore, by $b_{ij} = 9\gamma_{ij}$ and $b_{ijk} = b_{ik} + b_{jk} - b_{ij}$ we then have

$$\begin{aligned} w_{,\phi_1\phi_1} &= 18\gamma_{12}(1-\chi)^2, \\ w_{,\phi_1\phi_2} &= 36\gamma_{12}\chi(1-\chi), \\ w_{,\phi_1\phi_3} &= 9\gamma_{12}(1-\chi^2), \\ w_{,\phi_2\phi_2} &= 18\gamma_{12}\chi^2, \\ w_{,\phi_2\phi_3} &= 9\gamma_{12}(2-\chi)\chi, \\ w_{,\phi_3\phi_3} &= 18\gamma_{13} - 18\gamma_{12}\chi(1-\chi). \end{aligned}$$

Evaluating $v \cdot w_{,\boldsymbol{\phi\phi}}(\chi, 1-\chi, 0)v$ we obtain

$$\begin{aligned} v \cdot w_{,\boldsymbol{\phi\phi}}\left(\chi, 1-\chi, 0\right) v &= w_{,\phi_1\phi_1} + w_{,\phi_2\phi_2} + 2w_{,\phi_1\phi_2} + 4w_{,\phi_3\phi_3} - 4\left(w_{,\phi_1\phi_3} + w_{,\phi_2\phi_3}\right) \\ &= 72\gamma_{13} + 18\gamma_{12}(6\chi^2 - 6\chi - 1), \end{aligned}$$

which is non-negative, if $5\gamma_{12} \leq 8\gamma_{13}$. To see this we remark that

$$72\gamma_{13} + 18\gamma_{12}(6\chi^2 - 6\chi - 1) \geq 0$$

is equivalent to

$$12\left(\chi - \tfrac{1}{2}\right)^2 \geq \left(5 - 8\tfrac{\gamma_{13}}{\gamma_{12}}\right). \tag{2.56}$$

Since $\left(\chi - \frac{1}{2}\right)^2 \geq 0$ inequality (2.56) is fulfilled, if $5\gamma_{12} \leq 8\gamma_{13}$. Now, if $\gamma_{12} = 1.8$ and $\gamma_{13} = \gamma_{23} = 1.0$ condition (2.56), i.e. $\left(5 - 8\frac{\gamma_{13}}{\gamma_{12}}\right) > 0 = 12\left(\chi - \frac{1}{2}\right)^2$ at $\chi = \frac{1}{2}$. In fact, evaluating $v \cdot w_{,\boldsymbol{\phi\phi}}(\chi, 1-\chi, 0)v$ at $\chi = \frac{1}{2}$ we obtain

$$v \cdot w_{,\boldsymbol{\phi\phi}}\left(\tfrac{1}{2}, \tfrac{1}{2}, 0\right) v = 9(4\gamma_{13} + 4\gamma_{23} - 5\gamma_{12}) = -9 < 0,$$

which proves the assertion. □

Remark 2.3.10. Summarizing, for a system of three phases and surface energies γ_{12} and $\gamma_{13} = \gamma_{23}$ we can apply Theorem 3.3, if

$$5\gamma_{12} \leq 8\gamma_{13} \tag{2.57}$$

holds. If the surface energies are $\gamma_{12} = 1.8$ and $\gamma_{13} = \gamma_{23} = 1.0$ we have $5\gamma_{12} > 8\gamma_{13}$ and, in fact, Theorem 3.3 is not applicable. Nevertheless this choice of surface energies behaved numerically stable in our test simulations in Section 2.3.5.

Positive definiteness of the gradient energy discussed in section 2.3.3.

In Section 2.3.3 we introduced the gradient energy density

$$a(X) = \frac{1}{2}\sum_{i,j=1}^{N} -g_{ij}X_i \cdot X_j,$$

and the matrix $G = (-g_{ij})_{i,j=1}^{N}$. We now ask under which conditions the matrix G is positive definite on $T(\mathscr{G})$, if the numbers g_{ij} fulfill condition 2.3.3.c (ii) of Assumption 2.3.1. Precisely we assume that the following conditions are fulfilled.

(B5) The numbers g_{ij} are positive, if $i \neq j$, and $g_{ij} = 0$ if $i = j$.

(B6) The numbers g_{ij} are symmetric, i.e. $g_{ij} = g_{ji}$ for all index pairs (i, j).

(B7) The numbers g_{ij} fulfill a straightforward analogue of the no-wet condition (2.7), i.e.

$$g_{ij} < g_{ik} + g_{jk},$$

for all mutually different indices i, j, $k \in \{1, \ldots, N\}$.

Remark 2.3.11. Condition (B7) is clear from (2.7) and Remark 2.3.8, which suggests a direct connection between g_{ij} and γ_{ij}.

Since we will examine the definiteness of $G = (-g_{ij})_{i,j=1}^{N}$ only on the $(N-1)$-dimensional subspace $T(\mathscr{G}) \subset \mathbb{R}^N$, it suffices to consider an appropriate restriction $G|_T(\mathscr{G})$ given by a matrix $G' \in \mathbb{R}^{(N-1)\times(N-1)}$. For this purpose we take a basis $B(T(\mathscr{G})) = \{a_1, \ldots, a_{N-1}\}$ of $T(\mathscr{G})$ and let $G' = A^T G A$ where $A = (a_1, \ldots, a_{N-1}) \in \mathbb{R}^{N\times(N-1)}$. In the sequel we choose $a_j = (\delta_{i,1} - \delta_{i-1,j})_{i=1}^{N}$ as basis elements of $B(T(\mathscr{G}))$; hence we obtain

$$A = (\delta_{i,1} - \delta_{i-1,j})_{i,j=1}^{N,N-1} \text{ and } A^T = (\delta_{1,j} - \delta_{i,j-1})_{i,j=1}^{N-1,N}, \tag{2.58}$$

where $\delta_{i,j}$ is the Kronecker delta. We then obtain the matrix

$$G' = A^T G A = (g_{1,i+1} + g_{1,j+1} - g_{i+1,j+1})_{i,j=1}^{N-1},$$

whose definiteness we will examine.

Our first result yields positive definiteness of G' for a system of $N = 3$ phases.

Proposition 2.3.6. *We consider a system of $N = 3$ phases. Assume that for $G = (-g_{ij})_{i,j=1}^3$ the conditions (B5)-(B7) hold true. Then G is a positive definite matrix on the tangent space $T(\mathscr{G})$.*

Proof. We just consider the restriction $G' = A^T G A$ as introduced with A, A^T given by (2.58). Thus it remains to investigate the definiteness of a 2×2-matrix, which is

$$G' = A^T G A = \begin{pmatrix} 2g_{12} & (g_{12} + g_{13} - g_{23}) \\ (g_{12} + g_{13} - g_{23}) & 2g_{13} \end{pmatrix}.$$

Clearly the entry $2g_{12}$ is positive since $g_{12} > 0$. To apply Sylvester's definiteness criterion it remains to consider the determinant of $A^T G A$ which is

$$\det(A^T G A) = \left(4g_{12}g_{13} - (g_{12} + g_{13} - g_{23})^2\right),$$

and this term is positive if and only if

$$(g_{12} + g_{13} - g_{23})^2 < 4g_{12}g_{13}. \tag{2.59}$$

Now G fulfills (B7) from which follows

$$g_{12}^2 < g_{12}(g_{13} + g_{23}), \quad g_{13}^2 < g_{13}(g_{12} + g_{23}) \quad \text{and } g_{23}^2 < g_{23}(g_{12} + g_{13}). \tag{2.60}$$

Then we sum up over all inequalities in (2.60) and infer

$$g_{12}^2 + g_{13}^2 + g_{23}^2 < 2\left(g_{12}g_{13} + g_{12}g_{23} + g_{13}g_{23}\right),$$

which is equivalent to (2.59). Hence our assertion follows. □

Remark 2.3.12. The converse of Proposition 2.3.6 is not true: For this purpose take $\delta > 0$ sufficiently small, $g_{12} = g_{13} = 1.0$ and $g_{23} = 2.0 + \delta$. Then the matrix G' is positive definite but condition (B7) is obviously violated.

For systems with more than three phases we have to supplement (A.2.a)-(A.2.c) by additional assumptions on g_{ij} to obtain positive definiteness of G on $T(\mathscr{G})$. May we start with the following general result.

Theorem 2.3.4. *For a given system of N, ($N \geq 4$) phases let $G = (-g_{ij})_{i,j=1}^N$ fulfill the conditions (B5)-(B7). Besides we assume*

$$(N-4)g_{1i+1} + \sum_{\substack{j=1,\dots,N-1 \\ j\neq i}} g_{1j+1} < \sum_{\substack{j=1,\dots,N-1 \\ j\neq i}} g_{i+1j+1} \text{ for all } i \tag{2.61}$$

to be fulfilled. Then G is positive definite on $T(\mathscr{G})$.

Proof. Again we consider the matrix $G' = A^T G A$ where A, A^T are given by (2.58). To examine definiteness of G' we apply a standard result from linear algebra: Following Geršgorin's theorem, cf. [55, p. 39] we find for any eigenvalue $\lambda \in \mathbb{R}$ an index i such that

$$2g_{1i+1} - \lambda \leq \sum_{\substack{j=1,\dots,N \\ j\neq i}} (g_{1i+1} + g_{1j+1} - g_{i+1j+1})$$

or equivalently

$$(4-N)g_{1i+1} + \sum_{\substack{j=1,\dots,N-1 \\ j\neq i}} (g_{i+1j+1} - g_{1j+1}) = 2g_{1i+1} + \sum_{\substack{j=1,\dots,N-1 \\ j\neq i}} (g_{i+1j+1} - g_{1i+1} - g_{1j+1}) \leq \lambda,$$

where we have used condition (B7), i.e. $g_{1i+1} + g_{1j+1} - g_{i+1j+1} > 0$. Now condition (2.61) leads to

$$0 < (4-N)g_{1i+1} + \sum_{\substack{j=1,\dots,N-1 \\ j\neq i}} (g_{i+1j+1} - g_{1j+1}) \leq \lambda, \tag{2.62}$$

the desired result. □

Remark 2.3.13. Assume that (B5) - (B7) are fulfilled for $G = (-g_{ij})_{i,j=1}^N$ again, but condition (2.61) is relaxed to

$$(N-4)g_{1i+1} + \sum_{\substack{j=1,\dots,N-1 \\ j\neq i}} g_{1j+1} \leq \sum_{\substack{j=1,\dots,N-1 \\ j\neq i}} g_{i+1j+1} \text{ for all } i\,. \tag{2.63}$$

Then G is positive semidefinite on the tangent space $T(\mathscr{G})$. This follows easily, since (2.63) leads to (2.62) as well it allows for equality in (2.62). Hence G is positive semidefinite.

Now we can conclude positive semidefiniteness for four phase systems by the following theorem.

Theorem 2.3.5. *Assume that we are given a system of $N = 4$ phases and conditions (B5)-(B7) hold true for the matrix $G = (-g_{ij})_{i,j=1}^4$. Then G is positive semidefinite on $T(\mathscr{G})$.*

Proof. Without loss of generality we assume that the sum of each row in $G = (-g_{ij})_{i,j=1}^4$ is lower or equal than the sum of all elements of the first row, i.e.

$$-(g_{12} + g_{13} + g_{14}) \geq \sum_{\substack{i=1,\dots,N \\ i\neq j}} -g_{ij} \text{ for all } j. \tag{2.64}$$

Otherwise we consider a matrix $\tilde{G} = P^T G P$, where P is an appropriate permutation matrix such that the sum of every row in $\tilde{G}$ is in fact lower or equal than the sum accross the first row. Since $P^T P = I$ the matrix $\tilde{G}$ is orthogonally equivalent to G, i.e $\tilde{G}$ and G have the same eigenvalues and either both symmetric or not. For $q = (1,1,1,1)^T$ we clearly have

$\mathbb{R}^4 = \operatorname{span}\{q\} \dotplus T(\mathscr{G})$ and since $q = Pq$ holds $T(\mathscr{G})$ is an invariant subspace of P, i.e. $P(T(\mathscr{G})) \subset T(\mathscr{G})$. Assume $x \cdot Gx \geq 0$ for all $x \in T(\mathscr{G})$ then we obtain

$$x \cdot \tilde{G}x = Px \cdot GPx \geq 0,$$

thus $\tilde{G}$ is positive semidefinite on $T(\mathscr{G})$. Besides for $e_j = Pe_i$ we have $e_i \cdot \tilde{G}e_i = e_j \cdot Ge_j = 0$. Thus $\tilde{G}$ fulfills (B5) - (B7).

In view of this we assume (2.64) for the given matrix $G = (-g_{ij})_{i,j=1}^4$. Obviously inequality (2.64) turns into

$$s \leq g_{21} + g_{23} + g_{24}, \quad s \leq g_{31} + g_{32} + g_{34}, \text{ and } s \leq g_{41} + g_{42} + g_{43}, \tag{2.65}$$

where $s = g_{12} + g_{13} + g_{14}$. By subtracting equal summands on both sides in (2.65) we arrive at

$$g_{13} + g_{14} \leq g_{23} + g_{24}, \quad g_{12} + g_{14} \leq g_{32} + g_{34}, \text{ and } g_{12} + g_{13} \leq g_{42} + g_{43}, \tag{2.66}$$

which is just condition (2.63) for $N = 4$. Thus by Remark 2.3.13 $G = (-g_{ij})_{i,j=1}^4$ is positive semidefinite on $T(\mathscr{G})$. □

2.3.4 Anisotropic gradient energies.

In order to model anisotropic gradient energies we need to involve an explicite dependency on the interface orientation ν in our Ginzburg-Landau functional $\mathscr{F}$. Clearly the gradient energy of Section 2.3.3 does not allow for such a property. Therefore we assume our anisotropic gradient energy density is given by

$$a(X) = \frac{1}{4} \sum_{i \in I} \sum_{j \in I \setminus \{i\}} \left(\tilde{a}_{ij}(X_i) + \tilde{a}_{ij}(X_j) - \tilde{a}_{ij}(X_i + X_j) \right), \tag{2.67}$$

where $\tilde{a}_{ij} : \mathbb{R}^d \to \mathbb{R}$ are smooth functions that fulfill the following properties.

Assumption 2.3.2. Let our Ginzburg-Landau energy $\mathscr{F} : \mathscr{G} \to \mathbb{R}$ given by (2.27) with (2.67) as gradient energy density. For $q = (q_1, \ldots, q_d) \in \mathbb{R}^d$ the derivative $(\partial_{q_1} \tilde{a}_{ij}, \ldots, \partial_{q_d} \tilde{a}_{ij})(q)$ is denoted by $\tilde{a}'_{ij}(q)$. In addition let $\eta \in \mathbb{R}$ arbitrarily chosen. We then assume that the pair of functions (a, w) fulfills the following conditions:

(B8) The multi-well potential $w : \Sigma \to \mathbb{R}$ is a *non-negative polynomial* and given by (2.29).

(B9) The function $a : (T(\Sigma))^d \to \mathbb{R}$ is fulfills $a(X) > 0$ whenever $X \neq 0$. Besides assume $\tilde{a}_{ij} : \mathbb{R}^d \to \mathbb{R}$ are *symmetric,* i.e.

$$\tilde{a}_{ij}(q) = \tilde{a}_{ji}(q),$$

for all index pairs (i, j).

(B10) Every $\tilde{a}_{ij} : \mathbb{R}^d \to \mathbb{R}$ is *two-homogeneous*, i.e.

$$\tilde{a}_{ij}(\eta q) = \eta^2 \tilde{a}_{ij}(q), \tag{2.68}$$

for all index pairs (i, j) again.

(B11) The consistency conditions (2.35) and (2.39) are fulfilled.

Remark 2.3.14. Assume $\phi = \chi e_\beta + (1 - \chi)e_\alpha$ and $X = (e_\beta - e_\alpha) \otimes \nu$. Then we have

1. By symmetry, i.e. Assumption (B9) of 2.3.2 we have $a_{\alpha\beta}(\nu) = \tilde{a}_{\alpha\beta}(\nu) \geq 0$.
2. The partial derivatives $a_{,X_k}$ in X are

$$a_{,X_k}(X) = \begin{cases} -\frac{1}{2}\tilde{a}'_{\alpha\beta}(\nu) & \text{if } k = \alpha, \\ \frac{1}{2}\tilde{a}'_{\alpha\beta}(\nu) & \text{if } k = \beta, \\ \frac{1}{2}\left(\tilde{a}'_{\alpha k}(\nu) - \tilde{a}'_{\beta k}(\nu)\right) & \text{else.} \end{cases}$$

3. From 1. and 2. equation (2.38) follows by two-homogeneity. Then (2.67) leads to *equal interface thicknesses* along every phase boundary.

Theorem 2.3.6. *Let the function pair (a, w) given by (2.29) and (2.67) fulfill the conditions of Assumption 2.3.2. Then $\phi(z) = \chi(z)e_\beta + (1 - \chi(z)e_\alpha$ with $\chi(z)$ given by (2.17) is a critical point of (2.14). Hence this pair (a, w) is suitable to fulfill the properties I. and II. of the Task presented in the Introduction.*

Remark 2.3.15. By Proposition 2.3.5 all numbers $f(\nu) = \frac{a_{ij}(\nu)}{b_{ij}}$ are independent of the actual indices i and j. We then obtain from (2.10) that

$$\gamma_{ij}(\nu) = \frac{1}{3} b_{ij} \sqrt{f(\nu)}$$

holds. Then for given anisotropic surface energies $\gamma_{ij} = \gamma_{ij}(\nu)$ and an anisotropy function $f : S^{d-1} \to \mathbb{R}$, $f \geq 0$ we infer

$$b_{ij} = 3\frac{\gamma_{ij}(\nu)}{\sqrt{f(\nu)}} \text{ and } a_{ij}(\nu) = 3\gamma_{ij}(\nu)\sqrt{f(\nu)},$$

or rather familiar

$$b_{ij} = 9\frac{\gamma_{ij}(\nu)}{\sqrt{\tilde{f}(\nu)}} \text{ and } a_{ij}(\nu) = \gamma_{ij}(\nu)\sqrt{\tilde{f}(\nu)},$$

where $\tilde{f} = 9f$. Furthermore, by (2.37) we have

$$b_{ijk} = 9\frac{\gamma_{ik}(\nu) + \gamma_{jk}(\nu) - \gamma_{ij}(\nu)}{\sqrt{\tilde{f}(\nu)}}.$$

2.4 Numerical case studies.

In order to validate the theoretical predictions we now investigate the *qualitative behaviour* of the introduced gradient energy and multi-well potential numerically. Especially we expect vanishing third phase contribution if the third phase is equal to zero at initial state. In two space dimensions we expect further the validity of Youngs Law at triple junctions.

Throughout this paper the partial differential equations (2.26) were discretized in space using finite differences on a uniform grid with mesh size Δx. Gradients were replaced by forward difference quotients, divergences by backward difference quotients. In time, an explicit Euler scheme with time step Δt was used with $\Delta t \lesssim \Delta x^2$ for stability reasons.

2.4.1 Phase transitions in 1D-simulations

First we study systems of three and four phases in a spatial domain Ω that occupies a line segment of $\mathbb{R}$. We will examine third and fourth phase contributions in a two-phase transition as well as the correct approximation of the surface energies.

We start with a system of three and four phases where all surface energies γ_{ij}, are set to 1.0. The gradient energy density has been chosen as in Section 2.3.3, i.e. $a(\nabla \boldsymbol{\phi}) = \frac{1}{2}|\nabla \boldsymbol{\phi}|^2$ and the multi-well potential w as in (2.29), where we have set $b_{ijkl} = 0$ for all $i,\ j,\ k,\ l$. The remaining coefficients b_{ij} and b_{ijk} of the potential w we set as in Remark 2.3.8. Since $\sum_{j=1}^{N} \phi_j = 1$ we have

$$\nabla \phi_i = -\sum_{\substack{j=1 \\ j\neq i}}^{N} \nabla \phi_j \text{ and } |\nabla \phi_i|^2 = -\sum_{\substack{j=1 \\ j\neq i}}^{N} \nabla \phi_j \cdot \nabla \phi_i.$$

Thus $\frac{1}{2}|\nabla \boldsymbol{\phi}|^2 = \frac{1}{2}\sum_{i=1}^{N} |\nabla \phi_i|^2$ equals $\frac{1}{2}\sum_{i=1}^{N} -g_{ij} \nabla \phi_j \cdot \nabla \phi_i$ where $g_{ij} = 1$ for $i \neq j$ and $g_{ij} = 0$, if $i = j$. Then by Remark 2.3.10 Theorem 3.3 asserts stability since equal surface energies fulfill (2.57). In fact, the stability predicted by Theorem 3.3 has been validated in the following numerical simulations. Then we solve the gradient flow (2.26) on the interval $(0, 2)$ subject to homogeneous Neumann boundary conditions. As initial data we chose a sharp transition from phase 1 to phase 2, i.e. we set

$$\phi_1(0, x) = \begin{cases} 0 & \text{if } x \in [0, 1], \\ 1 & \text{if } x \in (1, 2], \end{cases} \tag{2.69}$$

and $\phi_2(0, x) = 1 - \phi_1(0, x)$, $\phi_3(0, x) = \phi_4(0, x) = 0$. We carried out our simulations with mesh sizes $\Delta x \in \{0.01, 0.005, 0.0025\}$ for our spatial grid on $[0, 2]$. The thickness parameter ε we have chosen $\varepsilon = 0.1$ and as time frame we chose the interval $[0.0, 0.055]$. The observed relaxation time varied between 0.0225 and 0.0300 due to different values of Δx. After relaxation we observed a phase profile for phase 1 which has been in good accordance with the profile (2.17), if the square root $\sqrt{\frac{w_{12}}{a_{12}}}$ equals $\frac{1}{\varepsilon}$ due to the rescaling in (2.3). In addition we observed no contributions of third and fourth phases, i.e. their contributions are (numerical) zero for all

spatial grids. Furthermore we computed the approximation of the surface energies γ_{12} of the 1-2-transition by the numeric approximation of the Ginzburg-Landau energy given by

$$\mathscr{F}_{approx} := \Delta x \sum_{i=0}^{K} \varepsilon\, a(\phi(x_i), \partial_x^{\Delta x}\phi(x_i)) + \frac{1}{\varepsilon} w(\phi(x_i)), \tag{2.70}$$

where $\partial_x^{\Delta x}\phi(x_i) = \frac{1}{\Delta x}(\phi(x_{i+1}) - \phi(x_i))$ and the $\{x_i\}_{i=0}^{K}$ are the grid points. We have performed

Δx	$N = 3,\ 4$
0.0100	0.9992478
0.0050	0.9998124
0.0025	0.9999531

Table 2.1: Ginzburg-Landau energies for systems of three and four phases and equal surface energies.

these computations for different values of Δx for systems of $N = 3$ and $N = 4$ phases. Table 2.1 shows that the approximations became better as the grid has been refined.

Secondly, we considered systems of three and four phases again, but with different surface energies γ_{ij}. In view of this we used the gradient energy density $a(\nabla\phi) = \frac{1}{2}\sum_{i,j} -g_{ij}\nabla\phi_i \cdot \nabla\phi_j$ as proposed in Section 2.3.3, where all remaining parameters and potentials are chosen as before. In this case we considered a three phase system where two surface energies are equal to 1.0, but the remaining one is set to 1.8. We run simulations for $\gamma_{12} = 1.8$, $\gamma_{13} = \gamma_{23} = 1.0$ as well as for $\gamma_{23} = 1.8$, $\gamma_{12} = \gamma_{13} = 1.0$. As expected we observed in both cases a zero third phase contribution after relaxation while the phase profiles for phase 1 show a good accordance with the standing wave solution (2.17).

Δx	$\gamma_{12} = 1.0$	$\gamma_{12} = 1.8$
0.0100	0.9992479	1.7986460
0.0050	0.9998124	1.7996623
0.0025	0.9999531	1.7999156

Table 2.2: Ginzburg-Landau energies for a three phase system for different values of γ_{12}.

Furthermore we computed the numerical approximation for γ_{12} as in (2.70). We observed for both configurations of surface energies a good agreement with the correct values 1.0 and 1.8 as shown in Table 2.2. Clearly the approximations became better the finer the spatial grid. In addition we considered a system of four phases, where we could use the values for γ_{ij} from the three phase simulations, supplemented by appropriate values for γ_{14}, γ_{24} and γ_{34}. Precisely we considered the cases $\gamma_{12} = 1.8$, $\gamma_{ij} = 1.0$ for $(i,j) \in \mathcal{A} \setminus \{(1,2),(2,1)\}$, $\gamma_{23} = 1.8$, $\gamma_{ij} = 1.0$ for $(i,j) \in \mathcal{A} \setminus \{(2,3),(3,2)\}$, and as additional possibility, $\gamma_{34} = 1.8$, $\gamma_{ij} = 1.0$ for $(i,j) \in \mathcal{A} \setminus \{(3,4),(4,3)\}$. Again, we kept all other parameters unchanged. As in the

case of equal surface energies we observed zero third and fourth phase contributions as well as a good accordance with the phase profiles of the nonzero phases ϕ_1 and ϕ_2. Finally the numerical approximations of the surface energies γ_{12} yield the same values as in Table 2.2 except for $\Delta x = 0.0100$, $\gamma_{12} = 1.0$ we observed a difference in the last given digit, precisely we computed for $N = 4$ the value $\gamma_{12} \approx 0.9992478$.

As an example for mutually different surface energies γ_{ij} we chose $\gamma_{12} = 0.8$, $\gamma_{13} = 1.0$, $\gamma_{23} = 1.6$ and $\gamma_{12} = 1.6$, $\gamma_{13} = 0.8$, $\gamma_{23} = 1.0$. Again we kept all other parameters unchanged and observed zero third phase contributions after relaxation.

Δx	$\gamma_{12} = 0.8$	$\gamma_{12} = 1.6$
0.0100	0.7993982	1.5987964
0.0050	0.7998499	1.5996998
0.0025	0.7999625	1.5999248

Table 2.3: Ginzburg-Landau energies for a three phase system (all surface energies are mutually different) for different values of γ_{12}.

For completeness we give the numerical approximations of the surface energies in Table 2.3.

As a result of our simulations in one space dimension we conclude that third and, if applicable fourth phase contributions remain zero during the simulation time, if a phase transition purely between phase 1 and phase 2 has been considered. This physically consistent behaviour could be observed in the case of equal and different surface energies. In addition, the numerical approximation for γ_{12} behaved robustly when a (zero) fourth phase has been added as well as another surface energy has been changed. Besides these approximations became the better the finer the spatial grid was.

Finally, we consider the surface energies

$$\gamma_{12} = 1.5,\ \gamma_{13} = 1.0,\ \text{and } \gamma_{23} = 0.7, \tag{2.71}$$

in a system of at least three phases. Clearly the choices in (2.71) fulfill the no-wet condition (2.7). We will briefly discuss the case of $N = 3$ phases. In this case we have

$$G(e_1 - e_2) = (\gamma_{12}, -\gamma_{12}, \gamma_{23} - \gamma_{13})^\top = (1.5, -1.5, -0.3)^\top,$$

and the vector $(1, 1, -2)^\top$ is obviously not G-orthogonal to $e_1 - e_2$. A vector $v \in T(\mathscr{G})$ that is also G-orthogonal to $e_1 - e_2$ is given by

$$v = \tfrac{1}{\gamma_{12}}(\gamma_{12} + \gamma_{23} - \gamma_{13}, \gamma_{12} + \gamma_{13} - \gamma_{23}, -2\gamma_{12})^\top = (0.8, 1.2, -2.0)^\top.$$

Then using (2.55) we evaluate $v \cdot w_{,\phi\phi}(\chi, 1-\chi, 0)v$ at $\chi = 1/2$ and we obtain

$$v \cdot w_{,\phi\phi}\left(\tfrac{1}{2}, \tfrac{1}{2}, 0\right) v = \tfrac{9}{\gamma_{12}}\left(-2\gamma_{13}\gamma_{23} + 4\gamma_{23}\gamma_{12} + 4\gamma_{12}\gamma_{13} + \gamma_{13}^2 + \gamma_{23}^2 - 5\gamma_{12}^2\right) = -5.76 < 0.$$

We did numerical simulations with the potential w given by (2.29) and the matrix G of Section 2.3.3 given by $G = (-g_{ij})_{i,j=1}^N$ subject to conditions (B1)-(B4) where we used (2.71) for the surface energies. The initial data we chose as $\phi_2(0,x) = 1 - \phi_1(0,x)$, $\phi_3(0,x) = 0$ and $\phi_1(0,x)$ is given by (2.69) and then we solved the gradient flow (2.26) with homogeneous Neumann boundary conditions. The results are nearly the same as in the one-dimensional simulations before: The phase variables ϕ_1 and ϕ_2 relaxed to a profile similar to the one given by (2.17) while third phase contributions vanished after relaxation.

For a system of $N = 4$ phases we considered the surface energies given by (2.71) supplemented by

$$\gamma_{14} = \gamma_{24} = \gamma_{34} = 1.0. \tag{2.72}$$

Again the choice (2.71,2.72) fulfills the no-wet condition (2.7). As one observes the vectors $(1,1,-2,0)^\top$ and $(1,1,-1,-1)^\top$ are not G-orthogonal to $e_1 - e_2$, since $G(e_1 - e_2)$ is now given by

$$G(e_1 - e_2) = (\gamma_{12}, -\gamma_{12}, \gamma_{23} - \gamma_{13}, \gamma_{24} - \gamma_{14})^\top = (1.5, -1.5, -0.3, 0)^\top.$$

Via orthogonalization with respect to the G-inner product we obtained vectors v, $u \in T(\mathscr{G})$ given by

$$v = \frac{1}{\gamma_{12}} \begin{pmatrix} \gamma_{12} + \gamma_{23} - \gamma_{13} \\ \gamma_{12} + \gamma_{13} - \gamma_{23} \\ -2\gamma_{12} \\ 0 \end{pmatrix} \text{ and } u = \frac{1}{2\gamma_{12}} \begin{pmatrix} 2\gamma_{12} - (\gamma_{13} - \gamma_{23} + \gamma_{14} - \gamma_{24}) \\ 2\gamma_{12} + (\gamma_{13} - \gamma_{23} + \gamma_{14} - \gamma_{24}) \\ -2\gamma_{12} \\ -2\gamma_{12} \end{pmatrix},$$

which are G-orthogonal to $e_1 - e_2$. Clearly, $v \cdot w_{,\phi\phi}(\chi, 1-\chi, 0, 0)v$ consists only of derivatives $w_{,\phi_i\phi_j}$ for i, $j \in \{1,2,3\}$. Besides, one verifies that each of these second derivatives equals the corresponding one in (2.55). Hence, we have $v \cdot w_{,\phi\phi}(\frac{1}{2}, \frac{1}{2}, 0, 0)v = -5.76$ as before. To evaluate $u \cdot w_{,\phi\phi}(\chi, 1-\chi, 0, 0)u$ we need the derivatives of w with respect to ϕ_4, i.e.

$$\begin{aligned}
w_{,\phi_1\phi_4}(\chi, 1-\chi, 0, 0) &= (1-\chi)\left((1-3\chi)(b_{24} - b_{14}) + (1+\chi)b_{12}\right), \\
w_{,\phi_2\phi_4}(\chi, 1-\chi, 0, 0) &= \chi\left((2-3\chi)(b_{24} - b_{14}) + (2-\chi)b_{12}\right), \\
w_{,\phi_3\phi_4}(\chi, 1-\chi, 0, 0) &= (b_{23} + b_{24})(1-\chi)^2 + (b_{13} + b_{14})\chi^2 - b_{34}(1 - 2\chi + 2\chi^2), \\
w_{,\phi_4\phi_4}(\chi, 1-\chi, 0, 0) &= 2b_{24}(1-\chi) - 2b_{12}\chi(1-\chi) + 2b_{14}\chi.
\end{aligned}$$

Then evaluating $u \cdot w_{,\phi\phi}(\chi, 1-\chi, 0, 0)u$ at $\chi = \frac{1}{2}$ we obtain

$$u \cdot w_{,\phi\phi}(\tfrac{1}{2}, \tfrac{1}{2}, 0, 0)u = -12.915 < 0,$$

which indicates that w is strongly non-convex at $\chi = \frac{1}{2}$.

We will now see that the configuration (2.71,2.72) is responsible for serious numerical difficulties: Again we assume w is given by (2.29) where G is given by $G = (-g_{ij})_{i,j=1}^N$ subject to conditions (B1)-(B4). We also set the initial values $\phi_2(0,x) = 1 - \phi_1(0,x)$, $\phi_3(0,x) =$

$\phi_4(0,x) = 0$ where $\phi_1(0,x)$ is given by (2.69). Solving the gradient flow (2.26) with a spatial mesh size $\Delta x = 0.005$ we observed apart from third and fourth phase contributions in the interfacial region a finite-time blow-up approximately at $t = 0.1210$. Table 2.4 shows the blow-up

t	$\|\phi_1(t)\|_\infty$	$\|\phi_3(t)\|_\infty$	$\|\phi_4(t)\|_\infty$
0.1200	1.1266	0.6753	0.5591
0.1205	2.7522	2.4910	2.1754
0.1210	Nan	Nan	Nan

Table 2.4: Numerical L^∞-norms of the phases 1, 3 and 4.

of the L^∞-norms at $t = 0.1210$.

2.4.2 Geometry at phase interfaces and triple junctions in two spatial dimensions.

For the following numerical tests let us introduce some notation and briefly motivate the physical laws at (sharp) interface boundaries.

Consider two distinct phases with open phase domains Ω_i, $\Omega_j \subset \Omega \subset \mathbb{R}^2$ such that $\Omega_i \cap \Omega_j = \emptyset$ and $\partial\Omega_i \cap \partial\Omega_j \neq \emptyset$. We then assume that the common phase boundary Γ_{ij} given by $\Gamma_{ij} = \partial\Omega_i \cap \partial\Omega_j$ admits a piecewise representation by twice differentiable curves. Thus we define the oriented interface normal $\nu = \nu_{ij} \in S^1$ pointing into Ω_j. Besides, we define the mean curvature $\kappa \in \mathbb{R}$ by $\kappa = -\nabla_\Gamma \cdot \nu$ where $\nabla_\Gamma \cdot \nu$ is the surface divergence of ν. Every such interface Γ_{ij} follows two physical laws:

First the *Gibbs-Thomson law* describes the motion of Γ_{ij} in dependence of the local interface geometry and bulk contributions, i.e.

$$V = -\gamma_{ij}\kappa + \text{(bulk contributions)}, \tag{2.73}$$

where $V \in \mathbb{R}$ denotes the normal velocity of the interface Γ_{ij} in direction of ν and $\gamma_{ij} > 0$ the surface energy density.

Secondly *Youngs law* predicts the correct contact angles at triple junctions. For this purpose we define τ_{ij} as the unit vector (i.e. $|\tau_{ij}| = 1$) tangential to the interface Γ_{ij} such that (ν_{ij}, τ_{ij}) is positively oriented. Then Youngs law at equilibrium says that the tangential forces at every Γ_{ij} given by $\gamma_{ij}\tau_{ij}$ will balance out, i.e.

$$\gamma_{ij}\tau_{ij} + \gamma_{ik}\tau_{ik} + \gamma_{jk}\tau_{jk} = 0, \tag{2.74}$$

which is Young's law at equlibrium, cf. [37].

Now we introduce the angle α_i as the angle between the tangents τ_{ij} and τ_{ik}. If we choose a local coordinate system such that $\tau_{12} = e_1$, then

$$\begin{aligned} \gamma_{12} + \gamma_{13}\cos\alpha_1 + \gamma_{23}\cos\alpha_2 &= 0, \\ \gamma_{13}\sin\alpha_1 - \gamma_{23}\sin\alpha_2 &= 0, \end{aligned} \tag{2.75}$$

holds, and likewise for $\tau_{23} = e_1$ we have

$$\gamma_{12} \sin \alpha_3 - \gamma_{23} \sin \alpha_2 = 0. \tag{2.76}$$

Then equations (2.75) and (2.76) yield

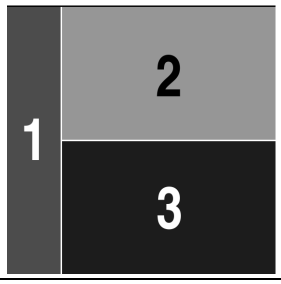
$$\frac{\sin \alpha_1}{\gamma_{23}} = \frac{\sin \alpha_2}{\gamma_{13}} = \frac{\sin \alpha_3}{\gamma_{12}}, \tag{2.77}$$

where $\alpha_1 + \alpha_2 + \alpha_3 = 2\pi$.

2.4.3 Simple three phase systems with triple junctions.

As an example in two space dimensions we now consider a system of three phases whose (phase) interfaces have initially the form of the capital letter 'T' rotated by 90 degree counter-clockwise:

Figure 2.3 Initial arrangement of the phase domains.



The three phase domains we have arranged as in Figure 2.3, i.e. phase 1 on the left neighboring phase 2 on the upper right, phase 3 on the lower right area of Ω.

As domain $\Omega \subset \mathbb{R}^2$ we chose a square of length $a = 1.005$, i.e. $\Omega = (0, a)^2$ and besides we chose a spatial grid of mesh size 0.005 in both directions. We then solved the gradient flow (2.26) with the explicit finite difference code as briefly described in Section 3.4 where we used the gradient potential $a(\nabla\phi) = \frac{1}{2}\sum_{i,j} -g_{ij}\nabla\phi_i \cdot \nabla\phi_j$ of Section 2.3.3 and the multi-well potential (2.29). Throughout these simulations we imposed homogeneous Neumann boundary conditions at $\partial\Omega$. Besides we chose the thickness parameter $\epsilon = 0.025$ and $[0.0, 0.15]$ as time interval.

Beyond the investigation of third phase contributions in a 1-2 phase transition we checked the angle condition of Young's Law (2.77) in the results of our simulations. Though the diffuse interface allows only for a rough estimate of the contact angles we could determine angle intervals of a size about 10^{-2} by use of a protractor.

A further possibility to analyze these simulation results is the comparison to the sharp interface model, where an analytic solution of the symmetric triple junction problem moving with constant velocity has been constructed in [39]. Given a two-dimensional cartesian coordinate system we identify the vertical axis in Figure 2.3 with the x_1-axis. We assume that our time-dependent phase interface is given by the curve $(t, x_1) \to (x_1, v(x_1) + ct) \in [0, a] \times \mathbb{R}$ with a

time-independent and continuous profile function $v : [0, a] \to \mathbb{R}$ and a constant transport velocity $c \in \mathbb{R}$. Besides assume that v is twice differentiable on the open interval $(0, a/2)$. Then, following [39] a solution $v : (0, a/2) \to \mathbb{R}$ is given by

$$v(x_1) = -\frac{\gamma_{12}}{c} \log \cos\left(\frac{c}{\gamma_{12}} x_1\right) + d, \tag{2.78}$$

where d is an appropriate constant and c is given by

$$c = \frac{2\gamma_{12}}{a} \arctan \sqrt{\frac{\gamma_{23}^2}{4\gamma_{12}^2 - \gamma_{23}^2}}. \tag{2.79}$$

The solution on $(a/2, a)$ is then given by $x_1 \mapsto v(a - x_1)$ for all $x \in (a/2, a)$. Then it is possible to compare the diffuse interface region with the exact sharp interface profile; on the other hand the exact sharp interface solution provides the exact transport velocity for the phase interface which may be compared with their numerical approximations. The numerical approximations are obtained as follows. First we computed the integral $\int_\Omega \phi_1 \, \mathrm{d}x$ numerically at neighboring times t and $t + \Delta t$, i.e. we computed

$$\sum_{i,j} \phi_1(ih, jh) h^2, \tag{2.80}$$

where $h = \Delta x_1 = \Delta x_2$ denotes the grid spacing in x_1- and x_2-direction. Since $\phi_1 \approx 1.0$ in the pure phase 1 and $\phi_1 \approx 0.0$ in the other phases equation (2.80) gives the approximate area occupied by phase 1. Now (2.78) and (2.79) provide a constantly transported interface profile, thus the exact area $\mathcal{L}^2(A(t, \phi_1))$ occupied by phase 1 changes due to

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathcal{L}^2(A(t, \phi_1)) = ac, \tag{2.81}$$

since $\Omega = (0, a)^2$. Thus the constant velocity c is approximately given by

$$c \approx \frac{h^2}{a} \frac{\sum_{i,j} \left(\phi_1(t + \Delta t; ih, jh) - \phi_1(t; ih, jh)\right)}{\Delta t}.$$

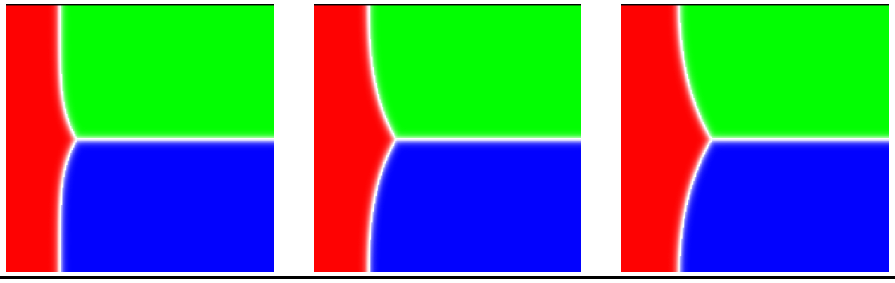
Equal surface energies.

At first we assumed all surface energies γ_{ij} equal to 1.0. As theoretically predicted we observed that along a transition between two phases outside a neighborhood around the triple junction the remaining phase is not present, i.e. it is equal to zero.

To validate Young's law we measured the contact angles at phase 2 and phase 3 which we have assumed to be equal. A rough estimate using a protractor led to contact angles varying between $\frac{2}{3}\pi - 0.0175$ and $\frac{2}{3}\pi + 0.0349$ which shows a good approximation of the exact contact angles of $\frac{2}{3}\pi$.

Since (2.78) gives an analytical solution for the sharp interface model of the symmetric triple junction evolution we compared the exact triple junction velocity with the numerically

Figure 2.4 Simulation results for equal surface energies: Solutions to $t = 0.01$, $t = 0.03$ and $t = 0.05$.



t	0.090	0.100	0.110	0.120	0.130	0.140	exact velocity
	1.0390	1.0389	1.0388	1.0387	1.0386	1.0386	1.0420

Table 2.5: Approximated triple junction velocities in a three phase system with equal surface energies.

approximated triple junction velocities given in Table 2.5. In comparison to the predicted velocity 1.0420 we observe that the numerical values are quite near to the exact velocity, but they have a slight decrease even though they are below the correct value.

As a consequence the exact phase interface given by (2.78) is more curved as the numerically computed one as depicted in Figure 2.5. This validates the observation of the contact angles as well as the transport velocities. The numerical computation of the interface has been done as follows: For the transition region between ϕ_1 and ϕ_2 the maximum of $\phi_1 \cdot \phi_2$ at every (horizontal) axis has been determined as well as the indices (i, j) of every grid point where this maximum is attained. These grid points of the interfacial region where $\phi_1 \cdot \phi_2$ attained its maximum are marked by the circles in Figure 2.5 and 2.7 rotated by $\frac{\pi}{2}$ counterclockwise.

Different surface energies.

Again we consider our two-dimensional triple junction problem with initial phase configuration as depicted in Figure 2.3. We now consider different surface energies γ_{ij}, precisely we assume γ_{23} as one of the values 1.2, 1.5 and 1.8 while the other surface energies γ_{12} and γ_{13} remain unchanged, i.e. they equal 1.0. All other parameters are set as introduced as well as the potentials.

γ_{23}	1.2	1.5	1.8
$\varepsilon = 0.025$	0.3430	0.8960	1.5640
$\varepsilon = 0.020$	0.2760	0.7230	1.2520
$\varepsilon = 0.015$	0.2050	0.5220	0.9470

Table 2.6: Third phase contributions given by $10^{-3} \cdot \phi_2$.

As a first test we examined third phase contributions in the transition region between the

Figure 2.5 Comparison of the numerical solution (dotted) to the exact boundary (solid) of the sharp interface problem. The vertical axis here corresponds to the x_2-axis (i.e. the horizontal axes of Figures 2.3 and 2.4); the horizontal one corresponds to x_1, where $x_1 = 0$ represents a part of the boundary $\partial\Omega$ and $x_1 = 0.5$ the horizontal coordinate of the triple junction.

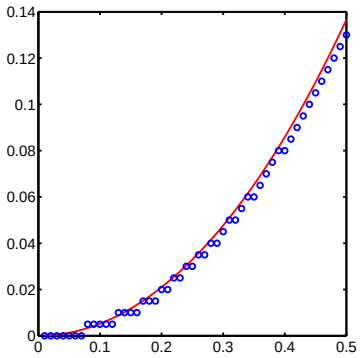
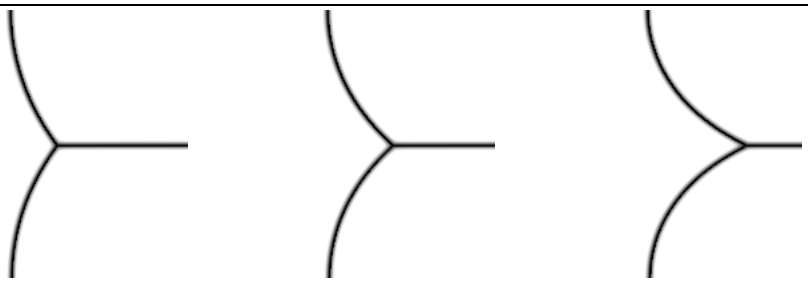


Figure 2.6 Simulation results for different surface energies: Solutions to $\gamma_{23} = 1.2$, $\gamma_{23} = 1.5$ and $\gamma_{23} = 1.8$ at $t = 0.15$.



other two phases. Precisely we had a look at the curved transition region between phase 1 and phase 3 after relaxation to the constantly transported profile $v : (a/2, a) \to \mathbb{R}$. Outside a sufficiently large neighborhood around the triple junction we expect $\phi_2 = 0$ in this transition region. But in contrast to the example before where all surface energies were equal we found now very small contributions of ϕ_2 in the curved transition region between phase 1 and phase 3, while in the plain one between phase 2 and phase 3 no contributions of ϕ_1 were found. The contributions of ϕ_2 are present along the whole transition region between ϕ_1 and ϕ_3; we have measured the maximum of ϕ_2 on the line $\{a\} \times [0, a]$ and depicted in Table 2.6. It turned out that these contributions depend on the deviation of γ_{23} to $\gamma_{12} = \gamma_{13}$ and on the thickness parameter ε. Table 2.6 shows that the values became smaller as γ_{23} narrowed $\gamma_{12} = \gamma_{13}$, likewise for decreasing $\varepsilon > 0$.

Secondly we had a look at the contact angles at the triple junction: Again we measured the contact angle α_3 at phase 3. Since the blurred interface prevents us to determine a unique value for α_3 we depicted the intervals where we measured the approximate values for α_3 in Table 2.7. The second column of Table 2.7 gives the exact contact angle resulting from Young's Law (2.75). We observed that the approximations are quite close to the exact contact angles. Nevertheless the approximations of α_3 became slightly worse as γ_{23} increased. Besides the ap-

γ_{23}	exact α_3	approximations of α_3
1.2	2.2143	$[\alpha_3 - 0.0675, \alpha_3 + 0.0197]$
1.5	2.4189	$[\alpha_3 - 0.0627, \alpha_3 + 0.0420]$
1.8	2.6906	$[\alpha_3 - 0.2471, \alpha_3 - 0.0028]$

Table 2.7: Contact angles α_3 at the triple junction and their approximations in the diffuse interface model.

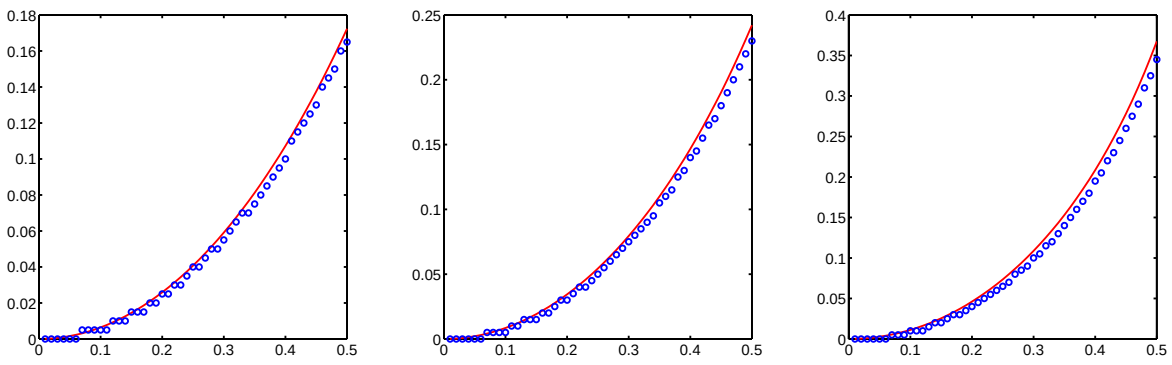
proximations of α_3 show a tendency to be smaller as the exact angles since the exact angles tend to the upper interval bound or even tend to be larger (in the case γ_{23}). Now, if the approximated value for α_3 is too small, it may happen that the curvature of the transition region between phase 1 and phase 3 is too small. In this case (2.73) would lead to a smaller normal velocity of the curved interface. We omitted measuring the curvature since the diffuse interface complicates such a procedure, nevertheless the approximated interface velocities are slightly below the exact ones as we will see below.

γ_{23}	$t = 0.090$	0.100	0.110	0.120	0.130	0.140	exact velocity
1.2	1.2766	1.2764	1.2762	1.2761	1.2760	1.2760	1.2806
1.5	1.6814	1.6811	1.6809	1.6808	1.6807	1.6806	1.6877
1.8	2.2189	2.2185	2.2183	2.2181	2.2179	2.2178	2.2284

Table 2.8: Approximated triple junction velocities in a three phase system with different surface energies.

As in the case of equal surface energies we computed numerical approximations of the triple junction velocities which are given in Table 2.8. Likewise we observed slightly decreasing values below the correct triple junction velocities.

Figure 2.7 Comparison of the numerical solution (dotted) to the exact boundary (solid) of the sharp interface problem for surface energies $\gamma_{23} = 1.2$, $\gamma_{23} = 1.5$ and $\gamma_{23} = 1.8$ at $t = 0.15$. The labelling of the coordinate axes is done as in Figure 2.5.



Again the exact phase interface given by (2.78) is more curved as the numerically computed

one as depicted in Figure 2.7.

2.4.4 A bubble-shaped three phase system in two space dimensions under phase volume conservation.

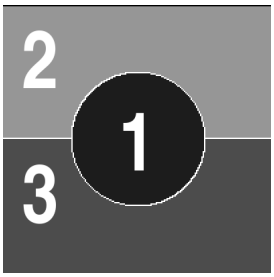
A further possibility to study the triple junction evolution in two space dimensions is provided by a bubble-shaped configuration as depicted in Figure 2.8. In addition we postulate the volume of every phase to be constant during the triple junction evolution. In general the initial configuration with its contact angles $\phi_1 = \pi$, $\phi_2 = \phi_3 = \frac{\pi}{2}$ violates Young's Law (2.74). On the other hand, since the circle minimizes the perimeter (and hence the surface energy) under all domains of equal area we expect relaxation to a domain bounded by two circular arcs that meet at the triple junctions where the contact angles will adjust according to Young's law (2.74). From this point of view it is posssible to construct an analytic solution of the sharp interface problem (2.73) supplemented by volume conservation. For this purpose we set the horizontal axis in Figure 2.8 as the x-axis and then we assume that every point (x, y) on the circular arc is given either by $(x, y) = (x, u(x))$ or $(x, y) = (x, -u(x))$ with a certain function $u = u(x)$. To give an explicite formula for $u(x)$ let θ be the half contact angle inside the bubble-shaped domain. Then u is given by a vertically shifted circular profile of radius R, i.e.

$$u(x) = \sqrt{R^2 - x^2} + d(\theta), \tag{2.82}$$

where $d(\theta)$ is given by $d(\theta) = -R\cos\theta$. For given domain area A a computation shows that the radius R is given by

$$R = \sqrt{\frac{A}{2(\theta - \sin\theta\cos\theta)}}.$$

Figure 2.8 Initial bubble configuration.



To incorporate volume conservation into the phase field model we need to add an additional Lagrange parameter ν_α to the gradient flow (2.26), i.e. we then have

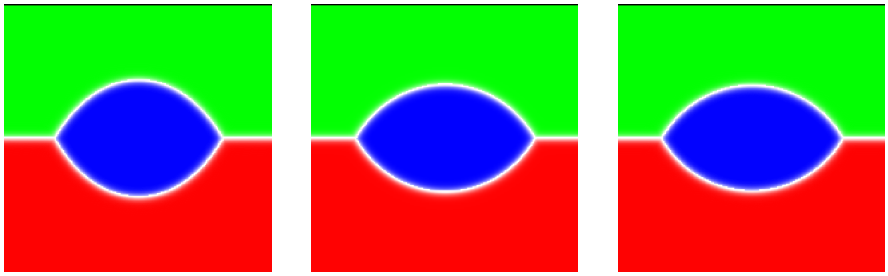
$$\varepsilon\partial_t\phi_\alpha = -\frac{\delta\mathscr{F}}{\delta\phi_\alpha} + \lambda + \nu_\alpha, \tag{2.83}$$

for all phase indices $\alpha \in \{1, \dots, N\}$. To achieve $\partial_t \int_\Omega \phi_\alpha \,\mathrm{d}x = 0$ for all $\alpha \in \{1, \dots, N\}$ we then infer

$$\nu_\alpha = -\frac{1}{\mathcal{L}^2(\Omega)} \int_\Omega \left(\frac{\delta\mathscr{F}}{\delta\phi_\alpha} - \lambda \right) \mathrm{d}x.$$

As domain $\Omega \subset \mathbb{R}^2$ we chose a square of length $a = 1.005$, i.e. $\Omega = (0, a)^2$ and besides we chose a spatial grid of mesh size 0.005 in both directions. We then solved the gradient flow (2.83) with the explicit finite difference code as briefly described in Section 3.4 where the sum of the forward differences $\frac{\phi_\alpha(t+\Delta t,x)-\phi_\alpha(t,x)}{\Delta t}$ over all spatial grid points $x \in \Omega$ had been used to compute the Lagrange multiplier ν_α. As before we used the gradient potential $a(\nabla\phi) = \frac{1}{2}\sum_{i,j} -g_{ij}\nabla\phi_i \cdot \nabla\phi_j$ of Section 2.3.3 and the multi-well potential (2.29). Throughout these simulations we imposed homogeneous Neumann boundary conditions on $\partial\Omega$. Besides we chose the thickness parameter $\epsilon = 0.0250$ and $[0.0, 0.45]$ as time frame. Finally we set the initial radius to 0.25 and the surface energies $\gamma_{12} = \gamma_{13} = 1.0$ while γ_{23} varies.

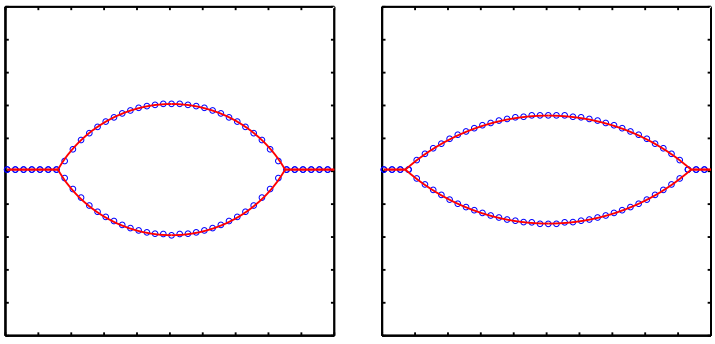
Figure 2.9 All phases at $t = 0.02$, 0.06 and 0.1.



Our first simulation involves identical surface tensions γ_{ij} set equal to 1.0. As in the previous paragraph we expect contact angles of $\frac{2}{3}\pi$. Then we have $\theta = \frac{1}{3}\pi$, $A = \pi/16$ and $R = 0.3990$.

In fact during the numerical simulations we observed a relaxation to a flat-shaped and curved bubble as depicted in Figure 2.9. Moreover, the contact angles as observed after relaxation are quite good approximations to the exact ones which equal $\frac{2\pi}{3}$.

Figure 2.10 Exact Boundary (as solid line) in comparison to the numerically computed phase boundary marked by circles. The left picture results from simulations with equal surface tensions; for the right one the surface tensions $\gamma_{12} = \gamma_{13} = 1.0$, $\gamma_{23} = 1.5$ has been used.

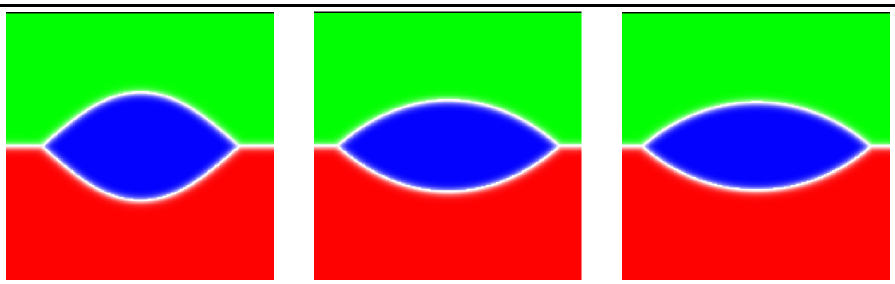


In addition the phase boundaries of phase 1 are quite near to the predicted ones given by (2.82): The left side of Figure 2.10 shows the comparison of the exact boundaries (solid) and the numerically computed ones (dotted) which are nearly equal to each other.

In our second simulation we use surface tensions

$$\gamma_{12} = \gamma_{13} = 1.0 \text{ and } \gamma_{23} = 1.5.$$

Figure 2.11 All phases at $t = 0.02$, 0.06 and 0.1.



The domain turned out to be large enough to avoid interactions between the curved phase interfaces and the domain boundary. As expected the bubble becomes more flat as in the example with equal surface tensions. This relaxation process is depicted in Figure 2.11. From Youngs Law (2.74) we derive $\theta = 0.7227$. With $A = \pi/16$ we obtain $R = 0.6569$. On the right side in Figure 2.10 we see the exact boundary given by (2.82) in comparison to the numerically computed phase boundary. Again there is almost no difference between the both marked lines.

Chapter 3

Models of Phase Transitions in Multi-Component Fluids.

3.1 Introduction.

In many applications phase transitions occur in interaction with fluid flow. Thus one is interested in a mathematical description of phase transitions in convective systems. For isothermal single- and multi-component systems as well as for non-isothermal one-component systems a lot work has been already done cf. [6, 11, 29, 47]. Finally, a widespread selection of topics and references is presented in [5].

In this Chapter, we derive a phase field model and a sharp interface model for multi-component systems with convection in a non-isothermal regime. For both models we consider general balance laws and an entropy inequality in integral form which are quite similar. Due to additional contributions on phase interfaces the integral balance laws for energy and momentum are slightly different in both models. Besides, the list of thermodynamic variables will either include a phase parameter and its derivatives or geometric and kinematic quantities of phase boundaries. We use the ideas of Liu and Müller [61], [66] to extract constitutive relations from an entropy principle for both models. In addition, we discuss relationships of these models to other convective models. Following Gurtin et al. [47] we consider a microforce balance law for the phase field model.

3.2 Classical fluid mechanics and balance equations.

Particle flow.

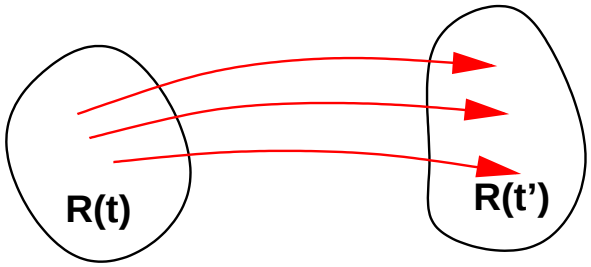
In a system of moving mass particles we can describe the position of any particle at time $t > 0$ by its path $t \mapsto \boldsymbol{s}(t, \boldsymbol{p}_0)$ where $\boldsymbol{p}_0$ is its position at a reference time $t_0 \in \mathbb{R}_+$. We assume that $t \mapsto \boldsymbol{s}(t, \boldsymbol{p}_0)$ is a smooth function for all $\boldsymbol{p}_0$. Furthermore we postulate that the considered

material is impenetrable: Two distinct particles do not meet at any time $t > 0$, i.e. $\boldsymbol{s}(t, \boldsymbol{p}_0) \neq \boldsymbol{s}(t, \boldsymbol{p}_1)$ for all t whenever $\boldsymbol{p}_0 \neq \boldsymbol{p}_1$. For simplicity we assume $t_0 = 0$. For the statement and analysis of the governing conservation laws we need the following definition:

Definition 3.2.1 (Material volume). Let $R(t)$, $t > 0$ be a time-dependent subset of $\mathbb{R}^d$. We say that $R(t)$ is a *material volume,* if it preserves *all* mass particles that originally were in $R(0)$. Conversely all mass particles of $R(t)$ were also present in $R(0)$. Paraphrasing, $R(t)$ is given by

$$R(t) = \boldsymbol{s}(t, R(0)) \stackrel{\text{def}}{=} \{\boldsymbol{x} \in \mathbb{R}^d | \text{ there exists a } \boldsymbol{p} \in R(0) \text{ such that } \boldsymbol{x} = \boldsymbol{s}(t, \boldsymbol{p})\}.$$

Figure 3.1 A material volume and mass flow ($t' > t$).



If $t \mapsto \boldsymbol{s}(t) = \boldsymbol{s}(t, \boldsymbol{p}_0)$ is differentiable, it is the solution of the ordinary differential equation

$$\begin{aligned} \dot{\boldsymbol{s}}(t) &= \boldsymbol{v}(t, \boldsymbol{s}(t)),\ t > 0, \\ \boldsymbol{s}(0) &= \boldsymbol{p}_0, \end{aligned}$$

where $\boldsymbol{v}$ is the *velocity* of the particle.

Remark 3.2.1 (Transport equations). Assume that $\phi : [0, T] \times \Omega \to \mathbb{R}$ is a smooth function that is constant along every particle path $\boldsymbol{s}(t) = \boldsymbol{s}(t, \boldsymbol{p}_0)$. Besides, let every particle path $\boldsymbol{s}(t)$ be differentiable on $[0, T)$. Then we have

$$\begin{aligned} 0 &= \frac{\mathrm{d}}{\mathrm{d}t}\left(\phi(t, \boldsymbol{s}(t))\right) \\ &= \partial_t \phi(t, \boldsymbol{s}(t)) + \boldsymbol{v}(t, \boldsymbol{s}(t)) \cdot \nabla \phi(t, \boldsymbol{s}(t)). \end{aligned}$$

Hence each $\boldsymbol{s}(t, \boldsymbol{p}_0)$ serves as characteristic curve for the transport equation

$$\partial_t \phi(t, \boldsymbol{x}) + \boldsymbol{v}(t, \boldsymbol{x}) \cdot \nabla \phi(t, \boldsymbol{x}) = 0. \tag{3.1}$$

If $\boldsymbol{v}$ is a constant then the particles are shifted parallel in direction of $\boldsymbol{v}$ and $\phi(t, \boldsymbol{x}) = \phi_0(\boldsymbol{x} - \boldsymbol{v}t)$ solves equation (3.1).

Although transport equations allow some insight into particle flow and propose a nice time derivative by (3.1) we cannot apply these calculations. In the following conservation laws ϕ represents an integral over a material volume $R = R(t)$ and of course we are interested how to interchange integration over $R(t)$ and differentiation with respect to t. The answer is given by *Reynold's transport theorem*:

Theorem 3.2.2 (Reynold's transport theorem). *Let $R(t) \subset \Omega \subset \mathbb{R}^d$ a material volume that is transported with velocity $\boldsymbol{v} : [0,T] \times \Omega \to \mathbb{R}^d$. Besides, $f : [0,T] \times \Omega \to \mathbb{R}$ denotes a differentiable function. Then the time derivative of its integral over $R(t)$ is given by*

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{R(t)} f(t,\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x} = \int_{R(t)} \partial_t f(t,\boldsymbol{x}) \, \mathrm{d}\boldsymbol{x} + \int_{\partial R(t)} f(t,\boldsymbol{x}) \boldsymbol{v} \cdot \boldsymbol{\nu}_R \, \mathrm{d}\mathcal{H}^{d-1},$$

for all $t \in (0,T)$ where $\boldsymbol{\nu}_R$ is the outer unit normal at $\partial R(t)$.

The proof follows from Corollary 2 of Appendix B via $\gamma = R$.

We now introduce the notation to derive the system of balance laws and the resulting models. We consider a system with N components and M phases. By c_i we denote the mass fraction of component i and $\boldsymbol{c} = (c_1, \ldots, c_N)$ is the concentration vector. We always require

$$\sum_{i=1}^{N} c_i = 1,$$

i.e.

$$\boldsymbol{c} \in \Sigma^N = \left\{ \boldsymbol{c}' \in \mathbb{R}^N \mid \quad \sum_{i=1}^{N} c_i' = 1 \right\}.$$

In addition we introduce a vector for the phase fields $\boldsymbol{\phi} = (\phi_1, \ldots \phi_M)$ where ϕ_i is the local fraction of phase i which implies that $\boldsymbol{\phi} \in \Sigma^M$. By

$$T\Sigma^N = \left\{ \boldsymbol{c}' \in \mathbb{R}^N \mid \quad \sum_{i=1}^{N} c_i' = 0 \right\}$$

we denote the tangent space to Σ.

As it is customary in *rational thermodynamics* we will start with only very few assumptions on the specific form of *constitutive relations*. We want to derive a phase field model which is a diffuse interface model based on a free energy that contains Ginzburg-Landau type gradient terms. But different to some other approaches, we will only state precise relations *after* we derive restrictions imposed by the *second law of thermodynamics*.

To formulate the balance laws and the second law of thermodynamics for a convective system we need to introduce the quantities mass density ϱ, velocity $\boldsymbol{v}$, internal energy density (per unit mass) E and entropy density (per unit mass) S. Furthermore $\boldsymbol{T}$ denotes the stress tensor and $\boldsymbol{k}$ denotes the density of volume forces (per unit mass). We formulate our theory in *Eulerian coordinates*. All quantities depend on $(\boldsymbol{x}, t)$ where $\boldsymbol{x}$ is the Eulerian coordinate vector and t is the time.

Definition 3.2.3 (Material derivative). By

$$\mathrm{D}_t \, u = \frac{\partial u}{\partial t} + (\boldsymbol{v} \cdot \nabla) u$$

we denote the *material derivative*.

Proposition 3.2.1 (Commutator rule). *Let $\phi : [0,T] \times \Omega \to \mathbb{R}^n$ twice differentiable with respect to to the spatial coordinates $\boldsymbol{x}$ and together with its first spatial derivatives differentiable with respect to to time t. Then we have*

$$\mathrm{D}_t\left(\partial_{x_k}\phi\right) = \partial_{x_k}\left(\mathrm{D}_t\,\phi\right) - \left(\partial_{x_k}\boldsymbol{v}\cdot\nabla\right)\phi,$$

and

$$\mathrm{D}_t\left(\nabla\phi\right) = \nabla\left(\mathrm{D}_t\,\phi\right) - \left(\nabla\boldsymbol{v}\nabla\right)\phi.$$

Proof. Using Definition 3.2.3 we compute

$$\begin{aligned}
\mathrm{D}_t\left(\partial_{x_k}\phi\right) &= \partial_t\left(\partial_{x_k}\phi\right) + \sum_{i=1}^{d} v_i\partial_{x_i}\left(\partial_{x_k}\phi\right)\\
&= \partial_{x_k}\left(\partial_t\phi\right) + \partial_{x_k}\left(\sum_{i=1}^{d} v_i\partial_{x_i}\phi\right) - \sum_{i=1}^{d}\left(\partial_{x_k}v_i\right)\partial_{x_i}\phi\\
&= \partial_{x_k}\left(\mathrm{D}_t\,\phi\right) - \left(\partial_{x_k}\boldsymbol{v}\right)\cdot\nabla\phi,
\end{aligned}$$

as desired. The second assertion is straightforward. □

After having determined the notation we discuss the principal balance laws as well as the entropy principle.

Conservation laws and entropy inequality.

To postulate the classical balance and imbalance laws we assume that $R = R(t)$ is an arbitrary material volume. Let us start with the conservation of mass. It is natural to postulate that all particles are kept in $R(t)$, i.e. there is no loss of mass. Thus *mass conservation* is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t)} \varrho\ \mathrm{d}\boldsymbol{x} = 0. \tag{3.2}$$

Using Reynold's transport theorem we obtain

$$\int_{R(t)}\left(\frac{\partial\varrho}{\partial t} + \nabla\cdot\left(\varrho\boldsymbol{v}\right)\right)\mathrm{d}\boldsymbol{x} = 0.$$

Since $R(t)$ is an arbitrary material volume we obtain the local version

$$\frac{\partial\varrho}{\partial t} + \nabla\cdot\left(\varrho\boldsymbol{v}\right) = 0. \tag{3.3}$$

We proceed by postulating that changes in the total momentum of $R(t)$ are due to forces $\boldsymbol{k}$ acting in the volume and acting on the surface. The latter forces are caused by *mechanical interactions* along the boundary $\partial R(t)$ like frictional forces or shear forces. Thus the *momentum balance* is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t)} \varrho\boldsymbol{v}\ \mathrm{d}\boldsymbol{x} = \int_{\partial R(t)} \boldsymbol{T}\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1} + \int_{R(t)} \varrho\boldsymbol{k}\ \mathrm{d}\boldsymbol{x} \tag{3.4}$$

where $\boldsymbol{\nu}_R$ is the outer unit normal to $\partial R(t)$ and $\mathrm{d}\mathcal{H}^{d-1}$ denotes integration with respect to the $(d-1)$-dimensional surface measure. Now we can derive in a standard manner (see e.g. [44]) the momentum balance in local form, using Reynold's transport theorem and the mass balance (3.3), i.e.

$$\varrho\left(\frac{\partial \boldsymbol{v}}{\partial t} + (\mathrm{D}\,\boldsymbol{v})\boldsymbol{v}\right) = \nabla\cdot\boldsymbol{T} + \varrho\boldsymbol{k} \tag{3.5}$$

where $\nabla\cdot\boldsymbol{T}$ is the *divergence* of the stress tensor $\boldsymbol{T}$ (for definition see e.g. [44]). We now postulate that the total energy of $R(t)$ consists of internal energy (with density E) and kinetic energy depending on the material velocity $\boldsymbol{v}$. Furthermore, we assume that changes of this total energy are due to work by the volume force density $\boldsymbol{k}$ and stress forces $\boldsymbol{T}\boldsymbol{\nu}_R$ as well as the energy flux density $\boldsymbol{J}_E$. Finally we will neglect external heat sources. Thus the *energy balance* is given by

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t)} \varrho\left(E + \frac{1}{2}|\boldsymbol{v}|^2\right)\,\mathrm{d}\boldsymbol{x} \qquad (3.6)\\ = \;& -\int_{\partial R(t)} \boldsymbol{J}_E\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\partial R(t)} (\boldsymbol{T}\boldsymbol{\nu}_R)\cdot\boldsymbol{v}\,\mathrm{d}\mathcal{H}^{d-1} + \int_{R(t)} \varrho(\boldsymbol{k}\cdot\boldsymbol{v})\,\mathrm{d}\boldsymbol{x}. \end{aligned}$$

The first term on the right hand side describes *energy outflow* with energy flux density $\boldsymbol{J}_E$, the second term accounts for the work by the *surface stress* and the third term accounts for the work by the *body forces*. The energy identity in its local form is given by

$$\frac{\partial}{\partial t}\left(\varrho\left(E + \frac{|\boldsymbol{v}|^2}{2}\right)\right) + \nabla\cdot\left(\varrho\boldsymbol{v}\left(E + \frac{|\boldsymbol{v}|^2}{2}\right) + \boldsymbol{J}_E - \boldsymbol{T}^\top\boldsymbol{v}\right) = \varrho\boldsymbol{k}\cdot\boldsymbol{v},$$

and using (3.3) and (3.5) we have

$$\varrho\left(\partial_t E + \boldsymbol{v}\cdot\nabla E\right) = -\nabla\cdot\boldsymbol{J}_E + \boldsymbol{T}^\top : \nabla\boldsymbol{v}. \tag{3.7}$$

We complete our balance laws by the *conservation of species* assuming that concentration changes are due to the concentration fluxes $\boldsymbol{J}_i$. We note that no chemical reactions take place. Then the *conservation of species* is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t)} \varrho c_i\,\mathrm{d}\boldsymbol{x} = -\int_{\partial R(t)} \boldsymbol{J}_i\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1} \tag{3.8}$$

where $\boldsymbol{J}_i$, $i = 1,\ldots,N$ denotes the *mass flux* of component i. Again, using Reynold's transport theorem we obtain

$$\varrho\left(\frac{\partial c_i}{\partial t} + \boldsymbol{v}\cdot\nabla c_i\right) + \nabla\cdot\boldsymbol{J}_i = 0. \tag{3.9}$$

For the fluxes $\boldsymbol{J}_i$ we require $\sum_{i=1}^N \boldsymbol{J}_i = 0$ in order to guarantee the constraint $\sum_{i=1}^N c_i = 1$ *during the evolution*. Besides, an important requirement of *irreversible thermodynamics* is that the *second law of thermodynamics* holds. This fundamental law follows from the following *entropy inequality*:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t)} \varrho S\,\mathrm{d}\boldsymbol{x} \geq -\int_{\partial R(t)} \boldsymbol{J}_S\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1}, \tag{3.10}$$

which has the local form

$$\varrho\left(\frac{\partial S}{\partial t}+\boldsymbol{v}\cdot\nabla S\right)+\nabla\cdot\boldsymbol{J}_S\geq 0. \tag{3.11}$$

Here $\boldsymbol{J}_S$ denotes the entropy flux. Using the notion of material derivatives, we obtain our system of balance laws:

$$\begin{aligned}
\mathrm{D}_t\,\varrho &= -\varrho\nabla\cdot\boldsymbol{v}, && (3.12)\\
\varrho\,\mathrm{D}_t\,c_i &= -\nabla\cdot\boldsymbol{J}_i, && (3.13)\\
\varrho\,\mathrm{D}_t\,\boldsymbol{v} &= \nabla\cdot\boldsymbol{T}+\varrho\boldsymbol{k}, && (3.14)\\
\varrho\,\mathrm{D}_t\,E &= -\nabla\cdot\boldsymbol{J}_E+\boldsymbol{T}^\top:\nabla\boldsymbol{v}, && (3.15)
\end{aligned}$$

supplemented by the entropy inequality

$$\varrho\,\mathrm{D}_t\,S\geq-\nabla\cdot\boldsymbol{J}_S. \tag{3.16}$$

The next result is a consequence of the principle of frame independence (cf. Section 1.2):

Theorem 3.2.4. *Assume that the principle of frame independence and the energy balance (3.15) hold. Then the bulk stress tensor $\boldsymbol{T}$ is symmetric, i.e. it suffices*

$$\boldsymbol{T}=\boldsymbol{T}^\top.$$

Proof. Let $\boldsymbol{Q}=\boldsymbol{Q}(t)$ be a rotation in $\mathbb{R}^d$ thus $\boldsymbol{Q}^\top\boldsymbol{Q}=\boldsymbol{I}$ and $\det(\boldsymbol{Q})=1$. Then from $\boldsymbol{x}^\star=\boldsymbol{Q}(t)\boldsymbol{x}$ we obtain $\boldsymbol{v}^\star=\dot{\boldsymbol{Q}}\boldsymbol{x}+\boldsymbol{Q}\boldsymbol{v}$. The transformed bulk fields $\varrho^\star$, $E^\star$, $\boldsymbol{J}_E^\star$ and $\boldsymbol{T}^\star$ must fulfill the energy balance

$$\varrho^\star\left(\frac{\partial E^\star}{\partial t}+\boldsymbol{v}^\star\cdot\nabla_{\boldsymbol{x}^\star}E^\star\right)=-\nabla_{\boldsymbol{x}^\star}\cdot\boldsymbol{J}_E^\star+\boldsymbol{T}^\star:\mathrm{D}_{\boldsymbol{x}^\star}\,\boldsymbol{v}^\star,$$

just as the original fields ϱ, E, $\boldsymbol{J}_E$ and $\boldsymbol{T}$. From the principle of frame independence we have

$$E^\star(t,\boldsymbol{x}^\star)=E(t,\boldsymbol{x}),\quad \boldsymbol{J}_E^\star(t,\boldsymbol{x}^\star)=\boldsymbol{Q}\boldsymbol{J}_E(t,\boldsymbol{x}),\ \text{and}\ \boldsymbol{T}^\star(t,\boldsymbol{x}^\star)=\boldsymbol{Q}\boldsymbol{T}(t,\boldsymbol{x})\boldsymbol{Q}^\top$$

as well as

$$\mathrm{D}_{\boldsymbol{x}^\star}\,\boldsymbol{v}^\star=\dot{\boldsymbol{Q}}\boldsymbol{Q}^\top+\boldsymbol{Q}\,\mathrm{D}_{\boldsymbol{x}}\,\boldsymbol{v}\boldsymbol{Q}^\top\ \text{and}\ \mathrm{D}_{\boldsymbol{x}^\star}\,\boldsymbol{J}_E^\star=\boldsymbol{Q}\,\mathrm{D}_{\boldsymbol{x}}\,\boldsymbol{J}_E\boldsymbol{Q}^\top.$$

Then we have $\partial_t E^\star=\partial_t E$ and

$$\begin{aligned}
\nabla_{\boldsymbol{x}^\star}\cdot\boldsymbol{J}_E^\star &= \boldsymbol{I}:\mathrm{D}_{\boldsymbol{x}^\star}\,\boldsymbol{J}_E^\star=\boldsymbol{I}:\boldsymbol{Q}\,\mathrm{D}_{\boldsymbol{x}}\,\boldsymbol{J}_E\boldsymbol{Q}^\top\\
&= \boldsymbol{Q}:\boldsymbol{Q}\,\mathrm{D}_{\boldsymbol{x}}\,\boldsymbol{J}_E=\boldsymbol{I}:\mathrm{D}_{\boldsymbol{x}}\,\boldsymbol{J}_E=\nabla\cdot\boldsymbol{J}_E.
\end{aligned}$$

Since $\boldsymbol{v}$ is *not* an objective field the evaluation of the following equations gives additional terms that lead to restrictions on the stress tensor. Therefore, we consider

$$\begin{aligned}
\boldsymbol{v}^\star\cdot\nabla_{\boldsymbol{x}^\star}E^\star &= (\dot{\boldsymbol{Q}}\boldsymbol{x}+\boldsymbol{Q}\boldsymbol{v})\cdot\boldsymbol{Q}\nabla E\\
&= \boldsymbol{Q}^\top\dot{\boldsymbol{Q}}\boldsymbol{x}\cdot\nabla E+\boldsymbol{v}\cdot\nabla E,
\end{aligned}$$

and for the stress tensor term

$$\begin{aligned} \boldsymbol{T}^\star : \mathrm{D}_{\boldsymbol{x}^\star}\, \boldsymbol{v}^\star &= \boldsymbol{Q}\boldsymbol{T}\boldsymbol{Q}^\top : (\dot{\boldsymbol{Q}} + \boldsymbol{Q}\, \mathrm{D}_{\boldsymbol{x}}\, \boldsymbol{v})\boldsymbol{Q}^\top \\ &= \boldsymbol{T} : \mathrm{D}_{\boldsymbol{x}}\, \boldsymbol{v} + \boldsymbol{Q}\boldsymbol{T} : \dot{\boldsymbol{Q}}. \end{aligned}$$

Thus

$$\boldsymbol{T} : \boldsymbol{Q}^\top \dot{\boldsymbol{Q}} = \boldsymbol{Q}^\top \dot{\boldsymbol{Q}} \boldsymbol{x} \cdot \nabla E$$

has to hold which is

$$(\boldsymbol{T} - \boldsymbol{x} \otimes \nabla E) : \boldsymbol{Q}^\top \dot{\boldsymbol{Q}} = 0$$

for all fields ∇E. In particular, $\boldsymbol{T} : \boldsymbol{Q}^\top \dot{\boldsymbol{Q}} = 0$ must be fulfilled. A short calculation shows that $\boldsymbol{Q}^\top \dot{\boldsymbol{Q}} = -(\boldsymbol{Q}^\top \dot{\boldsymbol{Q}})^\top$. Now fix two distinct indices $i, j \in \{1, \ldots, d\}$ and take $\boldsymbol{Q}$ as the rotation by t in the subspace spanned by the vectors $\boldsymbol{e}_i$ and $\boldsymbol{e}_j$. Let Q_{ij} be the 2×2-submatrix with that entries of $\boldsymbol{Q}$ where the rows i and j meet the columns i and j. Then we have

$$Q_{ij} = \begin{pmatrix} \cos t & \sin t \\ -\sin t & \cos t \end{pmatrix} \text{ and } \dot{Q}_{ij} = \begin{pmatrix} -\sin t & \cos t \\ -\cos t & -\sin t \end{pmatrix},$$

that leads to $\boldsymbol{Q}^\top \dot{\boldsymbol{Q}} = \boldsymbol{e}_i \wedge \boldsymbol{e}_j = \boldsymbol{e}_i \otimes \boldsymbol{e}_j - \boldsymbol{e}_j \otimes \boldsymbol{e}_i$. Then we have $t_{ij} = t_{ji}$ for the i, j-component of the stress tensor $\boldsymbol{T}$.

□

3.3 A multi-component phase field model.

Exploitation of the entropy principle.

In order to obtain phase field type equations which are derived from *free energies including gradients of the phase fields* we include $\nabla \boldsymbol{\phi}$ in the list of variables which we base our *constitutive theory*. Since in classical phase field theories time derivatives of the phase field enter the *entropy inequality* (see [11, 12, 37]) or the *energy balance* (see [33]) we also include the time derivative $\mathrm{D}_t\, \boldsymbol{\phi}$ into the list of variables. Precisely we assume that S, E, $\boldsymbol{T}$, $\boldsymbol{J}_E$, $\boldsymbol{J}_1$, ..., $\boldsymbol{J}_N$ depend on the variables

$$Y = (\varrho, \boldsymbol{c}, \nabla \boldsymbol{c}, \nabla \boldsymbol{v}, T, \nabla T, \boldsymbol{\phi}, \nabla \boldsymbol{\phi}, \mathrm{D}_t\, \boldsymbol{\phi}), \tag{3.17}$$

where T is the absolute temperature. Analogously to the ideas of Liu and Müller (see [61, 66]) we now use the method of *Lagrange multipliers* to derive restrictions on the constitutive relations which are enforced by the entropy inequality. We discuss in Appendix C under which conditions the existence of Lagrange multipliers can be guaranteed such that

$$\begin{aligned} &\varrho\, \mathrm{D}_t\, S + \nabla \cdot \boldsymbol{J}_S - \lambda_E\, (\varrho\, \mathrm{D}_t\, E + \nabla \cdot \boldsymbol{J}_E - \boldsymbol{T} : \nabla \boldsymbol{v}) - \lambda_\varrho\, (\mathrm{D}_t\, \varrho + \varrho \nabla \cdot \boldsymbol{v}) \\ &\quad - \sum_{i=1}^{N} \lambda_{c_i}\, (\varrho\, \mathrm{D}_t\, c_i + \nabla \cdot \boldsymbol{J}_i) - \lambda_{\boldsymbol{v}} \cdot (\varrho\, \mathrm{D}_t\, \boldsymbol{v} - \nabla \cdot \boldsymbol{T} - \boldsymbol{k}) \geq 0 \end{aligned} \tag{3.18}$$

holds for all fields $(\varrho, \boldsymbol{c}, \boldsymbol{v}, T, \boldsymbol{\phi})$. In particular we do not need to require that the balance laws (3.12)-(3.15) hold. In the following we will assume that $\lambda_E = \frac{1}{T}$ which can be obtained by an appropriate normalization of the temperature (see Alt and Pawlow [4] or arguments according to Müller, see [66, pp.16,184]). We now define the *free energy*

$$F = E - TS.$$

Then we obtain from (3.18) after *multiplying by* $-T$:

$$\begin{aligned}\varrho \,\mathrm{D}_t\, F + \nabla \cdot (\boldsymbol{J}_E - T\boldsymbol{J}_S) + \varrho S \,\mathrm{D}_t\, T + \boldsymbol{J}_S \cdot \nabla T - \boldsymbol{T} : \nabla \boldsymbol{v} + T\lambda_\varrho \left(\mathrm{D}_t\, \varrho + \varrho \nabla \cdot \boldsymbol{v}\right) \\ + T \sum_{i=1}^{N} \lambda_{c_i} \left(\varrho \,\mathrm{D}_t\, c_i + \nabla \cdot \boldsymbol{J}_i\right) + T\lambda_{\boldsymbol{v}} \cdot \left(\varrho \,\mathrm{D}_t\, \boldsymbol{v} - \nabla \cdot \boldsymbol{T} - \boldsymbol{k}\right) \leq 0. \quad (3.19)\end{aligned}$$

Using the chain rule for material derivatives we derive

$$\begin{aligned}\varrho \left(F_{,\varrho} + \frac{\lambda_\varrho}{\varrho} T\right) \mathrm{D}_t\, \varrho + \varrho \left(F_{,T} + S\right) \mathrm{D}_t\, T + \varrho F_{,\nabla T} \cdot \mathrm{D}_t\, \nabla T + \varrho \left(F_{,\boldsymbol{c}} + T\lambda_{\boldsymbol{c}}\right) \cdot \mathrm{D}_t\, \boldsymbol{c} \\ + \varrho \left(F_{,\nabla \boldsymbol{c}} : \mathrm{D}_t\, \nabla \boldsymbol{c} + F_{,\nabla \boldsymbol{v}} : \mathrm{D}_t\, \nabla \boldsymbol{v} + F_{,\boldsymbol{\phi}} \cdot \mathrm{D}_t\, \boldsymbol{\phi} + F_{,\nabla \boldsymbol{\phi}} : \mathrm{D}_t\, \nabla \boldsymbol{\phi} + F_{,\mathrm{D}_t\, \boldsymbol{\phi}} \cdot \mathrm{D}_t^2\, \boldsymbol{\phi}\right) \\ + \nabla \cdot (\boldsymbol{J}_E - T\boldsymbol{J}_S) + \boldsymbol{J}_S \cdot \nabla T - \boldsymbol{T} : \nabla \boldsymbol{v} + T\lambda_\varrho \varrho \nabla \cdot \boldsymbol{v} \\ + T \sum_{i=1}^{N} \lambda_{c_i} \nabla \cdot \boldsymbol{J}_i + T\lambda_{\boldsymbol{v}} \cdot \left(\varrho \,\mathrm{D}_t\, \boldsymbol{v} - \nabla \cdot \boldsymbol{T} - \boldsymbol{k}\right) \leq 0,\end{aligned}$$

where $F_{,T}$, $F_{,\nabla T}$ etc. denote the derivatives with respect to variables corresponding to T, ∇T etc. Since this inequality has to hold *for all fields* with $\boldsymbol{c} \in \Sigma^N$ and $\boldsymbol{\phi} \in \Sigma^M$ we obtain that the terms appearing linear will vanish. Hence we obtain

$$\begin{aligned}\lambda_\varrho &= -\frac{\varrho F_{,\varrho}}{T}, \\ S &= -F_{,T}, \\ F_{,\nabla T} &= 0, \\ \boldsymbol{\Pi}^N \lambda_{\boldsymbol{c}} &= -\frac{1}{T} \boldsymbol{\Pi}^N F_{,\boldsymbol{c}}, \\ \boldsymbol{\Pi}^N F_{,\nabla \boldsymbol{c}} &= 0, \\ F_{,\nabla \boldsymbol{v}} &= 0, \\ \boldsymbol{\Pi}^M F_{,\mathrm{D}_t\, \boldsymbol{\phi}} &= 0, \\ \lambda_{\boldsymbol{v}} &= 0,\end{aligned}$$

where $\boldsymbol{\Pi}^K$ is the projection on $T\Sigma^K$ and for a matrix $A = (A_{ij})_{i=1,\ldots,K,\, j=1,\ldots,d}$ we define

$$\left(\boldsymbol{\Pi}^K A\right)_{ij} = a_{ij} - \frac{1}{K} \sum_{k=1}^{K} a_{kj},$$

for $K \in \{M, N\}$.

Using the commutator rule and defining the *chemical potentials* $\boldsymbol{\mu}' = \boldsymbol{\Pi}^N F_{,\boldsymbol{c}}$ as well as $\boldsymbol{\mu} = (-1, \boldsymbol{\mu}')$ it yields the inequality

$$\begin{aligned}\varrho\left(F_{,\boldsymbol{\phi}} \cdot \mathrm{D}_t\,\boldsymbol{\phi} + F_{,\nabla\boldsymbol{\phi}} : \nabla\,\mathrm{D}_t\,\boldsymbol{\phi}\right) - \left(\boldsymbol{T} + F_{,\varrho}\varrho^2\boldsymbol{I} + F_{,\nabla\boldsymbol{\phi}} \otimes \nabla\boldsymbol{\phi}\right) : \nabla\boldsymbol{v}\\ +\nabla\cdot\left(\boldsymbol{J}_E - T\boldsymbol{J}_S - \sum_{i=1}^N \mu_i\boldsymbol{J}_i\right) + \boldsymbol{J}_S\cdot\nabla T + \sum_{i=1}^N \boldsymbol{J}_i\cdot\nabla\mu_i \le 0,\end{aligned}$$

where we have set $F_{,\nabla\boldsymbol{\phi}} \otimes \nabla\boldsymbol{\phi} = \sum_{i=1}^M F_{,\nabla\phi_i} \otimes \nabla\phi_i$. For simplicity we set $\boldsymbol{S} = \boldsymbol{T} + F_{,\varrho}\varrho^2\boldsymbol{I} + F_{,\nabla\boldsymbol{\phi}} \otimes \nabla\boldsymbol{\phi}$ and after elementary calculations we obtain

$$\begin{aligned}(\varrho F_{,\boldsymbol{\phi}} - \nabla\cdot(\varrho F_{,\nabla\boldsymbol{\phi}}))\cdot\mathrm{D}_t\,\boldsymbol{\phi} - \boldsymbol{S} : \nabla\boldsymbol{v} + \boldsymbol{J}_S\cdot\nabla T + \sum_{i=1}^N \boldsymbol{J}_i\cdot\nabla\mu_i +\\ \nabla\cdot\left(\boldsymbol{J}_E - T\boldsymbol{J}_S - \sum_{i=1}^N \mu_i\boldsymbol{J}_i + \varrho F_{,\nabla\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi}\right) \le 0.\end{aligned} \tag{3.20}$$

Since $\boldsymbol{\Pi}^M F_{,\mathrm{D}_t\,\boldsymbol{\phi}} = 0$ we have

$$0 = \left(\boldsymbol{\Pi}^M F_{,\mathrm{D}_t\,\boldsymbol{\phi}}\right)_{,c_i} = \boldsymbol{\Pi}^M F_{,c_i,\mathrm{D}_t\,\boldsymbol{\phi}}.$$

Hence $\boldsymbol{\Pi}^M \mu_{i,\mathrm{D}_t\,\boldsymbol{\phi}} = 0$ and $\mu_{i,\mathrm{D}_t\,\boldsymbol{\phi}}\cdot\partial_{x_k}\,\mathrm{D}_t\,\boldsymbol{\phi} = 0$, and then $\nabla\boldsymbol{\mu}$ does not depend on $\nabla\,\mathrm{D}_t\,\boldsymbol{\phi}$. In order to obtain a model with $F_{,\nabla\boldsymbol{\phi}} \neq 0$ we need that

$$\boldsymbol{J} = \boldsymbol{J}_E - T\boldsymbol{J}_S - \sum_{i=1}^N \mu_i\boldsymbol{J}_i$$

depends on $\mathrm{D}_t\,\boldsymbol{\phi}$. We do not aim to derive the most general models and hence we assume that $\boldsymbol{J}$ is *affine linear* in $\mathrm{D}_t\,\boldsymbol{\phi}$ (see also [3]), i.e.

$$\boldsymbol{J} = \boldsymbol{J}^1 + \boldsymbol{J}^2\,\mathrm{D}_t\,\boldsymbol{\phi}$$

where $\boldsymbol{J}^1$, $\boldsymbol{J}^2$ do not depend on $\mathrm{D}_t\,\boldsymbol{\phi}$. Then we obtain

$$\boldsymbol{J}^2 = -\varrho F_{,\nabla\boldsymbol{\phi}}.$$

We assume the representation

$$\begin{aligned}\boldsymbol{J}_E &= \boldsymbol{J}_E^1 + \boldsymbol{J}_E^2\,\mathrm{D}_t\,\boldsymbol{\phi},\\ \boldsymbol{J}_S &= \boldsymbol{J}_S^1 + \boldsymbol{J}_S^2\,\mathrm{D}_t\,\boldsymbol{\phi},\\ \boldsymbol{J}_i &= \boldsymbol{J}_i^1 + \boldsymbol{J}_i^2\,\mathrm{D}_t\,\boldsymbol{\phi},\ i = 1,\ldots,N,\end{aligned}$$

where $\boldsymbol{J}_E^1$, $\boldsymbol{J}_E^2$, $\boldsymbol{J}_S^1$, $\boldsymbol{J}_S^2$, $\boldsymbol{J}_i^1$, $\boldsymbol{J}_i^2$, $(i = 1,\ldots,N)$ do not depend on $\mathrm{D}_t\,\boldsymbol{\phi}$. Hence we obtain

$$\begin{aligned}\left(\varrho F_{,\boldsymbol{\phi}} - \nabla\cdot(\varrho F_{,\nabla\boldsymbol{\phi}}) + \sum_{i=1}^N \nabla\mu_i\boldsymbol{J}_i^2 + \nabla T\boldsymbol{J}_S^2\right)\cdot\mathrm{D}_t\,\boldsymbol{\phi}\\ -\boldsymbol{S} : \nabla\boldsymbol{v} + \nabla\cdot\boldsymbol{J}^1 + \sum_{i=1}^N \nabla\mu_i\cdot\boldsymbol{J}_i^1 + \nabla T\cdot\boldsymbol{J}_S^1 \le 0.\end{aligned}$$

Suppose that the fluxes for $\mathrm{D}_t\,\boldsymbol{\phi}$ have the standard form, i.e. $\boldsymbol{J}^1 = 0$ that is

$$\boldsymbol{J}_S^1 = \frac{1}{T}\boldsymbol{J}_E^1 - \sum_{i=1}^{N} \frac{\mu_i}{T} \cdot \boldsymbol{J}_i^1.$$

Then we obtain

$$\left(\varrho F_{,\boldsymbol{\phi}} - \nabla \cdot (\varrho F_{,\nabla\boldsymbol{\phi}}) + \sum_{i=1}^{N} \nabla\mu_i \boldsymbol{J}_i^2 + \nabla T \boldsymbol{J}_S^2 \right) \cdot \mathrm{D}_t\,\boldsymbol{\phi} \tag{3.21}$$
$$-\boldsymbol{S} : \nabla\boldsymbol{v} + T \sum_{i=1}^{N} \nabla\frac{\mu_i}{T} \cdot \boldsymbol{J}_i^1 - T\nabla\frac{1}{T} \cdot \boldsymbol{J}_E^1 \leq 0,$$

and this inequality must be fulfilled for all values of $\mathrm{D}_t\,\boldsymbol{\phi}$, $\nabla\boldsymbol{v}$, $\nabla\frac{\mu_0}{T}, \ldots, \nabla\frac{\mu_N}{T}$ where $\mu_0 = -1$. If we define $\frac{\boldsymbol{\mu}}{T} = (\frac{\mu_0}{T}, \ldots, \frac{\mu_N}{T})$ and $X = (\mathrm{D}_t\,\boldsymbol{\phi}, \nabla\boldsymbol{v}, \nabla\frac{\boldsymbol{\mu}}{T})$ inequality (3.21) admits the abstract form $-A(X) \cdot X \leq 0$ which has to hold for all tuples $X \in \Sigma^M \times \mathbb{R}^{(d\times d)\times((N+1)\times d)}$ where M denotes the number of phases. Then by Theorem 2 from Appendix B applied to (3.21) yields that there exist functions

$$\begin{aligned}
A_1(Y') : \Sigma^M &\to \mathbb{R}^M, \\
A_2(Y') : \mathbb{R}^{d\times d} &\to \mathbb{R}^M, \\
A_3(Y') : \mathbb{R}^{(N+1)\times d} &\to \mathbb{R}^M, \\
B_1(Y') : \Sigma^M &\to \mathbb{R}^{d\times d}, \\
B_2(Y') : \mathbb{R}^{d\times d} &\to \mathbb{R}^{d\times d}, \\
B_3(Y') : \mathbb{R}^{(N+1)\times d} &\to \mathbb{R}^{d\times d}, \\
C_1(Y') : \Sigma^M &\to \mathbb{R}^{(N+1)\times d}, \\
C_2(Y') : \mathbb{R}^{d\times d} &\to \mathbb{R}^{(N+1)\times d}, \\
C_3(Y') : \mathbb{R}^{(N+1)\times d} &\to \mathbb{R}^{(N+1)\times d},
\end{aligned}$$

which are linear for all tuples $Y' = \left(\varrho, \boldsymbol{c}, \nabla\boldsymbol{c}, \nabla\boldsymbol{v}, T, \nabla T, \boldsymbol{\phi}, \nabla\boldsymbol{\phi}, \mathrm{D}_t\,\boldsymbol{\phi}, \nabla\frac{\boldsymbol{\mu}}{T}\right)$ and these functions fulfill

$$\nabla \cdot (\varrho F_{,\nabla\boldsymbol{\phi}}) - \varrho F_{,\boldsymbol{\phi}} - \boldsymbol{J}_S^2 \cdot \nabla T - \sum_{i=1}^{N} \boldsymbol{J}_i^2 \cdot \nabla\mu_i = A_1\,\mathrm{D}_t\,\boldsymbol{\phi} + A_2\nabla\boldsymbol{v} + A_3\nabla\frac{\boldsymbol{\mu}}{T}, \tag{3.22}$$
$$\boldsymbol{S} = B_1\,\mathrm{D}_t\,\boldsymbol{\phi} + B_2\nabla\boldsymbol{v} + B_3\nabla\frac{\boldsymbol{\mu}}{T}, \tag{3.23}$$
$$(\boldsymbol{J}_E^1, \boldsymbol{J}_1^1, \ldots, \boldsymbol{J}_N^1) = C_1\,\mathrm{D}_t\,\boldsymbol{\phi} + C_2\nabla\boldsymbol{v} + C_3\nabla\frac{\boldsymbol{\mu}}{T}, \tag{3.24}$$

for all tuples $(\mathrm{D}_t\,\boldsymbol{\phi}, \nabla\boldsymbol{v}, \nabla\frac{\boldsymbol{\mu}}{T})$ again. By Theorem 2 from Appendix B the matrix

$$\begin{pmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{pmatrix}$$

is positive semidefinite on an appropriate subspace. Equation (3.22) gives a relation between thermodynamical driving forces on the left hand side and the derivatives of $\boldsymbol{\phi}$, $\boldsymbol{v}$, $\frac{\boldsymbol{\mu}}{T}$ on the right hand side. It turns out that (3.22) is a generalized phase field equation. Equations (3.23) and (3.24) give very general representations of $\boldsymbol{S}$ and the fluxes $\boldsymbol{J}_E$, $\boldsymbol{J}_1, \ldots, \boldsymbol{J}_N$ in terms of the quantities $\mathrm{D}_t\,\boldsymbol{\phi}$, $\nabla\boldsymbol{v}$ and $\nabla\frac{\boldsymbol{\mu}}{T}$ where the functions B_i and C_i may depend on Y' for $i \in \{1,2,3\}$. The following example shows that the usual choices for the phase field equations, the tensors and fluxes are special cases of (3.22)-(3.24).

Example.

Though the form of A_i, B_i and C_i, ($i \in \{1,2,3\}$) follows from Theorem 2 of Appendix B we assume that we can choose these functions. We assume that A_2, A_3, B_1, B_3, C_1, C_2 are equal to zero. Furthermore let

$$\begin{aligned} A_1(X) &= \beta(X)TI, \\ B_2(X)\nabla\boldsymbol{v} &= 2\nu\boldsymbol{E} + \lambda\,\mathrm{tr}(\boldsymbol{E})\boldsymbol{I}, \\ \boldsymbol{e}_l C_3(X)\boldsymbol{e}_m &= -(L_{ij})_{ij=0}^{N}, \text{ for all } l,\ m \in \{1,\ldots,d\}, \end{aligned}$$

with positive $\beta \in \mathbb{R}$ as well as $2\boldsymbol{E} = \nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T$ and appropriately chosen $\nu = \nu(T,\boldsymbol{\phi})$, $\lambda = \lambda(T,\boldsymbol{\phi}) \in \mathbb{R}$ such that $\boldsymbol{S}$ becomes a positive definite tensor. Finally let $(L_{ij}(T,\boldsymbol{c},\boldsymbol{\phi}))_{i,j=0}^{N}$ be a symmetric and positive semidefinite matrix with $\sum_{i=1}^{N} L_{ij} = 0$ as well as $\boldsymbol{J}_S^2 = \boldsymbol{J}^2$ and $\boldsymbol{J}_i^2 = 0$ for $i = 1,\ldots,N$. Then we extract the following equations:

$$\beta\,\mathrm{D}_t\,\boldsymbol{\phi} = \nabla\cdot\left(\frac{\varrho}{T}F_{,\nabla\boldsymbol{\phi}}\right) - \frac{\varrho}{T}F_{,\boldsymbol{\phi}}, \tag{3.25}$$

$$\begin{aligned} \boldsymbol{J}_i &= \sum_{j=0}^{N} L_{ij}\nabla\frac{-\mu_j}{T}, \\ \boldsymbol{J}_S &= \frac{1}{T}\boldsymbol{J}_E - \sum_{i,j=1}^{N}\frac{\mu_i}{T}L_{ij}\nabla\frac{-\mu_j}{T} + \frac{\varrho F_{,\nabla\boldsymbol{\phi}}}{T}\,\mathrm{D}_t\,\boldsymbol{\phi}. \end{aligned} \tag{3.26}$$

Then we derive from (3.21) that

$$-\beta T\left(\mathrm{D}_t\,\boldsymbol{\phi}\right)^2 - \boldsymbol{S} : \nabla\boldsymbol{v} - T\sum_{i,j=0}^{N}\nabla\frac{\mu_i}{T}L_{ij}\nabla\frac{\mu_j}{T} \le 0$$

holds. Thus the entropy inequality (3.11) holds.

Relation to other models.

Now we relate our model to other convective phase-field models, especially the model derived by Anderson, McFadden and Wheeler, cf. [6] and the one derived by Blesgen, cf. [11]. Since these models concern substances constituted by a single species we can drop the concentrations.

Besides both models follow from the general theory discussed in Section 3.2. Especially, as in the previous example we assume the tensor $\boldsymbol{S}$ to have classical form, i.e.

$$\boldsymbol{S} = 2\nu\boldsymbol{E} + \lambda \mathrm{tr}(\boldsymbol{E})\boldsymbol{I}, \tag{3.27}$$

with $\nu,\ \lambda \in \mathbb{R}$ such that $\boldsymbol{S}$ is positive definite. The balance equations for mass, momentum and energy used in [6, 11, 12] are the classical relations which we have also used in Section 3.2, cf. equations (3.3), (3.5) and (3.7).

Relation to the model of Blesgen.

This model studied in [11] allows for a system of *two pure phases* constituted by *two compressible fluids* having *isotropic* surface energies. To derive this model from our general one we assume that the balance laws (3.3), (3.5) and (3.7) are fulfilled where outer forces $\boldsymbol{k}$ are neglected. The stress tensor is assumed of the form

$$\boldsymbol{T} = \boldsymbol{S} - p\boldsymbol{I} - \delta\varrho T\nabla\boldsymbol{\phi}\otimes\nabla\boldsymbol{\phi},$$

where $\boldsymbol{S} = \nu\boldsymbol{E} + \lambda\,\mathrm{tr}(\boldsymbol{E})\boldsymbol{I}$ and $\boldsymbol{E} = \frac{1}{2}\left(\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^{\top}\right)$. Here $\sqrt{\delta}$ denotes the thickness of the transition layer. In a standard manner the flux of internal energy is set to

$$\boldsymbol{J}_E = -L\nabla T,$$

where $L > 0$ denotes the (scalar) thermal diffusivity. With these assumptions the balance laws (3.3), (3.5) and (3.7) become

$$\begin{aligned}
\partial_t\varrho &= -\nabla\cdot(\varrho\boldsymbol{v}),\\
\partial_t(\varrho\boldsymbol{v}) &= -\nabla\cdot(\varrho\boldsymbol{v}\otimes\boldsymbol{v} + \delta\varrho T\nabla\boldsymbol{\phi}\otimes\nabla\boldsymbol{\phi}) + \nabla\cdot\boldsymbol{S} - \nabla p,\\
\partial_t\tilde{E} &= \nabla\cdot\left(L\nabla T - \tilde{E}\boldsymbol{v} + \boldsymbol{T}\boldsymbol{v}\right),
\end{aligned}$$

as proposed in [11] where $\tilde{E} = \varrho\left(E + \frac{1}{2}|\boldsymbol{v}|^2\right)$ and p is the pressure. We now set the free energy density to be

$$F(\varrho, T, \boldsymbol{\phi}, \nabla\boldsymbol{\phi}) = T\left(\frac{\delta}{2}|\nabla\boldsymbol{\phi}|^2 + J(T, \varrho, \boldsymbol{\phi})\right),$$

where J denotes the thermodynamical driving force given by

$$J(T, \varrho, \boldsymbol{\phi}) = W(\boldsymbol{\phi}) + \frac{1}{T}\left(\phi_1 G_1(\varrho, T) + \phi_2 G_2(\varrho, T)\right). \tag{3.28}$$

Here $W : \Sigma^2 \to \mathbb{R}$ is a logarithmic potential given by

$$W(\boldsymbol{\phi}) = \phi_1\ln\phi_1 + \phi_2\ln\phi_2 = \phi_1\ln\phi_1 + (1-\phi_1)\ln(1-\phi_1).$$

The second term in (3.28) is a weighted average of the Gibbs energy densities G_1 and G_2 of every pure phase multiplied by $\frac{1}{T}$. In addition, the entropy flux is supposed to be

$$\boldsymbol{J}_S = \frac{1}{T}\boldsymbol{J}_E + \frac{\delta\varrho}{T}\nabla\boldsymbol{\phi}\,\mathrm{D}_t\,\boldsymbol{\phi}.$$

To obtain the phase field equation we choose A_i, B_i and C_i in (3.22)-(3.24) as in the example after these equations, i.e. A_2, A_3, B_1, B_3, C_1, C_2 are equal to zero. With $\beta = \varepsilon\varrho$ we obtain from (3.25) the phase field equation as presented in [11], e.g.

$$\varepsilon \, \mathrm{D}_t \, \boldsymbol{\phi} = \left(\frac{1}{\varrho} \nabla \cdot (\varrho \delta \nabla \boldsymbol{\phi}) - J_{,\boldsymbol{\phi}}(T, \varrho, \boldsymbol{\phi}) \right),$$

where ε is a kinetic coefficient related to the interfacial layer.

Relation to the model of Anderson, McFadden and Wheeler.

As already mentioned this model has been discussed elaborately in [6, 7]. This model describes *two phase* systems of *pure materials* which may have *anisotropic* surface energies. In these papers the $\boldsymbol{\xi}$-vector technique is used, defining the $\boldsymbol{\xi}$-vector by $\boldsymbol{\xi} = \Gamma_{,p}(p)$ with a gradient energy density $(\Gamma(\nabla\boldsymbol{\phi}))^2$ as part of the free energy F. This approach generalizes the ideas of Cahn and Hoffman (cf. [17, 18]). If we set $2a(\nabla\boldsymbol{\phi}) = (\Gamma(\nabla\boldsymbol{\phi}))^2$ we have $a_{,p}(p) = \Gamma(p)\Gamma_{,p}(p) = \Gamma(p)\boldsymbol{\xi}$. Hence there is a straightforward relation between the gradient energy densities $a(\nabla\boldsymbol{\phi})$ of Chapter 2 and the quantity Γ^2. Then it is possible to rewrite the leading order term $\nabla \cdot (a_{,p}(p)) = \nabla \cdot (\boldsymbol{\xi}\, \Gamma(p))$ as done in [6, 7]. For brevity we will write Γ^2 for $\Gamma^2(\nabla\boldsymbol{\phi})$ and $\Gamma\boldsymbol{\xi}$ for $\Gamma(\nabla\boldsymbol{\phi})\Gamma_{,p}(\nabla\boldsymbol{\phi})$. With this notation Anderson, McFadden and Wheeler derive the following balance laws:

$$\begin{aligned}
\mathrm{D}_t \, \varrho &= -\varrho \nabla \cdot \boldsymbol{v}, && (3.29)\\
\varrho \, \mathrm{D}_t \, \boldsymbol{v} &= \nabla \cdot \left(\left(-p + \tfrac{1}{2}\varepsilon_F^2 \Gamma^2 \right) \boldsymbol{I} - \varepsilon_F^2 \Gamma \boldsymbol{\xi} \otimes \nabla\boldsymbol{\phi} + \boldsymbol{S} \right), && (3.30)\\
\varrho \, \mathrm{D}_t \, e &= \nabla \cdot (k \nabla T) + \varepsilon_E^2 \nabla \cdot (\Gamma\boldsymbol{\xi}) \, \mathrm{D}_t \, \boldsymbol{\phi} && (3.31)\\
&+ \left(\left(-p + \tfrac{1}{2}\varepsilon_S^2 T \Gamma^2 \right) \boldsymbol{I} - T\varepsilon_S^2 \Gamma \boldsymbol{\xi} \otimes \nabla\boldsymbol{\phi} + \boldsymbol{S} \right) : \nabla \boldsymbol{v}, \\
\beta \, \mathrm{D}_t \, \boldsymbol{\phi} &= \varepsilon_F^2 \nabla \cdot (\Gamma\boldsymbol{\xi}) - \varrho e_{,\boldsymbol{\phi}}. && (3.32)
\end{aligned}$$

Here, as before, ϱ is the mass density, $\boldsymbol{v}$ the fluid velocity, p the pressure, T the temperature, e the internal energy without interfacial terms. In addition let $\boldsymbol{S} = 2\nu\boldsymbol{E} + \lambda \, \mathrm{tr}(\boldsymbol{E})\boldsymbol{I}$ positive semidefinite where $2\boldsymbol{E} = \nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^\top$. The quantity k is a positive constant and ε_E, $\varepsilon_S > 0$ are small constant parameters related to the interface thickness where $\varepsilon_F^2 = \varepsilon_E^2 + T\varepsilon_S^2$. Equation (3.29) is already (3.12) of our model. To obtain (3.30) we set

$$\boldsymbol{T} = \boldsymbol{S} + \left(-p + \tfrac{1}{2}\varepsilon_F^2 \Gamma^2 \right) \boldsymbol{I} - \varepsilon_F^2 \Gamma \boldsymbol{\xi} \otimes \nabla\boldsymbol{\phi}, \tag{3.33}$$

as in [6]. Then (3.14) without volume forces $\boldsymbol{k}$ becomes (3.30).

To obtain (3.31) and (3.32) we assume that the densities of internal energy E and entropy S in (3.15) and (3.16) have the form

$$E = e + \frac{\varepsilon_E^2}{2\varrho}\Gamma^2 \text{ and } S = s - \frac{\varepsilon_S^2}{2\varrho}\Gamma^2, \tag{3.34}$$

where e and s denote bulk densities without interfacial contributions. We define the free energy f as $f = e - Ts$. Furthermore, we assume the energy flux $\boldsymbol{J}_E$ and the entropy flux $\boldsymbol{J}_S$ to be

$$\boldsymbol{J}_S = -\frac{k}{T}\nabla T + \varepsilon_S^2 \Gamma \boldsymbol{\xi}\, \mathrm{D}_t\, \boldsymbol{\phi} \text{ and } \boldsymbol{J}_E = -k\nabla T - \varepsilon_E^2 \Gamma \boldsymbol{\xi}\, \mathrm{D}_t\, \boldsymbol{\phi}. \tag{3.35}$$

To derive (3.31) we consider $\frac{\mathrm{d}}{\mathrm{d}t}\int_R \varrho E \,\mathrm{d}\boldsymbol{x}$ which is $\frac{\mathrm{d}}{\mathrm{d}t}\int_R \left(\varrho e + \frac{1}{2}\varepsilon_E^2\Gamma^2\right)\,\mathrm{d}\boldsymbol{x}$ by use of (3.34). Hence, thanks to the mass balance (3.12) and Reynold's transport theorem,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_R \left(\varrho e + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\right)\,\mathrm{d}\boldsymbol{x} &= \int_R \left(\partial_t\left(\varrho e + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\right) + \nabla\cdot\left(\varrho e\boldsymbol{v} + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\boldsymbol{v}\right)\right)\mathrm{d}\boldsymbol{x}\\ &= \int_R \left(\varrho\,\mathrm{D}_t\, e + \tfrac{1}{2}\varepsilon_E^2\,\mathrm{D}_t\left(\Gamma^2\right) + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\nabla\cdot\boldsymbol{v}\right)\mathrm{d}\boldsymbol{x}\end{aligned}$$

holds. Then we have

$$\begin{aligned}\varrho\,\mathrm{D}_t\, E &= \varrho\,\mathrm{D}_t\, e + \tfrac{1}{2}\varepsilon_E^2\,\mathrm{D}_t\left(\Gamma^2\right) + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\nabla\cdot\boldsymbol{v}\\ &= \varrho\,\mathrm{D}_t\, e + \varepsilon_E^2\Gamma\boldsymbol{\xi}\,\mathrm{D}_t\,\nabla\boldsymbol{\phi} + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\boldsymbol{I} : \nabla\boldsymbol{v}.\end{aligned}$$

On the other hand,

$$\begin{aligned}-\nabla\cdot\boldsymbol{J}_E &= \nabla\cdot(k\nabla T) + \nabla\cdot\left(\varepsilon_E^2\Gamma\boldsymbol{\xi}\right)\mathrm{D}_t\,\boldsymbol{\phi} + \varepsilon_E^2\Gamma\boldsymbol{\xi}\nabla\,\mathrm{D}_t\,\boldsymbol{\phi}\\ &= \nabla\cdot(k\nabla T) + \varepsilon_E^2\nabla\cdot(\Gamma\boldsymbol{\xi})\,\mathrm{D}_t\,\boldsymbol{\phi} + \varepsilon_E^2\Gamma\boldsymbol{\xi}\,\mathrm{D}_t\,\nabla\boldsymbol{\phi} + \varepsilon_E^2\Gamma\boldsymbol{\xi} : (\nabla\boldsymbol{v})^\top\nabla\boldsymbol{\phi}\\ &= \nabla\cdot(k\nabla T) + \varepsilon_E^2\nabla\cdot(\Gamma\boldsymbol{\xi})\,\mathrm{D}_t\,\boldsymbol{\phi} + \varepsilon_E^2\Gamma\boldsymbol{\xi}\,\mathrm{D}_t\,\nabla\boldsymbol{\phi} + \varepsilon_E^2\Gamma\boldsymbol{\xi}\otimes\nabla\boldsymbol{\phi} : \nabla\boldsymbol{v},\end{aligned}$$

after we have used the commutator rule for material derivatives. Now we consider

$$\begin{aligned}\varrho\,\mathrm{D}_t\, E + \nabla\cdot\boldsymbol{J}_E &= \varrho\,\mathrm{D}_t\, e + \varepsilon_E^2\Gamma\boldsymbol{\xi}\,\mathrm{D}_t\,(\nabla\boldsymbol{\phi}) + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\boldsymbol{I} : \nabla\boldsymbol{v} - \nabla\cdot(k\nabla T)\\ &- \varepsilon_E^2\nabla\cdot(\Gamma\boldsymbol{\xi})\,\mathrm{D}_t\,\boldsymbol{\phi} - \varepsilon_E^2\Gamma\boldsymbol{\xi}\,\mathrm{D}_t\,\nabla\boldsymbol{\phi} - \varepsilon_E^2\Gamma\boldsymbol{\xi}\otimes\nabla\boldsymbol{\phi} : \nabla\boldsymbol{v}\\ &= \varrho\,\mathrm{D}_t\, e - \nabla\cdot(k\nabla T) + \tfrac{1}{2}\varepsilon_E^2\Gamma^2\boldsymbol{I} : \nabla\boldsymbol{v}\\ &- \varepsilon_E^2\nabla\cdot(\Gamma\boldsymbol{\xi})\,\mathrm{D}_t\,\boldsymbol{\phi} - \varepsilon_E^2\Gamma\boldsymbol{\xi}\otimes\nabla\boldsymbol{\phi} : \nabla\boldsymbol{v},\end{aligned} \tag{3.36}$$

and using $\varepsilon_F^2 = \varepsilon_E^2 + T\varepsilon_S^2$ we infer

$$\begin{aligned}\boldsymbol{T} : \nabla\boldsymbol{v} &= \boldsymbol{S} : \nabla\boldsymbol{v} + \left(-p + \tfrac{1}{2}T\varepsilon_S^2\Gamma^2\right)\boldsymbol{I} : \nabla\boldsymbol{v} - T\varepsilon_S^2\Gamma\boldsymbol{\xi}\otimes\nabla\boldsymbol{\phi} : \nabla\boldsymbol{v}\\ &+ \tfrac{1}{2}\varepsilon_E^2\Gamma^2\boldsymbol{I} : \nabla\boldsymbol{v} - \varepsilon_E^2\Gamma\boldsymbol{\xi}\otimes\nabla\boldsymbol{\phi} : \nabla\boldsymbol{v}.\end{aligned} \tag{3.37}$$

Using (3.36) and (3.37) equation (3.31) follows from (3.15) where $\boldsymbol{k}$ was assumed to be 0.

To derive the phase field equation from the entropy principle we rewrite (3.31) as

$$\varrho\,\mathrm{D}_t\, e = \boldsymbol{T} : \nabla\boldsymbol{v} - \tfrac{1}{2}\varepsilon_E^2\,\mathrm{D}_t\left(\Gamma^2\right) - \tfrac{1}{2}\varepsilon_E^2\Gamma^2\nabla\cdot\boldsymbol{v} - \nabla\cdot\boldsymbol{J}_E$$

as well as the entropy inequality

$$\varrho T\,\mathrm{D}_t\, s - \tfrac{1}{2}\varepsilon_S^2 T\,\mathrm{D}_t\left(\Gamma^2\right) - \tfrac{1}{2}\varepsilon_S^2 T\Gamma^2\nabla\cdot\boldsymbol{v} + T\nabla\cdot\boldsymbol{J}_S \geq 0. \tag{3.38}$$

We now employ the Gibbs identity (cf. [6])

$$\mathrm{D}_t\, e = T\,\mathrm{D}_t\, s + f_{,\varrho}\,\mathrm{D}_t\,\varrho + e_{,\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi},$$

to obtain for the left hand side of (3.38)

$$\begin{aligned}
& \varrho\,\mathrm{D}_t\, e - \varrho f_{,\varrho}\,\mathrm{D}_t\,\varrho - \varrho e_{,\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi} - \tfrac{1}{2}\varepsilon_S^2 T\,\mathrm{D}_t\left(\Gamma^2\right) - \tfrac{1}{2}\varepsilon_S^2 T\Gamma^2\nabla\cdot\boldsymbol{v} + T\nabla\cdot\boldsymbol{J}_S \\
= \;& \boldsymbol{T} : \nabla\boldsymbol{v} - \tfrac{1}{2}\varepsilon_F^2\,\mathrm{D}_t\left(\Gamma^2\right) - \tfrac{1}{2}\varepsilon_F^2\Gamma^2\nabla\cdot\boldsymbol{v} - \varrho f_{,\varrho}\,\mathrm{D}_t\,\varrho - \varrho e_{,\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi} \\
+ \;& \nabla\cdot(T\boldsymbol{J}_S - \boldsymbol{J}_E) - \boldsymbol{J}_S\cdot\nabla T \\
= \;& \left(\boldsymbol{T} + \varepsilon_F^2\left(\Gamma\boldsymbol{\xi}\otimes\nabla\boldsymbol{\phi} - \tfrac{1}{2}\Gamma^2\boldsymbol{I}\right)\right) : \nabla\boldsymbol{v} - \varepsilon_F^2\nabla\cdot(\Gamma\boldsymbol{\xi}\,\mathrm{D}_t\,\boldsymbol{\phi}) + \varepsilon_F^2\nabla\cdot(\Gamma\boldsymbol{\xi})\cdot\mathrm{D}_t\,\boldsymbol{\phi} \\
- \;& \varrho f_{,\varrho}\,\mathrm{D}_t\,\varrho - \varrho e_{,\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi} + \nabla\cdot\left(\varepsilon_F^2\Gamma\boldsymbol{\xi}\cdot\mathrm{D}_t\,\boldsymbol{\phi}\right) - \boldsymbol{J}_S\cdot\nabla T,
\end{aligned}$$

after we have used the structure of the fluxes and the commutator rule again. Now, using $p = \varrho^2 f_{,\varrho}$, the mass balance (3.12) and the definition (3.35) of the fluxes the entropy inequality reads

$$\begin{aligned}
0 \;\leq\; & \varrho\,\mathrm{D}_t\, e - \varrho f_{,\varrho}\,\mathrm{D}_t\,\varrho - \varrho e_{,\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi} - \tfrac{1}{2}\varepsilon_S^2 T\,\mathrm{D}_t\left(\Gamma^2\right) - \tfrac{1}{2}\varepsilon_S^2 T\Gamma^2\nabla\cdot\boldsymbol{v} + T\nabla\cdot\boldsymbol{J}_S \\
= \;& (\boldsymbol{S} - p\boldsymbol{I}) : \nabla\boldsymbol{v} + \varepsilon_F^2\nabla\cdot(\Gamma\boldsymbol{\xi})\cdot\mathrm{D}_t\,\boldsymbol{\phi} - \varrho f_{,\varrho}\,\mathrm{D}_t\,\varrho - \varrho e_{,\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi} - \boldsymbol{J}_S\cdot\nabla T \\
+ \;& \Gamma\boldsymbol{\xi}\cdot\nabla(\varepsilon_F^2) \\
= \;& \boldsymbol{S} : \nabla\boldsymbol{v} + \left(\varepsilon_F^2\nabla\cdot(\Gamma\boldsymbol{\xi}) - \varrho e_{,\boldsymbol{\phi}}\right)\cdot\mathrm{D}_t\,\boldsymbol{\phi} + \frac{k}{T}\left|\nabla T\right|^2,
\end{aligned}$$

where we have used $\nabla(\varepsilon_F^2) = \varepsilon_S^2\nabla T$. The entropy inequality is fulfilled, if we state the phase field equation as

$$\beta\,\mathrm{D}_t\,\boldsymbol{\phi} = \varepsilon_F^2\nabla\cdot(\Gamma\boldsymbol{\xi}) - \varrho e_{,\boldsymbol{\phi}},$$

which is just (3.32) where $\beta = \beta(\varrho, T, \boldsymbol{\phi}, \nabla\boldsymbol{\phi}) \geq 0$, and if we assume (3.27) which implies $\boldsymbol{S} : \nabla\boldsymbol{\phi} \geq 0$.

Microforce balance.

Now we aim to derive the *governing equations* by requiring a *balance law* for microforces which has been introduced by Gurtin (see e.g. [33, 46] and the references therein).

In addition to the balance laws discussed in Section 3.2 we consider microforces that act in response to changes in the local distribution of forces. To introduce these forces we need a stress $\boldsymbol{\xi}$ which attains values in

$$T_d(\Sigma^M) = \left\{ \boldsymbol{\zeta} = (\zeta_1, \ldots, \zeta_M)^\top,\ \zeta_i \in \mathbb{R}^d \text{ for all } i, \text{ with } \sum_{i=1}^{M} \zeta_i = \boldsymbol{0} \right\}.$$

With this definition we can state a balance law for microforces that reads

$$\int_{\partial R(t)} \boldsymbol{\xi}\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1} + \int_{R(t)} \boldsymbol{\pi}\,\mathrm{d}\boldsymbol{x} = 0,$$

where $\boldsymbol{\pi} \in \mathbb{R}^M$ stands for *internal microforces*.

In contrast to (3.7) the energy balance is now given as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t)} \varrho\left(E+\frac{|\boldsymbol{v}|^2}{2}\right)\,\mathrm{d}\boldsymbol{x} &= \int_{\partial R(t)} -\boldsymbol{J}_E\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1}+\int_{R(t)}\varrho(\boldsymbol{k}\cdot\boldsymbol{v})\,\mathrm{d}\boldsymbol{x}\\ &+ \int_{\partial R(t)}(\boldsymbol{T}\boldsymbol{v})\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1}+\int_{\partial R(t)}\mathrm{D}_t\,\boldsymbol{\phi}\cdot(\boldsymbol{\xi}\boldsymbol{\nu}_R)\,\mathrm{d}\mathcal{H}^{d-1}\\ &= \int_{\partial R(t)} -\boldsymbol{J}_E\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1}+\int_{R(t)}\varrho(\boldsymbol{k}\cdot\boldsymbol{v})\,\mathrm{d}\boldsymbol{x}\\ &+ \int_{\partial R(t)}(\boldsymbol{T}\boldsymbol{v})\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1}+\int_{\partial R(t)}(\mathrm{D}_t\,\boldsymbol{\phi}\otimes\boldsymbol{\nu}_R):\boldsymbol{\xi}\,\mathrm{d}\mathcal{H}^{d-1},\end{aligned}$$

where we have added a coupling term $\int_{\partial R(t)}\mathrm{D}_t\,\boldsymbol{\phi}\cdot(\boldsymbol{\xi}\boldsymbol{\nu}_R)\,\mathrm{d}\mathcal{H}^{d-1}$ that can be interpreted as the power acting across $\partial R(t)$ due to external configurations next to $\partial R(t)$. In a similar manner $\int_{R(t)}\boldsymbol{\pi}\cdot\mathrm{D}_t\,\boldsymbol{\phi}\,\mathrm{d}\boldsymbol{x}$ describes the lattice forces acting on the atoms. The remaining three terms are classical as in Section 3.2. In addition we postulate that the balance laws (3.12)-(3.15) as well as the entropy inequality (3.16) hold. Furthermore asuume that the variables are given by (3.17). The microforce balance can locally be expressed as

$$\nabla\cdot\boldsymbol{\xi}+\boldsymbol{\pi}=0, \tag{3.39}$$

as well as the energy balance

$$\varrho\,\mathrm{D}_t\,E+\nabla\cdot\left(\boldsymbol{J}_E-\boldsymbol{\xi}^\top\,\mathrm{D}_t\,\boldsymbol{\phi}\right)=\boldsymbol{T}:\nabla\boldsymbol{v}.$$

The quantity $\boldsymbol{J}_E-\boldsymbol{\xi}^\top\,\mathrm{D}_t\,\boldsymbol{\phi}$ can be interpreted as a *generalized heat flux*. In the approach of Gurtin it is now assumed that the entropy flux is given as

$$\boldsymbol{J}_S=\frac{1}{T}\boldsymbol{J}_E-\sum_{i=1}^N\frac{\mu_i}{T}\boldsymbol{J}_i.$$

The exploitation of the entropy principle analogously to the beginning of Section 3.3 yields the inequality

$$(\varrho F_{,\boldsymbol{\phi}}-\nabla\cdot(\varrho F_{,\nabla\boldsymbol{\phi}}))\cdot\mathrm{D}_t\,\boldsymbol{\phi}+\nabla\cdot\left((\varrho F_{,\nabla\boldsymbol{\phi}}-\boldsymbol{\xi}^\top)\,\mathrm{D}_t\,\boldsymbol{\phi}\right)-\boldsymbol{S}:\nabla\boldsymbol{v}+\boldsymbol{J}_S\cdot\nabla T+\sum_{i=1}^N\boldsymbol{J}_i\cdot\nabla c_i\le 0,$$

which is similar to (3.20). Using the commutator rule and $(\boldsymbol{\xi}^\top-\varrho F_{,\nabla\boldsymbol{\phi}})\otimes\nabla\boldsymbol{\phi}=\sum_{i=1}^M(\xi_i-\varrho F_{,\nabla\phi_i})\otimes\nabla\phi_i$ we obtain

$$\begin{aligned}0 &\ge \left(\varrho F_{,\boldsymbol{\phi}}-\nabla\cdot\boldsymbol{\xi}^\top\right)\cdot\mathrm{D}_t\,\boldsymbol{\phi}-\left(\boldsymbol{S}+(\boldsymbol{\xi}^\top-\varrho F_{,\nabla\boldsymbol{\phi}})\otimes\nabla\boldsymbol{\phi}\right):\nabla\boldsymbol{v}+\boldsymbol{J}_S\cdot\nabla T\\ &+ \sum_{i=1}^N\boldsymbol{J}_i\cdot\nabla c_i+\left(\varrho F_{,\nabla\boldsymbol{\phi}}-\boldsymbol{\xi}^\top\right):\mathrm{D}_t\,\nabla\boldsymbol{\phi},\end{aligned}$$

which has to hold for all fields $\mathrm{D}_t\,\nabla\boldsymbol{\phi}$. In view of (3.39) $\nabla\cdot\boldsymbol{\xi}^{\top}$ is independent of $\mathrm{D}_t\,\nabla\boldsymbol{\phi}$. Since all other terms are also independent of $\mathrm{D}_t\,\nabla\boldsymbol{\phi}$ we infer $\boldsymbol{\xi} = \varrho F^{\top}_{,\nabla\boldsymbol{\phi}}$ and from (3.39) we obtain $\boldsymbol{\pi} = -\nabla\cdot(\varrho F^{\top}_{,\nabla\boldsymbol{\phi}})$. Thus, the energy balance reads

$$\varrho\,\mathrm{D}_t\,E + \nabla\cdot(\boldsymbol{J}_E - \varrho F_{,\nabla\boldsymbol{\phi}}\,\mathrm{D}_t\,\boldsymbol{\phi}) = \boldsymbol{T} : \nabla\boldsymbol{v},$$

in contrast to (3.15).

3.4 Sharp interface theory.

Our goal is now to derive a *convective sharp interface model* using the methods of rational thermodynamics, as already done in Section 3.3. The sharp phase interface is modelled as a *free boundary* carrying interfacial energy contributions that complete the balance laws in the bulk regions with interfacial jump conditions for the relevant thermodynamical fields. Convective systems supplemented with several thermodynamic phases that are seperated by singular surfaces have been already considered in [8], [13], [19], [26], [32], [45], and [46]. The references [19], [32] and [45] provide a comprehensive treatment of stress and surface phenomena of one-component systems. In addition, [8], [45] and [46] provide a detailed mathematical analysis of evolving hypersurfaces. Beyond this, in [8], [13], and [26] convective systems influenced by chemical reactions have been considered and the latter both provide conservation laws on different length scales.

We will construct a sharp interface model that allows for an arbitrary number of phases and components where chemical reactions will be excluded. As in Section 3.2 the entropy inequality enters our initial assumptions again, thus our model is a priori thermodynamically consistent. Furthermore, we assume that the free boundaries representing phase interfaces carry energy contributions but no mass particles.

We consider a bounded domain $\Omega\subset\mathbb{R}^d$ with Lipschitz boundary. We further assume that Ω is occupied by M phase regions represented by a finite family $\{\Omega_i\}_{i\in I}$ of mutually disjoint subsets $\Omega_i = \Omega_i(t)\subset\Omega$ which are open and time-dependent regions with piecewise smooth boundary. Without loss of generality let $\overline{\Omega}^{+}$, $\overline{\Omega}^{-}\in\{\Omega_i\}_{i\in I}$ be two neighboring phase regions separated by a moving hypersurface $\Gamma = \Gamma_t = \overline{\Omega}^{+}\cap\overline{\Omega}^{-}$ subject to the conditions (F1)-(F4) of Appendix B.

Let $f:\Omega\to\mathbb{R}^n$ be a function such that its restrictions $f|_{\overline{\Omega}^{+}}:\overline{\Omega}^{+}\to\mathbb{R}^n$, $f|_{\overline{\Omega}^{-}}:\overline{\Omega}^{-}\to\mathbb{R}^n$ are continuous functions on $\overline{\Omega}^{+}$, $\overline{\Omega}^{-}$, but f may suffer from jump discontinuities at the interface Γ. We denote the unilateral limits of f at $\boldsymbol{x}\in\Gamma$ by

$$f^{+}(\boldsymbol{x}) = \lim_{\boldsymbol{y}^{+}\to\boldsymbol{x}} f(\boldsymbol{y}^{+}) \text{ and } f^{-}(\boldsymbol{x}) = \lim_{\boldsymbol{y}^{-}\to\boldsymbol{x}} f(\boldsymbol{y}^{-}),$$

where $\boldsymbol{y}^{+}\in\Omega^{+}$ and $\boldsymbol{y}^{-}\in\Omega^{-}$. Then we denote the jump of f at $\boldsymbol{x}\in\Gamma$ by

$$[f(\boldsymbol{x})] = f^{+}(\boldsymbol{x}) - f^{-}(\boldsymbol{x})$$

and the average of f by

$$\langle f(\boldsymbol{x})\rangle = \frac{1}{2}\left(f^+(\boldsymbol{x}) + f^-(\boldsymbol{x})\right).$$

Furthermore we denote with $T_{\boldsymbol{x}}(\Gamma)$ the *tangent space* of Γ at an arbitrary point $\boldsymbol{x} \in \Gamma$ and with $\boldsymbol{\nu}(\boldsymbol{x})$ the oriented unit normal at $\boldsymbol{x} \in \Gamma$. Then we refer to $\boldsymbol{P} = \boldsymbol{P}_{\boldsymbol{x}} = \boldsymbol{I} - \boldsymbol{\nu}(\boldsymbol{x}) \otimes \boldsymbol{\nu}(\boldsymbol{x})$ as the orthogonal projection onto $T_{\boldsymbol{x}}(\Gamma)$. For completeness, let $\boldsymbol{Q} = \boldsymbol{I} - \boldsymbol{P}$ its complementary projection. We refer to $\kappa = -\nabla_\Gamma \cdot \boldsymbol{\nu}$ as the (scalar) mean curvature and $\boldsymbol{\kappa} = \kappa\boldsymbol{\nu}$ the mean curvature vector. In addition, let V be the (scalar) normal velocity of the interface γ and $\boldsymbol{V} = V\boldsymbol{\nu}$. The quantity V_γ is the velocity of $\partial\gamma$ in direction of $\boldsymbol{\nu}_\gamma(\boldsymbol{x}) \in T_{\boldsymbol{x}}(\Gamma)$ with $\boldsymbol{\nu}_\gamma(\boldsymbol{x}) \cdot \tau \leq 0$ for all τ in the tangent cone of $\partial\gamma$ at $\boldsymbol{x} \in \partial\gamma$.

Now we state constitutive assumptions for the bulk quantities. Therefore we assume that S, E, $\boldsymbol{T}$, $\boldsymbol{J}_E$, $\boldsymbol{J}_1$, ..., $\boldsymbol{J}_N$ depend only on the variables ϱ, $\boldsymbol{c}$, $\nabla\boldsymbol{c}$, $\boldsymbol{v}$, $\nabla\boldsymbol{v}$, T, ∇T. Consequently we set

$$Y_B = (\varrho, \boldsymbol{c}, \nabla\boldsymbol{c}, \boldsymbol{v}, \nabla\boldsymbol{v}, T, \nabla T),$$

as the bulk variables.

Interfacial balance laws.

We derive balance laws at a $(d-1)$-dimensional hypersurface γ_t which represents the sharp boundary between two neighboring phases and which evolves during the time and fulfills (F1)-(F4) of Appendix B. We employ the calculus rules on evolving hypersurfaces from Appendix B, essentially the *pillbox lemma* (Lemma 3 of Appendix B), the *divergence theorem on hypersurfaces* (Theorem 3 of Appendix B) and the general *transport theorem* (Theorem 4 of Appendix B). Throughout this paragraph let $\{R(t,\varepsilon)\}_{t,\varepsilon>0}$ be a family of sets subject to the conditions (F5)-(F8) of Appendix B.

Starting with the mass balance given by (3.2) on $R(t,\varepsilon)$ and using the pillbox lemma we obtain

$$\int_{\gamma_t} [\varrho(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)]\,\mathrm{d}\mathcal{H}^{d-1} = 0.$$

Local variations of the above identity give

$$[\varrho(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)] = 0, \tag{3.40}$$

locally on γ_t, where V is the scalar normal velocity of the hypersurface γ_t.

Proceeding with the momentum balance as in Section 3.2 we supplement (3.4) with an additional interfacial term, that accounts for changes of momentum due to interfacial stress and shear forces:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t,\varepsilon)} \varrho\boldsymbol{v}\,\mathrm{d}\boldsymbol{x} = \int_{\partial R(t,\varepsilon)} \boldsymbol{T}\boldsymbol{\nu}_{R(t,\varepsilon)}\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\partial\gamma_t} \boldsymbol{T}_I\boldsymbol{\nu}_\gamma\,\mathrm{d}\mathcal{H}^{d-2},$$

where $\boldsymbol{T}_I$ denotes the interfacial stress tensor. Using the pillbox lemma and the divergence theorem we obtain in the limit, as $\varepsilon \to 0$,

$$[\varrho \boldsymbol{v}(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)] = [\boldsymbol{T}]\boldsymbol{\nu} + \nabla_\Gamma \cdot \boldsymbol{T}_I + \boldsymbol{T}_I\boldsymbol{\kappa}, \tag{3.41}$$

the momentum balance at the interface γ_t.

In order to include multi-component fluids we assume that changes of a single species on $R(t,\varepsilon)$ are given by (3.8), combined with the pillbox lemma we obtain

$$\int_{\gamma_t} [\varrho c_i(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)]\,\mathrm{d}\mathcal{H}^{d-1} = -\int_{\gamma_t} [\boldsymbol{J}_i]\cdot\boldsymbol{\nu}\,\mathrm{d}\mathcal{H}^{d-1}$$

that is in local form

$$[\varrho c_i(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)] = -[\boldsymbol{J}_i]\cdot\boldsymbol{\nu}. \tag{3.42}$$

We assume that changes of the total energy in the volume $R(t,\varepsilon)$ are effects of the energy fluxes $\boldsymbol{J}_E$ in the bulk and $\boldsymbol{j}_E$ on the surface as well as changes of the boundary $\partial\gamma$ which may enlarge or decrease the surface area. Therefore we postulate

$$\begin{aligned} 0 &= \frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{R(t,\varepsilon)} \varrho\left(E + \tfrac{1}{2}|\boldsymbol{v}|^2\right)\,\mathrm{d}\boldsymbol{x} + \int_{\gamma_t} e\,\mathrm{d}\mathcal{H}^{d-1}\right) + \int_{\partial R(t,\varepsilon)} \left(\boldsymbol{J}_E - \boldsymbol{T}^\top\boldsymbol{v}\right)\cdot\boldsymbol{\nu}_{R(t,\varepsilon)}\,\mathrm{d}\mathcal{H}^{d-1} \\ &+ \int_{\partial\gamma_t} (\boldsymbol{j}_E\cdot\boldsymbol{\nu}_\gamma - eV_\gamma)\,\mathrm{d}\mathcal{H}^{d-2}. \end{aligned}$$

with internal energy densities E of the bulk and e of the surface. We employ the pillbox lemma to obtain

$$\lim_{\varepsilon\to 0}\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t,\varepsilon)} \varrho\left(E + \tfrac{1}{2}|\boldsymbol{v}|^2\right)\,\mathrm{d}\boldsymbol{x} = \int_\gamma \left[\varrho\left(E + \tfrac{1}{2}|\boldsymbol{v}|^2\right)(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)\right]\mathrm{d}\mathcal{H}^{d-1}.$$

Proceeding by use of the transport theorem and the divergence theorem we arrive at

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int_{\gamma_t} e\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\partial\gamma_t} (\boldsymbol{j}_E\cdot\boldsymbol{\nu}_\gamma - eV_\gamma)\,\mathrm{d}\mathcal{H}^{d-2} \\ &= \int_{\gamma_t} (\partial^\circ e - e\boldsymbol{\kappa}\cdot\boldsymbol{V} + \nabla_\Gamma\cdot\boldsymbol{j}_E + \boldsymbol{\kappa}\cdot\boldsymbol{j}_E)\,\mathrm{d}\mathcal{H}^{d-1}, \end{aligned}$$

where $\partial^\circ e = \partial_{(1,\boldsymbol{V})}$ denotes the normal time derivative, i.e. the derivative in $(1,\boldsymbol{V})$-direction. Putting everything together we infer a local version of the energy balance at the interface γ, i.e.

$$\begin{aligned} 0 &= \left[\varrho\left(E + \tfrac{1}{2}|\boldsymbol{v}|^2\right)(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)\right] + \left[\boldsymbol{J}_E - \boldsymbol{T}^\top\boldsymbol{v}\right]\cdot\boldsymbol{\nu} \\ &+ \partial^\circ e - e\boldsymbol{\kappa}\cdot\boldsymbol{V} + \nabla_\Gamma\cdot\boldsymbol{j}_E + \boldsymbol{\kappa}\cdot\boldsymbol{j}_E. \end{aligned} \tag{3.43}$$

In a completely analogous manner we derive the entropy inequality. Therefore we assume that changes to the total entropy in $R(t,\varepsilon)$ are due to the entropy fluxes $\boldsymbol{J}_S$ in the bulk and $\boldsymbol{j}_S$ on the surface as well as entropy changes through the variation of the boundary $\partial\gamma$. We assume

$$\begin{aligned} 0 &\le \frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{R(t,\varepsilon)} \varrho S\,\mathrm{d}\boldsymbol{x} + \int_{\gamma_t} s\,\mathrm{d}\mathcal{H}^{d-1}\right) + \int_{\partial R(t,\varepsilon)} \boldsymbol{J}_S\cdot\boldsymbol{\nu}_{R(t,\varepsilon)}\,\mathrm{d}\mathcal{H}^{d-1} \\ &+ \int_{\partial\gamma_t} (\boldsymbol{j}_S\cdot\boldsymbol{\nu}_\gamma - sV_\gamma)\,\mathrm{d}\mathcal{H}^{d-2}, \end{aligned}$$

where S denotes the entropy density in the bulk and s the entropy density on the surface. In a similar way we obtain the local version

$$0 \leq [\varrho S(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)] + [\boldsymbol{J}_S\cdot\boldsymbol{\nu}] + (\partial^\circ s - s\boldsymbol{\kappa}\cdot\boldsymbol{V} + \nabla_\Gamma\cdot\boldsymbol{j}_S + \boldsymbol{\kappa}\cdot\boldsymbol{j}_S). \tag{3.44}$$

Furthermore, from (3.40) we deduce that the mass flux $m = \varrho(\boldsymbol{v}\cdot\boldsymbol{\nu} - V)$ is continuous across the interface γ_t. Hence, following [32] our interfacial balance laws become

$$\begin{aligned}
[m] &= 0 && (3.45)\\
m[\boldsymbol{v}] - [\boldsymbol{T}]\cdot\boldsymbol{\nu} &= \nabla_\Gamma\cdot\boldsymbol{T}_I + \boldsymbol{T}_I\boldsymbol{\kappa} && (3.46)\\
m[c_i] + [\boldsymbol{J}_i]\cdot\boldsymbol{\nu} &= 0 && (3.47)\\
m\left[E + \tfrac{1}{2}|\boldsymbol{v}|^2\right] + [\boldsymbol{J}_E - \boldsymbol{T}\boldsymbol{v}]\cdot\boldsymbol{\nu} &= -(\partial^\circ e - e\boldsymbol{\kappa}\cdot\boldsymbol{V} + (\nabla_\Gamma + \boldsymbol{\kappa})\cdot\boldsymbol{j}_E) && (3.48)\\
m[S] + [\boldsymbol{J}_S]\cdot\boldsymbol{\nu} &\geq -(\partial^\circ s - s\boldsymbol{\kappa}\cdot\boldsymbol{V} + (\nabla_\Gamma + \boldsymbol{\kappa})\cdot\boldsymbol{j}_S). && (3.49)
\end{aligned}$$

In the bulk region the balance laws (3.12)-(3.15) and the entropy inequality (3.16) are valid.

Remark 3.4.1. Let $\boldsymbol{f}$ be a vector field and $\boldsymbol{G}$ a tensor field. Then we have

$$(\nabla_\Gamma + \boldsymbol{\kappa})\cdot\boldsymbol{f} = \nabla_\Gamma\cdot(\boldsymbol{P}\boldsymbol{f}) \quad \text{and} \quad \nabla_\Gamma\cdot\boldsymbol{G} + \boldsymbol{G}\boldsymbol{\kappa} = \nabla_\Gamma\cdot(\boldsymbol{G}\boldsymbol{P}).$$

Remark 3.4.2. A possible choice of the interfacial tensor $\boldsymbol{T}_I$ is

$$\boldsymbol{T}_I = \sigma\boldsymbol{P} = \sigma(\boldsymbol{I} - \boldsymbol{\nu}\otimes\boldsymbol{\nu}),$$

where σ is the (isotropic) surface tension. Then we have using Remark 3.4.1

$$\nabla_\Gamma\cdot\boldsymbol{T}_I = \sigma\kappa\boldsymbol{\nu} + \nabla_\Gamma\sigma,$$

as a constituent part of the interface contributions in the momentum balance (3.46). This relation is established in [9, p.68 f.]

Relation to the model of Gurtin.

In [45, pp. 119-123] a two-phase and single-component system has been discussed. As sharp interface model this system includes an evolving interface γ_t separating the two phase regions in the plane $\mathbb{R}^2$ and besides, this system excludes convection. Nevertheless this model gives some insights to the forces -mainly capillary and frictional forces- acting at the interface γ_t. The equations of this model are

$$c\partial_t T = -\nabla\cdot\boldsymbol{J}_E, \tag{3.50}$$

in the bulk, and

$$\begin{aligned}
bV &= f\kappa + \partial_s\xi + [F], && (3.51)\\
[E]V &= [\boldsymbol{J}_E]\cdot\boldsymbol{\nu} + \partial^\circ e - e\kappa V + \partial_s(\xi V), && (3.52)
\end{aligned}$$

on the one-dimensional surface (cf. [45, Eq. 17, p.128]). Here b is a positive function depending on T and the interface orientation and ξ is the surface shear.

Calculus of plane curves.

Here the interface γ_t reduces to a planar curve thus we can represent its unit normal $\boldsymbol{\nu}$ by its angular coordinates, i.e.

$$\boldsymbol{\nu} = (\cos\vartheta, \sin\vartheta)^\top,$$

where ϑ denotes the angle between the vector $\boldsymbol{\nu}$ and the horizontal coordinate axis. The corresponding tangent vector $\boldsymbol{\tau}$ is denoted by

$$\boldsymbol{\tau} = (\sin\vartheta, -\cos\vartheta)^\top.$$

Then every function F depending on the unit normal $\boldsymbol{\nu}$ fulfills

$$F_{,\vartheta} = F_{,\boldsymbol{\nu}} \cdot \frac{\mathrm{d}\boldsymbol{\nu}}{\mathrm{d}\vartheta} = -F_{,\boldsymbol{\nu}} \cdot \boldsymbol{\tau}. \tag{3.53}$$

For an arc-length parametrization $\gamma : s \to \gamma(s)$ the differential operators on γ admit the representation

$$\nabla_\Gamma F = \partial_s F \boldsymbol{\tau},\ \nabla_\Gamma \cdot \boldsymbol{F} = \partial_s \boldsymbol{F} \cdot \boldsymbol{\tau} \text{ and } (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{F} = \partial_s(\boldsymbol{F} \cdot \boldsymbol{\tau}).$$

Constitutive assumptions and interfacial laws.

In the absence of fluid flow and varying density we assume $\boldsymbol{v} = 0$ and $\varrho = 1$, then our balance and imbalance laws (3.48) and (3.49) reduce to

$$\begin{aligned} V[E] - [\boldsymbol{J}_E] \cdot \boldsymbol{\nu} - \partial^\circ e + e\kappa V - (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_E &= 0 && (3.54)\\ V[S] - [\boldsymbol{J}_S] \cdot \boldsymbol{\nu} - \partial^\circ s + s\kappa V - (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_S &\leq 0. && (3.55) \end{aligned}$$

Now we assume that all bulk potentials and forces depend on

$$Y_B = (T, \nabla T),$$

whereas the corresponding interfacial fields depend on

$$Y_I = (T, V, \boldsymbol{\nu}).$$

For brevity we set

$$f = e - Ts \text{ and } \boldsymbol{j} = \boldsymbol{j}_E - T\boldsymbol{j}_S$$

and following classical thermodynamics we assume $\boldsymbol{J}_E - T\boldsymbol{J}_S = 0$. Now we multiply (3.55) by T and then subtract it from (3.54), that is

$$\begin{aligned} 0 &\leq V[F] - \partial^\circ f - s\partial^\circ T + f\kappa V - (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} - \boldsymbol{j}_S \cdot \nabla_\Gamma T \\ &= V[F] + f\kappa V - (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} - \boldsymbol{j}_S \cdot \nabla_\Gamma T \qquad (3.56)\\ &- f_{,T}\partial^\circ T - f_{,V}\partial^\circ V - f_{,\boldsymbol{\nu}}\partial^\circ \boldsymbol{\nu} - s\partial^\circ T, \end{aligned}$$

where we have set $F = E - TS$, $f = e - Ts$ as free energies. We extract first constitutive laws, i.e. $s = -f_{,T}$ and $f_{,V} = 0$. These restrictions lead to $f = f(T, \boldsymbol{\nu})$ and $s = s(T, \boldsymbol{\nu})$. Using $f = e - Ts$ we infer $e = e(T, \boldsymbol{\nu})$. Besides, we assume that $\boldsymbol{j}$, $\boldsymbol{j}_E$ and $\boldsymbol{j}_S$ admit the decompositions

$$\boldsymbol{j} = \boldsymbol{j}^1 + \boldsymbol{j}^2 V,\ \boldsymbol{j}_E = \boldsymbol{j}_E^1 + \boldsymbol{j}_E^2 V,\ \boldsymbol{j}_S = \boldsymbol{j}_S^1 + \boldsymbol{j}_S^2 V, \tag{3.57}$$

where $\boldsymbol{j}^k$, $\boldsymbol{j}_E^k$, $\boldsymbol{j}_S^k$ are independent of V and $k \in \{1, 2\}$. Then we have

$$(\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} = (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}^1 + V\,(\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}^2 + \boldsymbol{j}^2 \cdot \nabla_\Gamma V. \tag{3.58}$$

For simplicity we assume $\boldsymbol{j}^1 = \boldsymbol{j}_E^1 - T\boldsymbol{j}_S^1 = 0$ as we have already done for the bulk fields $\boldsymbol{J}_E$ and $\boldsymbol{J}_S$. Besides, let $\boldsymbol{j}_S^1 = 0$ and using (3.58) our entropy inequality (3.56) turns into

$$\begin{aligned} 0 &\leq V[F] + f\kappa V - f_{,\boldsymbol{\nu}} \partial^\circ \boldsymbol{\nu} - V\,(\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}^2 - \boldsymbol{j}^2 \cdot \nabla_\Gamma V - \boldsymbol{j}_S \cdot \nabla_\Gamma T \\ &= (f_{,\boldsymbol{\nu}} - \boldsymbol{j}^2) \cdot \nabla_\Gamma V + V\left([F] + f\kappa - (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}^2 - \boldsymbol{j}_S^2 \cdot \nabla_\Gamma T\right), \end{aligned}$$

where we have used Lemma 1 of Appendix B. Thus we have $\boldsymbol{P} f_{,\boldsymbol{\nu}} = \boldsymbol{P}\boldsymbol{j}^2$ where $\boldsymbol{P}$ is the orthogonal projection onto $T_{\boldsymbol{x}}(\Gamma)$ and arrive at

$$\begin{aligned} 0 &\leq V\left([F] + f\kappa - (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}^2 - \boldsymbol{j}_S^2 \cdot \nabla_\Gamma T\right) \\ &= V\left([F] + f\kappa - \nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^2) - \boldsymbol{j}_S^2 \cdot \nabla_\Gamma T\right). \end{aligned}$$

Using $\boldsymbol{P} f_{,\boldsymbol{\nu}} = \boldsymbol{P}\boldsymbol{j}^2$ and Theorem 2 of Appendix B we obtain

$$\begin{aligned} bV &= f\kappa - (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot f_{,\boldsymbol{\nu}} + [F] - \boldsymbol{j}_S^2 \cdot \nabla_\Gamma T \\ &= f\kappa - \partial_s(f_{,\boldsymbol{\nu}} \cdot \boldsymbol{\tau}) - \boldsymbol{j}_S^2 \cdot \boldsymbol{\tau}\partial_s T + [F], \end{aligned} \tag{3.59}$$

where $b > 0$. Now the compatibility theorem [45, p.126] assures thermodynamical consistency, if the following conditions hold:

(i) The surface shear $\xi \in \mathbb{R}$ is equal to $\xi = -f_{,\boldsymbol{\nu}} \cdot \boldsymbol{\tau}$.

(ii) The essential thermodynamical fields, i.e. interfacial internal energy, surface shear and interfacial entropy are independent of the interface velocity V.

We now assume $\boldsymbol{j}_S^2 = 0$ then equation (3.59) turns into

$$bV = f\kappa + \partial_s \xi + [F],$$

which is exactly equation (3.51) of Gurtins Model.

In order to justify the other interfacial relation (3.52) we consider

$$\begin{aligned} (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_E &= \partial_s(\boldsymbol{j}_E \cdot \boldsymbol{\tau}) \\ &= \partial_s\left((\boldsymbol{j}_E^1 + V\boldsymbol{j}_E^2) \cdot \boldsymbol{\tau}\right) \\ &= \partial_s(\boldsymbol{j}_E^1 \cdot \boldsymbol{\tau}) - \partial_s(V\xi). \end{aligned}$$

Assuming $\boldsymbol{j}_E^1 = 0$ we obtain the second interfacial relation (3.52) by applying the interfacial energy balance (3.54). The bulk equation given by (3.50) is straightforward.

Single-component fluid flow.

We now consider a one-component *fluid flow* whose fluid velocity $\boldsymbol{v}$ does not jump across the interface Γ. The bulk regions are described by (3.3), (3.5), (3.7) and (3.11), where in the interfacial regions (3.40), (3.41), (3.43) and (3.44) hold, i.e. we have

$$\begin{aligned} \nabla_\Gamma \cdot (\boldsymbol{T}_I \boldsymbol{P}) + [\boldsymbol{T}]\boldsymbol{\nu} &= 0, && (3.60)\\ m\,[E] + [\boldsymbol{J}_E - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu} &= -\left(\partial^\circ e - e\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_E\right), && (3.61)\\ m[S] + [\boldsymbol{J}_S] \cdot \boldsymbol{\nu} &\geq -\left(\partial^\circ s - s\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_S\right), && (3.62) \end{aligned}$$

on the interface. To derive constitutive relations we assume that our interface fields depend on

$$Y_I = (T, \nabla_\Gamma T, V, \boldsymbol{\nu}, \boldsymbol{v})\,.$$

From (3.61) and (3.62) we deduce a quasilinear form given by

$$\begin{aligned} 0 &= e_{,Y_I} \cdot X - e\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_E + m\,[E] + [\boldsymbol{J}_E - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu} && (3.63)\\ 0 &\leq s_{,Y_I} \cdot X - s\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_S + m[S] + [\boldsymbol{J}_S] \cdot \boldsymbol{\nu}, && (3.64) \end{aligned}$$

where $X = \partial^\circ Y_I$. Since $\partial^\circ T$ depends only on the normal contributions of ∇T we infer that Y_I and X can be chosen independently. Therefore, we can apply Liu's lemma from Appendix C to (3.63) and (3.64) to obtain

$$\begin{aligned} 0 &\leq (s_{,Y_I} - \lambda e_{,Y_I}) \cdot X - (s - \lambda e)\,\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_S - \lambda\,(\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}_E && (3.65)\\ &+ m\,[S - \lambda E] + [\boldsymbol{J}_S - \lambda(\boldsymbol{J}_E - \boldsymbol{T}\boldsymbol{v})] \cdot \boldsymbol{\nu}, \end{aligned}$$

for all X.

Proposition 3.4.1. *Let (3.65) be fulfilled and $s_{,T} > 0$ for all $T > 0$. Then we have $\lambda = 1/e_{,s}$.*

Proof. Clearly (3.65) has to hold for all fields $\partial^\circ T$. Since $\partial^\circ T$ appears neither in the variables Y_I nor anywhere else in (3.65) except in X this leads to

$$s_{,T} - \lambda e_{,T} = 0. \tag{3.66}$$

Since $s_{,T} > 0$ we can define $T = T(s, Z)$ if we solve $s = s(T, Z)$. In particular, we have $1 = s_{,T} T_{,s}$, thus by $e = e(s, Z)$ we obtain $e_{,T} = e_{,s} s_{,T}$. In view of (3.66) the assertion follows. □

Remark 3.4.3. If the absolute temperature is defined as $T = e_{,s}$ we have $\lambda = 1/T$. We will henceforth assume $\lambda = 1/T$.

We proceed further by setting $F = E - TS$, $f = e - Ts$ and use $\lambda = 1/T$. Then we have

$$\begin{aligned} 0 &\geq \partial^\circ f + s\partial^\circ T - f\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} + \boldsymbol{j}_S \cdot \nabla_\Gamma T + m\,[F] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu}\\ &= f_{,T}\partial^\circ T + f_{,\nabla_\Gamma T}\partial^\circ \nabla_\Gamma T + f_{,V}\partial^\circ V + f_{,\boldsymbol{\nu}} \cdot \partial^\circ \boldsymbol{\nu} + f_{,\boldsymbol{v}} \cdot \partial^\circ \boldsymbol{v} + s\partial^\circ T && (3.67)\\ &- f\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} + \boldsymbol{j}_S \cdot \nabla_\Gamma T + m\,[F] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu}, \end{aligned}$$

where we have set $\boldsymbol{J} = \boldsymbol{J}_E - T\boldsymbol{J}_S$ and $\boldsymbol{j} = \boldsymbol{j}_E - T\boldsymbol{j}_S$. Thus we obtain

$$\begin{aligned} f_{,T} &= -s, && (3.68)\\ f_{,\nabla_\Gamma T} &= 0, && (3.69)\\ f_{,V} &= 0, && (3.70)\\ f_{,\boldsymbol{v}} &= 0. && (3.71) \end{aligned}$$

For simplicity, we assume that $\boldsymbol{j}$, $\boldsymbol{j}_E$ and $\boldsymbol{j}_S$ admit the decompositions as in (3.57) where $\boldsymbol{j}^k$, $\boldsymbol{j}_E^k$, $\boldsymbol{j}_S^k$ are independent of V and $k \in \{1, 2\}$. Then (3.67) becomes

$$0 \;\geq\; f_{,\boldsymbol{\nu}} \cdot \partial^\circ \boldsymbol{\nu} + (\boldsymbol{j} - f\boldsymbol{V}) \cdot \boldsymbol{\kappa} + \nabla_\Gamma \cdot \boldsymbol{j} + \boldsymbol{j}_S \cdot \nabla_\Gamma T + m\,[F] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu},$$

for all vectors $\boldsymbol{\kappa}$. Thus $\boldsymbol{j} - f\boldsymbol{V}$ is a tangential field, i.e.

$$\boldsymbol{P}(\boldsymbol{j} - f\boldsymbol{V}) = \boldsymbol{P}\boldsymbol{j} = \boldsymbol{j} - f\boldsymbol{V}$$

holds. Then we have

$$f\boldsymbol{V} = \boldsymbol{Q}\boldsymbol{j} = \boldsymbol{Q}\boldsymbol{j}^1 + V\boldsymbol{Q}\boldsymbol{j}^2 \text{ and } fV = \boldsymbol{j}^1 \cdot \boldsymbol{\nu} + V\boldsymbol{j}^2 \cdot \boldsymbol{\nu}.$$

If $V = 0$, we infer $\boldsymbol{j}^1 \cdot \boldsymbol{\nu} = 0$ and since $\boldsymbol{j}^1$ and $\boldsymbol{\nu}$ are independent of V we have

$$f = \boldsymbol{j}^2 \cdot \boldsymbol{\nu} \text{ and } \boldsymbol{j}^1 \cdot \boldsymbol{\nu} = 0$$

for all $V \in \mathbb{R}$.

In a next step, we will determine the remaining derivative $f_{,\boldsymbol{\nu}}$. Therefore, by use of $\nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}) = (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j}$ we obtain

$$\begin{aligned} 0 \;&\geq\; f_{,\boldsymbol{\nu}} \cdot \partial^\circ \boldsymbol{\nu} - f\kappa V + \nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^1) + V\nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^2) + \boldsymbol{P}\boldsymbol{j}^2 \cdot \nabla_\Gamma V\\ &+\; \boldsymbol{j}_S \cdot \nabla_\Gamma T + m\,[F] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu}\\ &=\; (\boldsymbol{j}^2 - f_{,\boldsymbol{\nu}}) \cdot \nabla_\Gamma V - f\kappa V + \nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^1) + V\nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^2) \qquad (3.72)\\ &+\; \boldsymbol{j}_S \cdot \nabla_\Gamma T + m\,[F] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu}, \end{aligned}$$

where we have used Lemma 1 from Appendix B. Hence $\boldsymbol{P}\boldsymbol{j}^2 = \boldsymbol{P}f_{,\boldsymbol{\nu}}$ holds. Now we assume $\boldsymbol{P}\boldsymbol{j}^1 = 0$, $\boldsymbol{J} = 0$ and define $\boldsymbol{S} = \boldsymbol{T} - \varrho F\boldsymbol{I}$. Then (3.72) turns into

$$\begin{aligned} 0 \;&\leq\; V\left(f\kappa + [\varrho F] - \nabla_\Gamma \cdot (\boldsymbol{P}f_{,\boldsymbol{\nu}})\right) \qquad (3.73)\\ &+\; \boldsymbol{v} \cdot [\boldsymbol{S}]\boldsymbol{\nu} - \boldsymbol{j}_S \cdot \nabla_\Gamma T, \end{aligned}$$

as an inequality in the variables $(V, \nabla_\Gamma T, \boldsymbol{v})$. Now (3.73) has to be fulfilled for all tuples $(V, \nabla_\Gamma T, \boldsymbol{v})$. Then by Theorem 2 of Appendix B there exist functions

$$\begin{aligned} &A_1(Y_I) : \mathbb{R} \to \mathbb{R}, \;\; A_i(Y_I) : \mathbb{R}^d \to \mathbb{R},\\ &B_1(Y_I) : \mathbb{R} \to \mathbb{R}^d,\, B_i(Y_I) : \mathbb{R}^d \to \mathbb{R}^d,\\ &C_1(Y_I) : \mathbb{R} \to \mathbb{R}^d,\, C_i(Y_I) : \mathbb{R}^d \to \mathbb{R}^d, \quad i \in \{2, 3\}, \end{aligned}$$

which are linear for all tuples $Y_I = (T, \nabla_\Gamma T, V, \boldsymbol{\nu}, \boldsymbol{v})$. Moreover, these functions fulfill

$$\begin{aligned} A_1 V + A_2 \nabla_\Gamma T + A_3 \boldsymbol{v} &= f\kappa + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot f_{,\boldsymbol{\nu}} + [\varrho F], \\ B_1 V + B_2 \nabla_\Gamma T + B_3 \boldsymbol{v} &= -\boldsymbol{j}_S, \\ C_1 V + C_2 \nabla_\Gamma T + C_3 \boldsymbol{v} &= [\boldsymbol{S}]\boldsymbol{\nu}, \end{aligned} \tag{3.74}$$

for all tuples $(V, \nabla_\Gamma T, \boldsymbol{v})$ again. Since $[\boldsymbol{S}]$ and $\boldsymbol{\nu}$ do not depend on V we assume $C_1 = \mathbf{0}$. For $\nabla_\Gamma T = \mathbf{0}$, $\boldsymbol{v} = \mathbf{0}$ equation (3.74) leads to

$$A_1 V^2 = V\left(f\kappa + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot f_{,\boldsymbol{\nu}} + [\varrho F]\right) \geq 0,$$

due to (3.73). Hence we assume $A_1 \geq 0$. Equation (3.74) may be considered as generalized Gibbs-Thomson law.

Now we assume that the interfacial stress tensor $\boldsymbol{T}_I$ fulfills $f\boldsymbol{P} = \boldsymbol{P}\boldsymbol{T}_I\boldsymbol{P}$. Clearly $\boldsymbol{T}_I$ restricted on the tangent space is symmetric, i.e. $\boldsymbol{P}\boldsymbol{T}_I\boldsymbol{P} = \boldsymbol{P}\boldsymbol{T}_I^\top\boldsymbol{P}$. Using

$$\begin{aligned} \nabla_\Gamma \cdot (\boldsymbol{Q}\boldsymbol{T}_I\boldsymbol{P}) &= \nabla_\Gamma \cdot (\boldsymbol{\nu} \otimes \boldsymbol{\nu}\boldsymbol{T}_I\boldsymbol{P}) = \nabla_\Gamma \cdot \left(\boldsymbol{\nu} \otimes (\boldsymbol{P}\boldsymbol{T}_I^\top\boldsymbol{\nu})\right) \\ &= \nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{T}_I^\top\boldsymbol{\nu})\boldsymbol{\nu} + \nabla_\Gamma\boldsymbol{\nu}\boldsymbol{P}\boldsymbol{T}_I^\top\boldsymbol{\nu} \end{aligned}$$

the interfacial momentum balance reduces to

$$\begin{aligned} [\boldsymbol{T}]\boldsymbol{\nu} &= -\nabla_\Gamma \cdot (\boldsymbol{T}_I\boldsymbol{P}) \\ &= -\nabla_\Gamma \cdot (f\boldsymbol{P}) - \nabla_\Gamma \cdot (\boldsymbol{Q}\boldsymbol{T}_I\boldsymbol{P}) \\ &= -(\nabla_\Gamma + \boldsymbol{\kappa})f - \nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{T}_I^\top\boldsymbol{\nu})\boldsymbol{\nu} - \nabla_\Gamma\boldsymbol{\nu}\boldsymbol{P}\boldsymbol{T}_I^\top\boldsymbol{\nu}, \end{aligned} \tag{3.75}$$

where $\boldsymbol{P}\boldsymbol{T}_I^\top\boldsymbol{\nu}$ describes shear forces at the interface Γ. It is similar to the concept of surface shear at test volumes, cf. [19, p. 95]. Neglecting this effect we obtain

$$[\boldsymbol{T}]\boldsymbol{\nu} = -f\boldsymbol{\kappa} - \nabla_\Gamma f,$$

which may be regarded as *generalized Young-Laplace law*, especially if $\nabla\boldsymbol{v}$ does not jump across the interface Γ we have $[p] = f\kappa$.

Multi-component fluid flow.

Now we generalize the single-component system to a convective system of several components. In addition, the fluid velocity $\boldsymbol{v}$ is allowed to jump across the interface Γ. Hence, the system of interfacial balance and imbalance laws is given by (3.45)-(3.49) where the bulk relations are of the form (3.12)-(3.16). We will work with (3.47)-(3.49) and assume that the interface fields depend on

$$Y_I = \left(T, \nabla_\Gamma T, V, \boldsymbol{\nu}, \boldsymbol{v}^+, \boldsymbol{v}^-, \boldsymbol{c}^+, \boldsymbol{c}^-\right).$$

As before, we define

$$F = E - TS,\ f = e - Ts,\ \boldsymbol{J} = \boldsymbol{J}_E - T\boldsymbol{J}_S - \sum_{i=1}^{N} \mu_i \boldsymbol{J}_i,\ \text{and } \boldsymbol{j} = \boldsymbol{j}_E - T\boldsymbol{j}_S.$$

Recalling the method of Lagrange multipliers as in Section 3.3 we subtract the interfacial concentration balance (3.47) that has been multiplied with an appropriate vector $\boldsymbol{\lambda} = (\lambda_i)_i$ to obtain

$$\begin{aligned}
0 \;&\geq\; \partial^\circ f + s\partial^\circ T - f\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} + \boldsymbol{j}_S \cdot \nabla_\Gamma T \\
&+\; m\left[F + \tfrac{1}{2}|\boldsymbol{v}|^2\right] + [\boldsymbol{J}_E - T\boldsymbol{J}_S - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu} - \sum_{i=1}^{N} \lambda_i [mc_i + \boldsymbol{J}_i \cdot \boldsymbol{\nu}] \\
&=\; f_{,T}\partial^\circ T + f_{,\nabla_\Gamma T}\partial^\circ \nabla_\Gamma T + f_{,V}\partial^\circ V + f_{,\boldsymbol{\nu}} \cdot \partial^\circ \boldsymbol{\nu} + f_{,\boldsymbol{v}^+} \cdot \partial^\circ \boldsymbol{v}^+ + f_{,\boldsymbol{v}^-} \cdot \partial^\circ \boldsymbol{v}^- \\
&+\; f_{,\boldsymbol{c}^+} \cdot \partial^\circ \boldsymbol{c}^+ + f_{,\boldsymbol{c}^-} \cdot \partial^\circ \boldsymbol{c}^- + s\partial^\circ T - f\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} + \boldsymbol{j}_S \cdot \nabla_\Gamma T \\
&+\; m\left[F + \tfrac{1}{2}|\boldsymbol{v}|^2\right] + [\boldsymbol{J}_E - T\boldsymbol{J}_S - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu} - \sum_{i=1}^{N} \lambda_i [mc_i + \boldsymbol{J}_i \cdot \boldsymbol{\nu}].
\end{aligned}$$

In addition to (3.68) - (3.71) we infer $f_{,\boldsymbol{v}^\pm} = 0$ and $f_{,\boldsymbol{c}^\pm} = 0$. With $\lambda_i = \mu_i$ we then have

$$\begin{aligned}
0 \;&\geq\; f_{,\boldsymbol{\nu}} \cdot \partial^\circ \boldsymbol{\nu} - f\kappa V + (\nabla_\Gamma + \boldsymbol{\kappa}) \cdot \boldsymbol{j} + \boldsymbol{j}_S \cdot \nabla_\Gamma T \\
&+\; m\left[F + \tfrac{1}{2}|\boldsymbol{v}|^2 - \sum_{i=1}^{N} \mu_i c_i\right] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu}.
\end{aligned}$$

In a next step we will determine the remaining derivative $f_{,\boldsymbol{\nu}}$. For this purpose we split our fluxes as $\boldsymbol{j}$, $\boldsymbol{j}_S$ as in (3.57) where $\boldsymbol{j}^1$, $\boldsymbol{j}^2$, $\boldsymbol{j}_E^1$, $\boldsymbol{j}_E^2$, $\boldsymbol{j}_S^1$, $\boldsymbol{j}_S^2$ do not depend on V. We employ (3.58) to obtain

$$\begin{aligned}
0 \;&\geq\; f_{,\boldsymbol{\nu}} \cdot \partial^\circ \boldsymbol{\nu} - f\kappa V + \nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^1) + V\nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^2) + \boldsymbol{j}^2 \cdot \nabla_\Gamma V \\
&+\; \boldsymbol{j}_S \cdot \nabla_\Gamma T + m\left[F + \tfrac{1}{2}|\boldsymbol{v}|^2 - \sum_{i=1}^{N} \mu_i c_i\right] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu} \\
&=\; \left(\boldsymbol{j}^2 - f_{,\boldsymbol{\nu}}\right) \cdot \nabla_\Gamma V - f\kappa V + \nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^1) + V\nabla_\Gamma \cdot (\boldsymbol{P}\boldsymbol{j}^2) \\
&+\; \boldsymbol{j}_S \cdot \nabla_\Gamma T + m\left[F + \tfrac{1}{2}|\boldsymbol{v}|^2 - \sum_{i=1}^{N} \mu_i c_i\right] + [\boldsymbol{J} - \boldsymbol{T}\boldsymbol{v}] \cdot \boldsymbol{\nu},
\end{aligned}$$

where we have used Lemma 1 from Appendix B. Since all thermodynamic fields are independent of $\nabla_\Gamma V$ we infer $\boldsymbol{P}\boldsymbol{j}^2 = \boldsymbol{P}f_{,\boldsymbol{\nu}}$. As before, we assume $\boldsymbol{P}\boldsymbol{j}^1 = 0$, $\boldsymbol{J} = 0$ and define $\boldsymbol{S} = \boldsymbol{T} - \varrho\left(F + \frac{1}{2}|\boldsymbol{v}|^2 - \sum_{i=1}^{N} \mu_i c_i\right)\boldsymbol{I}$ and obtain

$$\begin{aligned}
0 \;&\leq\; V\left(F\kappa - \nabla_\Gamma \cdot (\boldsymbol{P}F_{,\boldsymbol{\nu}}) + \left[\varrho\left(F + \tfrac{1}{2}|\boldsymbol{v}|^2 - \sum_{i=1}^{N} \mu_i c_i\right)\right]\right) \\
&-\; \boldsymbol{j}_S \cdot \nabla_\Gamma T + [\boldsymbol{S}\boldsymbol{v}] \cdot \boldsymbol{\nu} \\
&=\; V\left(F\kappa - \nabla_\Gamma \cdot (\boldsymbol{P}F_{,\boldsymbol{\nu}}) + \left[\varrho\left(F + \tfrac{1}{2}|\boldsymbol{v}|^2 - \sum_{i=1}^{N} \mu_i c_i\right)\right]\right) \\
&-\; \boldsymbol{j}_S \cdot \nabla_\Gamma T + \boldsymbol{v}^+ \cdot \boldsymbol{S}^+\boldsymbol{\nu} - \boldsymbol{v}^- \cdot \boldsymbol{S}^-\boldsymbol{\nu}.
\end{aligned} \tag{3.76}$$

Inequality (3.76) must be fulfilled for all tuples $(V, \nabla_\Gamma T, \boldsymbol{v}^+, \boldsymbol{v}^-)$, then by Theorem 2 of Appendix B there exist functions

$$
\begin{aligned}
&A_1(Y_I) : \mathbb{R} \to \mathbb{R}, \quad A_i(Y_I) : \mathbb{R}^d \to \mathbb{R},\\
&B_1(Y_I) : \mathbb{R} \to \mathbb{R}^d, \; B_i(Y_I) : \mathbb{R}^d \to \mathbb{R}^d,\\
&C_1(Y_I) : \mathbb{R} \to \mathbb{R}^d, \; C_i(Y_I) : \mathbb{R}^d \to \mathbb{R}^d,\\
&D_1(Y_I) : \mathbb{R} \to \mathbb{R}^d, \; D_i(Y_I) : \mathbb{R}^d \to \mathbb{R}^d, \quad i \in \{2,3,4\},
\end{aligned}
$$

which are linear for all Y_I, such that

$$
\begin{aligned}
& A_1 V + A_2 \nabla_\Gamma T + A_3 \boldsymbol{v}^+ + A_4 \boldsymbol{v}^- \qquad (3.77)\\
= \;& f\kappa - \nabla_\Gamma \cdot (\boldsymbol{P} f_{,\boldsymbol{\nu}}) + \left[\varrho \left(F + \tfrac{1}{2}|\boldsymbol{v}|^2\right)\right] - \sum_{i=1}^{N} \mu_i [\varrho c_i],\\
-\boldsymbol{j}_S \;=\; & B_1 V + B_2 \nabla_\Gamma T + B_3 \boldsymbol{v}^+ + B_4 \boldsymbol{v}^-,\\
\boldsymbol{S}^+\boldsymbol{\nu} \;=\; & C_1 V + C_2 \nabla_\Gamma T + C_3 \boldsymbol{v}^+ + C_4 \boldsymbol{v}^-,\\
\boldsymbol{S}^-\boldsymbol{\nu} \;=\; & D_1 V + D_2 \nabla_\Gamma T + D_3 \boldsymbol{v}^+ + D_4 \boldsymbol{v}^-,
\end{aligned}
$$

for all variables $(V, \nabla_\Gamma T, \boldsymbol{v}^+, \boldsymbol{v}^-)$. As before, (3.77) is the generalized Gibbs-Thomson law.

Chapter 4

Regularity and Existence Results.

A rather theoretical point of interest concerns the *existence theory* of a given system of phase field equations. In a customary manner this will be done by an *approximation method* like *Galerkin's ansatz, fix point iterations* or *implicit time discretization*. These constructive methods lead to a sequence of *approximate solutions*, but their *convergence to a solution is in question*. Usually this sequence has a *weak limit*, but in general this convergence is *insufficient for nonlinear equations*. Thus one employs compactness results to prove a better convergence. Usually classical compactness arguments as *Aubin-Lions' lemma* (cf. Lions [60], Showalter [74]) lead to the desired convergence that is sufficient to prove an *existence result*. Other methods make explicit use of the *structure* of the given equation, as the method of *compensated compactness*.

In this chapter we consider a model problem for a given *one-component thermodynamic system of N distinguished phases* that is considered as a *time-dependent, closed and isothermal system without particle flow*. In addition we allow *different surface tensions* along the phase interfaces. For this model problem we will employ a Galerkin ansatz and for spatial dimension $d = 1$ it is possible to prove *higher regularity*. From this regularity results we can extract the sufficient convergence results.

In spite of these simplifications the difficulties arise from the *nonlinear structure* even in the terms of lower order in connection with the critical growth complicating the derivation of uniform estimates. Since our model problem is a system of equations maximum principles from parabolic theory are not applicable.

4.1 A model problem for isothermal multi-component phase field systems.

Statement of the problem.

Introduction.

We consider an isothermal and one-component system of N phases, besides we neglect convection phenomena and chemical reactions. Thus our system of partial differential equations reduces to the phase field equations (1.8). The main difficulties arise first from the coupling of every phase field to one another and second from the nonlinear structure of the evolution operator. For an arbitrarily fixed $\alpha \in \{0, 1\}$ we will slightly modify our notation by introducing the affine (if $\alpha \neq 0$) linear space

$$\Sigma_\alpha = \{\boldsymbol{r} = (r_i)_{i=1}^N \in \mathbb{R}^N |\ r_1 + \cdots + r_N = \alpha\}.$$

Now let $\Omega \subset \mathbb{R}^d$ represent the space, where the formation of different phases will take place, i.e. we will consider our model problem in Ω. Precisely we assume $\Omega \subset \mathbb{R}^d$ to be a domain of finite measure with a closed C^2-boundary $\partial\Omega$. As usual let $\phi_i : \Omega \to \mathbb{R}$ represent the volume fraction of phase i and for a system of N distinct phases let $\boldsymbol{\phi} = (\phi_i)_{i=1}^N$ denote the *N-dimensional phase field* subject to the normalization condition $\sum_{i=1}^N \phi_i = 1$ or $\boldsymbol{\phi} \in \Sigma_1$, respectively. Let $\mathcal{M}_\alpha \subset H^{1,2}\left(\Omega; \mathbb{R}^N\right)$ the set of functions $\boldsymbol{\zeta} \in H^{1,2}\left(\Omega; \mathbb{R}^N\right)$ such that $\boldsymbol{\zeta}(\boldsymbol{x}) \in \Sigma_\alpha$ for almost all $\boldsymbol{x} \in \Omega$, that is $H^{1,2}\left(\Omega; \Sigma_\alpha\right)$. Now let $\mathcal{M}_1$ the class of admissible phase fields and $\mathcal{M}_0$ the linear space of admissible variations (or test functions) of elements in $\mathcal{M}_1$. Besides we assume that our *Ginzburg-Landau energy* as defined in (1.9) is a *non-negative* function on $\mathcal{M}_1$ and *independent of temperature and concentration*, i.e. it simplifies to

$$\mathscr{F}(\boldsymbol{\phi}) = \int_\Omega \left(F\left(\boldsymbol{\phi}\right) + \left(\varepsilon a\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) + \frac{1}{\varepsilon} w\left(\boldsymbol{\phi}\right) \right) \right) \,\mathrm{d}\boldsymbol{x}.$$

As usual the function $a : \mathbb{R}^N \times \mathbb{R}^{N\times d} \to \mathbb{R}_+$ represents a gradient energy density depending on $\boldsymbol{\phi}$ as well as on its spatial derivatives. Furthermore $w : \mathbb{R}^N \to \mathbb{R}_+$ is given by a smooth multistable potential that has *N distinct global minima*, that correspond to each of the N pure phases. Hence the formation of different phases will be driven by the potential w. Since w does not depend on the derivatives of $\boldsymbol{\phi}$ its minima might have jump discontinuities in general. To keep minimizers $\boldsymbol{\phi}$ in the admissible class $\mathcal{M}_1$ or to guarantee convergence of minimzing sequences at least in $H^{1,2}\left(\Omega; \mathbb{R}^N\right)$ the term $a\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right)$ penalizes large gradients of $\boldsymbol{\phi}$ as some generalization of elliptic regularization. Finally the term $F\left(\boldsymbol{\phi}\right)$ denotes the bulk density of the free energy. For brevity let us define

$$\psi\left(\boldsymbol{\phi}\right) = F\left(\boldsymbol{\phi}\right) + \frac{1}{\varepsilon} w\left(\boldsymbol{\phi}\right) \text{ and } A(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) = \varepsilon a\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) + \psi\left(\boldsymbol{\phi}\right).$$

Principal assumptions.

Now we fix the assumptions on the structure of $a(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi})$ and $\psi(\boldsymbol{\phi})$ which will be essential for applying variational methods hereafter. For technical reasons we define intervals I_1, $I_2 \subset \bar{\mathbb{R}}$ by

$$I_1 = \begin{cases} [1,\infty] & \text{if } d=1, \\ [1,\infty) & \text{if } d=2, \\ \left[1, \frac{d}{d-2}\right] & \text{if } d>2, \end{cases} \text{ and } I_2 = \begin{cases} [1,\infty] & \text{if } d=1, \\ [1,\infty) & \text{if } d=2, \\ \left[1, \frac{d+2}{d-2}\right] & \text{if } d>2. \end{cases}$$

May we begin with the gradient term $a : \mathbb{R}^N \times \mathbb{R}^{N\times d} \to \mathbb{R}_+$, where $a : (\boldsymbol{z}, \boldsymbol{p}) \mapsto a(\boldsymbol{z}, \boldsymbol{p})$, that we assume to fulfill the following properties.

(D1) *Convexity* of $a(\boldsymbol{z}, \boldsymbol{p})$ in $\boldsymbol{p} \in \mathbb{R}^{N\times d}$ for all $\boldsymbol{z} \in \mathbb{R}^N$, i.e.

$$a(\boldsymbol{z}, \lambda \boldsymbol{p}_1 + (1-\lambda)\,\boldsymbol{p}_2) \le \lambda a(\boldsymbol{z}, \boldsymbol{p}_1) + (1-\lambda)\, a(\boldsymbol{z}, \boldsymbol{p}_2) \tag{4.1}$$

holds for $0 \le \lambda \le 1$ and all $\boldsymbol{p}_1, \boldsymbol{p}_2 \in \mathbb{R}^{N\times d}$.

(D2) *Coercivity* of $a(\boldsymbol{z}, \boldsymbol{p})$ in $\boldsymbol{p}$. There exist numbers $c_0 > 0$ and $c_1 \ge 0$ such that

$$a(\boldsymbol{z}, \boldsymbol{p}) \ge c_0 |\boldsymbol{p}|^2 - c_1 \tag{4.2}$$

holds for all $\boldsymbol{z} \in \mathbb{R}^N$ and $\boldsymbol{p} \in \mathbb{R}^{N\times d}$.

(D3) *Controlled growth* of $a_{,\boldsymbol{p}}(\boldsymbol{z}, \boldsymbol{p})$ and $a_{,\boldsymbol{\phi}}(\boldsymbol{z}, \boldsymbol{p})$ in $\boldsymbol{p}$. There exist numbers $c_{\boldsymbol{\phi}},\ c_{\boldsymbol{p}} > 0$ and $p \in I_1$ such that

$$|a_{,\boldsymbol{p}}(\boldsymbol{z}, \boldsymbol{p})| \le c_{\boldsymbol{p}} \left(1 + |\boldsymbol{z}|^p + |\boldsymbol{p}|\right) \text{ and } |a_{,\boldsymbol{\phi}}(\boldsymbol{z}, \boldsymbol{p})| \le c_{\boldsymbol{\phi}} \left(1 + |\boldsymbol{z}|^{p-1} + |\boldsymbol{p}|^2\right) \tag{4.3}$$

holds for all $\boldsymbol{z} \in \mathbb{R}^N$ and $\boldsymbol{p} \in \mathbb{R}^{N\times d}$.

(D4) *Continuity* of $a(\boldsymbol{z}, \boldsymbol{p})$, $a_{,\boldsymbol{\phi}}(\boldsymbol{z}, \boldsymbol{p})$ and $a_{,\boldsymbol{p}}(\boldsymbol{z}, \boldsymbol{p})$ in $\boldsymbol{z}$ as well as in $\boldsymbol{p}$.

(D5) Let $a(\boldsymbol{z}, \boldsymbol{0}) = 0$ for all $\boldsymbol{z} \in \mathbb{R}^N$.

For the gradient-free term $\psi = \psi(\boldsymbol{z})$ we postulate the following conditions.

(D6) *Lower bound* for $\psi(\boldsymbol{z})$, i.e. we assume that there exist numbers $b_0 > 0$ and $b_1 \ge 0$ as well as $q \ge 1$ such that

$$\psi(\boldsymbol{z}) \ge b_0 |\boldsymbol{z}|^q - b_1 \tag{4.4}$$

is fulfilled.

(D7) *Upper bound* for $\psi_{,\boldsymbol{\phi}}(\boldsymbol{z})$, i.e. we assume that there exist numbers $b_{\boldsymbol{\phi}} > 0$ and $p' \in I_2$ such that

$$|\psi_{,\boldsymbol{\phi}}(\boldsymbol{z})| \le b_{\boldsymbol{\phi}} \left(|\boldsymbol{z}|^{p'} + 1\right) \tag{4.5}$$

is valid.

(D8) *Continuity* of $\psi_{,\boldsymbol{\phi}}(\boldsymbol{z})$ with respect to $\boldsymbol{z}$.

Remark 4.1.1. Assume that (D1)-(D5) hold true. Then the convexity of $a(\boldsymbol{z},\boldsymbol{p})$ in $\boldsymbol{p}$ leads to coercivity of $a_{,\boldsymbol{p}}(\boldsymbol{z},\boldsymbol{p})$ similar to (4.2) as well as it leads to growth estimates for $a(\boldsymbol{z},\boldsymbol{p})$ similar to (4.3(1)). Precisely from (D2) and (D5) follows

$$c_0|\boldsymbol{p}|^2 - c_1 \leq a(\boldsymbol{z},\boldsymbol{p}) \leq a_{,\boldsymbol{p}}(\boldsymbol{z},\boldsymbol{p}) : \boldsymbol{p},$$

as well as

$$a(\boldsymbol{z},\boldsymbol{p}) \leq a_{,\boldsymbol{p}}(\boldsymbol{z},\boldsymbol{p}) : \boldsymbol{p} \leq |a_{,\boldsymbol{p}}(\boldsymbol{z},\boldsymbol{p})|\,|\boldsymbol{p}| \leq c_{\boldsymbol{p}}\left(1+|\boldsymbol{z}|^p+|\boldsymbol{p}|\right)|\boldsymbol{p}|.$$

Thus $a(\boldsymbol{z},\boldsymbol{p})$ and $a_{,\boldsymbol{p}}(\boldsymbol{z},\boldsymbol{p}) : \boldsymbol{p}$ have essentially the same upper and lower bounds with equal growth exponents.

Spaces and sets of functions.

To build up our framework we will use several spaces of integrable and weakly differentiable functions. As *central function spaces* we will use spaces based on $L^2(\Omega) = L^2(\Omega;\mathbb{R})$ and $H^{1,2}(\Omega) = H^{1,2}(\Omega;\mathbb{R})$ as well as on its dual counterparts $L^2(\Omega)'$ and $(H^{1,2}(\Omega))'$. To be more precise we will need their M-fold cartesian products, i.e.

$$\begin{aligned} L^2(\Omega;\mathbb{R}^M) &\stackrel{\text{def}}{=} \left(L^2(\Omega)\right)^M, \\ H^{1,2}(\Omega;\mathbb{R}^M) &\stackrel{\text{def}}{=} \left(H^{1,2}(\Omega)\right)^M, \\ \left(H^{1,2}(\Omega;\mathbb{R}^M)\right)' &\stackrel{\text{def}}{=} \left(\left(H^{1,2}(\Omega)\right)'\right)^M. \end{aligned}$$

For brevity we will henceforth write

$$\mathcal{H}^M \stackrel{\text{def}}{=} L^2(\Omega;\mathbb{R}^M), \quad \mathcal{V}^M \stackrel{\text{def}}{=} H^{1,2}(\Omega;\mathbb{R}^M) \text{ and } \left(\mathcal{V}^M\right)' \stackrel{\text{def}}{=} \left(H^{1,2}(\Omega;\mathbb{R}^M)\right)'.$$

In this context we have $\mathcal{M}_\alpha \subset \mathcal{V}^N \subset \mathcal{H}^N$.

In addition it is necessary to introduce spaces of functions f which have values in Banach spaces, i.e. $f : t \mapsto f(t) \in \mathcal{X}$ where $t \in I \subset \mathbb{R}$ and $\mathcal{X}$ is a Banach space. For definition of p-integrable functions $f : I \to \mathcal{X}$ we refer to [87, § 24]. For $T > 0$ we just introduce the following function spaces:

$$\begin{aligned} L^p\left(0,T;\mathcal{H}^M\right) &\stackrel{\text{def}}{=} L^p\left(0,T;L^2(\Omega;\mathbb{R}^M)\right), \\ L^p\left(0,T;\mathcal{V}^M\right) &\stackrel{\text{def}}{=} L^p\left(0,T;H^{1,2}(\Omega;\mathbb{R}^M)\right), \\ L^{p'}\left(0,T;\left(\mathcal{V}^M\right)'\right) &\stackrel{\text{def}}{=} L^{p'}\left(0,T;\left(H^{1,2}(\Omega;\mathbb{R}^M)\right)'\right), \\ L^p\left(0,T;\mathcal{M}_\alpha\right) &\stackrel{\text{def}}{=} L^p\left(0,T;H^{1,2}(\Omega;\Sigma_\alpha)\right). \end{aligned}$$

In the sequel M is either equal to one or equals the number of different phases, i.e. $M = N$.

To carry out the following computations we will henceforth assume one of the following two conditions:

(D9) The spatial dimension d is equal to one.

(D10) The gradient energy $a = a(\boldsymbol{z}, \boldsymbol{p})$ is *homogeneous of degree two* in both variables $\boldsymbol{z}$ and $\boldsymbol{p}$. Besides we assume $a(\boldsymbol{z}, \boldsymbol{p})$ to be *convex* also in the $\boldsymbol{z}$-variable.

The Euler-Lagrange equations.

Proposition 4.1.1. *We assume that (D1)-(D8) and either (D9) or (D10) hold true. Then for every $\boldsymbol{\phi}, \boldsymbol{\zeta} \in \mathcal{V}^N$ the integrals*

$$\int_\Omega a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x},\ \int_\Omega a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) : \mathrm{D}\,\boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x},\ \int_\Omega \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x},$$

exist and are finite.

Proof. First assume that (D9) is valid. Thus by Sobolev's embedding theorem (cf. Appendix B and [35, Chs. 10 & 11]) we have $\boldsymbol{\phi}, \boldsymbol{\zeta} \in L^\infty(\Omega; \mathbb{R}^N)$ and

$$\begin{aligned} |a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}| &\leq c_{\boldsymbol{\phi}} \|\boldsymbol{\zeta}\|_{L^\infty(\Omega;\mathbb{R}^N)} \left(1 + |\boldsymbol{\phi}|^{p-1} + |\,\mathrm{D}\,\boldsymbol{\phi}|^2\right), && (4.6)\\ |\psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}| &\leq b_{\boldsymbol{\phi}} \|\boldsymbol{\zeta}\|_{L^\infty(\Omega;\mathbb{R}^N)} \left(1 + |\boldsymbol{\phi}|^{p'}\right), && (4.7) \end{aligned}$$

holds. In addition we estimate

$$\begin{aligned} |a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) : \mathrm{D}\,\boldsymbol{\zeta}| &\leq c_{\boldsymbol{p}} \left(1 + |\boldsymbol{\phi}|^p + |\,\mathrm{D}\,\boldsymbol{\phi}|\right) |\,\mathrm{D}\,\boldsymbol{\zeta}| && (4.8)\\ &\leq \frac{c_{\boldsymbol{p}}}{2} \left(1 + |\boldsymbol{\phi}|^{2p} + |\,\mathrm{D}\,\boldsymbol{\phi}|^2 + |\,\mathrm{D}\,\boldsymbol{\zeta}|^2\right). && (4.9) \end{aligned}$$

Since $\boldsymbol{\phi}, \boldsymbol{\zeta} \in \mathcal{V}^N$ the terms $|\,\mathrm{D}\,\boldsymbol{\zeta}|^2$, $|\,\mathrm{D}\,\boldsymbol{\phi}|^2$ and $|\boldsymbol{\phi}|^q$, ($q \in \{p', p-1, 2p\}$) are integrable; hence the assertion follows in case of (D9).

Secondly we assume (D10) instead of (D9). Then we estimate by use of (D3)

$$|a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) : \mathrm{D}\,\boldsymbol{\zeta}| \leq c_{\boldsymbol{p}} \left(1 + |\boldsymbol{\phi}|^{2p} + 2|\,\mathrm{D}\,\boldsymbol{\phi}|^2 + 2|\,\mathrm{D}\,\boldsymbol{\zeta}|^2\right) \tag{4.10}$$

where the last term is integrable since $\boldsymbol{\phi}, \boldsymbol{\zeta} \in \mathcal{V}^N$ and $2p(d-2) \leq 2d$. Furthermore we can estimate

$$\begin{aligned} a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\zeta} &= a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\phi} + a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot (\boldsymbol{\zeta} - \boldsymbol{\phi})\\ &\leq a(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) + a(\boldsymbol{\zeta}, \mathrm{D}\,\boldsymbol{\phi}), \end{aligned}$$

and similarly

$$a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot (-\boldsymbol{\zeta}) \leq a(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) + a(-\boldsymbol{\zeta}, \mathrm{D}\,\boldsymbol{\phi}) \leq a(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) + a(\boldsymbol{\zeta}, \mathrm{D}\,\boldsymbol{\phi}),$$

by two-homogeneity. Then by (D3) and Remark 4.1.1 we infer

$$\begin{aligned} |a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}| &\leq 2c_{\boldsymbol{p}} \left(1 + |\boldsymbol{\phi}|^p + |\boldsymbol{\zeta}|^p + |\,\mathrm{D}\,\boldsymbol{\phi}|\right) |\,\mathrm{D}\,\boldsymbol{\phi}|\\ &\leq c_{\boldsymbol{p}} \left(1 + 5|\,\mathrm{D}\,\boldsymbol{\phi}|^2 + |\boldsymbol{\phi}|^{2p} + |\boldsymbol{\zeta}|^{2p}\right). && (4.11) \end{aligned}$$

Again the right hand side is integrable since $\boldsymbol{\phi} \in \mathcal{V}^N$ and $2p(d-2) \leq 2d$. Then it remains to estimate:

$$\begin{aligned} |\psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}| &\leq b_{\boldsymbol{\phi}} \left(1 + |\boldsymbol{\phi}|^{p'}\right) |\boldsymbol{\zeta}| \\ &\leq b_{\boldsymbol{\phi}} \left(|\boldsymbol{\zeta}| + \frac{1}{q'} |\boldsymbol{\phi}|^{p'q'} + \frac{1}{q} |\boldsymbol{\zeta}|^q \right), \end{aligned} \tag{4.12}$$

by Youngs inequality where $q > 1$ is chosen such that q, $p' \cdot q' \leq \frac{2d}{d-2}$. Then the right hand side is integrable again and integrability of $a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) : \mathrm{D}\,\boldsymbol{\zeta}$, $a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}$, $\psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}$ follows in case of (D10). □

This enables us to apply the following variational methods. We have defined $\mathcal{M}_1$ as admissible class for our Ginzburg-Landau energy. Obviously for any given $\eta > 0$ and all functions $\boldsymbol{\phi} \in \mathcal{M}_1$, $\boldsymbol{\zeta} \in \mathcal{M}_0$ the variation $\boldsymbol{\phi} + \eta\boldsymbol{\zeta}$ is admissible again (i.e. it is an element of $\mathcal{M}_1$) and hence the first variation in direction of $\boldsymbol{\zeta}$ is defined for all $\boldsymbol{\zeta} \in \mathcal{M}_0$, precisely it is given via

$$\begin{aligned} \left\langle \boldsymbol{\zeta}, \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right\rangle &= \left. \frac{\mathrm{d}\mathscr{F}\left(\boldsymbol{\phi} + \eta\boldsymbol{\zeta}\right)}{\mathrm{d}\eta} \right|_{\eta=0} \\ &= \int_\Omega \left(A_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) \cdot \boldsymbol{\zeta} + A_{,\boldsymbol{p}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) : \mathrm{D}\,\boldsymbol{\zeta} \right) \mathrm{d}\boldsymbol{x} \\ &= \varepsilon \int_\Omega \left(a_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) \cdot \boldsymbol{\zeta} + a_{,\boldsymbol{p}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) : \mathrm{D}\,\boldsymbol{\zeta} \right) \mathrm{d}\boldsymbol{x} \\ &+ \int_\Omega \psi_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}\right) \cdot \boldsymbol{\zeta} \, \mathrm{d}\boldsymbol{x}. \end{aligned}$$

Here we have set

$$\left\langle \boldsymbol{\zeta}, \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right\rangle = \sum_{i=1}^N \left\langle \zeta_i, \frac{\delta \mathscr{F}}{\delta \phi_i}(\boldsymbol{\phi}) \right\rangle,$$

for brevity. From classical calculus of variations it is well-known that a *minimizer* $\boldsymbol{\phi}$ of $\mathscr{F} : \mathcal{M}_1 \to \mathbb{R}_+$ satisfies the *Euler-Lagrange equations*

$$\left\langle \boldsymbol{\zeta}, \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right\rangle = 0 \text{ for all } \boldsymbol{\zeta} \in \mathcal{M}_0. \tag{4.13}$$

In order to state a strong form of (4.13) we will now prove a generalization of (4.13). Moreover this generalization is essential for applying the Galerkin method.

Proposition 4.1.2. *Let $\boldsymbol{\Pi}^N : \mathbb{R}^N \to \Sigma_0$ the orthogonal projection onto Σ_0, given by $\boldsymbol{\Pi}^N = \boldsymbol{I} - \frac{1}{N}\mathbf{1} \otimes \mathbf{1}$, where $\mathbf{1} = (1, \ldots, 1)^\top \in \mathbb{R}^N$. Then $\boldsymbol{\phi} \in \mathcal{M}_1$ fulfills (4.13), i.e.*

$$\left\langle \boldsymbol{\zeta}, \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right\rangle = 0 \textit{ for all } \boldsymbol{\zeta} \in \mathcal{M}_0,$$

if and only if it fulfills

$$\left\langle \boldsymbol{\zeta}, \boldsymbol{\Pi}^N \left(\frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right) \right\rangle = 0 \textit{ and } \left\langle \boldsymbol{\zeta}, \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) - \boldsymbol{\lambda} \right\rangle = 0 \textit{ for all } \boldsymbol{\zeta} \in \mathcal{V}^N, \tag{4.14}$$

where $\boldsymbol{\lambda}$ *is a vector-valued* Lagrange multiplier *given by* $\boldsymbol{\lambda} = (\lambda)_{i=1}^N \in \mathbb{R}^N$ *and*

$$\lambda = \tfrac{1}{N} \sum_{i=1}^{N} \frac{\delta \mathscr{F}}{\delta \phi_i}(\boldsymbol{\phi}).$$

Proof. For any given $\boldsymbol{\zeta} \in \mathcal{V}^N$ let $\boldsymbol{\zeta}^N = \boldsymbol{\Pi}^N \boldsymbol{\zeta}$, which is an admissible test function in (4.13). Then we have

$$\begin{aligned} \left\langle \boldsymbol{\zeta}^N, \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right\rangle &= \int_\Omega \left(A_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) \cdot \boldsymbol{\Pi}^N \boldsymbol{\zeta} + A_{,\boldsymbol{p}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) : \mathrm{D}\left(\boldsymbol{\Pi}^N \boldsymbol{\zeta}\right)\right) \mathrm{d}\boldsymbol{x} \\ &= \int_\Omega \left(A_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) \cdot \boldsymbol{\Pi}^N \boldsymbol{\zeta} + A_{,\boldsymbol{p}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) : \boldsymbol{\Pi}^N \mathrm{D}\,\boldsymbol{\zeta}\right) \mathrm{d}\boldsymbol{x}, \end{aligned}$$

since $\partial_{x_k}\left(\boldsymbol{\Pi}^N \boldsymbol{\zeta}\right) = \boldsymbol{\Pi}^N \partial_{x_k} \boldsymbol{\zeta}$. By $\boldsymbol{\Pi}^N = \left(\boldsymbol{\Pi}^N\right)^\top$ we have

$$\begin{aligned} \left\langle \boldsymbol{\zeta}^N, \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right\rangle &= \int_\Omega \left(\boldsymbol{\Pi}^N \left(A_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right)\right) \cdot \boldsymbol{\zeta} + \left(\boldsymbol{\Pi}^N A_{,\boldsymbol{p}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right)\right) : \mathrm{D}\,\boldsymbol{\zeta}\right) \mathrm{d}\boldsymbol{x} \\ &= \left\langle \boldsymbol{\zeta}, \boldsymbol{\Pi}^N \left(\frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right) \right\rangle \end{aligned}$$

what proves (4.14(1)). By definition of $\boldsymbol{\Pi}^N$ we have

$$N \boldsymbol{e}_k \cdot \left(\boldsymbol{\Pi}^N \left(\frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right) \right) = N \frac{\delta \mathscr{F}}{\delta \phi_k}(\boldsymbol{\phi}) - \mathbf{1} \cdot \frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) = N \frac{\delta \mathscr{F}}{\delta \phi_k}(\boldsymbol{\phi}) - \sum_{i=1}^{N} \frac{\delta \mathscr{F}}{\delta \phi_i}(\boldsymbol{\phi}). \tag{4.15}$$

By $\lambda = \frac{1}{N} \sum_{i=1}^N \frac{\delta \mathscr{F}}{\delta \phi_i}(\boldsymbol{\phi})$ equation (4.21) is

$$\boldsymbol{e}_k \cdot \left(\boldsymbol{\Pi}^N \left(\frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right) \right) = \frac{\delta \mathscr{F}}{\delta \phi_k}(\boldsymbol{\phi}) - \lambda.$$

Hence we obtain (4.14(2)). The equivalence of (4.14(1)) and (4.13) follows from $\boldsymbol{\Pi}^N \boldsymbol{\zeta} = \boldsymbol{\zeta}$ for all $\boldsymbol{\zeta} \in \mathcal{M}_0$. □

By (4.14) we have derived a sufficiently general formulation of our variational problem that allows for test functions $\boldsymbol{\zeta} \in \mathcal{V}^N$. Hence we can state a strong formulation via

$$\nabla \cdot \left(\boldsymbol{\Pi}^N A_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \right) - \boldsymbol{\Pi}^N A_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) = \mathbf{0} \text{ in } \Omega,$$

and *no-flux boundary conditions*

$$\boldsymbol{\Pi}^N a_{,\boldsymbol{p}}\left(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}\right) \boldsymbol{\nu}_\Omega = \mathbf{0} \text{ on } \partial\Omega.$$

The time-dependent problem as gradient flow.

So far we have discussed a *time-independent* variational problem for a given Ginzburg-Landau functional. Such a variational problem allows for description of *equilibrium state*, where all

interesting fields are *independent of* time t. If several equilibrium problems of this type at distinct times are considered it remains to fix assumptions on the mechanism that correlates two such problems to different (or "infinitesimally neighboring") times. In this context we get *time-dependent* fields and the term *equilibrium* is no longer justified. Hence we postulate that the *time evolution* of $\boldsymbol{\phi}$ is given by the gradient flow

$$\frac{\partial \boldsymbol{\phi}}{\partial t} = -\boldsymbol{\Pi}^N \left(\frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) \right) = - \left(\frac{\delta \mathscr{F}}{\delta \boldsymbol{\phi}}(\boldsymbol{\phi}) - \boldsymbol{\lambda} \right), \tag{4.16}$$

for sufficiently smooth $\boldsymbol{\phi}$. We will supplement this setting to a parabolic initial-boundary problem by no-flux boundary conditions, i.e.

$$\boldsymbol{\Pi}^N a_{,\boldsymbol{p}} \left(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi} \right) \boldsymbol{\nu}_\Omega = \mathbf{0} \text{ on } \partial\Omega \tag{4.17}$$

and the initial condition

$$\boldsymbol{\phi}\left(0, \boldsymbol{x}\right) = \boldsymbol{\phi}_0\left(\boldsymbol{x}\right), \tag{4.18}$$

for a given function $\boldsymbol{\phi}_0\left(\boldsymbol{x}\right) \in \mathcal{M}_1$.

By (4.17) we can pass to the weak form of (4.16) which is given by (4.18) and

$$\begin{aligned} \int_0^T \left\langle \boldsymbol{\zeta}, \frac{\partial \boldsymbol{\phi}}{\partial t} \right\rangle \mathrm{d}t = &-\varepsilon \int_{\Omega_T} \left(a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi}) : \mathrm{D}\, \boldsymbol{\zeta} + a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi}) \cdot \boldsymbol{\zeta} \right) \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \\ &- \int_{\Omega_T} \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \\ &+ \frac{1}{N}\varepsilon \int_{\Omega_T} \left((a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi})\mathbf{1}) \cdot (\mathrm{D}\, \boldsymbol{\zeta}\mathbf{1}) \right) \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \\ &+ \frac{1}{N}\varepsilon \int_{\Omega_T} (a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi}) \cdot \mathbf{1})(\boldsymbol{\zeta} \cdot \mathbf{1})\ \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \\ &+ \frac{1}{N} \int_{\Omega_T} (\psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \mathbf{1})(\boldsymbol{\zeta} \cdot \mathbf{1})\ \mathrm{d}\boldsymbol{x}\, \mathrm{d}t, \end{aligned} \tag{4.19}$$

which holds for all $\boldsymbol{\zeta} \in L^2\left(0, T; \mathcal{V}^N\right)$. Here we understand $\int_0^T \left\langle \boldsymbol{\zeta}, \frac{\partial \boldsymbol{\phi}}{\partial t} \right\rangle \mathrm{d}t$ as

$$\int_0^T \left\langle \boldsymbol{\zeta}, \frac{\partial \boldsymbol{\phi}}{\partial t} \right\rangle \mathrm{d}t = \lim_{n\to\infty} \int_0^T \left\langle \boldsymbol{\zeta}, \frac{\partial \boldsymbol{\phi}^{(n)}}{\partial t} \right\rangle \mathrm{d}t, \ \int_0^T \left\langle \boldsymbol{\zeta}, \frac{\partial \boldsymbol{\phi}^{(n)}}{\partial t} \right\rangle \mathrm{d}t = \int_{\Omega_T} \boldsymbol{\zeta} \cdot \frac{\partial \boldsymbol{\phi}^{(n)}}{\partial t}\ \mathrm{d}\boldsymbol{x}\, \mathrm{d}t, \tag{4.20}$$

where $\boldsymbol{\zeta} \in L^2(0, T; \mathcal{V}^N)$, $\frac{\partial \boldsymbol{\phi}^{(n)}}{\partial t} \in L^2(0, T; \mathcal{H}^N)$ for all $n \in \mathbb{N}$ and $\frac{\partial \boldsymbol{\phi}^{(n)}}{\partial t} \rightharpoonup \frac{\partial \boldsymbol{\phi}}{\partial t}$ in $L^2(0, T; \left(\mathcal{V}^N\right)')$. If we set $\bar{\boldsymbol{\zeta}} = \frac{1}{N}\boldsymbol{\zeta} \cdot \mathbf{1} = \frac{1}{N}\sum_{i=1}^N \zeta_i$ this simplifies to

$$\begin{aligned} \int_0^T \left\langle \boldsymbol{\zeta}, \frac{\partial \boldsymbol{\phi}}{\partial t} \right\rangle \mathrm{d}t \ &= \ -\varepsilon \int_{\Omega_T} \left(a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi}) : \mathrm{D}\, \boldsymbol{\zeta} + a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi}) \cdot \boldsymbol{\zeta} \right) \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \\ &- \ \int_{\Omega_T} \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \\ &+ \ \varepsilon \int_{\Omega_T} \left((a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi})\mathbf{1}) \cdot \nabla\bar{\boldsymbol{\zeta}} + (a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\, \boldsymbol{\phi}) \cdot \mathbf{1})\bar{\boldsymbol{\zeta}} \right) \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \\ &+ \ \int_{\Omega_T} (\psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \mathbf{1})\bar{\boldsymbol{\zeta}}\ \mathrm{d}\boldsymbol{x}\, \mathrm{d}t \end{aligned}$$

which holds for all $\boldsymbol{\zeta} \in L^2\left(0,T;\mathcal{V}^N\right)$ again.

Galerkin approximation.

We are now going to construct a sequence of approximate solutions $\boldsymbol{\phi}^{(n)} : (0,T) \to \mathcal{V}^N$, whose images belong to an ascending scale of finite-dimensional (i.e. n-dimensional) subspaces of $\mathcal{V}^N$. For this purpose we consider the following elliptic eigenvalue problem supplemented by homogeneous Neumann conditions:

$$\begin{aligned} -\Delta w &= \lambda w \text{ in } \Omega, \\ \boldsymbol{\nu}_\Omega \cdot \nabla w &= 0 \text{ on } \partial\Omega, \end{aligned} \tag{4.21}$$

where $\lambda \in \mathbb{C}$. Since Ω has C^2-boundary we have $w \in H^{2,2}(\Omega)$ according to standard elliptic regularity theory, cf. [42, §§ 8.3 and 8.4].

Proposition 4.1.3. *Let $\{w_k, \lambda_k\}_{k\in I}$, $\lambda_k \in \mathbb{C}$, $w_k \in H^{2,2}(\Omega)$ the family of solutions of (4.21).*

1. *The eigenvalue problem (4.21) admits an at most countable family $\{\lambda_k\}_{k\in I}$ of distinct eigenvalues $\lambda_k \in \mathbb{R}_+$ that fulfill $\lambda_k \to \infty$ as k tends to infinity.*
2. *Every eigenspace $\mathcal{E}(\lambda_k)$ is of finite dimension and eigenspaces to different eigenvalues are orthogonal in $L^2(\Omega)$ as well as in $H^{1,2}(\Omega)$.*
3. *The family $\{w_k\}_{k\in I}$ is (up to appropriate scaling factors) a* complete orthonormal system *of $L^2(\Omega)$.*
4. *In addition, $\lambda_1 \stackrel{\text{def}}{=} 0$ is an eigenvalue in (4.21) and the eigenspace $\mathcal{E}(\lambda_1 = 0)$ is spanned by all constants, i.e. $w_1 = \text{const}$.*

Sketch of the Proof. Ad 1: From Riesz-Schauder theory (cf. [87, §§ 12 and 13]) follows that $\{\lambda_k\}_{k\in I}$ is at most countable and $|\lambda_k| \to \infty$ as k tends to infinity. Since $-\Delta$ is symmetric we have $\lambda_k \in \mathbb{R}$ for all k. Moreover the *weak version* of (4.21), precisely

$$\int_\Omega \nabla\zeta \cdot \nabla w \, \mathrm{d}\boldsymbol{x} = \lambda \int_\Omega \zeta w \, \mathrm{d}\boldsymbol{x}, \text{ for all } \zeta \in H^{1,2}(\Omega),$$

leads to $\lambda_k \in \mathbb{R}_+$ for all k. Otherwise, if $\lambda_i < 0$ is an eigenvalue we would get

$$\int_\Omega |\nabla w_i|^2 \, \mathrm{d}\boldsymbol{x} = \lambda_i \int_\Omega w_i^2 \, \mathrm{d}\boldsymbol{x} \leq 0,$$

which holds true only if $w_i = 0$. In this case λ_i is *not* an eigenvalue in (4.21), thus all eigenvalues are non-negative, i.e. $\lambda_k \in \mathbb{R}_+$.

Ad 2 and 3: The orthogonality relations follow from spectral theory of self-adjoint and Fredholm operators, cf. [87, §§ 12 and 13] again as well as [27, pp. 126 ff.].

Ad 4: Finally $w_1 = \text{const} \neq 0$ solves (4.21) for $\lambda_1 = 0$. □

The functions $\{w_k\}_{k\in\mathbb{N}}$ form a basis of orthogonal functions in $L^2(\Omega)$ as well as in $H^{1,2}(\Omega)$. In the sequel we assume w_i orthonormal in $L^2(\Omega)$. Especially for $w_1 = \text{const}$ we then infer

$$1 = \int_\Omega w_1^2 \, \mathrm{d}\boldsymbol{x} = \mathcal{L}(\Omega) w_1^2,$$

thus $w_1 = \frac{1}{\sqrt{\mathcal{L}(\Omega)}}$ holds. Moreover, every eigenfunction w_i to λ_i with $i > 1$ has zero mean, i.e. $\int_\Omega w_i \, \mathrm{d}\boldsymbol{x} = 0$.

Now we define for $n \in \mathbb{N}$ our finite-dimensional ansatz spaces $\mathcal{V}_n \subset H^{1,2}(\Omega)$ by

$$\mathcal{V}_n = \operatorname{span}\{w_1, w_2, \ldots, w_n\} \text{ and } \mathcal{V}_n^N = (\mathcal{V}_n)^N,$$

and finite-dimensional approximations $\phi_k^{(n)} : [0,T] \to \mathcal{V}_n$ and $\boldsymbol{\phi}^{(n)} : [0,T] \to \mathcal{V}_n^N$ via

$$\phi_k^{(n)}(t) = \sum_{j=1}^{n} \alpha_{k,j}^{(n)}(t) \, w_j \text{ and } \boldsymbol{\phi}^{(n)}(t) = \left(\phi_k^{(n)}(t)\right)_{k=1}^{N}, \tag{4.22}$$

with unknown functions $\alpha_{k,j}^{(n)}(t)$. The initial values for $\alpha_{k,j}^{(n)}(t)$ we assume to fulfill

$$\alpha_{k,j} \overset{\text{def}}{=} \alpha_{k,j}^{(n)}(0) = \int_\Omega w_j \phi_k(0) \, \mathrm{d}\boldsymbol{x}. \tag{4.23}$$

Then state our system of Galerkin equations via

$$\begin{aligned}
\int_\Omega \boldsymbol{\zeta} \cdot \frac{\partial \boldsymbol{\phi}^{(n)}}{\partial t} \, \mathrm{d}\boldsymbol{x} = &-\varepsilon \int_\Omega \left(a_{,\boldsymbol{p}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) : \mathrm{D}\,\boldsymbol{\zeta} + a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta} \right) \mathrm{d}\boldsymbol{x} \\
&- \int_\Omega \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta} \, \mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N}\varepsilon \int_\Omega ((a_{,\boldsymbol{p}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)})\mathbf{1}) \cdot (\mathrm{D}\,\boldsymbol{\zeta}\mathbf{1}) \, \mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N}\varepsilon \int_\Omega (a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) \cdot \mathbf{1})(\boldsymbol{\zeta} \cdot \mathbf{1}) \, \mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N} \int_\Omega (\psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}) \cdot \mathbf{1})(\boldsymbol{\zeta} \cdot \mathbf{1}) \, \mathrm{d}\boldsymbol{x},
\end{aligned} \tag{4.24}$$

which holds for all $\boldsymbol{\zeta} \in \mathcal{V}_n^N$. Written for the k-th component this is

$$\begin{aligned}
\int_\Omega \zeta \frac{\partial \phi_k^{(n)}}{\partial t} \, \mathrm{d}\boldsymbol{x} = &- \int_\Omega \varepsilon a_{,\boldsymbol{p}_k}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) \cdot \nabla\zeta \, \mathrm{d}\boldsymbol{x} \\
&- \int_\Omega \left(\varepsilon a_{,\phi_k}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) + \psi_{,\phi_k}\left(\boldsymbol{\phi}^{(n)}\right)\right) \zeta \, \mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N} \sum_{i=1}^{N} \int_\Omega \varepsilon a_{,\boldsymbol{p}_i}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) \cdot \nabla\zeta \, \mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N} \sum_{i=1}^{N} \int_\Omega \left(\varepsilon a_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) + \psi_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}\right)\right) \zeta \, \mathrm{d}\boldsymbol{x},
\end{aligned} \tag{4.25}$$

which holds for all $\zeta \in \mathcal{V}_n$.

Remark 4.1.2. Per construction $\boldsymbol{\phi}^{(n)}(t)$ is weakly differentiable up to second order, i.e.$\boldsymbol{\phi}^{(n)}(t) \in H^{2,2}(\Omega;\mathbb{R}^N)$ for appropriate $t \in \mathbb{R}_+$. Thus (4.25) admits a strong formulation. In this case $\boldsymbol{\phi}^{(n)}(t)$ has fulfill two boundary conditions:

1. Since $\boldsymbol{\phi}^{(n)}(t) \in \mathcal{V}_n^N$ it fulfills $\mathrm{D}\,\boldsymbol{\phi}^{(n)}(t)\boldsymbol{\nu}_\Omega = \mathbf{0}$ on $\partial\Omega$.
2. In addition, to obtain the strong version of (4.25) $\boldsymbol{\phi}^{(n)}(t)$ has to fulfill
$$\boldsymbol{\Pi}^N a_{,\boldsymbol{p}}(\boldsymbol{\phi}^{(n)}(t), \mathrm{D}\,\boldsymbol{\phi}^{(n)}(t))\boldsymbol{\nu}_\Omega = \mathbf{0} \text{ on } \partial\Omega.$$

Then by $\zeta = w_l$ and $\boldsymbol{\alpha}_j^{(n)} = \left(\alpha_{k,j}^{(n)}\right)_{k=1}^N$ we obtain from (4.25)

$$\begin{aligned}
\frac{\partial \alpha_{k,l}^{(n)}}{\partial t} = &- \int_\Omega \varepsilon a_{,\boldsymbol{p}_k}\left(\sum_j \boldsymbol{\alpha}_j^{(n)} w_j, \sum_j \boldsymbol{\alpha}_j^{(n)} \mathrm{D}\, w_j\right) \cdot \nabla w_l \,\mathrm{d}\boldsymbol{x} \\
&- \int_\Omega \varepsilon a_{,\phi_k}\left(\sum_j \boldsymbol{\alpha}_j^{(n)} w_j, \sum_j \boldsymbol{\alpha}_j^{(n)} \mathrm{D}\, w_j\right) \,\mathrm{d}\boldsymbol{x} \\
&- \int_\Omega \psi_{,\phi_k}\left(\sum_j \boldsymbol{\alpha}_j^{(n)} w_j\right) w_l \,\mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N}\sum_{i=1}^N \int_\Omega \varepsilon a_{,\boldsymbol{p}_i}\left(\sum_j \boldsymbol{\alpha}_j^{(n)} w_j, \sum_j \boldsymbol{\alpha}_j^{(n)} \mathrm{D}\, w_j\right) \cdot \nabla w_l \,\mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N}\sum_{i=1}^N \int_\Omega \varepsilon a_{,\phi_i}\left(\sum_j \boldsymbol{\alpha}_j^{(n)} w_j, \sum_j \boldsymbol{\alpha}_j^{(n)} \mathrm{D}\, w_j\right) \,\mathrm{d}\boldsymbol{x} \\
&+ \frac{1}{N}\sum_{i=1}^N \int_\Omega \psi_{,\phi_i}\left(\sum_j \boldsymbol{\alpha}_j^{(n)} w_j\right) w_l \,\mathrm{d}\boldsymbol{x}
\end{aligned} \tag{4.26}$$

which is a system of (nonlinear) ordinary differential equations for $\boldsymbol{\alpha}_j^{(n)} = \boldsymbol{\alpha}_j^{(n)}(t)$ for each $n \in \mathbb{N}$. By virtue of (D4) and (D8) the right hand side is continuous in its variables. Hence by Peano's Theorem, cf. [21, p. 6] there exists an interval $[0, h(n)] \subseteq [0, T]$ and a local solution $\boldsymbol{\alpha}_j^{(n)} \in C^1([0, h(n)])$ which fulfills (4.23) and (4.26). For a global solution $\boldsymbol{\alpha}_j^{(n)} \in C^1([0, T])$ we refer to the next Subsection where uniform estimates will be proved.

Proposition 4.1.4. *Assume that* $\sum_{k=1}^N \phi_k^{(n)}(0) = 1$. *Then we have* $\sum_{k=1}^N \phi_k^{(n)}(t) = 1$ *for all* t *in the existence interval.*

Proof. Since
$$\sum_{k=1}^N \int_\Omega \zeta \frac{\partial \phi_k^{(n)}}{\partial t} \,\mathrm{d}\boldsymbol{x} = 0,$$
we obtain $\sum_{k=1}^N \frac{\partial \alpha_{k,l}^{(n)}}{\partial t} = 0$ using $\zeta = w_l$. On the other hand,
$$\sum_{k=1}^N \alpha_{k,j}^{(n)}(0) = \sum_{k=1}^N \int_\Omega w_j \phi_k(0) \,\mathrm{d}\boldsymbol{x} = \begin{cases} \sqrt{\mathcal{L}(\Omega)} & \text{if } j = 1, \\ 0 & \text{else.} \end{cases}$$

Thus we have

$$\sum_{k=1}^{N} \alpha_{k,j}^{(n)}(t) = \sum_{k=1}^{N} \alpha_{k,j}^{(n)}(0) = \begin{cases} \sqrt{\mathcal{L}(\Omega)} & \text{if } j = 1, \\ 0 & \text{else,} \end{cases}$$

for all t in the existence interval. Then we arrive at

$$\sum_{k=1}^{N} \phi_k^{(n)}(t) = \sum_{k=1}^{N} w_1 \alpha_{k,1}^{(n)}(t) = \frac{1}{\sqrt{\mathcal{L}(\Omega)}} \sqrt{\mathcal{L}(\Omega)} = 1.$$

□

A-priori estimates.

First we differentiate our Ginzburg-Landau functional with respect to time to obtain the following key result.

Proposition 4.1.5. *The sequence of Galerkin solutions $\{\boldsymbol{\phi}^{(n)}\}_{n\in\mathbb{N}}$ fulfills*

$$\int_{\Omega} |\partial_t \boldsymbol{\phi}^{(n)}(t)|^2 \, \mathrm{d}\boldsymbol{x} = -\frac{\mathrm{d}}{\mathrm{d}t} \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(t)\right), \tag{4.27}$$

for all $n \in \mathbb{N}$.

Proof. Clearly, differentiation of $\mathscr{F}\left(\boldsymbol{\phi}^{(n)}\right)$ with respect to t gives

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \mathscr{F}\left(\boldsymbol{\phi}^{(n)}\right) &= \int_{\Omega} \left(\varepsilon a_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) + \psi_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}^{(n)}\right)\right) \cdot \partial_t \boldsymbol{\phi}^{(n)} \, \mathrm{d}\boldsymbol{x} \\ &+ \int_{\Omega} \varepsilon a_{,\boldsymbol{p}}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) : \partial_t\left(\mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) \mathrm{d}\boldsymbol{x} \\ &= \int_{\Omega} \left(\varepsilon a_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) + \psi_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}^{(n)}\right)\right) \cdot \partial_t \boldsymbol{\phi}^{(n)} \, \mathrm{d}\boldsymbol{x} \\ &+ \int_{\Omega} \varepsilon a_{,\boldsymbol{p}}\left(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}\right) : \mathrm{D}\left(\partial_t \boldsymbol{\phi}^{(n)}\right) \mathrm{d}\boldsymbol{x}, \end{aligned}$$

where we have used $\partial_t\left(\partial_{x_k}\boldsymbol{\phi}^{(n)}\right) = \partial_{x_k}\left(\partial_t\boldsymbol{\phi}^{(n)}\right)$. Besides, since $\partial_t\boldsymbol{\phi}^{(n)} \in \mathcal{M}_0$ we have $\mathbf{1} \cdot \partial_t\boldsymbol{\phi}^{(n)} = 0$. Thus by (4.24) we arrive at

$$\int_{\Omega} |\partial_t \boldsymbol{\phi}^{(n)}(t)|^2 \, \mathrm{d}\boldsymbol{x} = -\frac{\mathrm{d}}{\mathrm{d}t} \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(t)\right),$$

what proves our result. □

Corollary 4.1.1. *From (4.27) we obtain that the Ginzburg-Landau energy decreases as time t proceeds forward, i.e.*

$$\frac{\mathrm{d}}{\mathrm{d}t} \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(t)\right) \leq 0 \text{ and } \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(s)\right) \leq \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(t)\right),$$

for almost all $t,\ s \in [0,T]$ with $s \geq t$.

Remark 4.1.3. In *isolated thermodynamical systems* (which are modeled by *no-flux* boundary conditions for essentially all fields) the free energy *cannot* increase during a time period. This is just the statement of Corollary 4.1.1; hence our gradient flow dynamics (4.16) models an *energy-dissipating* process that is quite reasonable for nonlinear diffusion phenomena.

For our exact initial state $\boldsymbol{\phi}_0$ we obtain from (4.23) that

$$\|\boldsymbol{\phi}^{(n)}(0)\|_{\mathcal{H}^N} \leq \|\boldsymbol{\phi}_0\|_{\mathcal{H}^N} \text{ as well as } \|\mathrm{D}\,\boldsymbol{\phi}^{(n)}(0)\|_{\mathcal{H}^N} \leq \|\mathrm{D}\,\boldsymbol{\phi}_0\|_{\mathcal{H}^N}$$

holds. By Remark 4.1.1 we then have $C\left(1+\|\boldsymbol{\phi}(0)\|_{\mathcal{V}^N}^2\right)$ as an uniform bound for $\mathscr{F}\left(\boldsymbol{\phi}^{(n)}(0)\right)$. Thus, for almost all $t \in (0,T)$ there exist appropriate constants C_0, $C_1 > 0$ such that

$$\begin{aligned} C_0\left(\|\boldsymbol{\phi}^{(n)}(t)\|_{\mathcal{V}^N}^2 - 1\right) &\leq \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(t)\right) \\ &\leq \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(0)\right) \leq C_1\left(\|\boldsymbol{\phi}_0\|_{\mathcal{V}^N}^2 + 1\right), \end{aligned} \tag{4.28}$$

where we have used assumption (D2). Besides, by integration of (4.27) with respect to t we obtain

$$\begin{aligned} \int_0^T \|\partial_t \boldsymbol{\phi}^{(n)}(t)\|_{L^2(\Omega)}^2 \,\mathrm{d}t &= \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(0)\right) - \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(T)\right) \\ &\leq \mathscr{F}\left(\boldsymbol{\phi}^{(n)}(0)\right) \leq C_1\left(\|\boldsymbol{\phi}_0\|_{\mathcal{V}^N}^2 + 1\right), \end{aligned}$$

by use of (4.28). Thus there exists a constant $C > 0$ such that

$$\int_0^t \|\partial_t \boldsymbol{\phi}^{(n)}(s)\|_{\mathcal{H}^N}^2 \,\mathrm{d}s + \|\boldsymbol{\phi}^{(n)}(t)\|_{\mathcal{V}^N}^2 \leq C, \tag{4.29}$$

uniformly in $n \in \mathbb{N}$ and almost all $t \in (0,T)$.

By (D4) and (D8) the right hand side in (4.26) is also continuous with respect to to $\alpha_{k,j}^{(n)}$, then by Peano's Theorem there exists a number $h = h(n) \in (0,T)$ and a local solution $\alpha_{k,j}^{(n)}$ on $(0,h)$. Following (4.29) we have an uniform bound for $\alpha_{k,j}^{(n)}$ for all n. Thus we can extend $\alpha_{k,j}^{(n)}$ beyond $(0,h)$ to obtain a global solution $\alpha_{k,j}^{(n)}$ on $(0,T)$. Clearly this solution is again uniformly bounded thanks to (4.29).

4.2 Antisymmetric differences and higher regularity.

In [58] there has been proposed the concept of antisymmetric differences to model free energies. The antisymmetric differences are given by

$$\boldsymbol{q}_{ij} = \phi_i \nabla \phi_j - \phi_j \nabla \phi_i.$$

This approach has been introduced for phase field modeling in [30] to model the gradient-based terms of interfacial free energies. In its variants it allows for isotropic as well as anisotropic materials.

In the sequel we assume that our gradient energy density $a(\boldsymbol{z}, \boldsymbol{p})$ is a function of these differences $\boldsymbol{q}_{ij}$ as just introduced. For this purpose we assume that the following assumption is fulfilled.

(D11) We assume that the gradient energy density $a(\boldsymbol{z}, \boldsymbol{p})$ admits the form

$$a(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) = \frac{1}{2}\sum_{i,j=1}^{N} a_{ij}|\phi_i \nabla\phi_j - \phi_j \nabla\phi_i|^2,$$

where $a_{ij} = a_{ji}$ for all indices i and j. In addition we assume that there exist constants $0 < \beta_1 \leq \beta_2$ such that $\beta_1 \leq a_{ij} \leq \beta_2$ holds for all indices i and j again.

Proposition 4.2.1. *Let $\boldsymbol{\phi} \in H^{2,2}(\Omega; \mathscr{G})$. The term $N\sum_{i,j=1}^{N} a_{ij}\left|\phi_i\Delta\phi_j - \phi_j\Delta\phi_i\right|^2$ is an upper bound for $\beta_1\sum_{i=1}^{N}\left|\Delta\phi_i\right|^2$, i.e.*

$$\beta_1\sum_{i=1}^{N}\left|\Delta\phi_i\right|^2 \leq N\sum_{i,j=1}^{N} a_{ij}\left|\phi_i\Delta\phi_j - \phi_j\Delta\phi_i\right|^2, \tag{4.30}$$

holds true.

Proof. Since $\sum_{i=1}^{N}\phi_i = 1$ and $\sum_{i=1}^{N}\Delta\phi_i = 0$ we obtain

$$\begin{aligned}\left|\Delta\phi_i\right|^2 &= \left(\sum_{j=1}^{N}\phi_i\Delta\phi_j - \sum_{j=1}^{N}\phi_j\Delta\phi_i\right)^2 \\ &\leq N\sum_{j=1}^{N}\left(\phi_i\Delta\phi_j - \phi_j\Delta\phi_i\right)^2\end{aligned}$$

and

$$\beta_1\sum_{i=1}^{N}\left|\Delta\phi_i\right|^2 \leq N\sum_{i,j=1}^{N} a_{ij}\left(\phi_i\Delta\phi_j - \phi_j\Delta\phi_i\right)^2,$$

which proves our result. □

4.3 Higher regularity in one space dimension.

We henceforth assume that condition (D9) is fulfilled. As a consequence we obtain

$$\operatorname{ess\,sup}_{t\in(0,T)}\|\boldsymbol{\phi}^{(n)}(t)\|_{L^\infty(\Omega;\mathbb{R}^N)} \leq C, \tag{4.31}$$

uniformly for all $n \in \mathbb{N}$. This follows directly from the estimate (4.29) and Sobolev's Embedding Theorem. Furthermore we assume that (D1)-(D8) and (D11) are fulfilled. In addition we have from (4.6), (4.7) and (4.8)

$$\int_\Omega \left(\varepsilon a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) + \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)})\right)\cdot\boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x} \leq \tilde{C}\|\boldsymbol{\zeta}\|_{L^\infty(\Omega;\mathbb{R}^N)} \leq C\|\boldsymbol{\zeta}\|_{H^{1,2}(\Omega;\mathbb{R}^N)}$$

as well as

$$\int_\Omega a_{,\boldsymbol{p}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) : \mathrm{D}\,\boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x} \le C\|\,\mathrm{D}\,\boldsymbol{\zeta}\|_{L^2(\Omega;\mathbb{R}^N)}.$$

Hence we obtain from (4.24) by integrating over $[0,T]$:

$$\left|\int_{\Omega_T} \boldsymbol{\zeta}\cdot\frac{\partial\boldsymbol{\phi}^{(n)}}{\partial t}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t\right| \le \tilde{C}\int_0^T \|\boldsymbol{\zeta}\|_{H^{1,2}(\Omega;\mathbb{R}^N)}\,\mathrm{d}t \le C\|\boldsymbol{\zeta}\|_{L^2(0,T;\mathcal{V}^N))},$$

where the constant C can be chosen independently of n. Thus $\partial_t\boldsymbol{\phi}^{(n)}$ is a linear and bounded functional on $L^2(0,T;H^{1,2}(\Omega;\mathbb{R}^N))$ and

$$\left\|\frac{\partial\boldsymbol{\phi}^{(n)}}{\partial t}\right\|_{L^2(0,T;(\mathcal{V}^N)')} \le C \tag{4.32}$$

holds uniformly for all $n\in\mathbb{N}$.

Now we will state and prove our fundamental estimate.

Lemma 4.3.1. *Let $\boldsymbol{\phi}^{(n)}$ be a solution of our Galerkin problem. Then*

$$\int_0^T \|\Delta\boldsymbol{\phi}^{(n)}\|^2_{L^2(\Omega;\mathbb{R}^N)}\,\mathrm{d}t \le \int_0^T C\left(1+\|\,\mathrm{D}\,\boldsymbol{\phi}^{(n)}\|^4_{L^4(\Omega;\mathbb{R}^{N\times d})}\right)\mathrm{d}t,$$

holds.

Proof. Since $\phi_k^{(n)}\in H^{2,2}(\Omega)$ we take $\boldsymbol{\zeta}=\Delta\boldsymbol{\phi}^{(n)}$ as test function in (4.25). Then we have

$$\begin{aligned}
&-\int_{\Omega_T}\sum_{i=1}^N\left(\partial_t\phi_i^{(n)}+\psi_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}\right)\right)\Delta\phi_i^{(n)}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t \qquad (4.33)\\
&=\int_{\Omega_T}\sum_{i,j=1}^N a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
&+\int_{\Omega_T}\sum_{i,j=1}^N a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\left(-\phi_j^{(n)}\nabla\Delta\phi_i^{(n)}\right)\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t.
\end{aligned}$$

Now by partial integration in the second summand of the right hand side of (4.33) we infer

$$\begin{aligned}
&-\int_{\Omega_T}\sum_{i=1}^N\left(\partial_t\phi_i^{(n)}+\psi_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}\right)\right)\Delta\phi_i^{(n)}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
&=\int_{\Omega_T}\sum_{i,j=1}^N a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
&+\int_{\Omega_T}\sum_{i,j=1}^N a_{ij}\nabla\cdot\left(\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\phi_j^{(n)}\right)\Delta\phi_i^{(n)}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t,\\
&=\int_{\Omega_T}2\sum_{i,j=1}^N a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
&+\int_{\Omega_T}\sum_{i,j=1}^N a_{ij}\left(\phi_i^{(n)}\Delta\phi_j^{(n)}-\phi_j^{(n)}\Delta\phi_i^{(n)}\right)\phi_j^{(n)}\Delta\phi_i^{(n)}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t.
\end{aligned}$$

Besides an easy observation shows

$$\sum_{i,j=1}^{N} a_{ij}\left(\phi_i^{(n)}\Delta\phi_j^{(n)}-\phi_j^{(n)}\Delta\phi_i^{(n)}\right)\phi_j^{(n)}\Delta\phi_i^{(n)}=-\sum_{i<j}a_{ij}\left|\phi_i^{(n)}\Delta\phi_j^{(n)}-\phi_j^{(n)}\Delta\phi_i^{(n)}\right|^2,$$

what results in

$$\begin{aligned}
&\int_{\Omega_T}\sum_{i=1}^{N}\left(\partial_t\phi_i^{(n)}+\psi_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}\right)\right)\Delta\phi_i^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
=\;&-\int_{\Omega_T}2\sum_{i,j=1}^{N}a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
+\;&\int_{\Omega_T}\sum_{i<j}a_{ij}\left|\phi_i^{(n)}\Delta\phi_j^{(n)}-\phi_j^{(n)}\Delta\phi_i^{(n)}\right|^2\mathrm{d}\boldsymbol{x}\,\mathrm{d}t. \qquad (4.34)
\end{aligned}$$

Now by Proposition 4.2.1 we can bound (4.34) from below and we obtain

$$\begin{aligned}
&\frac{\beta_1}{N}\int_{\Omega_T}\left(\sum_{i=1}^{N}\left|\Delta\phi_i^{(n)}\right|^2\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\;&\int_{\Omega_T}\sum_{i=1}^{N}\left(\partial_t\phi_i^{(n)}+\psi_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}\right)\right)\Delta\phi_i^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t \qquad (4.35)\\
+\;&\int_{\Omega_T}2\sum_{i,j=1}^{N}a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t. \qquad (4.36)
\end{aligned}$$

Now we prove upper estimates for (4.35, 4.36). Let us start with (4.35), that we estimate with Young's inequality, i.e.

$$\begin{aligned}
&\int_{\Omega_T}\left(\partial_t\phi_i^{(n)}+\psi_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}\right)\right)\Delta\phi_i^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\;&\int_{\Omega_T}\left(\frac{\delta}{2}\left|\Delta\phi_i^{(n)}\right|^2+\frac{1}{2\delta}\left(\left|\partial_t\phi_i^{(n)}\right|^2+\left|\psi_{,\phi_i}\left(\boldsymbol{\phi}^{(n)}\right)\right|^2\right)\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t.
\end{aligned}$$

It remains to estimate (4.36). Since our spatial dimension d is equal to one we employ estimate (4.31) to obtain

$$\begin{aligned}
&\int_{\Omega_T}2\sum_{i,j=1}^{N}a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)}-\phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\;&\tilde{C}\int_{\Omega_T}\sum_{i,j=1}^{N}\left(\left|\phi_i^{(n)}\right|\left|\Delta\phi_i^{(n)}\right|\left|\nabla\phi_j^{(n)}\right|^2+\left|\phi_j^{(n)}\right|\left|\Delta\phi_i^{(n)}\right|\left|\nabla\phi_i^{(n)}\right|\left|\nabla\phi_j^{(n)}\right|\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\;&C\int_{\Omega_T}\sum_{i,j=1}^{N}\left(\left|\Delta\phi_i^{(n)}\right|\left|\nabla\phi_j^{(n)}\right|^2+\left|\Delta\phi_i^{(n)}\right|\left|\nabla\phi_i^{(n)}\right|\left|\nabla\phi_j^{(n)}\right|\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t.
\end{aligned}$$

Then by Young's inequality we infer

$$\begin{aligned}
&\int_{\Omega_T} 2\sum_{i,j=1}^{N} a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)} - \phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\ & C\int_{\Omega_T}\sum_{i,j=1}^{N}\left|\Delta\phi_i^{(n)}\right|\left(\left|\nabla\phi_j^{(n)}\right|^2 + \left|\nabla\phi_i^{(n)}\right|\left|\nabla\phi_j^{(n)}\right|\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\ & \int_{\Omega_T}\sum_{i,j=1}^{N}\left(\delta\left|\Delta\phi_i^{(n)}\right|^2 + \frac{C}{\delta}\left(\left|\nabla\phi_j^{(n)}\right|^2 + \left|\nabla\phi_i^{(n)}\right|\left|\nabla\phi_j^{(n)}\right|\right)^2\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\ & \int_{\Omega_T}\sum_{i=1}^{N}\left(\delta N\left|\Delta\phi_i^{(n)}\right|^2 + \frac{4C}{\delta}\left|\nabla\phi_i^{(n)}\right|^4\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t.
\end{aligned}$$

Let us briefly summarize our estimates for (4.35, 4.36), i.e.

$$\begin{aligned}
&\int_{\Omega_T}\left(\partial_t\phi_i^{(n)} + \psi_{,\phi_i}\right)\Delta\phi_i^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\ & \int_{\Omega_T}\left(\frac{\delta}{2}\left|\Delta\phi_i^{(n)}\right|^2 + \frac{1}{2\delta}\left(\left|\partial_t\phi_i^{(n)}\right|^2 + |\psi_{,\phi_i}|^2\right)\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t,
\end{aligned}\tag{4.37}$$

where $\psi_{,\phi_i}$ is evaluated at $\boldsymbol{\phi}^{(n)}$ and

$$\begin{aligned}
&\int_{\Omega_T} 2\sum_{i,j=1}^{N} a_{ij}\left(\phi_i^{(n)}\nabla\phi_j^{(n)} - \phi_j^{(n)}\nabla\phi_i^{(n)}\right)\cdot\Delta\phi_i^{(n)}\nabla\phi_j^{(n)}\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
\leq\ & \int_{\Omega_T}\sum_{i=1}^{N}\left(\delta N\left|\Delta\phi_i^{(n)}\right|^2 + \frac{4C}{\delta}\left|\nabla\phi_i^{(n)}\right|^4\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t.
\end{aligned}\tag{4.38}$$

Then, using both (4.37) and (4.38) in the inequality (4.35, 4.36) we have

$$\begin{aligned}
\frac{\beta_1}{N}\int_{\Omega_T}\left|\Delta\boldsymbol{\phi}^{(n)}\right|^2\mathrm{d}\boldsymbol{x}\,\mathrm{d}t &= \frac{\beta_1}{N}\int_{\Omega_T}\left(\sum_{i=1}^{N}\left|\Delta\phi_i^{(n)}\right|^2\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t &(4.39)\\
&\leq \int_{\Omega_T}\sum_{i=1}^{N}\left(\frac{\delta}{2}\left|\Delta\phi_i^{(n)}\right|^2 + \frac{1}{2\delta}\left(\left|\partial_t\phi_i^{(n)}\right|^2 + |\psi_{,\phi_i}|^2\right)\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
&+ \int_{\Omega_T}\sum_{i=1}^{N}\left(\delta N\left|\Delta\phi_i^{(n)}\right|^2 + \frac{4C}{\delta}\left|\nabla\phi_i^{(n)}\right|^4\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t\\
&\leq \tilde{\delta}\int_{\Omega_T}\left|\Delta\boldsymbol{\phi}^{(n)}\right|^2\mathrm{d}\boldsymbol{x}\,\mathrm{d}t &(4.40)\\
&+ C\int_{\Omega_T}\left(\left|\mathrm{D}\,\boldsymbol{\phi}^{(n)}\right|^4 + \left|\partial_t\boldsymbol{\phi}^{(n)}\right|^2 + \left|\psi_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}^{(n)}\right)\right|^2\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t,
\end{aligned}$$

where the derivatives $\psi_{,\phi_i}$ of ψ are evaluated at $\boldsymbol{\phi}^{(n)}$ again. Now we take $\tilde{\delta} > 0$ sufficiently small, such that $\beta_1 - N\tilde{\delta} > 0$ and by subtracting (4.40) from (4.39) we obtain

$$\left(\beta_1 - N\tilde{\delta}\right)\int_{\Omega_T}\left|\Delta\boldsymbol{\phi}^{(n)}\right|^2\mathrm{d}\boldsymbol{x}\,\mathrm{d}t \leq C\int_{\Omega_T}\left(\left|\mathrm{D}\,\boldsymbol{\phi}^{(n)}\right|^4 + \left|\partial_t\boldsymbol{\phi}^{(n)}\right|^2 + \left|\psi_{,\boldsymbol{\phi}}\left(\boldsymbol{\phi}^{(n)}\right)\right|^2\right)\mathrm{d}\boldsymbol{x}\,\mathrm{d}t$$

that is

$$\int_0^T \|\Delta\boldsymbol{\phi}^{(n)}\|^2_{L^2(\Omega;\mathbb{R}^N)}\,\mathrm{d}t \le \int_0^T \tilde{C}\left(1+\|\,\mathrm{D}\,\boldsymbol{\phi}^{(n)}\|^4_{L^4(\Omega;\mathbb{R}^{N\times d})}\right)\mathrm{d}t, \tag{4.41}$$

our desired estimate. □

In order to get rid of the L^4-norm of $\mathrm{D}\,\boldsymbol{\phi}^{(n)}$ we apply *Gagliardo-Nirenberg's inequality* and *Calderón-Zygmund's inequality* (both see Appendix B) to get

$$\begin{aligned}\int_0^T \|\,\mathrm{D}\,\boldsymbol{\phi}^{(n)}\|^4_{L^4(\Omega;\mathbb{R}^{N\times d})}\,\mathrm{d}t &\le C\int_0^T \left(\|\,\mathrm{D}^2\,\boldsymbol{\phi}^{(n)}\|_{L^2(\Omega;\mathbb{R}^{N\times d\times d})}\|\,\mathrm{D}\,\boldsymbol{\phi}^{(n)}\|^3_{L^2(\Omega;\mathbb{R}^{N\times d})}+1\right)\mathrm{d}t\\ &\le C\int_0^T \left(\|\Delta\boldsymbol{\phi}^{(n)}\|_{L^2(\Omega;\mathbb{R}^N)}+1\right)\mathrm{d}t\\ &\le \varepsilon\int_0^T \|\Delta\boldsymbol{\phi}^{(n)}\|^2_{L^2(\Omega;\mathbb{R}^N)}\,\mathrm{d}t + C_\varepsilon.\end{aligned}$$

But then, we can absorb $\varepsilon\|\Delta\boldsymbol{\phi}^{(n)}\|^2_{L^2}$ into the left hand side of (4.41) and apply Calderón-Zygmund's inequality once again we obtain

$$c_0\int_0^T \|\,\mathrm{D}^2\,\boldsymbol{\phi}^{(n)}\|_{L^2(\Omega;\mathbb{R}^{N\times d\times d})}\,\mathrm{d}t \le \int_0^T \|\Delta\boldsymbol{\phi}^{(n)}\|^2_{L^2(\Omega;\mathbb{R}^N)}\,\mathrm{d}t \le C, \tag{4.42}$$

where $c_0, C>0$ are constants independent of $\boldsymbol{\phi}^{(n)}$.

Thus we have uniform bounds for

$$\begin{gathered}\operatorname{ess\,sup}_{0\le t\le T}\|\boldsymbol{\phi}^{(n)}(t)\|_{H^{1,2}(\Omega;\mathbb{R}^N)},\\ \operatorname{ess\,sup}_{0\le t\le T}\|\boldsymbol{\phi}^{(n)}(t)\|_{L^\infty(\Omega;\mathbb{R}^N)},\\ \int_0^T \|\,\mathrm{D}^2\,\boldsymbol{\phi}^{(n)}(t)\|^2_{L^2\left(\Omega;\mathbb{R}^{N\times d\times d}\right)}\,\mathrm{d}t.\end{gathered}$$

4.4 Convergence and existence result.

Our a priori-estimate (4.29) from Section 4.1 leads to the following convergence results for an appropriate subsequence $\boldsymbol{\phi}^{(n)}$:

$$\partial_t\boldsymbol{\phi}^{(n)} \rightharpoonup \partial_t\boldsymbol{\phi} \text{ in } L^2(0,T;\mathcal{H}^N), \tag{4.43}$$

$$\boldsymbol{\phi}^{(n)} \overset{*}{\rightharpoonup} \boldsymbol{\phi} \text{ in } L^\infty(0,T;\mathcal{V}^N). \tag{4.44}$$

Moreover, if assumption (D9) and (D11) are valid, we infer additional convergence results, i.e.

$$\partial_t\boldsymbol{\phi}^{(n)} \rightharpoonup \partial_t\boldsymbol{\phi} \text{ in } L^2\left(0,T;\left(\mathcal{V}^N\right)'\right), \tag{4.45}$$

$$\boldsymbol{\phi}^{(n)} \rightharpoonup \boldsymbol{\phi} \text{ in } L^2(0,T;H^{2,2}(\Omega;\mathbb{R}^N)) \tag{4.46}$$

which follow from (4.32) and (4.42), possibly after extracting an appropriate subsequence.

From the following Remark (cf. Elliott and Garcke [28]) we infer improved convergence results for $\boldsymbol{\phi}^{(n)}$.

Remark 4.4.1. Let B_1, B and B_2 Banach spaces where the embedding $B_1 \hookrightarrow B$ is compact and $B \hookrightarrow B_2$ continuous. Then the embeddings

$$\{\boldsymbol{\phi} \in L^2(0,T;B_1) |\ \partial_t \boldsymbol{\phi} \in L^2(0,T;B_2)\} \hookrightarrow L^2(0,T;B)$$

and

$$\{\boldsymbol{\phi} \in L^\infty(0,T;B_1) |\ \partial_t \boldsymbol{\phi} \in L^2(0,T;B_2)\} \hookrightarrow C([0,T];B)$$

are compact.

A proof is given in Simon, [75].

Corollary 4.4.1. *By Remark 4.4.1 we now conclude: From* (4.43), (4.46) *we infer*

$$\boldsymbol{\phi}^{(n)} \to \boldsymbol{\phi} \text{ in } L^2(0,T;\mathcal{V}^N). \tag{4.47}$$

Furthermore, from (4.44), (4.45) *we have*

$$\boldsymbol{\phi}^{(n)} \to \boldsymbol{\phi} \text{ in } C([0,T];\mathcal{H}^N). \tag{4.48}$$

As a consequence of (4.47) *we can extract a subsequence such that*

$$\boldsymbol{\phi}^{(n)} \to \boldsymbol{\phi} \text{ and } \mathrm{D}\,\boldsymbol{\phi}^{(n)} \to \mathrm{D}\,\boldsymbol{\phi} \text{ almost everywhere in } \Omega_T. \tag{4.49}$$

Now, since $a_{,\boldsymbol{p}}$, $a_{,\boldsymbol{\phi}}$ and $\psi_{,\boldsymbol{\phi}}$ are continuous due to (D4) and (D8) we obtain for a test function $\boldsymbol{\zeta} \in H^{1,2}(\Omega;\mathbb{R}^N)$ that

$$\begin{aligned} a_{,\boldsymbol{p}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) : \mathrm{D}\,\boldsymbol{\zeta} &\to a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) : \mathrm{D}\,\boldsymbol{\zeta}, \\ a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta} &\to a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}, \\ \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta} &\to \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}, \end{aligned}$$

almost everywhere in Ω_T. Similarly to Proposition 4.1.1, (4.9) we have

$$a_{,\boldsymbol{p}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) : \mathrm{D}\,\boldsymbol{\zeta} \le c_{\boldsymbol{p}} \left(1 + |\boldsymbol{\phi}^{(n)}|^{2p} + |\,\mathrm{D}\,\boldsymbol{\phi}^{(n)}|^2 + |\,\mathrm{D}\,\boldsymbol{\zeta}|^2\right),$$

where the right hand side is integrable. Likewise we have

$$a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta} \le c_{\boldsymbol{\phi}} \|\boldsymbol{\zeta}\|_{L^\infty(\Omega;\mathbb{R}^N)} \left(1 + |\boldsymbol{\phi}^{(n)}|^{p-1} + |\,\mathrm{D}\,\boldsymbol{\phi}^{(n)}|^2\right)$$

and

$$\psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta} \le b_{\boldsymbol{\phi}} \|\boldsymbol{\zeta}\|_{L^\infty(\Omega;\mathbb{R}^N)} \left(1 + |\boldsymbol{\phi}^{(n)}|^{p'}\right)$$

just as in (4.6) and (4.7) of Proposition 4.1.1. Again the right hand sides are integrable. Thus by Lebesgue's Theorem on dominated convergence we have

$$\begin{aligned} \int_{\Omega_T} a_{,\boldsymbol{p}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) : \mathrm{D}\,\boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t &\to \int_{\Omega_T} a_{,\boldsymbol{p}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) : \mathrm{D}\,\boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t, \\ \int_{\Omega_T} a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}, \mathrm{D}\,\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t &\to \int_{\Omega_T} a_{,\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathrm{D}\,\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t, \\ \int_{\Omega_T} \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}^{(n)}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t &\to \int_{\Omega_T} \psi_{,\boldsymbol{\phi}}(\boldsymbol{\phi}) \cdot \boldsymbol{\zeta}\ \mathrm{d}\boldsymbol{x}\,\mathrm{d}t, \end{aligned}$$

as $n \to \infty$. Now we integrate (4.24) over $[0,T]$, and by the weak convergence of $\frac{\partial \boldsymbol{\phi}^{(n)}}{\partial t}$ to $\frac{\partial \boldsymbol{\phi}}{\partial t}$ in $L^2\left(0,T;\left(\mathcal{V}^N\right)'\right)$ we can pass to the limit on both sides, and by (4.20) obtain that (4.19) is fulfilled for the limit $\boldsymbol{\phi}$. Besides, from (4.48) and $\boldsymbol{\phi}^{(n)}(0) \to \boldsymbol{\phi}_0$ in $L^2(\Omega;\mathbb{R}^N)$ we obtain $\boldsymbol{\phi}(0) = \boldsymbol{\phi}_0$ for the limit function $\boldsymbol{\phi}$. In addition, since $\sum_{k=1}^N \phi_k^{(n)} = 1$ almost everywhere in Ω_T we obtain from (4.49) $\sum_{k=1}^N \phi_k = 1$ in the limit.

We have proved the following result:

Theorem 4.4.1. *Assume that we are given the parabolic equation* (4.19) *with initial condition* (4.18)*. Furthermore we assume that the gradient energy density $a(\boldsymbol{z},\boldsymbol{p})$ fulfills (D1)-(D5) and (D11) as well as $\psi(\boldsymbol{z})$ fulfills (D6)-(D8). Moreover assume that the spatial dimension is equal to one, that is (D9). Then there exists a function $\boldsymbol{\phi} \in L^\infty(0,T;\mathcal{V}^N) \cap C([0,T];\mathcal{H}^N) \cap L^2(0,T;H^{2,2}(\Omega;\mathbb{R}^N))$ that fulfills* (4.19) *for all test functions $\boldsymbol{\zeta} \in L^2(0,T;\mathcal{V}^N)$. In addition this function $\boldsymbol{\phi}$ fulfills the initial condition* (4.18) *almost everywhere in Ω and $\sum_{k=1}^N \phi_k = 1$ almost everywhere in Ω_T.*

Appendix A- List of Notation.

$a(\boldsymbol{z}, \boldsymbol{p})$	gradient energy density (Sect. 2.1 f & 4.1 f)
c_i	concentration of component i (Sect. 3.2 f)
$\boldsymbol{c}$	vector of concentrations $\boldsymbol{c} = (c_i)_{i=1}^N$ (Sect. 3.2 f)
d	spatial dimension
$\mathcal{E}$	d-dimensional Euclidean space (Sect. 1.2)
$\mathscr{E}$	internal energy (Sect. 1.2)
E	(bulk) density of internal energy (Sect. 1.2 & 3.2 f)
e	surface density of internal energy (Sect. 3.4)
$\mathscr{F}$	free energy (Sect. 1.2, 2.1 f & 4.1)
F	(bulk) density of free energy (Sect 1.2 & 3.3 f)
f	surface density of free energy (Sect. 3.4)
$\mathscr{G}$	Gibbs simplex, $\mathscr{G} = \left\{\boldsymbol{x} = (x_i)_{i=1}^N \in \Sigma \middle\vert\ x_i \geq 0\right\}$ (Sect. 2.1)
Γ, Γ_t	evolving $(d-1)$-dimensional hyperplane (Sect. 3.4)
γ, γ_t	bounded subset of Γ (Sect. 3.4)
$\boldsymbol{J}_i$	bulk density of concentration flux (Sect. 1.2 & 3.2 f)
$\boldsymbol{J}_E$	(bulk) density of the energy flux (Sect. 1.2 & 3.2 f)
$\boldsymbol{j}_E$	surface density of the energy flux (Sect. 3.4)
$\boldsymbol{J}_S$	(bulk) density of the entropy flux (Sect. 3.2 f)
$\boldsymbol{j}_S$	surface density of the entropy flux (Sect. 3.4)
μ_i	chemical potential of component i (Sect. 3.3)
$\boldsymbol{\mu}'$	vector of all chemical potentials $\boldsymbol{\mu}' = (\mu_i)_{i=1}^N$ (Sect. 3.3)
$\boldsymbol{\mu}$	the vector $(-1, \boldsymbol{\mu}')$ (Sect. 3.3)
$\boldsymbol{\nu}_R$	oriented unit normal at ∂R (Sect. 1.2, 3.2 f & 4.1 f)
$\boldsymbol{\nu}$	oriented unit normal at Γ (Sect. 3.4)
$\boldsymbol{\Pi}^N$	orthogonal projection onto $T(\Sigma)$ (Sect. 3.3 & 4.1)
$\boldsymbol{P}$	$\boldsymbol{P} = \boldsymbol{I} - \boldsymbol{\nu} \otimes \boldsymbol{\nu}$ projection onto $T_{\boldsymbol{x}}(\Gamma)$ (Sect. 3.4)
$\boldsymbol{Q}$	$\boldsymbol{Q} = \boldsymbol{I} - \boldsymbol{P}$ projection onto $(T_{\boldsymbol{x}}(\Gamma))^{\perp}$ (Sect. 3.4)
ϕ_i	phase field variable of phase i (Chapts. 1, 2, 3 & 4)
$\boldsymbol{\phi}$	vector of all phase fields, $\boldsymbol{\phi} = (\phi_i)_{i=1}^N$ (Chapts. 1, 2, 3 & 4)
Φ	frame of reference (Sect. 1.2)

$\mathbb{R}_+$	non-negative real numbers $a \in \mathbb{R}$ with $a \geq 0$
ϱ	mass density (Sect. 1.2 & 3.2 f)
$\boldsymbol{s}$	path of a material point or a point on Γ (Sect. 1.2 & 3.2)
$\mathscr{S}$	entropy (Sect. 1.2)
S	(bulk) density of entropy (Sect. 3.2 f)
s	surface density of entropy (Sect. 3.4)
Σ	the hyperplane $\left\{\boldsymbol{x} = (x_i)_{i=1}^N \in \mathbb{R}^N \middle\vert \ \sum_{i=1}^N x_i = 1\right\}$ (Sect. 2.2)
t	time
$\boldsymbol{T}$	stress tensor (Sect. 3.2 f)
$\boldsymbol{T}_I$	interfacial stress tensor (Sect. 3.4)
T	absolute temperature
$T(\mathscr{G}), T\Sigma$	tangent space $\left\{\boldsymbol{x} = (x_i)_{i=1}^N \in \mathbb{R}^N \middle\vert \ \sum_{i=1}^N x_i = 0\right\}$ (Sect. 2.2 f)
$\boldsymbol{v}$	velocity of a material point (Sect 1.2 & Sect. 3.2 f)
w	multi-well potential (Sect. 2.1 f & 4.1 f)
$\mathcal{W}$	Newtonian space-time (Sect. 1.2)
$\boldsymbol{a} \cdot \boldsymbol{b}$, $\boldsymbol{a},\ \boldsymbol{b} \in \mathbb{R}^n$	inner product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ given by $\sum_{i=1}^n a_i b_i$
$\lvert\boldsymbol{a}\rvert$, $\boldsymbol{a} \in \mathbb{R}^n$	canonical length of a vector $\boldsymbol{a}$ given by $\lvert\boldsymbol{a}\rvert^2 = \boldsymbol{a} \cdot \boldsymbol{a}$
$\boldsymbol{a} \otimes \boldsymbol{b}$, $\boldsymbol{a} \in \mathbb{R}^n$, $\boldsymbol{b} \in \mathbb{R}^m$	tensor product of $(\boldsymbol{a} \otimes \boldsymbol{b})(\boldsymbol{x}) = (\boldsymbol{b} \cdot \boldsymbol{x})\boldsymbol{a}$
$\boldsymbol{a} \wedge \boldsymbol{b}$, $\boldsymbol{a},\ \boldsymbol{b} \in \mathbb{R}^n$	outer product of $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{a} \wedge \boldsymbol{b} = \boldsymbol{a} \otimes \boldsymbol{b} - \boldsymbol{b} \otimes \boldsymbol{a}$
$\boldsymbol{A} : \boldsymbol{B},\ \boldsymbol{A},\ \boldsymbol{B} \in \mathbb{R}^{m \times n}$	inner product of two matrices or tensors $\boldsymbol{A}$, $\boldsymbol{B}$, usually given by $\sum_{i,j=1}^{m,n} A_{ij} B_{ij}$
$\lvert\boldsymbol{A}\rvert$, $\boldsymbol{A} \in \mathbb{R}^{m \times n}$	norm of a matrix or tensor $\boldsymbol{A}$, $\lvert\boldsymbol{A}\rvert^2 = \boldsymbol{A} : \boldsymbol{A}$
D, $\mathrm{D}_{\boldsymbol{x}}$, $\mathrm{D}_{\boldsymbol{y}}$	Frechet derivative with respect to $\boldsymbol{x}$, $\boldsymbol{y}$
∇	Gradient, $\nabla f = (\mathrm{D}\, f)^\top$
∇_Γ	Surface gradient

Appendix B- Calculus.

Auxiliary material.

Theorem 1 (Divergence theorem). *Let $\Omega \subset \mathbb{R}^d$ a domain with C^1-boundary up to a set of $\mathcal{H}^{d-1}$-measure zero. Then we have for any differentiable function $\boldsymbol{f} : \Omega \to \mathbb{R}^d$ that*

$$\int_\Omega \nabla \cdot \boldsymbol{f} \, \mathrm{d}\boldsymbol{x} = \int_{\partial\Omega} \boldsymbol{f} \cdot \boldsymbol{\nu}_\Omega \, \mathrm{d}\mathcal{H}^{d-1}$$

holds, provided both integrals exist. Here $\boldsymbol{\nu}_\Omega$ denotes the outer unit normal at $\partial\Omega$ which exists almost everywhere wrt. the $\mathcal{H}^{d-1}$-measure.

For a proof of this theorem see for example [73, pp. 272 ff.]

Theorem 2 (Linearization). *Let $\boldsymbol{A} : \mathbb{R}^N \to \mathbb{R}^N$ a continuously differentiable function such that*

$$\boldsymbol{A}(\boldsymbol{X}) \cdot \boldsymbol{X} \geq 0$$

holds for all $\boldsymbol{X} \in U$ where $U \subseteq \mathbb{R}^N$ is a linear subspace and $P_U : \mathbb{R}^N \to U$ the orthogonal projection onto U. Then we have $P_U \boldsymbol{A}(0) = 0$. Besides $P_U \boldsymbol{A}(\boldsymbol{X})$ decomposes into $P_U \boldsymbol{A}(\boldsymbol{X}) = \boldsymbol{B}(\boldsymbol{X})\boldsymbol{X}$ with a matrix-valued function $\boldsymbol{B} : \mathbb{R}^N \to \mathbb{R}^{N \cdot N}$. The matrix $\boldsymbol{B}$ is positive semidefinite on the subspace U.

Proof. For any $\boldsymbol{X} \in \mathbb{R}^N$ and $r > 0$ consider $\boldsymbol{A}(rP_U\boldsymbol{X}) \cdot P_U\boldsymbol{X}$. Clearly

$$\boldsymbol{A}(rP_U\boldsymbol{X}) \cdot P_U\boldsymbol{X} = \frac{1}{r}\left(\boldsymbol{A}(rP_U\boldsymbol{X}) \cdot rP_U\boldsymbol{X}\right) \geq 0$$

holds. By continuity of $\boldsymbol{A}$ we have $P_U\boldsymbol{A}(0) \cdot \boldsymbol{X} = \lim_{r \searrow 0} \boldsymbol{A}(rP_U\boldsymbol{X}) \cdot P_U\boldsymbol{X} \geq 0$ and thus replacing $\boldsymbol{X}$ by $-\boldsymbol{X}$ we clearly have $P_U\boldsymbol{A}(0) \cdot \boldsymbol{X} \leq 0$. Now from the principal theorem of calculus we have

$$P_U\boldsymbol{A}(\boldsymbol{X}) = \int_0^1 \tfrac{\mathrm{d}}{\mathrm{d}t} P_U\boldsymbol{A}(t\boldsymbol{X}) \, \mathrm{d}t = \int_0^1 P_U\boldsymbol{A}_{,\boldsymbol{X}}(t\boldsymbol{X})\boldsymbol{X} \, \mathrm{d}t = \boldsymbol{B}(\boldsymbol{X})\boldsymbol{X},$$

with $\boldsymbol{B}(\boldsymbol{X}) = \int_0^1 P_U\boldsymbol{A}_{,\boldsymbol{X}}(t\boldsymbol{X}) \, \mathrm{d}t$ a matrix-valued function of $\boldsymbol{X}$. That proves our theorem. □

Corollary 1. *Let $\boldsymbol{X} = (\boldsymbol{X}_1, \boldsymbol{X}_2)$ and*

$$\boldsymbol{A}_1(\boldsymbol{X}) \cdot \boldsymbol{X} + \boldsymbol{A}_2(\boldsymbol{X}_1) \cdot \boldsymbol{X} \geq 0$$

for all $\boldsymbol{X} \in \mathbb{R}^N$. Then we have $\boldsymbol{A}_1(\boldsymbol{X}) = \boldsymbol{B}_1(\boldsymbol{X})\boldsymbol{X}$ and $\boldsymbol{A}_2(\boldsymbol{X}_1) = \boldsymbol{B}_2(\boldsymbol{X}_1)\boldsymbol{X}_1$.

Evolving hypersurfaces.

The development and analysis of *sharp interface models* and *free boundary problems* requires some helpful notation concerning the geometry of the phase interface and the free boundary, resp. Therefore we present some convenient material that is mainly used in Section 4 of Chapter 3 where a sharp interface model for multi-component fluid flows is derived. For further reading we refer to [48] or [46, p. 93 f.]. As first we introduce $\{\Gamma_t\}_{t\in I}$ as a family of hypersurfaces that evolves during the time range I. We assume that $\{\Gamma_t\}_{t\in I}$ has the following properties:

(F1) For all $t \in I$ we assume $\Gamma_t \subset \mathbb{R}^d$ is an orientable hypersurface of fixed dimension lower than d and there exists an orientation that depends continuously on $(t, \boldsymbol{x})$ for all $t \in I$ and almost all $\boldsymbol{x} \in \Gamma_t$.

(F2) Every $\Gamma_t \subset \mathbb{R}^d$ admits a local representation via a parametrization $\boldsymbol{\gamma}(t, .) : P \to \gamma_t \subset \Gamma_t$ that is also an isometric C^2-diffeomorphism on between P and γ_t.

(F3) For distinguished times $s, t \in I$ the hypersurfaces Γ_s and Γ_t have the same dimension.

(F4) The set I is assumed to be connected and nonempty. Besides $\boldsymbol{\gamma}(., \boldsymbol{p})$ is supposed to be continuously differentiable on I for all local parametrizations $\boldsymbol{\gamma}$.

We denote with $\boldsymbol{\nu} = \boldsymbol{\nu}(t, \boldsymbol{x})$ the (oriented) *unit normal vector* at Γ_t and

$$T(\Gamma_t) = T_{\boldsymbol{x}}(\Gamma_t) = \{\boldsymbol{\tau}(t, \boldsymbol{x}) \in \mathbb{R}^d \mid \boldsymbol{\tau} \cdot \boldsymbol{\nu} = 0\}$$

as the *tangent space* of Γ_t, where the elements of $T(\Gamma_t)$ are referred to as *tangent vectors*. Let $\boldsymbol{P} = \boldsymbol{P}(t, \boldsymbol{x})$ the orthogonal projection on $T(\Gamma_t)$, i.e. $\boldsymbol{P}$ suffices $\boldsymbol{P} = \boldsymbol{I} - \boldsymbol{\nu} \otimes \boldsymbol{\nu}$. We refer to $\boldsymbol{\kappa} = \nabla \cdot \boldsymbol{P}$ as the *mean curvature vector* and $\kappa = \boldsymbol{\kappa} \cdot \boldsymbol{\nu}$ as the *scalar mean curvature*. For any vector field $\boldsymbol{f} : I \times \mathbb{R}^d \to \mathbb{R}^n$ we define the *intrinsic derivative* on Γ_t by

$$\mathrm{D}_\Gamma(\boldsymbol{f} \circ \boldsymbol{\gamma}) = (\mathrm{D}_{\boldsymbol{x}} \boldsymbol{f}\, \boldsymbol{P}) \circ \boldsymbol{\gamma},$$

for any parametrization $\boldsymbol{\gamma}$ of Γ_t. Then for $f : I \times \mathbb{R}^d \to \mathbb{R}$ and $\boldsymbol{f} : I \times \mathbb{R}^d \to \mathbb{R}^d$ we define

$$\nabla_\Gamma f = \boldsymbol{P} \nabla f \text{ and } \nabla_\Gamma \cdot \boldsymbol{f} = \boldsymbol{P} : \mathrm{D}_{\boldsymbol{x}} \boldsymbol{f} = \mathrm{tr}(\boldsymbol{P}\, \mathrm{D}_{\boldsymbol{x}} \boldsymbol{f}\,)$$

as the *surface gradient* and the *surface divergence*, resp. Let t_0 be an inner point of I and for $\varepsilon > 0$ let $B = \{t \in I \mid |t - t_0| < \varepsilon\}$. For any $\boldsymbol{x}_0 \in \Gamma_{t_0}$ we define $\boldsymbol{s} : B \to \cup_{t\in B}\Gamma_t$ where $\boldsymbol{x}_0 = \boldsymbol{s}(t_0)$ as the *path* of $\boldsymbol{x} = \boldsymbol{s}(t) \in \Gamma_t$ through $\boldsymbol{x}_0$. Every *normal field* $\boldsymbol{V} : B \times (\cup_{t\in B}\Gamma_t) \to \mathbb{R}^d$ that is also a *velocity field* for $\boldsymbol{s}$, i.e. $\boldsymbol{V}$ suffices

$$\boldsymbol{V} \cdot \boldsymbol{\tau} = 0 \text{ for all } \boldsymbol{\tau} \in T(\Gamma) \quad \text{ and } \quad \dot{\boldsymbol{s}}(t) = \boldsymbol{V}(t, \boldsymbol{s}(t)) \text{ for all } t \in B$$

we refer to as *normal velocity*. Besides we use frequently its scalar variant $V = \boldsymbol{V} \cdot \boldsymbol{\nu}$. Finally we introduce the *time normal derivative* of $f : I \times \mathbb{R}^d \to \mathbb{R}$ as the derivative in $(1, \boldsymbol{V})$-direction, i.e. $\partial^\circ f = \partial_t f + \boldsymbol{V} \cdot \nabla f$.

If there is no risk of confusion, we will drop the time index t, i.e. we write Γ and γ instead of Γ_t and γ_t. Now we extract some kinematic properties and establish a first convenient result.

Lemma 1. *Let $\{\Gamma_t\}_{t\in I}$ a family of evolving hypersurfaces subject to the conditions (F1) - (F4). With the introduced notation we have*

$$\partial^\circ \boldsymbol{\nu} = -\nabla_\Gamma V. \tag{A.1}$$

Proof. Just as in the spirit of phase field modelling we introduce a level-set function $\phi : I \times \mathbb{R}^d \to \mathbb{R}$ with the following properties:

1. For all $\boldsymbol{x} \in \gamma_t$ we have $\phi(t, \boldsymbol{x}) = 0$, $\phi(t, \boldsymbol{x}) > 0$ for $(\boldsymbol{x} - \boldsymbol{P}\boldsymbol{x}) \cdot \boldsymbol{\nu} > 0$ and $\phi(t, \boldsymbol{x}) < 0$ for $(\boldsymbol{x} - \boldsymbol{P}\boldsymbol{x}) \cdot \boldsymbol{\nu} < 0$.

2. The functions $\phi(t, .), \nabla\phi(t, .)$ are continuously differentiable across γ_t for all $0 < t < T$.

3. The function $\phi(t, .)$ is monotone across γ_t for all $0 < t < T$, furthermore $\nabla\phi(t, .)$ does not vanish on γ_t.

Then we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi(\boldsymbol{s}(t), t) = \partial_t\phi(\boldsymbol{s}(t), t) + \dot{\boldsymbol{s}}(t) \cdot \nabla\phi(\boldsymbol{s}(t), t) = 0,$$

where $\boldsymbol{s}$ is defined as above and since $\dot{\boldsymbol{s}}(t) = \boldsymbol{V}(\boldsymbol{s}(t), t)$ holds ϕ solves the following *transport equation* given by

$$\partial_t\phi + \boldsymbol{V} \cdot \nabla\phi = 0, \tag{A.2}$$

which has $\boldsymbol{s}$ as characteristics. Since $\nabla\phi$ is a normal field we have (without loss of generality) $\boldsymbol{\nu} = \nabla\phi/|\nabla\phi|$ and we obtain

$$\partial_t\phi = -\boldsymbol{V} \cdot \boldsymbol{\nu}|\nabla\phi| = -V|\nabla\phi|,$$

a Hamilton-Jacobi equation. Now by elementary calculations we are led to

$$\begin{aligned}
\partial_t\left(|\nabla\phi|\boldsymbol{\nu}\right) &= |\nabla\phi|\partial_t\boldsymbol{\nu} + \boldsymbol{\nu}\partial_t\left(\nabla\phi \cdot \boldsymbol{\nu}\right) \\
&= |\nabla\phi|\partial_t\boldsymbol{\nu} + \boldsymbol{\nu}\left(\partial_t\nabla\phi \cdot \boldsymbol{\nu} + \nabla\phi \cdot \partial_t\boldsymbol{\nu}\right) \\
&= |\nabla\phi|\partial_t\boldsymbol{\nu} - \boldsymbol{\nu}\left(|\nabla\phi|\boldsymbol{\nu} \cdot \nabla(\boldsymbol{V} \cdot \boldsymbol{\nu}) - \nabla\phi \cdot \partial_t\boldsymbol{\nu}\right) \\
&= |\nabla\phi|\left(\partial_t\boldsymbol{\nu} - \boldsymbol{\nu} \otimes \boldsymbol{\nu}\nabla V\right) + \nabla\phi \cdot \partial_t\boldsymbol{\nu}\boldsymbol{\nu}.
\end{aligned}$$

Proceeding forward by using $\nabla\phi = (\nabla\phi \cdot \boldsymbol{\nu})\boldsymbol{\nu}$ we have

$$\boldsymbol{\nu}\nabla\phi \cdot \partial_t\boldsymbol{\nu} = \boldsymbol{\nu}\boldsymbol{\nu} \cdot \partial_t\nabla\phi - \boldsymbol{\nu}\partial_t\left(\nabla\phi \cdot \boldsymbol{\nu}\right) = -\boldsymbol{\nu}\nabla\phi \cdot \partial_t\boldsymbol{\nu},$$

which is fulfilled if and only if $\boldsymbol{\nu}\nabla\phi \cdot \partial_t\boldsymbol{\nu} = 0$. We then have

$$\begin{aligned}
\partial_t(\nabla\phi) &= |\nabla\phi|\left(\partial_t\boldsymbol{\nu} + \boldsymbol{P}\nabla V\right) - |\nabla\phi|\nabla V \\
&= |\nabla\phi|\left(\partial_t\boldsymbol{\nu} + \boldsymbol{P}\nabla V\right) + \partial_t(\nabla\phi) + \partial_t\phi\nabla\left(\frac{1}{|\nabla\phi|}\right)
\end{aligned}$$

and furthermore

$$\begin{aligned} 0 &= \partial_t \boldsymbol{\nu} + \boldsymbol{P}\nabla V - \frac{\partial_t \phi}{|\nabla\phi|^2}\nabla|\nabla\phi| \\ &= \partial_t \boldsymbol{\nu} + \nabla_\Gamma V + \frac{V}{|\nabla\phi|}\frac{\mathrm{D}^2\phi\nabla\phi}{|\nabla\phi|} \\ &= \partial_t \boldsymbol{\nu} + \nabla_\Gamma V + V\boldsymbol{\nu}\cdot\nabla\boldsymbol{\nu}, \end{aligned}$$

thus we have

$$\partial_t \boldsymbol{\nu} + \boldsymbol{V}\cdot\nabla\boldsymbol{\nu} = -\nabla_\Gamma V,$$

the desired result. □

Lemma 2. *Let $f : I \times \mathbb{R}^d \to \mathbb{R}$, then we have*

$$\int_{\gamma'} f(t,\boldsymbol{x})\,\mathrm{d}\mathcal{H}^d = \int_0^T \int_{\gamma_t} f(t,\boldsymbol{x})\sqrt{1+V^2}\,\mathrm{d}\mathcal{H}^{d-1}\,\mathrm{d}t. \tag{A.3}$$

Theorem 3 (Divergence theorem). *Let $\Gamma \subset \mathbb{R}^d$ be an n-dimensional C^2-manifold, $\gamma \subset \Gamma$ an open submanifold with piecewise C^1-boundary and $\boldsymbol{f} : \bar{\gamma} \to \mathbb{R}^d$ continuous and differentiable on γ. Besides assume that $\nabla_\Gamma \cdot \boldsymbol{f}$ is $\mathcal{H}^n$-integrable. Then*

$$\int_\gamma (\nabla_\Gamma \cdot \boldsymbol{f} + \boldsymbol{\kappa}\cdot\boldsymbol{f})\,\mathrm{d}\mathcal{H}^n = \int_{\partial\gamma} \boldsymbol{f}\cdot\boldsymbol{\nu}_\gamma\,\mathrm{d}\mathcal{H}^{n-1}$$

holds, where $\boldsymbol{\kappa}(\boldsymbol{x}) \subset T_{\boldsymbol{x}}(\Gamma)^\perp$ is the vectorial curvature of Γ and $\boldsymbol{\nu}_\gamma(\boldsymbol{x}) \subset T_{\boldsymbol{x}}(\Gamma)$ the unique unit vector with $\boldsymbol{\tau}\cdot\boldsymbol{\nu}_\gamma(\boldsymbol{x}) \le 0$ for all $\boldsymbol{\tau} \in T_{\boldsymbol{x}}(\bar{\gamma})$.

For a proof see [2].

Theorem 4 (Transport theorem). *Let $\{\Gamma_t\}_{t\in I}$ a family of evolving hypersurfaces subject to the conditions (F1) - (F4) and $\gamma_t \subset \Gamma_t$. Besides assume $f : \bar{\gamma} \to \mathbb{R}$ to be continuous and differentiable on γ_t. Then we have*

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{\gamma_t} f\,\mathrm{d}\mathcal{H}^{d-1}\right) = \int_{\gamma_t} (\partial^\circ f - f\kappa V)\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\partial\gamma_t} f V_\gamma\,\mathrm{d}\mathcal{H}^{d-2}.$$

Proof. For $(t_1,t_2) \subset (0,T)$ we consider a subfamily $\{\Gamma_t\}_{t\in[t_1,t_2]}$ of $\{\Gamma_t\}_{t\in[0,T]}$ and let $\Gamma' = \cup_{t\in[t_1,t_2]}\{t\}\times\Gamma_t \subset \mathbb{R}^{d+1}$. Given an orthonormal basis $\{\boldsymbol{\tau}_i\}_{i=1}^{d-1}$ of a single $\Gamma_t \subset \mathbb{R}^d$ we construct an orthonormal basis of Γ' by

$$\boldsymbol{t}_0 = \frac{\alpha}{|\alpha|} \text{ and } \boldsymbol{t}_i = (0,\boldsymbol{\tau}_i)^\top,$$

for $i = 1,\dots,d-1$ and $\alpha = (1,\boldsymbol{V})^\top$. We introduce

$$\nabla_{\Gamma'}\cdot\mathbf{f} = \sum_{i=0}^{d-1} \boldsymbol{t}_i\cdot\partial_{\boldsymbol{t}_i}\mathbf{f} \text{ and } \nabla_\Gamma\cdot\mathbf{g} = \sum_{i=1}^{d-1}\boldsymbol{\tau}_i\cdot\partial_{\boldsymbol{\tau}_i}\mathbf{g},$$

as the intrinsic divergence operators on Γ' and Γ_t. Then we have

$$\begin{aligned}
\nabla_{\Gamma'} \cdot (\boldsymbol{t}_0 f) &= f \nabla_{\Gamma'} \cdot \boldsymbol{t}_0 + \boldsymbol{t}_0 \cdot \nabla_{\Gamma'} f \\
&= f \nabla_{\Gamma'} \cdot \boldsymbol{t}_0 + \boldsymbol{t}_0 \cdot \boldsymbol{t}_0 \partial_{\boldsymbol{t}_0} f + \boldsymbol{t}_0 \cdot \left(\sum_{i=1}^{d-1} \boldsymbol{t}_i \partial_{\boldsymbol{t}_i} f \right) \\
&= f \nabla_{\Gamma'} \cdot \boldsymbol{t}_0 + \partial_{\boldsymbol{t}_0} f,
\end{aligned}$$

since $\boldsymbol{t}_0$ is orthogonal to all other $\boldsymbol{t}_i$. With $\partial_\alpha f = |\alpha| \partial_{\boldsymbol{t}_0} f$ we then have

$$\begin{aligned}
\nabla_{\Gamma'} \cdot (\boldsymbol{t}_0 f) &= \frac{1}{|\alpha|} \partial_\alpha f + f \nabla_{\Gamma'} \cdot \boldsymbol{t}_0 \\
&= \frac{1}{|\alpha|} \partial_{(1, \boldsymbol{V})} f + f \left(\boldsymbol{t}_0 \cdot \partial_{\boldsymbol{t}_0} \boldsymbol{t}_0 + \sum_{i=1}^{d-1} \boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \boldsymbol{t}_0 \right) \\
&= \frac{1}{|\alpha|} \partial^\circ f + f \left(\tfrac{1}{2} \partial_{\boldsymbol{t}_0} |\boldsymbol{t}_0|^2 + \sum_{i=1}^{d-1} \boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \boldsymbol{t}_0 \right).
\end{aligned}$$

For $\boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \boldsymbol{t}_0$ we obtain

$$\begin{aligned}
\boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \boldsymbol{t}_0 &= \boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \left(\frac{\alpha}{|\alpha|} \right) \\
&= \frac{1}{|\alpha|} \left(\boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \alpha - \boldsymbol{t}_i \cdot \boldsymbol{t}_0 \partial_{\boldsymbol{t}_i} |\alpha| \right) \\
&= \frac{1}{|\alpha|} \boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \alpha,
\end{aligned}$$

for $i \geq 1$. Then

$$\begin{aligned}
|\alpha| \nabla_{\Gamma'} \cdot (\boldsymbol{t}_0 f) &= \partial^\circ f + \sum_{i=1}^{d-1} \boldsymbol{t}_i \cdot \partial_{\boldsymbol{t}_i} \alpha \\
&= \partial^\circ f + \sum_{i=1}^{d-1} \boldsymbol{\tau}_i \cdot \partial_{\boldsymbol{\tau}_i} \boldsymbol{V} \\
&= \partial^\circ f + \nabla_\Gamma \cdot (V \boldsymbol{\nu}) \\
&= \partial^\circ f + V \nabla_\Gamma \cdot \boldsymbol{\nu} = \partial^\circ f - f \kappa V
\end{aligned}$$

holds since $\boldsymbol{\nu} \cdot \nabla_\Gamma V = 0$. Now the divergence theorem (Theorem 4) leads to

$$\begin{aligned}
\int_{\gamma'} \nabla_{\Gamma'} \cdot (\boldsymbol{t}_0 f)\, \mathrm{d}\mathcal{H}^d &= \int_{\partial\gamma'} \boldsymbol{\nu}_{\gamma'} \cdot \boldsymbol{t}_0 f \, \mathrm{d}\mathcal{H}^{d-1} - \int_{\Gamma'} \boldsymbol{\kappa}' \cdot \boldsymbol{t}_0 f \, \mathrm{d}\mathcal{H}^{d-1} \\
&= \int_{\partial\gamma'} \boldsymbol{\nu}_{\gamma'} \cdot \boldsymbol{t}_0 f \, \mathrm{d}\mathcal{H}^{d-1} \\
&= \sum_{t=t_1,t_2} \int_{\gamma_t} \boldsymbol{\nu}_{\gamma'} \cdot \boldsymbol{t}_0 f \, \mathrm{d}\mathcal{H}^{d-1} + \int_{t_1}^{t_2} \int_{\partial\gamma_t} \boldsymbol{\nu}_{\gamma'} \cdot \boldsymbol{t}_0 f |\alpha| \, \mathrm{d}\mathcal{H}^{d-2} \, \mathrm{d}t \\
&= \int_{\gamma_{t_2}} \boldsymbol{t}_0 \cdot \boldsymbol{t}_0 f \, \mathrm{d}\mathcal{H}^{d-1} + \int_{\gamma_{t_1}} -\boldsymbol{t}_0 \cdot \boldsymbol{t}_0 f \, \mathrm{d}\mathcal{H}^{d-1} \\
&+ \int_{t_1}^{t_2} \int_{\partial\gamma_t} \boldsymbol{\nu}_{\gamma'} \cdot \boldsymbol{t}_0 f |\alpha| \, \mathrm{d}\mathcal{H}^{d-2} \, \mathrm{d}t
\end{aligned}$$

since $\boldsymbol{\kappa}'$ is perpendicular to all tangent vectors of Γ'. On the other hand we have

$$\int_{\gamma'} \nabla_{\Gamma'} \cdot (\boldsymbol{t}_0 f)\, \mathrm{d}\mathcal{H}^d = \int_{t_1}^{t_2} \int_{\gamma_t} (\partial^\circ f - f\kappa V)\, \mathrm{d}\mathcal{H}^{d-1}\, \mathrm{d}t.$$

Then we have by $s = t$ and $t = t_2$

$$\left\{ \int_{\gamma_s} f \, \mathrm{d}\mathcal{H}^{d-1} \right\}_{t_1}^{t} + \int_{t_1}^{t} \int_{\partial\gamma_s} \boldsymbol{\nu}_{\gamma'} \cdot \boldsymbol{t}_0 f |\alpha| \, \mathrm{d}\mathcal{H}^{d-2} \, \mathrm{d}s = \int_{t_1}^{t} \int_{\gamma_s} (\partial^\circ f - f\kappa V)\, \mathrm{d}\mathcal{H}^{d-1}\, \mathrm{d}s.$$

Differentiate this with respect to t we have

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\gamma_t} f \, \mathrm{d}\mathcal{H}^{d-1} + \int_{\partial\gamma_t} \boldsymbol{\nu}_{\gamma'} \cdot \boldsymbol{t}_0 f |\alpha| \, \mathrm{d}\mathcal{H}^{d-2} = \int_{\gamma_t} (\partial^\circ f - f\kappa V)\, \mathrm{d}\mathcal{H}^{d-1}. \tag{A.4}$$

It remains to determine $\boldsymbol{\nu}_{\gamma'}$ on the lateral boundary as done in [41]. Therefore we construct an orthogonal system $\{\boldsymbol{t}_0, \ldots, \boldsymbol{t}_d\}$ of vectors as follows. We set $\boldsymbol{t}_0 = (1, \boldsymbol{V})$ and $\boldsymbol{t}_i = (0, \boldsymbol{\tau}_i)$ for $i \in \{1, \ldots, d\}$. Without loss of generality we choose $\boldsymbol{\tau}_1 = \boldsymbol{\nu}_{\gamma_t}$. Now for $(t, \boldsymbol{x}) \in \partial\gamma'$ we choose a curve $(\tau, \boldsymbol{s}(\tau)) \in \partial\gamma'$ such that $(t, \boldsymbol{s}(t)) = (t, \boldsymbol{x})$. Thus $(1, \partial_\tau \boldsymbol{s}(t))$ is tangential to $\partial\gamma'$ as well as it is tangential to γ'. The latter clearly leads to

$$(1, \partial_\tau \boldsymbol{s}(t)) = (1, \boldsymbol{V}) + \sum_{i=1}^{d} \alpha_i \boldsymbol{t}_i.$$

Since $V_\gamma = \partial_\tau \boldsymbol{s}(t) \cdot \boldsymbol{\nu}_{\gamma_t}$ and $\boldsymbol{\nu}_{\gamma_t} \cdot \boldsymbol{t}_i = \boldsymbol{t}_1 \cdot \boldsymbol{t}_i$ for $i > 1$ we obtain $\alpha_1 = V_\gamma$. Hence $(1, \boldsymbol{V}) + (0, V_\gamma \boldsymbol{\nu}_{\gamma_t})$ is tangential to $\partial\gamma'$. In view of this we try to find numbers a, $b \in \mathbb{R}$ such that

$$(\boldsymbol{t}_0 + V_\gamma \boldsymbol{t}_1) \cdot (a\boldsymbol{t}_0 + b\boldsymbol{t}_1) = 0.$$

In addition $\boldsymbol{\nu}_{\gamma'} = a\boldsymbol{t}_0 + b\boldsymbol{t}_1$ has to fulfil $|\boldsymbol{\nu}_{\gamma'}| = 1$. By $\boldsymbol{t}_0 \cdot \boldsymbol{t}1 = 0$ we arrive at

$$a|\boldsymbol{t}_0|^2 = -bV_\gamma |\boldsymbol{t}_1|^2 \text{ or } a(1 + V^2) = -bV_\gamma,$$

by $|\boldsymbol{t}_0|^2 = 1+V^2$ and $|\boldsymbol{t}_1|^2 = 1$. We define $a_0 = -V_\gamma$, $b_0 = 1+V^2$ and thus we obtain

$$\begin{aligned} |a_0\boldsymbol{t}_0 + b_0\boldsymbol{t}_1|^2 &= V_\gamma^2(1+V^2) + (1+V^2)^2 \\ &= (1+V^2)(V_\gamma^2 + 1 + V^2). \end{aligned}$$

Then we set

$$a = \frac{a_0}{\sqrt{1+V^2}\sqrt{1+V^2+V_\gamma^2}} = -\frac{V_\gamma}{\sqrt{1+V^2}\sqrt{1+V^2+V_\gamma^2}},$$

auch that $|\boldsymbol{\nu}_{\gamma'}| = 1$. On the other hand,

$$\begin{aligned} \boldsymbol{t}_0 \cdot \boldsymbol{\nu}_{\gamma'} &= (1+V^2)a \\ &= -\sqrt{1+V^2}\frac{V_\gamma}{\sqrt{1+V^2+V_\gamma^2}}, \end{aligned}$$

that is

$$\frac{(1,\boldsymbol{V})\cdot\boldsymbol{\nu}_{\gamma'}}{\sqrt{1+V^2}} = -\frac{V_\gamma}{\sqrt{1+V^2+V_\gamma^2}}.$$

Then we have

$$\int_{\partial\gamma'\setminus(\gamma_{t_2}\cup\gamma_{t_1})} \frac{f(1,\boldsymbol{V})\cdot\boldsymbol{\nu}_{\gamma'}}{\sqrt{1+V^2}}\,\mathrm{d}\mathcal{H}^{d-1} = -\int_{\partial\gamma'\setminus(\gamma_{t_2}\cup\gamma_{t_1})} \frac{fV_\gamma}{\sqrt{1+V^2+V_\gamma^2}}\,\mathrm{d}\mathcal{H}^{d-1}.$$

By (A.3) we then obtain

$$-\int_{\partial\gamma'\setminus(\gamma_{t_2}\cup\gamma_{t_1})} \frac{fV_\gamma}{\sqrt{1+V^2+V_\gamma^2}}\,\mathrm{d}\mathcal{H}^{d-1} = -\int_{t_1}^{t_2}\int_{\gamma_t} fV_\gamma\,\mathrm{d}\mathcal{H}^{d-2}\,\mathrm{d}t. \tag{A.5}$$

Then by inserting (A.5) into (A.4) we have proved our claim. □

Corollary 2. *Let $\gamma_t \subset \Gamma$ a hypersurface embedded in a time-independent manifold Γ. Then it is clear that γ_t evolves in Γ and thus its velocity is a tangential field. Thus the normal velocity $\boldsymbol{V} = 0$ and we have*

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{\gamma_t} f\,\mathrm{d}\mathcal{H}^{d-1}\right) = \int_{\gamma_t} \partial_t f\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\partial\gamma_t} fV_\gamma\,\mathrm{d}\mathcal{H}^{d-2}.$$

In case of $\Gamma = \mathbb{R}^d$ we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\gamma_t} f\ \mathrm{d}\boldsymbol{x} = \int_{\gamma_t} \partial_t f\ \mathrm{d}\boldsymbol{x} + \int_{\partial\gamma_t} fV_\gamma\,\mathrm{d}\mathcal{H}^{d-1}, \tag{A.6}$$

where V_γ is the normal velocity of the boundary $\partial\gamma_t$.

Let $\{R(t,\varepsilon)\}_{t,\varepsilon>0}$ be a family of sets such that:

(F5) Every $R(t,\varepsilon) \subset \mathbb{R}^d$ is compact.

(F6) For any fixed $\varepsilon_0 > 0$ the set $R(t,\varepsilon_0)$ is a material volume for all $t > 0$.

(F7) For any fixed $t_0 > 0$ the sets $R(t_0, \varepsilon)$ fulfill $\gamma_{t_0} \subset R(t_0, \varepsilon) \subset R(t_0, \varepsilon')$ for all $0 < \varepsilon < \varepsilon'$.

(F8) For any fixed $t_0 > 0$ the d-dimensional measure $\mathcal{L}(R(t_0, \varepsilon))$ tends to zero as $\varepsilon \to 0$.

Now we can prove the following result:

Lemma 3 (Pillbox lemma). *Let $\{\Gamma_t\}_{t\in I}$ a family of evolving hypersurfaces subject to the conditions (F1) - (F4) and let $\{R(t,\varepsilon)\}_{\varepsilon\in(0,\varepsilon_0)}$ a family of compact sets subject to the conditions (F5)-(F8). Then we have*

$$\begin{aligned}\lim_{\varepsilon\to 0}\left\{\int_{\partial R(t,\varepsilon)} \boldsymbol{f}\cdot\boldsymbol{\nu}_R \,\mathrm{d}\mathcal{H}^{d-1}\right\}_{t=t_0} &= \int_{\gamma_{t_0}} [\boldsymbol{f}]\cdot\boldsymbol{\nu}\,\mathrm{d}\mathcal{H}^{d-1},\\ \lim_{\varepsilon\to 0}\left\{\frac{\mathrm{d}}{\mathrm{d}t}\int_{R(t,\varepsilon)} f\,\mathrm{d}\boldsymbol{x}\right\}_{t=t_0} &= \int_{\gamma_{t_0}} [f(\boldsymbol{v}\cdot\boldsymbol{\nu}-V)]\,\mathrm{d}\mathcal{H}^{d-1},\end{aligned}$$

with unit normal $\boldsymbol{\nu}_R$ at $\partial R(t,\varepsilon)$.

Proof. We split $R(t,\varepsilon) = R = R_+ \cup \gamma_{t_0} \cup R_-$ and $R_+ \cap R_- = \emptyset$. By the Divergence Theorem in $\mathbb{R}^d$ we have

$$\begin{aligned}\int_{\partial R(t,\varepsilon)} \boldsymbol{f}\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1} &= \int_{\partial R\cap\partial R_+} \boldsymbol{f}_+\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\partial R\cap\partial R_-} \boldsymbol{f}_-\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1}\\ &= \int_{\partial R_+} \nabla\cdot\boldsymbol{f}_+\,\mathrm{d}\boldsymbol{x} + \int_{R_-}\nabla\cdot\boldsymbol{f}_-\,\mathrm{d}\boldsymbol{x} + \int_{\gamma_{t_0}} (\boldsymbol{f}_+\cdot\boldsymbol{\nu}-\boldsymbol{f}_-\cdot\boldsymbol{\nu})\,\mathrm{d}\mathcal{H}^{d-1}\\ &= \int_{\partial R_+} \nabla\cdot\boldsymbol{f}_+\,\mathrm{d}\boldsymbol{x} + \int_{R_-}\nabla\cdot\boldsymbol{f}_-\,\mathrm{d}\boldsymbol{x} + \int_{\gamma_{t_0}} [\boldsymbol{f}]\cdot\boldsymbol{\nu}\cdot\boldsymbol{\nu}\,\mathrm{d}\mathcal{H}^{d-1}.\end{aligned}$$

Since $\lim_{\varepsilon\to 0}|R_+| = \lim_{\varepsilon\to 0}|R_-| = 0$ we obtain the first identity for $\varepsilon \to 0$.

The second equation follows from (A.6) that reads

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_R f\,\mathrm{d}\boldsymbol{x} &= \int_R \partial_t f\,\mathrm{d}\boldsymbol{x} + \int_{\partial R} f V_R\,\mathrm{d}\mathcal{H}^{d-1}\\ &= \int_R \partial_t f\,\mathrm{d}\boldsymbol{x} + \int_{\partial R_+\cap\partial R} f_+\boldsymbol{v}\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\partial R_-\cap\partial R} f_-\boldsymbol{v}\cdot\boldsymbol{\nu}_R\,\mathrm{d}\mathcal{H}^{d-1}\\ &+ \int_{\gamma_{t_0}} f_+(\boldsymbol{v}_+\cdot\boldsymbol{\nu}-V)\,\mathrm{d}\mathcal{H}^{d-1} + \int_{\gamma_{t_0}} -f_-(\boldsymbol{v}_-\cdot\boldsymbol{\nu}-V)\,\mathrm{d}\mathcal{H}^{d-1}\\ &= \int_{R_+} (\partial_t f_+ + \nabla\cdot(f_+\boldsymbol{v}))\,\mathrm{d}\boldsymbol{x} + \int_{R_-}(\partial_t f_- + \nabla\cdot(f_-\boldsymbol{v}))\,\mathrm{d}\boldsymbol{x}\\ &+ \int_{\gamma_{t_0}} [f(\boldsymbol{v}\cdot\boldsymbol{\nu}-V)]\,\mathrm{d}\mathcal{H}^{d-1}.\end{aligned}$$

Again for $\varepsilon \to 0$ we obtain the second identity. □

Inequalities in Lebesgue and Sobolev spaces.

For any integrable function $u : \Omega \to \mathbb{R}$ we adopt the notion $(u)_\Omega = |\Omega|^{-1} \int_\Omega u \, \mathrm{d}\boldsymbol{x}$ from [31, p. 275]. Besides let $B_r(\boldsymbol{x}_0) \subset \mathbb{R}^d$ the open ball of radius $r > 0$ around center $\boldsymbol{x}_0 \in \mathbb{R}^d$. $(u)_{\boldsymbol{x}_0,r}$ denotes the average $|B_r(\boldsymbol{x}_0)|^{-1} \int_{B_r(\boldsymbol{x}_0)} u \, \mathrm{d}\boldsymbol{x}$ of an integrable function $u : B_r(\boldsymbol{x}_0) \to \mathbb{R}$.

Let us begin with a standard result.

Lemma 4 (Sobolev embedding). *Let $\Omega \subset \mathbb{R}^d$ a bounded domain and $u \in H^{1,p}(\Omega)$. Then the embedding $H^{1,p}(\Omega) \hookrightarrow L^q(\Omega)$ is continuous for $1 - \frac{d}{p} = -\frac{d}{q}$ and there exists a $C > 0$ such that*

$$\|u\|_{L^q(\Omega)} \leq C \|u\|_{H^{1,p}(\Omega)}$$

holds.

For a proof see [35, Chs. 10 & 11] The following two results are used to prove the Gagliardo-Nirenberg inequality.

Lemma 5 (Sobolev-Poincaré inequality). *Let Ω be a bounded domain of $\mathbb{R}^d$ and $u \in H^{1,p}(\Omega)$. Then there exists a constant $C > 0$ independent of u such that*

$$\|u - (u)_\Omega\|_{L^q(\Omega)} \leq C \|\nabla u\|_{L^p(\Omega)},$$

where $1 - \frac{d}{p} = -\frac{d}{q}$.

Proof. Using the classical Poincaré inequality as presented in [31, p. 275] and the Sobolev embedding theorem we obtain

$$c\|u - (u)_\Omega\|_{L^q} \leq \|u - (u)_\Omega\|_{L^p} + \|\nabla u\|_{L^p} \leq C \|\nabla u\|_{L^p}$$

□

Lemma 6 (Interpolation inequality). *Let $\Omega \subset \mathbb{R}^d$ be a bounded domain and $u \in L^p(\Omega)$ where $1 < r < q < p$. Then*

$$\|u\|_{L^q(\Omega)} \leq \|u\|^{\gamma}_{L^r(\Omega)} \|u\|^{1-\gamma}_{L^p(\Omega)}$$

holds for suitable $\gamma > 0$ with $\frac{1}{q} = \frac{\gamma}{r} + \frac{1-\gamma}{p}$.

Proof. Consider $\|u\|^q_{L^q(\Omega)}$ and employ Hölder's inequality

$$\int_\Omega |u|^q \, \mathrm{d}\boldsymbol{x} \leq \left(\int_\Omega |u|^{\gamma q t} \, \mathrm{d}\boldsymbol{x} \right)^{\frac{1}{t}} \left(\int_\Omega |u|^{(1-\gamma) q s} \, \mathrm{d}\boldsymbol{x} \right)^{\frac{1}{s}},$$

with $\frac{1}{s} + \frac{1}{t} = 1$. Let $\gamma q t = r$ and $(1 - \gamma) q s = p$. After Elimination of s and t it follows $\frac{1}{q} = \frac{\gamma}{r} + \frac{1-\gamma}{p}$ as well as

$$\|u\|_{L^q(\Omega)} \leq \|u\|^{\gamma}_{L^r(\Omega)} \|u\|^{1-\gamma}_{L^p(\Omega)},$$

the desired result. □

Lemma 7 (Gagliardo-Nirenberg inequality). *Let $\Omega \subset \mathbb{R}^d$ be a bounded domain and $u \in H^{1,p}(\Omega)$ and $1 < r < q$. Then*

$$\|u - (u)_\Omega\|_{L^q(\Omega)} \leq C\|\nabla u\|^\gamma_{L^p(\Omega)}\|u - (u)_\Omega\|^{1-\gamma}_{L^r(\Omega)}$$

holds for

$$\gamma = \left(\frac{1}{r} - \frac{1}{q}\right)\left(\frac{1}{d} - \frac{1}{p} + \frac{1}{r}\right)^{-1}. \tag{A.7}$$

Proof. To prove (A.7) we employ the interpolation inequality for $u - (u)_\Omega$ to get

$$\|u - (u)_\Omega\|_{L^q(\Omega)} \leq C\|u - (u)_\Omega\|^\gamma_{L^s(\Omega)}\|u - (u)_\Omega\|^{1-\gamma}_{L^r(\Omega)},$$

where $q < s$ and $\frac{1}{q} = \frac{\gamma}{s} + \frac{1-\gamma}{r}$. Then using Sobolev-Poincaré inequality we have

$$\|u - (u)_\Omega\|_{L^q(\Omega)} \leq C\|\nabla u\|^\gamma_{L^p(\Omega)}\|u - (u)_\Omega\|^{1-\gamma}_{L^r(\Omega)},$$

for $1 - \frac{d}{p} = -\frac{d}{s}$ from which (A.7) follows. □

Lemma 8 (Calderón-Zygmund inequality). *Assume $u \in C^k(\Omega),\ (k \geq 2)$ fulfils a homogeneous Dirichlet or Neumann boundary condition at $\partial\Omega$. Then we have*

$$\|\,\mathrm{D}^2\, u\|_{L^2(\Omega)} \leq c\|\Delta u\|_{L^2(\Omega)}$$

Proof. Consider the second partial derivative in $i,\ j$-direction, i.e.

$$\int_\Omega \partial_{x_i x_j} u \partial_{x_i x_j} u \ \mathrm{d}\boldsymbol{x} = \int_\Omega \partial_{x_i x_j} u \partial_{x_j x_j} u \ \mathrm{d}\boldsymbol{x},$$

after two partial integrations. From Cauchy-Schwartz' inequality we obtain

$$\int_\Omega |\partial_{x_i x_j} u|^2 \ \mathrm{d}\boldsymbol{x} \leq c \int_\Omega |\Delta u|^2 \ \mathrm{d}\boldsymbol{x}.$$

□

Appendix C- Lagrange Multipliers.

As an important challenge in irreversible thermodynamics there arises the statemant and analysis of the second law. As already discussed this law is given as an inequality for the change of entropy. The constitutive relations in the resulting models will strongly depend on this entropy principle. The probably most famous statement of the entropy principle is the Clausius-Duhem inequality which is precisely a combination of the energy and entropy law. Moreover this inequality involves the assumption that fluxes and sources of entropy equal their energetic counterparts divided by temperature. As an important result constitutive relations and dependencies admit a simple and plain form, if once the Clausius-Duhem inequality holds. This inequality and its consequences are the central part of the entropy principle and its exploitation discussed by Coleman and Noll in [23] and Coleman and Mizel in [22].

Now an essential requirement on entropy principles is their consistence to the kinetic theory and statistical mechanics. While in thermodynamics the entropy arises from an axiomatic approach, it admits a precise definition in the framework of statistical mechanics and kinetic theory. Consequently, as a quite reasonable requirement the entropy principle of thermodynamics should be consistent with statistical mechanics. In view of this the Coleman-Noll theory can be validated in many important applications. Nevertheless there are some interesting cases where this procedure leads to inconsistent models.

In [65] Müller proposed an entropy principle that drops the a-priori assumption on the relation between entropy and energy fluxes or sources, respectively. Although it neglects entropy and energy sources it is rather general than the approaches based on the Clausius-Duhem inequality. Moreover, in cases where the Coleman-Noll procedure is inconsistent Müllers entropy principle provides a hopefully consistent alternative. Nevertheless the exploitation of this entropy principle is rather difficult than the methods of Coleman and Noll. In his article [61] Liu proposed a method that is similar to the theory of Lagrange multipliers in constrained optimization problems. In this spirit his method has been called method of Lagrange multipliers. Its central part is the following lemma which reduces the analytical problem to a linear and algebraic one.

Theorem 5 (Liu's lemma). *Let* $A : \mathbb{R}^N \to \mathbb{R}^M$, $a : \mathbb{R}^N \to \mathbb{R}$ *two linear mappings,* $B \in \mathbb{R}^M$, $b \in \mathbb{R}$ *and* $S = \{X \in \mathbb{R}^N : \ AX + B = 0\}$. *The following three statements are equivalent:*

1. *For all* $X \in S$

$$a \cdot X + b \geq 0$$

is fulfilled.

2. *There exist numbers (called Lagrange multipliers)* $\Lambda \in \mathbb{R}^M$ *such that*

$$a \cdot X + b - \Lambda \cdot (AX + B) \geq 0,$$

for all $X \in \mathbb{R}^N$.

3. *There exist numbers (called Lagrange multipliers)* $\Lambda \in \mathbb{R}^M$ *such that*

$$\begin{aligned} a - \Lambda \cdot A &= 0, \\ b - \Lambda \cdot B &\geq 0. \end{aligned}$$

For a proof see [61].

Thus it is sufficient to transform a given system of balance-imbalance relations to a linear-algebraic problem.

We consider a system of conservation laws supplemented by an entropy inequality, given by

$$A(Z)\,\mathrm{D}_t\, Z + B(Z)\,\mathrm{D}_{\boldsymbol{x}}\, Z + C(Z) = 0, \tag{4.50}$$

$$a(Z) \cdot \mathrm{D}_t\, Z + b(Z) : \mathrm{D}_{\boldsymbol{x}}\, Z + c(Z) \geq 0, \tag{4.51}$$

where $\mathrm{D}_t\, Z$ denotes either the partial derivative with respect to t or the material derivative. Here $Z \in \mathbb{R}^n$ denotes the tableau of variables and B is a tableau $B = (B^{(1)}, \ldots, B^{(d)})$ of $m \times n$-matrices $B^{(i)}$ such that

$$B(Z)\,\mathrm{D}_{\boldsymbol{x}}\, Z = \sum_{i=1}^{d} B^{(i)} \partial_{\boldsymbol{x}_i} Z$$

holds. In addition A is also a $m \times n$-matrix, while b is a $n \times d$-matrix. We now assume that Z splits into simple thermodynamical fields regarded as variables and composed ones which depend on the simple fields. This contributes to the fact that in our applications appear simple fields as ϱ, $\boldsymbol{c}$ and $\boldsymbol{v}$ as well as complicated ones as E, $\boldsymbol{J}_E$ etc. In view of this we assume that there exist $Z_i \in \mathbb{R}^{n_i}$, $i \in \{1, 2\}$ such that

$$Z = (Z_1, Z_2(Z_1)) \text{ and } n = n_1 + n_2$$

hold. Then by $J = \frac{\partial Z_2}{\partial Z_1}$ we have

$$\mathrm{D}_t\, Z_2 = J\,\mathrm{D}_t\, Z_1 \text{ and } \partial_{\boldsymbol{x}_i} Z_2 = J \partial_{\boldsymbol{x}_i} Z_1. \tag{4.52}$$

In addition we define A_1, A_2 and B_1, B_2 via

$$A\,\mathrm{D}_t\, Z = A_1\,\mathrm{D}_t\, Z_1 + A_2\,\mathrm{D}_t\, Z_2 \text{ and } B\,\mathrm{D}_{\boldsymbol{x}}\, Z = B_1\,\mathrm{D}_{\boldsymbol{x}}\, Z_1 + B_2\,\mathrm{D}_{\boldsymbol{x}}\, Z_2,$$

hence $A = (A_1, A_2)$ and $B = (B_1, B_2)$ holds and by (4.52) we have

$$A\,\mathrm{D}_t\,Z = A_1\,\mathrm{D}_t\,Z_1 + A_2 J\,\mathrm{D}_t\,Z_1 \text{ and } B\,\mathrm{D}_{\boldsymbol{x}}\,Z = B_1\,\mathrm{D}_{\boldsymbol{x}}\,Z_1 + B_2 J\,\mathrm{D}_{\boldsymbol{x}}\,Z_1.$$

Then our balance-imbalance system (4.50) and (4.51) turns into

$$\begin{aligned}(A_1 + A_2 J)\,\mathrm{D}_t\,Z_1 + (B_1 + B_2 J)\,\mathrm{D}_{\boldsymbol{x}}\,Z_1 + C &= 0, &(4.53)\\ (a_1 + J^\top a_2)\cdot \mathrm{D}_t\,Z_1 + (b_1 + J^\top b_2) : \mathrm{D}_{\boldsymbol{x}}\,Z_1 + c &\geq 0 &(4.54)\end{aligned}$$

We set $A_0 = A_1 + A_2 J$, $B_0 = B_1 + B_2 J$, $a_0 = a_1 + J^\top a_2$, $b_0 = b_1 + J^\top b_2$. Then we obtain

$$\begin{aligned}A_0\,\mathrm{D}_t\,Z_1 + B_0\,\mathrm{D}_{\boldsymbol{x}}\,Z_1 + C &= 0, &(4.55)\\ a_0\cdot \mathrm{D}_t\,Z_1 + b_0 : \mathrm{D}_{\boldsymbol{x}}\,Z_1 + c &\geq 0. &(4.56)\end{aligned}$$

In general $\mathrm{D}_t\,Z_1$ and $\mathrm{D}_{\boldsymbol{x}}\,Z_1$ contain fields of Z_1 thus they are not independent. Therefore we assume $Z_1 = (X_1, Y_1)$ and $Z_1 = (X_2, Y_2)$ where $\mathrm{D}_t\,Y_1$ contains all fields of $\mathrm{D}_t\,Z_1$ that are also fields of Z_1, similarly let $\mathrm{D}_{\boldsymbol{x}}\,X_2$ contain all fields of $\mathrm{D}_{\boldsymbol{x}}\,Z_1$ that are fields of Z_1. Then we define A_X, A_Y and B_X, B_Y via

$$A_0\,\mathrm{D}_t\,Z_1 = A_X\,\mathrm{D}_t\,X_1 + A_Y\,\mathrm{D}_t\,Y_1 \text{ and } B_0\,\mathrm{D}_{\boldsymbol{x}}\,Z_1 = B_X\,\mathrm{D}_{\boldsymbol{x}}\,X_2 + B_Y\,\mathrm{D}_{\boldsymbol{x}}\,Y_2,$$

as well as a_X, a_Y and b_X, b_Y by

$$a_0\cdot \mathrm{D}_t\,Z_1 = a_X\cdot \mathrm{D}_t\,X_1 + a_Y\cdot \mathrm{D}_t\,Y_1 \text{ and } b_0 : \mathrm{D}_{\boldsymbol{x}}\,Z_1 = b_X : \mathrm{D}_{\boldsymbol{x}}\,X_2 + b_Y : \mathrm{D}_{\boldsymbol{x}}\,Y_2.$$

Then (4.53) and (4.54) turn into

$$\begin{aligned}A_X\,\mathrm{D}_t\,X_1 + A_Y\,\mathrm{D}_t\,Y_1 + B_X\,\mathrm{D}_{\boldsymbol{x}}\,X_2 + B_Y\,\mathrm{D}_{\boldsymbol{x}}\,Y_2 + C &= 0,\\ a_X\cdot \mathrm{D}_t\,X_1 + a_Y\cdot \mathrm{D}_t\,Y_1 + b_X : \mathrm{D}_{\boldsymbol{x}}\,X_2 + b_Y : \mathrm{D}_{\boldsymbol{x}}\,Y_2 + c &\geq 0.\end{aligned}$$

We set $C_0 = C + A_Y\,\mathrm{D}_t\,Y_1 + B_X\,\mathrm{D}_{\boldsymbol{x}}\,X_2$, $c_0 = c + a_Y\cdot \mathrm{D}_t\,Y_1 + b_X : \mathrm{D}_{\boldsymbol{x}}\,X_2$ and $X = \mathrm{D}_t\,X_1$, $Y = \mathrm{D}_{\boldsymbol{x}}\,Y_2$. With this setting A_X, B_Y, C_0, a_X, b_Y, c_0 depend only on Z_1. Then we have

$$\begin{aligned}A_X X + B_Y Y + C_0 &= 0, &(4.57)\\ a_X\cdot X + b_Y : Y + c_0 &\geq 0, &(4.58)\end{aligned}$$

now with free variables X and Y that are independent of Z_1. In order to apply Theorem 5 let $(t', \boldsymbol{x}')$ a fixed point of the time-space and $Z_1' = Z_1(t', \boldsymbol{x}')$. Now by the Cauchy-Kowalewsky existence theorem (cf. [24]) we obtain existence of a unique solution $Z_1(t, \boldsymbol{x})$ in a neighborhood of $(t', \boldsymbol{x}')$ for real analytic functions A_X, B_Y, C_0, a_X, b_Y, c_0 and arbitrary but analytic initial data $Z_1(t', \boldsymbol{x})$, provided A_X has maximal rank at $Z_1' = Z_1(t', \boldsymbol{x}')$. To validate the presumptions of Theorem 5 we have to check that $X = \mathrm{D}_t\,X_1$, $Y = \mathrm{D}_{\boldsymbol{x}}\,Y_2$ can be arbitrarily prescribed. In fact by Taylor series expansion

$$\begin{aligned}X_1(t'', \boldsymbol{x}') &= X_1(t', \boldsymbol{x}') + \partial_t X_1(t', \boldsymbol{x}')(t'' - t') + \ldots &(4.59)\\ X_1(t', \boldsymbol{x}'') &= X_1(t', \boldsymbol{x}') + \nabla X_1(t', \boldsymbol{x}')\cdot(\boldsymbol{x}'' - \boldsymbol{x}') + \ldots &(4.60)\\ Y_2(t', \boldsymbol{x}'') &= Y_2(t', \boldsymbol{x}') + \nabla Y_2(t', \boldsymbol{x}')\cdot(\boldsymbol{x}'' - \boldsymbol{x}') + \ldots &(4.61)\end{aligned}$$

the values for all first and higher derivatives of X_1 and Y_2 can be prescribed arbitrarily in $(t', \boldsymbol{x}')$, since $X_1(t'', \boldsymbol{x}')$, $X_1(t', \boldsymbol{x}'')$, $Y_2(t', \boldsymbol{x}'')$ can be chosen also arbitrarily. Thus it does not matter which values of $X_1(t'', \boldsymbol{x}')$, $X_1(t', \boldsymbol{x}'')$, $Y_2(t', \boldsymbol{x}'')$ result from the choice of the right hand sides of (4.59) - (4.61). Then by Theorem 5 there exists a Λ such that

$$\begin{aligned} 0 &\leq a_X \cdot X + b_Y : Y + c_0 - \Lambda \cdot (A_X X + B_Y Y + C_0) \\ &= (a_X - A_X^\top \Lambda) \cdot X + (b_Y - B_Y^\top \Lambda) : Y + c_0 - C_0 \cdot \Lambda, \end{aligned} \tag{4.62}$$

provided $Z_1 = Z_1'$ is kept fixed and for all fields X and Y. Clearly (4.57) is

$$\begin{aligned} 0 &\leq (a_0 - A_0^\top \Lambda) \cdot \mathrm{D}_t\, Z_1 + (b_0 - B_0^\top \Lambda) : \mathrm{D}_{\boldsymbol{x}}\, Z_1 + c - \Lambda \cdot C \\ &= (a_1 + J^\top a_2) \cdot \mathrm{D}_t\, Z_1 - \Lambda \cdot (A_1 + A_2 J)\, \mathrm{D}_t\, Z_1 \\ &+ (b_1 + J^\top b_2) : \mathrm{D}_{\boldsymbol{x}}\, Z_1 - \Lambda \cdot (B_1 + B_2 J)\, \mathrm{D}_{\boldsymbol{x}}\, Z_1 + c - \Lambda \cdot C. \end{aligned}$$

Then by $J = \frac{\partial Z_2}{\partial Z_1}$ we obtain

$$\begin{aligned} 0 &\leq a_1 \cdot \mathrm{D}_t\, Z_1 + a_2 \cdot \mathrm{D}_t\, Z_2 - \Lambda \cdot (A_1\, \mathrm{D}_t\, Z_1 + A_2\, \mathrm{D}_t\, Z_2) \\ &+ b_1 : \mathrm{D}_{\boldsymbol{x}}\, Z_1 + b_2 : \mathrm{D}_{\boldsymbol{x}}\, Z_2 - \Lambda \cdot (B_1\, \mathrm{D}_{\boldsymbol{x}}\, Z_1 + B_2\, \mathrm{D}_{\boldsymbol{x}}\, Z_2) + c - \Lambda \cdot C \\ &= a \cdot \mathrm{D}_t\, Z + b : \mathrm{D}_{\boldsymbol{x}}\, Z + c - \Lambda \cdot (A\, \mathrm{D}_t\, Z + B\, \mathrm{D}_{\boldsymbol{x}}\, Z + C). \end{aligned}$$

Hence for (4.50, 4.51) there exists a Λ such that

$$0 \leq a \cdot \mathrm{D}_t\, Z + b : \mathrm{D}_{\boldsymbol{x}}\, Z + c - \Lambda \cdot (A\, \mathrm{D}_t\, Z + B\, \mathrm{D}_{\boldsymbol{x}}\, Z + C) \tag{4.63}$$

for all X and Y such that $X, Y \notin Z$ and $X = \mathrm{D}_t\, Z_X$, $Y = \mathrm{D}_t\, Z_Y$ for appropriate $Z_X,\ Z_Y \subset Z$. We are now going to apply inequality (4.63) to our system of balance and imbalance laws given by (3.12)-(3.16). For this purpose we expand the free energy $\mathrm{D}_t\, F$ as

$$\mathrm{D}_t\, F = F_{,Z_1} : \mathrm{D}_t\, Z_1,$$

which admits to proceed with (4.55) and (4.56). Consequently we choose $Z = (Z_1, Z_2)$ as

$$Z_1 = (\varrho, \boldsymbol{c}, \nabla \boldsymbol{c}, \nabla \boldsymbol{v}, T, \nabla T, \boldsymbol{\phi}, \nabla \boldsymbol{\phi}, \mathrm{D}_t\, \boldsymbol{\phi})\ ,\ Z_2 = (S, \boldsymbol{J}_E, \boldsymbol{J}_S, \boldsymbol{J}, \boldsymbol{T}).$$

It remains to show that $F_{,X_1}$ ($X_1 = (\varrho, \boldsymbol{c}, \nabla \boldsymbol{c}, \nabla \boldsymbol{v}, T, \nabla T, \boldsymbol{\phi}, \nabla \boldsymbol{\phi})$) has maximal rank at Z_1 in $(t_0, \boldsymbol{x})$. Then the Cauchy-Kowalewsky existence theorem asserts the existence of an unique analytic solution $(\varrho, \boldsymbol{v}, \boldsymbol{c}, E)$ provided all terms of (3.3)-(3.9) are real analytic functions as well as the initial data in $(t_0, \boldsymbol{x})$. From the discussion of Taylor series we can allow arbitrary values of

$$\left(\mathrm{D}_t\, \varrho, \mathrm{D}_t\, \boldsymbol{c}, \mathrm{D}_t\, \nabla \boldsymbol{c}, \mathrm{D}_t\, \nabla \boldsymbol{v}, \mathrm{D}_t\, T, \mathrm{D}_t\, \nabla T, \mathrm{D}_t^2\, \boldsymbol{\phi}\right).$$

In view of this one can expect *constitutive relations* for

$$F_{,\varrho},\ F_{,\boldsymbol{c}},\ F_{,\nabla \boldsymbol{c}},\ F_{,\nabla \boldsymbol{v}},\ F_{,T},\ F_{,\nabla T},\ F_{,\mathrm{D}_t\, \boldsymbol{\phi}},$$

from inequality (4.63). In fact this is done in Section 3.3.

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