# Investigations of Microstructural Changes in Lead-Free Solder Alloys by Means of Phase Field Theories 

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Damit war später für sie bewiesen, dass die Mathematik, Mutter der exakten Naturwissenschaft, Großmutter der Technik, auch Erzmutter jenes Geistes ist, aus dem schließlich auch Giftgase und Kampfflieger aufgestiegen sind.

Robert Musil, (1880-1942)

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## Preface

The present thesis reflects my work during the last three years at the Chair of Continuum Mechanics and Materials Theory at the Institute of Mechanics of the Technische Universität Berlin. During this time I was supported by many persons, who gave me their advise, or inspired me in various discussions. Furthermore I always enjoyed the familiar and friendly atmosphere at the Institute of Mechanics as well as the intensively scientific cooperation with the research group Thermodynamic Modeling and Analysis of Phase Transitions at the Weierstrass Institute for Applied Analysis and Stochastics (WIAS) in Berlin. In the following I want to thank some people more explicitly.

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## Zusammenfassung

In der vorliegenden Arbeit wird der Prozess der spinodalen Entmischung und der einhergehenden Vergröberung am Beispiel des bleifreien, binären Hartlotes $\mathrm{Ag}-\mathrm{Cu}$ sowohl theoretisch als auch experimentell untersucht.

Wir starten in Abschnitt 1 mit einer Einleitung in die Problematik. Hierbei werden zuerst die technologischen und die ökologischen Tendenzen im Bereich der Mikroelektronik diskutiert und Schlussfolgerungen bzgl. der Aufgaben und Probleme aus Sicht der Materialwissenschaften gezogen.

Abschnitt 2 konzentriert sich auf die kontinuumsmechanische und thermodynamische Beschreibung der Phasenbildung in elastisch deformierten Festkörpern. Hierzu beginnen wir mit den fundamentalen Prinzipien der Thermodynamik, insbesondere mit dem zweiten Hauptsatz, und entwickeln die notwendigen Materialgleichungen, die zur Beschreibung der auftretenden Diffusionsprozesse in mehrphasigen Systemen notwendig sind. Es wird gezeigt, dass die aus dem postulierten Entropie Prinzip gewonnenen Resultate im Einklang mit der klassischen Thermodynamik der Fluide stehen. Anschließend wird eine Phasenfeldtheorie, basierend auf der Einführung sog. höherer Gradienten, entwickelt. Hierbei wird für den Spezialfall von binären Legierungen eine erweiterte Diffusionsgleichung abgeleitet, die es erlaubt, Phasenseparation und Vergröberung unter Berücksichtigung von thermo-elastischen Verzerrungen im Festkörper zu beschreiben.

Im darauf folgenden Abschnitt 3 widmen wir uns der Bestimmung der für die Simulation notwendigen Materialparameter. Insbesondere wird eine atomistische Theorie entwickelt, um die elastischen Konstanten als auch die aus der Phasenfeldtheorie stammenden Höheren Gradienten Koeffizienten (HGKs) theoretisch zu berechnen. Grundlage hierbei sind so genannte interatomare Wechselwirkungspotentiale auf der Basis der Embedded-Atom-Method, aus denen ein Energieausdruck für den Festkörper abgeleitet werden kann. Dieser wiederum gestattet es, die elastischen Konstanten als auch die HGKs als Funktionen der Konzentration und der Verzerrungen zu berechnen. Abschließend wird der feste Bereich des Ag-Cu Phasendiagramms berechnet, dessen gute Übereinstimmung mit den Literaturwerten die Zuverlässigkeit der gewonnenen Materialdaten untermauert.

Im Anschluss daran werden in Abschnitt 4 numerische Simulationen vorgestellt. Wir beginnen mit einem kurzen Abriss der notwendigen numerischen Werkzeuge, die zum

Lösen der erweiterten Diffusionsgleichung, einer nichtlineare partielle Differentialgleichung (PDG) vierter Ordnung, notwendig sind. Insbesondere verwenden wir hierbei die Methode der Diskreten Fourier Transformation sowie sog. Einschritt- Zeitintegrationsverfahren und lösen die PDG für den eindimensionalen und zweidimensionalen Fall. Verschiedene Szenarien werden untersucht und bzgl. ihres numerischen Aufwandes als auch ihres Vergröberungsverhalten diskutiert.

Abschnitt 5 bezieht sich auf die experimentelle Untersuchung der in Abschnitt 4 simulierten Phasenevolution in $\mathrm{Ag}-\mathrm{Cu}$. Hierzu werden eingangs die verwendeten experimentellen Methoden, insbesondere die metallografische Präparation, die Mikroskopie und die digitale Bildanalyse, vorgestellt. Anschließend erläutern wir, wie die gewonnenen mikroskopischen Aufnahmen bzgl. der Phasenvergröberung quantifiziert werden können. Der Abschnitt schließt mit der Darstellung verschiedener Bildreihen und mit der empirischen Bestimmung eines Vergröberungsgesetzes.

Die vorliegende Doktorarbeit endet mit einem Vergleich der theoretischen und experimentellen Resultate sowie deren Diskussion. Außerdem wird abschließend eine Zusammenfassung der Arbeit als auch ein kleiner Ausblick auf eventuell weiterzuführende Untersuchungen gegeben.

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## Chapter 1

## Introduction

### 1.1 Tendencies in Microelectronic Packaging

### 1.1.1 Technological Trends

As a consequence of the "technological revolution" in the last 20 years there is an ongoing miniaturization in the area of microelectronics driven by an increasing requirement for mobility (e.g., mobile phones or notebooks) and more complex functionalities (e.g., multimedia or fly-by-wire systems). Therefore the minimal feature size ${ }^{1}$ within semiconductors continuously decreases whereas the number of transistors rapidly grows (cf., Fig. 1.1). This process results in the use of smaller and smaller amounts of matter, and, consequently, the demands on strength and lifetime of the used materials considerably rise while the structural size is continuously reduced.

### 1.1.2 Environmental Concerns

In addition to the technological trends environmental initiatives become increasingly important, in particular in the high-technology countries. The purpose of these activities is the reduction of electronic waste and/or the hazardous substances within (e.g., $\mathrm{Cd}, \mathrm{Hg}, \mathrm{Pb})$. So, for instance the annual amount of the German electronic waste is more than four times of the volume of the 140 m high ChEOPs pyramid in Egypt (estimation of the German environmental organization BUND, [118]) or 130 million cell phones were estimated to be retired in 2005 in the US. This value corresponds to 81.250 pounds of lead resulting from the lead solder used in the printed wiring boards, which enter the waste stream. (estimation of the environmental organization InFORM, [48]).

[^0]

Figure 1.1: The development of the minimal feature size (partially expected) and the number of transistors in microelectronics, source: Intel, [62] and ITRS, [63].

These citations underscore the problems following from the technological progress and, thus, environmental initiatives are strongly necessary. In what follows the ecological efforts are briefly explained for the three regions of Europe, Asia, and the USA. However, although the regulations differ, the remaining time for broad-scale use of traditional Sn - Pb -based solders is certainly limited and, consequently, adequate leadfree materials must be investigated and evaluated, in particular from a theoretical and experimental materials science point of view.

## a. Europe, in particular Germany

In the EU two initiatives are worth mentioning: the directives WEEE (directive on Waste Electrical and Electronic Equipment, [33]) and the RoHS (Restriction of the use of certain Hazardous Substances in electrical and electronic equipment, [32]), which require the industry to take care of the disposal of electronic devices and which regulate/forbid the use of certain substances, such as $\mathrm{Pb}, \mathrm{Hg}$, or Cd in electronics. These directives must be transposed into national law by the member states. Germany, for example, passed the so-called "ElektroG" law, [53], which, among other things, restricts the use of Pb as of July, 1st, 2006. However, the technological progress could not follow the original RoHS restrictions in the pre-defined period, so that exemptions ${ }^{2}$ were subsequently included, [56].

[^1]
## b. Asia, in particular Japan and China

Undoubtedly, Japan represents the "trendsetter" in the area of so-called "green electronics". Already since 1990 the Japanese companies voluntarily committed in socalled Environmental Protection Charters to avoid waste and to save natural recourses. Based on the JEIDA ${ }^{3}$ roadmap, [50], which appeared in 1999 these agreements were successively extended by specific aims, in particular with respect to the lead-free legalization process in the microelectronic sector. In April 2001 (i.e., two years before the adequate EU directive WEEE were passed) the Home Electric Appliance Recycling Law were put into full force, which regulates the response of the manufacturer for the disposal of old electronics, [107].

The fast environmental progress in Japan is also based on the fact, that the leading electronic companies, such as Fujitsu, Toshiba, Sony or Panasonic use the environmental awareness for marketing strategies and compete for an ecological image. For instance, Sony already introduced in March 2001 the first lead-free camcorder on the market, [50]. Moreover, up to the middle of 2002 about $50 \%$ of the Pb solders were eliminated by the most Japanese electronic companies compared with the level of 1997, [95].

In China the Ministry of Information Industry has introduced an RoHS-like law called Management Methods for Pollution Prevention and Control in the Production of Electronic Information Products, [95], which represents Chinese policy on reduction of hazardous substances used in electronic information products. It includes manufacturing, imports, and packing, but explicitly exclude exporting products. In a first step, products containing certain toxic constituent parts must be labeled since March 2007, [49]. First concrete restriction, and without exceptions as in the RoHS, are planned for 2008.

## c. USA

The U.S. Environmental Protection Agency has introduced a Toxic Release Inventory rule, which lowers the reporting thresholds for the emission of lead and lead compounds to 100 pounds (approx. 45 kg ) for facilities and companies, [95], by April 2001. Furthermore one finds in different states rules regulating the use of lead for example in paint and batteries. However, although various states plan lead-free and/or recycling regulations for electronic appliances, there is no communicated federal position.

In 2003 California passed the so-called Electronic Waste Recycling Act, which includes the recycling and the design of optical electronic equipment, [95]. Furthermore the law restrict, similar to the EU RoHS directive, the use of certain hazardous substances

[^2](e.g. $\mathrm{Pb}, \mathrm{Hg}, \mathrm{Cd})$ by January 2007, [49].

Beside these "governmental efforts" various globally acting companies increasingly head toward lead-free products. For example, Intel recently announced the change to lead-free processors, [99].

### 1.2 Solder Materials

### 1.2.1 Solders in Microelectronic Packaging

The last paragraph already indicates the key role of solder materials in microelectronics. Consequently the question arise: Where and for which reasons solders are used in microelectronic packaging. Figure 1.2 illustrates various packaging variants typically used. Obviously, solder materials assume two important tasks: (a) they guarantee

## "flexible interposer CSPs"



Figure 1.2: Different types of Chip Scale Packaging (CSPs).
the electrical connection between the chip-unit and the electronic circuits within the substrate and (b) they provide the mechanical connection of the different electronic components on the printed circuit board. Consequently there is a specific demand on strength and lifetime of the used materials.

Furthermore the assembling by means of Surface Mount Technology ${ }^{4}$ (SMT) and reflow soldering ${ }^{5}$ requires moderate melting temperatures for the solder materials,

[^3]so that the supersensitive chip units do not fail during the joining process. Indeed, the above manufacturing procedures allow an extremely compact packaging (e.g., the application of chips on both sides of the substrate), but, in contradiction to the conventional Pin-Through-Hole (PTH) assembling, SMT solder joints increasingly tend to rupture, [105]. Here the conventional eutectic $\mathrm{Sn}-\mathrm{Pb}$ solder $\left(c_{\mathrm{Sn}}=0.63\right)$ represents a good compromise. On the one hand both components as well as the mixtures have sufficiently low melting temperatures, namely, [119, 1]:
$$
T_{\mathrm{Sn}}^{\text {melt }}=232^{\circ} \mathrm{C} \quad, \quad T_{\mathrm{Pb}}^{\text {melt }}=327^{\circ} \mathrm{C} \quad, \quad T_{\mathrm{Sn}-\mathrm{Pb}}^{\text {eut }}=183^{\circ} \mathrm{C} .
$$

On the other hand the containing Pb enables the components at the joint interface, e.g., Sn and Cu , to immediately form InterMetallic Compounds (IMCs) in the molten state (see also Section 1.3). Additionally, Pb reduces the surface tension of Sn , which, in turn, increases the wetting properties of Sn, [1]. Hence lead plays an important role for the resistance of the joining connection and, under the background of the lead-free legalization process, the question about an adequate alternative arises.

### 1.2.2 Lead-free Materials

In the last years various lead-free alloys became important for the use in microelectronics. Table 1.1 shows different solders, which are under consideration. Here the first five items represent so-called soft solders, whereas the last item, $\mathrm{Ag}-\mathrm{Cu}$, identifies a typical brazing alloy (i.e., $T^{\text {melt }}>450^{\circ} \mathrm{C}$ ). Obviously, there is no material, which is uniquely favored by the companies due to diverse application fields, country-specific material costs or different material properties. For instance $\mathrm{Sn}-\mathrm{Cu}$ cannot be used for reflow soldering since the relatively high melting temperature ( $c f$. ., Table 1.1) does not allow sufficiently long soldering time. Here experts recommend to use $\mathrm{Sn}-\mathrm{Ag}$, whereas $\mathrm{Sn}-\mathrm{Cu}$ is considered for wave soldering applications, [1].

| Solder | Composition (mass concentration) | $T^{\text {melt }}$ in ${ }^{\circ} \mathrm{C}$ |
| :--- | :--- | :--- |
| $\mathrm{Sn}-\mathrm{Ag}-\mathrm{Cu}$ | $c_{\mathrm{Ag}}=0.038, c_{\mathrm{Cu}}=0.007$ (eutectic) | 217 |
| $\mathrm{Sn}-\mathrm{Bi}$ | $c_{\mathrm{Bi}}=0.580$ (eutectic) | 138 |
| $\mathrm{Sn}-\mathrm{Cu}$ | $c_{\mathrm{Cu}}=0.007$ (eutectic) | 227 |
| $\mathrm{Sn}-\mathrm{Ag}$ | $c_{\mathrm{Ag}}=0.035$ (eutectic) | 221 |
| $\mathrm{Sn}-\mathrm{Zn}$ | $c_{\mathrm{Zn}}=0.090$ | 199 |
| $\mathrm{Ag}-\mathrm{Cu}$ | $c_{\mathrm{Cu}}=0.290$ (eutectic) | 778 |

Table 1.1: Various lead-free solder materials under discussion, source: [83],[112]
In contrast to soft solders, brazing materials, such as the binary solder $\mathrm{Ag}-\mathrm{Cu}$, are usually employed for highly-stressed or high temperature connections, e.g., for gas pipe joints. In particular, in microelectronics brazing materials are used for highperformance applications, in which - due to lower thermal expansion - ceramicsbased packages are preferred over plastics. Here the silicon chip must be fixed to
a metallized ceramic substrate, whereas the occurring ceramic-metal connection is realized by means of brazing solders, [69, 97].

However, soft solders as well as brazing materials show similar material phenomena, in particular micro-structural changes.

### 1.3 Microstructures in Solders

### 1.3.1 Phenomenology

From a microscopic point-of-view solder balls as illustrated in Figure 1.2 are basically subjected to four different micro-structural changes, cf., Fig. 1.3:


Figure 1.3: Various mircrostructural effects observed in solder materials. 1st row (left): IMC scallops $\left(\mathrm{Cu}_{6} \mathrm{Sn}_{5}\right)$ at the interface solder/substrate. 1st row (right): IMC needles $\left(\mathrm{Ag}_{3} \mathrm{Sn}\right)$ in the solder bulk, source: [92]. 2nd row (left): Phase separation by spinodal decomposition in eutectic $\mathrm{Ag}-\mathrm{Cu}$ after 40h heat treatment. 2nd row (right): Kirkendall void formation in the thin $\mathrm{Cu}_{3} \mathrm{Sn}$ layer at the interface solder/substrate, source: [120].
(a) Formation and growth of scallop-shaped InterMetallic Compounds ${ }^{6}$ (IMCs) at the interface solder/substrate: Here the IMCs are formed and grow in the molten state due to an interfacial reaction. In the case of a Cu substrate and an Sn -containing solder (e.g., $\mathrm{Sn}-\mathrm{Ag}-\mathrm{Cu}$ ) this reaction takes place between Cu and Sn and necessitates a mass transport from the substrate to the solder, [70]. Primarily by means of repeating reflow soldering the "scallops" further expand and may have a positive influence on the strength and lifetime of the solder joints, because they guarantee a "dovetail connection". In contrast, there are stress peaks in the vicinity of the IMCs leading to crack initiation. Consequently, the positive effects are limited by a critical size of the scallops.
(b) IMC formation in the interior of the solder: One of the most popular examples for this phenomenon are $\mathrm{Ag}_{3} \mathrm{Sn}$ precipitates observed in lead-free SAC solders ( $\mathrm{Sn}-\mathrm{Ag}-\mathrm{Cu}$ ). These IMCs typically occur in form of needles or plates and are formed due to a chemical reaction in the molten state during soldering. However, once developed, they do not essentially grow within the solid state. Nevertheless, the IMCs are - in contradiction to the solder - extremely stiff and brittle, which yields stress peaks and mismatching during, e.g., thermal cycling of the electronic device.
(c) Phase separation and coarsening through spinodal decomposition and Ostwald ripening in the solder bulk: In contrast to IMC-formation phase separation and coarsening are diffusion processes exclusively driven by aspects of thermodynamical stability and interfacial energy minimization, cf., Section 1.3.2 and [23]. The resulting "composite" of different phases can be interpreted as a "particle reinforced material" in which the stiffer phase acts as the reinforcement. Unfortunately mechanical failure, such as cracks, favorably grow along the phase boundary (cf., Figure 1.4) which result, among other reasons, from thermal mismatching. Thus the benefit of phase dispersion is limited by a critical phase size.
(d) Kirkendall voiding at the interface solder/substrate: Generally speaking, the Kirkendall effect is induced due to a difference in the diffusion coefficients of to neighboring regions, [25]. In particular the occurring IMCs show considerably different diffusion coefficients with respect to Cu . Therefore, the diffusion of Cu from the pad via the interface $\mathrm{Cu} / \mathrm{Cu}_{3} \mathrm{Sn}$ into $\mathrm{Cu}_{3} \mathrm{Sn}$ is much slower than the diffusion of Cu from $\mathrm{Cu}_{3} \mathrm{Sn}$ into the $\mathrm{Cu}_{6} \mathrm{Sn}_{5}$ scallops, which also cannot be corrected by the invers diffusion of Sn through the $\mathrm{Cu}_{6} \mathrm{Sn}_{5} / \mathrm{Cu}_{3}$ interface, [120]. As a consequence vacancies on the lattice sites remain within the $\mathrm{Cu}_{3} \mathrm{Sn}$ layer, which coalesce to macroscopic voids by means of vacancy diffusion. Additionally, stress peaks in the vicinity of the voids result in further void growth and micro crack formation, which may proceed failure.

[^4]

Figure 1.4: Mechanical failure by crack initiation and propagation along the phase boundary. Left: Crack propagation in the bulk, [76]. Right: Global and zoomed view on rupture of a solder bump, [47].

It is reasonable that the various evolving microstructures influent the material properties, which, in turn, also change in time. In particular they considerably determine strength and lifetime of the solders and, therefore, there is a considerable interest in predicting the micro-structural evolution. Note that the form of appearance and the source of the above explained microstructures is completely different. Hence the development of a common theory suitable for a unique description of all these phenomena is quite sophisticated, if not impossible.

For this reason the present work is subjected to the theoretical and experimental investigation of phase separation and coarsening, cf., item (c). The different phases resulting from these phenomena and two typical failure mechanism are illustrated in Figure 1.4 for eutectic $\mathrm{Sn}-\mathrm{Pb}\left(c_{\mathrm{Sn}}=0.63\right)$, [76, 47]. Here crack propagation primarily occurs at the phase boundary and probably results in total loss of the solder joint. Furthermore the binary brazing alloy $\mathbf{A g}-\mathbf{C u}$ is chosen to be in the focus of this work, in which spinodal decomposition and Ostwald ripening yields two equilibrium phases, the Ag -rich $\alpha$-phase and the Cu-rich $\beta$-phase, cf., Fig. 1.3 (lower left). It has qualitatively a similar miscibility gap (i.e., phase equilibrium data) as the $\mathrm{Sn}-\mathrm{Pb}$ solder, illustrated in Figure 1.4 and all required material parameters can easily be obtained.

### 1.3.2 Spinodal Decomposition and Coarsening

From a thermodynamical point-of-view a binary alloy A-B decomposes below a critical temperature $T_{\text {crit }}$ into two equilibrium phases $\alpha$ and $\beta$ due to a miscibility gap resulting in a gain of the GibBS free energy $G(y, T)$, which is a function of particle concentration $y \equiv y_{\mathrm{B}}$ (with $y_{\mathrm{A}}+y_{\mathrm{B}}=1$ ) and temperature $T$. Without loss of generality we consider
an initially eutectic mixture ( $T_{\text {crit }} \equiv T_{\text {eut }}$ ), which is quenched from $T>T_{\text {eut }}$ (liquid) to $T<T_{\text {eut }}$ (solid), cf., Figure 1.5 (first row).

In the liquid state the GIBBS free energy of the system is given by the energetically advantageous convex curve illustrated in Figure 1.5 (upper left). Obviously the mixture is stable to all fluctuations. This fact becomes evident if we imagine in Figure 1.5 (upper left) a fluctuated two-phase-system, represented by the concentrations $y_{1}$ and $y_{2}$ in the neighborhood of the original one-phase-state given by $y_{0}$. The resulting energy $G$ of the two-phase-mixture is given by the energetically disadvantageous connecting line. Therefore the system remains in the one-phase-state with the concentration $y_{0}$.

This fact changes for the solid state as illustrated in Figure 1.5 (upper right). In this case the crucial curve of $G(y, T)$ is piecewise concave. This region is called the spinodal area, enclosed by the spinodal concentrations $y_{1 / 2}^{s p}$ :

$$
\begin{equation*}
\left.\frac{\partial^{2} G(y, T)}{\partial y^{2}}\right|_{y_{1 / 2}^{s p}}=0 \quad \text { (spinodal concentrations) } \tag{1.1}
\end{equation*}
$$

The spinodal area, in which the curvature of $G$ is negative, characterizes the concentrations for which the system is unstable. Evidently any fluctuating system represented by the connecting line of the neighboring perturbed states is energetically advantageous. Consequently the system will decompose until it reaches a state, in which the connecting line of two pertubated neighboring states is completely situated above the original curve of $G$. Such a state is given by the equilibrium concentrations $y_{\alpha / \beta}$, which can be constructed by the so-called common tangent rule resulting from a thermodynamical stability analysis by assuming a uniform stress field, [89]:

$$
\begin{equation*}
\left.\frac{\partial G(y, T)}{\partial y}\right|_{y=y_{\alpha / \beta}}=\frac{G\left(y_{\beta}, T\right)-G\left(y_{\alpha}, T\right)}{y_{\beta}-y_{\alpha}} . \tag{1.2}
\end{equation*}
$$

Figure 1.5 (upper right) illustrates the construction of the equilibrium concentrations $y_{\alpha / \beta}$ of the two solid phases $\alpha$ and $\beta$. The process, during which a one-phase system is quenched into the unstable area and subsequently decomposes into different equilibrium phases is called spinodal decomposition.

Figure 1.5 (upper middle) displays the intermediate situation for the critical temperature $T=T_{\text {eut }}$, which is passed during the quenching process. Here the common tangent rule yields three equilibrium concentrations, so that three phases coexist within the systems: two solid phases with the concentrations $y_{\alpha / \beta}$ and one liquid phase with the concentration $y_{0}$. Constructing the various equilibrium phases for different temperatures yields so-called phase diagrams as given in Figure 1.5 (second row) exemplarily for the binary mixture $\mathrm{Ag}-\mathrm{Cu},[83]$.



Figure 1.5: First row: Illustration of the eutectic solidification process and of the characteristic concentrations within the miscibility gap. Second row: Phase diagram of $\mathrm{Ag}-\mathrm{Cu}$, source [83].

After the whole system reaches the equilibrium concentrations coarsening begins in such a way that the number of precipitated phase regions decreases whereas the size of the phases increases. Here the bigger phases grow at the expense of the smaller ones due to the Gibbs-Thomson effect, [116]. In particular, the concentration on the boundary of the smaller phases is greater due to the larger curvature. Consequently there is an (uphill) diffusion flux from the smaller phases to the bigger ones. This process is often called coarsening or Ostwald-ripening, [96], and minimizes the total interfacial energy of the system, $[79,116,115]$.

### 1.4 Organisation of this Work

In what follows the process of spinodal decomposition and coarsening, in particular for the brazing alloy $\mathrm{Ag}-\mathrm{Cu}$, is investigated theoretically as well as experimentally.

The presented work starts in Chapter 2 with fundamental thermodynamical consid-
erations allowing for the description of diffusion processes in multi-component and multi-phase solid mixtures. First, we show that the introduced thermodynamical principles reproduce the classical results of fluid thermodynamics. Subsequently a phase field theory is developed by means of so-called Higher Gradient (HG) terms. The section ends with the special cases of binary alloys, for which an Extended Diffusion Equation (EDE) can be derived, which is suitable to investigate the spinodal decomposition and coarsening process in binary solid mixtures under the presence of thermo-elastic stresses.

In the following Chapter 3 an atomistic approach for the exact calculation of the socalled Higher Gradient Coefficients (HGCs) is presented. These coefficients enter the theory due to the phase field model, in which the free energy not only depends on the composition but also on gradients of the composition. Based on the Embedded-AtomMethod (EAM) the HGCs are calculated for the binary alloy $\mathrm{Ag}-\mathrm{Cu}$ as functions of concentration and strains.

Subsequently, the derived theories are applied to numerical simulations. Based on Discrete Fourier Transforms (DFT) and discrete time integration methods the EDE is solved for the one and two dimensional case. Different case studies are investigated for illustrating purposes and in order to point out the numerical difficulties.

Chapter 6 is devoted to the experimental investigation of the micromorphological changes in Ag-Cu. Starting with an explanation of the experimental methods it is outlined how the observed micromorphologies can be exploited for the quantification of the coarsening process. After that various obtained micrographs are presented and analyzed with respect to coarsening.

The work ends with a critical discussion of the obtained results and gives a brief outlook on receivable investigations.

## Chapter 2

## A Higher Gradient Theory of Mixtures ${ }^{1}$

### 2.1 Historical Remarks about Diffusion

Due to the explanations in Chapter 1 it is reasonable that the theoretical description of diffusion processes in solid mixtures represents an important aspect in modern materials science. A review of the literature shows that the theoretical description of diffusion processes in mixtures has a history of more than 150 years. In 1855 Fick proposed to treat diffusion analogously to Fourier's law of heat conduction, [46]. The resulting first and second Fick's laws allow the characterization of "downhill" diffusion, i.e., of material transfers from high to low concentrations. However, they are not suitable to explain "uphill" diffusion, such as spinodal decomposition during which concentrations gradients are amplified. Although this process is well-known from the experimental point of view, cf., [96], a commonly accepted general theory for the effective prediction of interfaces, phase boundaries and other diffusion-induced inhomogeneities in solids, in particular under the consideration of arbitrary conditions (e.g., thermal misfits, local stresses, etc.), is still a pending problem.

However, there are various pioneering works in the literature dedicated to diffusion under the presence of inhomogeneities. Already GibBS (1892) was concerned about the conditions for the stability and formation of "discontinuities" in liquids and solids, [55]. However, it seems that the first popular theoretical work stems from Becker \& Döring (1935) in which they present a statistical model for the nucleation of liquid droplets, [8]. In 1937 Becker also published a molecular model in order to describe the formation of superstructures and precipitations within binary solids, [7]. Based on that work Hillert (1961) developed a one dimensional model for the qualitative prediction of the nonuniform concentration field by spinodal decomposition and nucleation in "inhomogeneous solids" (sic!), [61]. This approach was generalized in 1958

[^5]by Cahn and Hilliard ${ }^{2}$, [24]. They first presented a general phenomenological theory of spinodal decomposition and nucleation adding interfacial energy contributions to the free energy by means of concentration gradient terms in order to characterize the nonuniform concentration field. The resulting Cahn-Hilliard equation, cf., [22, 23], allows for an explicit simulation of the formation and growth of (coarsening) phases separated by smooth interfaces and denotes the starting point for so-called Phase Field Models (PFM). From then on phase field equations were studied from different point-of-views, e.g. [74], and one finds a multitude of modifications, [54], extentions, e.g. [2], and generalizations, [58].

Parallel to this chronology so-called Sharp Interface Models (SIM) were developed in which the nonuniform system is assumed to involve well-defined phases separated by sharp interfaces whose motion is determined by the jump conditions following from the balances on discontinuities. It is reasonable to postulate that the SIM equations must follow from the equations according to the PFM. For that reason one has to reduce "suitably" the finite width of the smooth interfaces into sharp interfaces which is usually done by transforming the corresponding equations to the limit case of infinite width, [59, 39]. However, note that it is also possible to treat a nonzero interface width within the SIM framework, [45]. A "subgroup" within SIM are so-called $L S W$ theories, named after the seminal works of Lifshitz and Slyozov (1961) and Wagner (1961), [79, 116]. They start from the Gibbs-Thomson effect and investigate the temporal development of the radius distribution of spherical precipitations embedded in supersaturated solutions. Due to a dissolving process they found that the average radius $\bar{r}(t)$ increases with $t^{-1 / 3}$ whereas the number of precipitates $N(t)$ reduces with $t^{-1}$. Thus bigger inclusions grow at the expense of smaller ones. On the other hand experimental investigations could not reflect these predictions quantitatively, cf., [4]. For example, the theoretically predicted distribution function is too narrow and the coarsening rate depends on the precipitate's volume fraction, originally assumed to be infinitely small. However, according to these shortcomings various improvements were developed, cf., [115].

Nevertheless, in view of the ongoing miniaturization, e.g., in microelectronic solders, questions about the impact of local mechanical fields on diffusion increasingly raised. Indeed, Cahn incorporated ad hoc a separate elastic energy term for isotropic solids, [22, 23]. However, consequences on the interfacial energy contributions or eigenstrain effects due to a misfit between the different phases did not enter the theory. These shortcomings were, in fact, later partially diminished by Larché and Cahn, [75]. They modified the elastic energy expression by a concentration dependent stiffness matrix but questions about the influence of strains to the interfacial energy remain.

Regardless of the open questions the focus has recently changed to quantitative numerical simulations initiated by the fast increasing computational capacities. The applied algorithms are mainly based on discrete Fourier transforms, [117], or finite

[^6]elements, [52], in order to solve the governing PDEs. In particular PFMs have been applied to simulations of the microstructure in solders, cf., [37, 113] as well as to solidification problems, [9].

In the present Chapter we want to turn the attention back to the theoretical aspects of diffusion. The purpose is to provide both a general and a systematic theoretical framework in order to investigate nonuniform mixtures subjected to thermo-mechanical fields. We start with the classical local balance equations for mass, momentum and internal energy density and exploit the Second Law of Thermodynamics in order to deduce the required constitutive relations for the diffusion flux, the stress tensor and the heat flux. For that reason four statements of an entropy principle are proposed, which reflect the "undisputed elements" within the already existing principles (cf., Section 2.3.4). For the sake of transparency and in order to emphasize the potential of the presented procedure we, first, consider a single phase of a mixture and illustrate the consistency of the obtained results with classical thermodynamics. Second, we turn the attention to multiphase and multicomponent solids including so-called higher gradients into the domain of the constitutive equations and demonstrate how the classical results change, due to the heterogeneities of the material. We end with the specialization of the theory to binary mixtures in order to predict the phase evolution within the brazing alloy $\mathrm{Ag}-\mathrm{Cu}$.

### 2.2 Symbols and Notation

For better readability we present various symbols, that are frequently used. Additional symbols, which are used only occasionally are explained when required. Furthermore throughout this work the sum convention $x^{i} y^{i} \doteq \sum_{i=1}^{3} x^{i} y^{i}$ holds ${ }^{3}$.

```
quantities of motion
Xi}\quad\mathrm{ LAGRANGE position (cartesian)
x i}=\mp@subsup{\chi}{}{i}(\mp@subsup{X}{}{j},t)\quad\mathrm{ current position
u}\mp@subsup{u}{}{i}=\mp@subsup{x}{}{i}-\mp@subsup{X}{}{i}\quad\mathrm{ displacements
v}=\textrm{d}\mp@subsup{x}{}{i}/\textrm{d}t=\mp@subsup{\dot{x}}{}{i}\quad\mathrm{ (barycentric) velocity
F}\mp@subsup{}{}{ij}=\partial\mp@subsup{\chi}{}{i}(\mp@subsup{X}{}{k},t)/\partial\mp@subsup{X}{}{j}\quad\mathrm{ deformation gradient
J=\operatorname{det}\mp@subsup{F}{}{ij}\geq0\quad JACOBIan
C ij}=\mp@subsup{F}{}{mi}\mp@subsup{F}{}{mj}\wedge\operatorname{det}\mp@subsup{C}{}{ij}=\mp@subsup{J}{}{2}\quad\mathrm{ right CaUChY-Green tensor
c}\mp@subsup{}{}{ij}=\mp@subsup{J}{}{-2/3}\mp@subsup{C}{}{ij}\wedge\operatorname{det}\mp@subsup{c}{}{ij}=1\quad\mathrm{ unimodular right CAUCHY-GreEN tensor
\sigma}\mp@subsup{\sigma}{}{ij}\quad\mathrm{ CAUCHY stress tensor
tij}=J(\mp@subsup{F}{}{im}\mp@subsup{)}{}{-1}\mp@subsup{\sigma}{}{mn}(\mp@subsup{F}{}{jn}\mp@subsup{)}{}{-1}\quad\mathrm{ 2nd PIOLA-KirchHOFF tensor
```

[^7]| $\nu$ | number of components of the mixture |
| :---: | :---: |
| $\alpha \in\{1, \ldots, \nu\}$ | label for the constituents |
| $N_{\alpha}$ | number of particles of the component $\alpha$ |
| $N=\sum_{\alpha=1}^{\nu} N_{\alpha}$ | total number of particles of the mixture |
| $n_{\alpha}$ | particle density of component $\alpha$ |
| $n=\sum_{\alpha=1}^{\nu} n_{\alpha}$ | particle density of the mixture |
| $y_{\alpha}=n_{\alpha} / n=N_{\alpha} / N$ | Mole fraction/particle concentration of $\alpha$ |
| $m_{H}=1.66 \cdot 10^{-27} \mathrm{~kg}$ | $1 / 12$ of the carbon 12 isotope (reference mass) |
| $M_{\alpha}$ | molecular weight (dimensionless) |
| $m_{\alpha}=m_{H} M_{\alpha}$ | molecular mass (in kg ) of component $\alpha$ |
| $m=\sum_{\alpha=1}^{\nu} N_{\alpha} m_{\alpha}$ | total mass (in kg) |
| $\rho_{\alpha}=m_{\alpha} n_{\alpha}$ | mass density of component $\alpha$ |
| $\rho=\sum_{\alpha=1}^{\nu} m_{\alpha} n_{\alpha}$ | total mass density of the mixture |
| $M=\tilde{M}\left(y_{\alpha}\right)=\sum_{\alpha=1}^{\nu} M_{\alpha} y_{\alpha}$ | mean molecular weight of a mixture particle |
| $c_{\alpha}=\rho_{\alpha} / \rho=n_{\alpha} m_{\alpha} /(n m)$ | mass concentration of component $\alpha$ |
| T, $p, V$ | (absolute) temperature, pressure, total volume |
| $\epsilon, \eta$ | internal energy, entropy per unit mass |
| $\varphi=\epsilon-T \eta$ | Helmholtz free energy per unit mass |
| $\psi=\varphi+p / \rho$ | GibBS free energy per unit mass |
| $\mu_{\alpha}$ | chemical potential (in J/particle) of component $\alpha$ |
| $j_{\alpha}^{i}$ | particle diffusion flux of component $\alpha$ |
| $J_{\alpha}^{i}$ | mass diffusion flux of component $\alpha$ |
| $q^{i}$ | heat flux |

### 2.3 Elements of Nonequilibrium Thermodynamics

### 2.3.1 Description of Motion and Deformation

In order to measure the motion and deformation of a body a reference state $\left(t=t_{0}\right)$ is required, in which the position of the material points is referred to $X^{i}$. The symbol $x^{i}$ denotes the position at time $t$ of that material point which is at $X^{i}$ in the reference configuration, and the function

$$
\begin{equation*}
x^{i}=\chi^{i}\left(t, X^{1}, X^{2}, X^{3}\right) \tag{2.1}
\end{equation*}
$$

is called the motion of the body.
The function $\chi^{i}$ can be used to determine the barycentric velocity $v_{0}^{i}$ as well as the
displacements of the material points, viz.:

$$
\begin{equation*}
v_{0}^{i}\left(t, X^{j}\right)=\frac{\partial \chi^{i}\left(t, X^{j}\right)}{\partial t} \quad \text { and } \quad U^{i}=U^{i}\left(t, X^{j}\right)=\chi^{i}\left(t, X^{j}\right)-X^{j} \tag{2.2}
\end{equation*}
$$

Furthermore the displacement gradient $H^{i j}$ and the deformation gradient $F^{i j}$ is defined as:

$$
\begin{equation*}
H^{i j}=\frac{\partial U^{i}}{\partial X^{j}} \quad \text { and } \quad F^{i j}=\frac{\partial \chi^{i}}{\partial X^{j}}=\delta^{i j}+H^{i j} \tag{2.3}
\end{equation*}
$$

Note that the quantities introduced above contain the reference position $X^{j}$ as arguments, i.e., a LAGRANGE or material description is used. However, one can alternatively use the so-called Euler or spatial description. To this end we assume the Jacobian $J=\operatorname{det} F^{i j}>0$, so that we may invert $x^{i}=\chi^{i}\left(t, X^{j}\right)$. We write:

$$
\begin{equation*}
X^{i}=\left(\chi^{-1}\right)^{i}\left(t, x^{j}\right) \tag{2.4}
\end{equation*}
$$

Analogously to Eq. (2.2) and (2.3) we note (also see Section 2.2):

$$
\begin{array}{ll}
v^{i}\left(t, x^{j}\right)=v_{0}^{i}\left(t,\left(\chi^{-1}\right)^{j}\left(t, x^{k}\right)\right), & u^{i}\left(t, x^{j}\right)=U^{i}\left(t,\left(\chi^{-1}\right)^{j}\left(t, x^{k}\right)\right) \\
h^{i j}=H^{i j}\left(t,\left(\chi^{-1}\right)^{j}\left(t, x^{k}\right)\right)=\frac{\partial u^{i}}{\partial x^{j}} \quad, \quad\left(F^{-1}\right)^{i j}=\frac{\partial\left(\chi^{-1}\right)^{i}}{\partial x^{j}}=\delta^{i j}-h^{i j} \tag{2.5}
\end{array}
$$

Beyond this, further "measures of strain" can be considered, e.g., the right CauchyGreen tensor, $C^{i j}$, the Green strain tensor, $G^{i j}$ or the linearized strains, $\varepsilon^{i j}$. It holds:

$$
\begin{equation*}
C^{i j}=F^{m i} F^{m j} \quad, \quad G^{i j}=\frac{1}{2}\left(C^{i j}-\delta^{i j}\right) \quad \text { and } \quad \varepsilon^{i j}=\frac{1}{2}\left(H^{i j}-H^{j i}\right) \tag{2.6}
\end{equation*}
$$

Other than $C^{i j}$ the unimodular right Cauchy-Green tensor, $c^{i j}$, will prove very useful. It results from the decomposition of the deformation gradient into a pure volume-changing part, $J^{1 / 3} \delta^{m i}$, and into a unimodular part, $F_{\mathrm{u}}^{m j}$, as follows:

$$
\begin{equation*}
F^{i j}=\left(J^{1 / 3} \delta^{m i}\right) F_{\mathrm{u}}^{m j} \quad \Rightarrow \quad C^{i j}=J^{2 / 3} F_{\mathrm{u}}^{m i} F_{\mathrm{u}}^{m j}=J^{2 / 3} c^{i j} \tag{2.7}
\end{equation*}
$$

Thus $C^{i j}$ is split into a pure volume-changing, $J^{2 / 3}$, and into a volume-preserving part, $c^{i j}$ ( with $\operatorname{det} c^{i j}=1$ ), which describes pure changes of the shape of the body.

### 2.3.2 Balance Equations and Mass Diffusion Flux

In order to investigate mixtures, in particular the temporal change of the internal composition, the partial mass density $\rho_{\alpha}\left(x^{j}, t\right)$ of the different constituents, the barycentric velocity $v^{i}\left(x^{j}, t\right)$ (in case of liquids) or the displacements $u^{i}\left(x^{j}, t\right)$ (in case of solids), and the internal energy density $\rho \epsilon\left(x^{j}, t\right)$ of the thermodynamical system need to be determined. These fields are used in the partial mass balance, the momentum balance and in the internal energy balance which read in regular points in case of absence of external forces and energy supplies:

$$
\begin{align*}
\frac{\partial \rho_{\alpha}}{\partial t} & =-\frac{\partial\left(\rho_{\alpha} v_{\alpha}^{i}\right)}{\partial x^{i}}+\tau_{\alpha}^{\rho}  \tag{2.8}\\
\frac{\partial \rho v^{i}}{\partial t} & =-\frac{\partial}{\partial x^{j}}\left(\rho v^{j} v^{i}-\sigma^{i j}\right) \tag{2.9}
\end{align*} \quad \text { (partial mass balance) }, ~(\text { momentum balance) },
$$

Note that the internal energy density is used instead of the temperature $T$ because $\rho \epsilon$ appears under the time derivative $\partial / \partial t$ in Eq. (2.10). The temperature, which is more important from a experimental point of view, will be defined later. In general the different components of a mixture can react chemically, which gives rise to a production term, $\tau_{\alpha}^{\rho}$, on the right hand side of Eq. (2.8). Consequently the conservation of mass does not hold for the individual component $\alpha$.

By summation of Eq. (2.8) w.r.t. all constituents $\alpha \in\{1, \ldots, \nu\}$ the conservation law of mass for the whole mixture results. We write:

$$
\begin{align*}
& \frac{\partial \rho}{\partial t}=-\frac{\partial\left(\rho v^{i}\right)}{\partial x^{i}}  \tag{2.11}\\
& \text { with } \sum_{\alpha=1}^{\nu} \rho_{\alpha} \stackrel{\text { (def) }}{=} \rho \quad, \quad \sum_{\alpha=1}^{\nu} \rho_{\alpha} v_{\alpha}^{i} \stackrel{\text { deff }}{=} \rho v^{i}, \quad \sum_{\alpha=1}^{\nu} \tau_{\alpha}^{\rho}=0 . \tag{2.12}
\end{align*}
$$

An alternative form of Eq. (2.11) is given by $J=\rho_{0} / \rho$ where $\rho_{0}$ represents the mass density of the reference state, cf., [86]. This relation follows by integrating Eq. (2.11) and by using the relation $\mathrm{d} J / \mathrm{d} t=J \cdot \partial v^{i} / \partial x^{i}$, cf., Eq. (A.2).

The mass diffusion flux characterizes the mass transport resulting from the deviation between the partial velocity of the component $\alpha, v_{\alpha}^{i}$, and the barycentric velocity and is defined as:

$$
\begin{equation*}
J_{\alpha}^{i} \stackrel{(\text { def })}{=} \rho_{\alpha}\left(v_{\alpha}^{i}-v^{i}\right) \quad \text { which implies } \quad \sum_{\alpha=1}^{\nu} J_{\alpha}^{i}=0 \tag{2.13}
\end{equation*}
$$

by means of Eq. $(2.12)_{2}$. The definition of the mass diffusion flux, viz. Eq. $(2.13)_{1}$,
can be used in order to rewrite Eq. (2.8) in the following form:

$$
\begin{equation*}
\frac{\partial \rho_{\alpha}}{\partial t}=-\frac{\partial\left(\rho_{\alpha} v^{i}+J_{\alpha}^{i}\right)}{\partial x^{i}}+\tau_{\alpha}^{\rho} \quad \text { (alternative partial mass balance). } \tag{2.14}
\end{equation*}
$$

### 2.3.3 Particle Diffusion Flux

A general mixture theory of solids should also allow for the treatment of vacancies which may be considered as massless constituents. Therefore it is more practical to examine the balance of the individual particle densities $n_{\alpha}\left(x^{i}, t\right)$ instead of Eq. (2.8). By means of $\rho_{\alpha}=m_{\alpha} n_{\alpha}$ one finds:

$$
\begin{equation*}
\frac{\partial n_{\alpha}}{\partial t}=-\frac{\partial\left(n_{\alpha} v_{\alpha}^{i}\right)}{\partial x^{i}}+\tau_{\alpha}^{n} \quad \text { with } \quad \tau_{\alpha}^{\rho}=m_{\alpha} \tau_{\alpha}^{n} \quad, \quad \sum_{\alpha=1}^{\nu} m_{\alpha} \tau_{\alpha}^{n}=0 \tag{2.15}
\end{equation*}
$$

The particle diffusion flux is defined analogously to Eq. (2.13), viz.:

$$
\begin{equation*}
j_{\alpha}^{i} \stackrel{(\text { def })}{=} n_{\alpha}\left(v_{\alpha}^{i}-v^{i}\right) \quad \text { and } \quad J_{\alpha}^{i}=m_{\alpha} j_{\alpha}^{i} \quad, \quad \sum_{\alpha=1}^{\nu} m_{\alpha} j_{\alpha}^{i}=0 \tag{2.16}
\end{equation*}
$$

Hence Eq. (2.15) can be written correspondingly to Eq. (2.14):

$$
\begin{equation*}
\frac{\partial n_{\alpha}}{\partial t}=-\frac{\partial\left(n_{\alpha} v^{i}+j_{\alpha}^{i}\right)}{\partial x^{i}}+\tau_{\alpha}^{n} \quad \text { (alternative partial particle balance). } \tag{2.17}
\end{equation*}
$$

It is worth mentioning that the sum $\sum_{\alpha} \tau_{\alpha}^{n}$ is not necessarily zero: due to chemical reactions an overall particle conservation of the mixture does not hold.

We use the quantities that occur under the time derivative in the balances, viz. $\left\{\rho_{\alpha}\right.$ or $n_{\alpha}, v^{i}$ or $\left.u^{i}, \rho \epsilon\right\}$, as primary variables. Beyond these variables further quantities, so-called constitutive quantities, such as $\sigma^{i j}, q^{i}, J_{\alpha}^{i}, j_{\alpha}^{i}$ and $\tau_{\alpha}^{\rho / n}$, occur. They must be specified by means of constitutive equations which relate them to the variables and their derivatives in a material-dependent manner. The resulting so-called field equations represent a system of Partial Differential Equations (PDE) for the variables, which, in turn, can be solved with initial/boundary conditions.

### 2.3.4 Entropy Principle

Clausius introduced the concept of entropy in the 19th century, cf., [38] for a detailed overview of the physical and historical background. Originally his objective was to
establish a rational basis to Carnot's study which had lead to an upper bound for the maximal work that can be produced by a heat engine. Clausius was aware of many serious errors in Carnot's paper, which he had to correct at first. The most prominent error concerns the fact that even the conservation law of energy, the $1^{\text {st }}$ Law of Thermodynamics, is found to be violated, i.e. Carnot assumed that the heat that is needed to produce mechanical work is conserved during the process. Surprisingly, Carnot's final result is correct and Clausius re-derived it from the simple axiom: Heat cannot flow by it itself from a colder body to a hotter body. This is the first version of the $2^{\text {nd }}$ Law of Thermodynamics. Based on his axiom Clausius, however, derived a further law that goes far beyond the characterization of efficiencies of heat engines. Nowadays this law is called the $2^{\text {nd }}$ Law of Thermodynamics (2 $2^{\text {nd }}$ law), and it reads without a contribution from radiation:

$$
\begin{equation*}
\frac{\mathrm{d} S}{\mathrm{~d} t} \geq \frac{\dot{Q}}{T} \quad \text { or } \quad \frac{\mathrm{d}}{\mathrm{~d} t} \int_{V} \rho \eta \mathrm{~d} V \geq-\frac{1}{T} \oint_{\partial V} q^{i} n^{i} \mathrm{~d} A \tag{2.18}
\end{equation*}
$$

The inequality concerns an arbitrary body with volume $V$, whose surface $\partial V$ may exchange heat with the environment with rate $\dot{Q}$ at a homogeneous temperature $T$. By means of this version of the $2^{\text {nd }}$ Law Clausius introduced a new additive quantity, which he called the entropy of the body. The equality sign holds in equilibrium and in non-equilibrium the variation of the entropy is larger than $\dot{Q} / T$.

After some generalizations, which we will explain in the following, the entropy inequality is used today for many purposes. Among them we have: (i) it restricts the admissible class of constitutive functions, (ii) it establishes stability criteria for thermodynamic processes, (iii) it may guarantee uniqueness of initial boundary value problems, (iv) it controls the approach to equilibrium of a technical system and it gives the possible equilibria.

In this paper we focus on the materials science point-of-view, and here the Eq. (2.18) is rather impracticable and the question about a local form of the inequality must be posed. However, the usual procedure (REynold's transport theorem) that transforms Eq. $(2.18)_{2}$ into a local form fails since the temperature stands outside the integral. In other words, the question about the local form of the (non-convective part of the) entropy flux $\phi^{i}$ occurring in Eq. $(2.35)_{1}$ arises.

Various attempts were undertaken in the past to find a general form for the entropy flux. The most obvious way is to simply "write" the temperature $T$ under the integral. The resulting equation is called the Clausius-Duhem inequality:

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{~d} t} \int_{V} \rho \eta \mathrm{~d} V \geq-\oint_{\partial V} \frac{q^{i} n^{i}}{T} \mathrm{~d} A \Rightarrow \frac{\partial \rho \eta}{\partial t}+\nabla_{i}\left(\rho \eta v^{i}+\frac{q^{i}}{T}\right) \geq 0 \tag{2.19}
\end{equation*}
$$

Consequently the entropy flux is $\phi^{i}=q^{i} / T$, as used in [27] or [57]. However, this form of $\phi^{i}$ already fails in case of ideal gases, cf., [38], or binary fluid mixtures, cf.,
[84]. This shortcoming was, as far as we know, in a systematic manner first remedied by the seminal works of Müller (1968) and, later, Liu (1972), [84, 80]. Here, in contradiction to the preliminary definition of the local form of $\phi^{i}$, the entropy flux is considered to be a material-dependent quantity and thus relies on a constitutive law whose explicit form results from the exploitation of the 2nd law according to the strategies of Müller and Liu. However, recent investigations show that the explicit determination of the entropy flux by means of the eponymous method of Liu, which uses the balance equations as constraints during the exploitation of the 2nd law, might become impossible or at least very subtle if complex materials are under consideration, for example those that need higher derivatives in their constitutive laws. In such a case the entropy density and entropy flux may do not form a unique pair, $c f$. ., [51]. In particular it is a priori not clear, as to whether only the balances or, additionally, higher derivatives of the balances must be considered. Therefore we present a revision of the entropy principle based on four, well accepted statements, which - in an astonishing simple, but general way - allows to exploit the 2nd law in order to examine the constitutive relations for complex materials. It avoids the difficulties of the existing methods by prescribing a particular form of the entropy production, $\zeta$, based on established thermodynamical concepts.

## a. Simple One-dimensional Example: Thermoelasticity with Strain Gradients

In this section we give a simple illustration how an a priori assumption on the entropy flux can be avoided in order to base the entropy principle on firm grounds.

To this end we consider a one-dimensional thermo-elastic body with reference mass density $\rho_{0}=1 \mathrm{~kg} / \mathrm{m}^{3}$, whose state at time $t$ is given by the fields internal energy density, $e(t, x)$, or temperature, $T(t, x)$, and the displacement $u(t, x)$ which we consider as the basic variables. In this section $x$ denotes a Lagrange coordinate.

The field equations for the variables rely on the equations of balance for momentum and internal energy

$$
\begin{equation*}
\ddot{u}-\frac{\partial \sigma}{\partial x}=0, \quad \dot{e}+\frac{\partial q}{\partial x}=\sigma \dot{u}_{x} . \tag{2.20}
\end{equation*}
$$

For abbreviation we indicate in this section the spatial derivatives of the displacement by $u_{x}, u_{x x}$ and so on.

In order to end up with a closed set of field equation we have to relate the two quantities stress, $\sigma$, and and heat flux, $q$, which are not among the basic variables, via constitutive laws to the variables and their derivatives. Within the setting of a phase field model, a popular constitutive law for the stress to describe phase transitions in
a thermo-elastic body is given by

$$
\begin{equation*}
\sigma=\sigma_{0}\left(e, u_{x}\right)-a\left(e, u_{x}\right) u_{x x x}-b\left(e, u_{x}\right) u_{x x}^{2} \tag{2.21}
\end{equation*}
$$

where $\sigma_{0}$ is a non-monotone function of $u_{x}$ of VAN DER WAALS type and $a$ and $b$ are not specified in more detail at this moment. The constitutive law for the heat flux will be given later on.

As we shall see, the structure of the system (2.20) with (2.21) is already sufficiently rich to allow an interesting consequence. We start the following discussion with the introduction of a function that relates the entropy density $s$ to the variables and their derivatives, viz.

$$
\begin{equation*}
s=h\left(e, u_{x}, u_{x x}, u_{x x x}\right) . \tag{2.22}
\end{equation*}
$$

We do not discuss here how to obtain that function. For example, it could be calculated within the framework of statistical mechanics, as it is in fact usually done, cf., [11].

We now form the time derivative of $s$ :

$$
\begin{equation*}
\dot{s}=\frac{\partial h}{\partial e} \dot{e}+\frac{\partial h}{\partial u_{x}} \dot{u}_{x}+\frac{\partial h}{\partial u_{x x}} \dot{u}_{x x}+\frac{\partial h}{\partial u_{x x x}} \dot{u}_{x x x} \tag{2.23}
\end{equation*}
$$

and proceed with the elimination of $\dot{e}$ by means of the balance equation $(2.20)_{2}$. Next the product rule is used to rearrange terms. The result is:

$$
\begin{align*}
\dot{s}= & -\frac{\partial}{\partial x}\left(\frac{\partial h}{\partial e} q-\left(\frac{\partial h}{\partial u_{x x}}-\frac{\partial}{\partial x} \frac{\partial h}{\partial u_{x x x}}\right) \dot{u}_{x}+\frac{\partial h}{\partial u_{x x x}} \dot{u}_{x x}\right)+ \\
& +\left(\frac{\partial h}{\partial u_{x}}-\frac{\partial}{\partial x} \frac{\partial h}{\partial u_{x x}}+\frac{\partial^{2}}{\partial x^{2}} \frac{\partial h}{\partial u_{x x x}}+\frac{\partial h}{\partial e} \sigma\right) \dot{u}_{x}+q \frac{\partial}{\partial x} \frac{\partial h}{\partial e} . \tag{2.24}
\end{align*}
$$

This identity forms the basis to establish the entropy inequality by two definitions, Clausius' axiom and a conclusion.

1. We define the (absolute) temperature, $T$, and subsequently define the entropy flux, $\phi$, according to:

$$
\begin{equation*}
\frac{1}{T}=\frac{\partial h}{\partial e}, \quad \text { and } \quad \phi=\frac{q}{T}-\left(\frac{\partial h}{\partial u_{x x}}-\frac{\partial}{\partial x} \frac{\partial h}{\partial u_{x x x}}\right) \dot{u}_{x}+\frac{\partial h}{\partial u_{x x x}} \dot{u}_{x x} . \tag{2.25}
\end{equation*}
$$

2. We satisfy Clausius' axiom, according to which heat cannot flow by itself from a cold to a hot place, by:

$$
\begin{equation*}
q \frac{\partial \frac{1}{T}}{\partial x} \geq 0 \tag{2.26}
\end{equation*}
$$

i.e., the heat flux must be antiparallel to the temperature gradient.
3. The identity (2.24) is linear in the velocity gradient $\dot{u}_{x}$, however, it can arbitrarily chosen to construct an arbitrary solution of the system (2.20) and (2.21). In particular, it can be chosen so that the last line of (2.24) becomes negative. This can only be avoided by the requirement that the factor of $\dot{u}_{x}$ in (2.24) must vanish, i.e.:

$$
\begin{equation*}
\frac{\sigma}{T}=-\frac{\partial h}{\partial u_{x}}+\frac{\partial}{\partial x} \frac{\partial h}{\partial u_{x x}}-\frac{\partial^{2}}{\partial x^{2}} \frac{\partial h}{\partial u_{x x x}} . \tag{2.27}
\end{equation*}
$$

Thus the identity (2.24) has turned into the entropy inequality:

$$
\begin{equation*}
\dot{s}+\frac{\partial \phi}{\partial x} \geq 0 \tag{2.28}
\end{equation*}
$$

which results here as a consequence of the field equations and some additional assumptions: (i) The definition $(2.25)_{1}$ of the temperature in non-equilibrium is the same as in equilibrium. (ii) The entropy production is of the form irreversible flux $\times$ driving force, which is in a thermoelastic body the heat flux times the derivative of $1 / T$. (iii) The constitutive functions for the stress and for the heat flux, are restricted by (2.27), and (2.26), respectively, so that the field equations imply a further equation of balance, viz. (2.28), with a non-negative production.

Note that the described strategy requires in particular, as a prerequisite, the identification of the irreversible fluxes and the corresponding driving forces in the system of field equations. These are those that are known to be zero in equilibrium.

We now proceed to exploit the consequences of the entropy principle concerning the constitutive laws for the stress and the heat flux. We start from the assumption that the entropy density (2.22) is given by the representation

$$
\begin{equation*}
s=h_{0}\left(e, u_{x}\right)-\frac{1}{2} \alpha\left(e, u_{x}\right) u_{x x}^{2}+\gamma\left(e, u_{x}\right) u_{x x x} . \tag{2.29}
\end{equation*}
$$

In order to describe two existing phases, the function $h_{0}\left(e, u_{x}\right)$ is non-concave with respect to $u_{x}$, and $\alpha>0$, so that the homogeneous body has maximal entropy.

The exploitation of $(2.25)_{2}$ and (2.27) then yields the entropy flux

$$
\begin{equation*}
\phi=\left(\alpha+\gamma^{\prime}\right) u_{x x} \dot{u}_{x}-\gamma u_{x x}, \tag{2.30}
\end{equation*}
$$

and the constitutive function for the stress

$$
\begin{equation*}
\frac{\sigma}{T}=-h_{0}^{\prime}-\left(\alpha+2 \gamma^{\prime}\right) u_{x x x}-\frac{1}{2}\left(\alpha^{\prime}+2 \gamma^{\prime \prime}\right) u_{x x}^{2} \tag{2.31}
\end{equation*}
$$

A comparison of this result with (2.21) implies that we have $\sigma_{0}=-T h_{0}^{\prime}, a=T(\alpha+$ $\left.2 \gamma^{\prime}\right)$ and $b=T \frac{1}{2}\left(\alpha^{\prime}+2 \gamma^{\prime \prime}\right)$. We conclude that the entropy principle requires that the coefficient functions $a$ and $b$ are not independent of each other but must satisfy

$$
\begin{equation*}
b=\frac{1}{2} a^{\prime} . \tag{2.32}
\end{equation*}
$$

A further important conclusion is that the alternative choices $(\alpha \neq 0, \gamma=0)$ or $(\alpha=0, \gamma \neq 0)$ lead to the same stress-strain relation. Thus there is no unique correspondence between the chosen entropy/entropy flux pair and the constitutive law for the stress.

Finally we give the constitutive law for the heat flux by the simplest possibility to satisfy the inequality (2.26), which is the classical Fourier law

$$
\begin{equation*}
q=-\kappa \frac{\partial T}{\partial x} \quad \text { with } \quad \kappa>0 \tag{2.33}
\end{equation*}
$$

Note that Dunn \& Serrin, [41], obtained a different law for the heat flux because they relied their treatment of the same subject on the Clausius-Duhem inequality.

The complete procedure to change from the energy density $e$ to the temperature $T$ as a variable is described in detail in Section 2.4.2.

## b. Statement of the Entropy Principle

The entropy principle presented here consists of four parts:
§1) We postulate the existence of the constitutive quantities called entropy density, $\rho \eta$, and entropy flux, $\phi^{i}$. The constitutive relation of $\rho \eta$ has the form:

$$
\begin{equation*}
\rho \eta=\mathcal{S} \text { (variables, (functions of) derivatives of the variables), } \tag{2.34}
\end{equation*}
$$

in which the variables are the arguments of the time derivatives of the balances. All constitutive equations are of this type but, by abandoning the Principle of Equipresence, [110], the arguments can differ.
§2) There exists a local entropy balance

$$
\begin{equation*}
\frac{\partial \rho \eta}{\partial t}+\frac{\partial\left(\rho \eta v^{k}+\phi^{k}\right)}{\partial x^{k}}=\zeta \quad \text { with } \quad \zeta \geq 0 \quad \text { (dissipation inequality). } \tag{2.35}
\end{equation*}
$$

The constraint of Eq. (2.35) $)_{2}$, viz. the non-negative entropy-production $\zeta$, represents the Second Law of Thermodynamics.
§3) We define the absolute temperature to be:

$$
\begin{equation*}
\frac{1}{T} \stackrel{(\text { def })}{=} \frac{\partial \rho \eta}{\partial \rho \epsilon} \tag{2.36}
\end{equation*}
$$

which corresponds to the concept of the integrating factor within classical thermodynamics.
§4) (a) Analogously to the concept of thermodynamical fluxes $\left(F_{z}\right)$ and driving forces $\left(D_{z}\right)$ known from the Thermodynamics of Irreversible Processes, [43], we postulate the following form for the entropy production:

$$
\begin{equation*}
\zeta=\sum_{z} F_{z} D_{z} \quad, \quad F_{z} \stackrel{\text { e.g. }}{=}\left\{j_{\alpha}^{k} \text { or } J_{\alpha}^{k}, \sigma_{\text {diss }}^{i j}, q^{k}\right\} . \tag{2.37}
\end{equation*}
$$

$\sigma_{\text {diss }}^{i j}\left(\right.$ with $\left.\sigma^{i j}=\sigma_{\text {el }}^{i j}+\sigma_{\text {diss }}^{i j}\right)$ gives the dissipative, also called irreversible, contribution to the stress. Note that there was no such part in the example of the last section. It is well known, [43], that the driving forces corresponding to the fluxes in (2.37) are

$$
\begin{equation*}
D_{z}=\left\{\nabla_{i}\left(\frac{\mu_{\alpha}-\mu_{\nu}}{T}\right), \nabla_{(i} v^{j)}, \nabla_{i}(1 / T)\right\}, \tag{2.38}
\end{equation*}
$$

The newly introduced quantities $\mu_{\alpha}$ are the chemical potentials, see Section 2.4 for their definition in the current study.
(b) For equilibrium the fluxes $F_{z}$ vanish, i.e., $\left.F_{z}\right|_{\mathrm{eq}} \doteq 0$, which, in turn, guarantees the absence of dissipation, i.e., $\left.\zeta\right|_{\text {eq }}=0$, within equilibrium. Hence it follows that $\left.\zeta\right|_{\text {eq }}$ is minimal. Relying on the assumption that the $F_{z}$ depend on the $D_{z}$, we may conclude that $\left.D_{z}\right|_{\text {eq }}=0$ holds additionally.

## c. The Role of the 2nd Law

The field equations (i.e., balances + constitutive relations) represent a system of partial differential equations for the determination of the variables. Such a solution must satisfy the 2nd law (cf., Statement 2 of the last paragraph) and consequently the constitutive relations must be constructed such, that the 2nd law follows for any solution of the field equations.

For that reason we interpret the balances $(2.9,2.10,2.14)$ as a system of algebraic equations, in which the right hand sides can be chosen arbitrarily in order to calculate the left hand sides, see also [3]. Due to the product rule the arbitrary terms on the right hand sides are:

$$
\begin{equation*}
\{\underbrace{\rho_{\alpha}, \frac{\partial v^{i}}{\partial x^{i}}, v^{i}, \frac{\partial \rho_{\alpha}}{\partial x^{i}}, \frac{\partial J_{\alpha}^{i}}{\partial x^{i}}, \tau_{\alpha}^{\rho}}_{\text {partial mass balance }}, \underbrace{\rho, \rho v^{i}, \frac{\partial v^{\langle i}}{\partial x^{j\rangle}}, \frac{\partial \sigma^{i j}}{\partial x^{j}}}_{\text {momentum balance }}, \underbrace{\rho \epsilon, \frac{\partial \rho \epsilon}{\partial x^{i}}, \frac{\partial q^{i}}{\partial x^{i}}, \sigma^{i j}}_{\text {internal energy balance }}\} . \tag{2.39}
\end{equation*}
$$

Alternatively, in order to investigate particle diffusion (cf., Section 2.3.3), one must consider the balances (2.9, 2.10,2.17). Hence the quantities $\rho_{\alpha}, J_{\alpha}^{i}$ and $\tau_{\alpha}^{\rho}$ in Eq. (2.39) must be replaced by $n_{\alpha}, j_{\alpha}^{i}$ and $\tau_{\alpha}^{n}$.

Thus one has to construct the constitutive relations such that the 2nd law follows for an arbitrary choice of the list of elements in Eq. (2.39) representing an arbitrary solution of the balances.

### 2.4 Investigations of a Single Phase

### 2.4.1 Exploitation of the 2nd Law for non-reacting, thermoelastic Solids

In what follows we consider a thermo-elastic solid mixture consisting of $\nu$ non-reacting components, i.e., $\sigma_{\text {diss }}^{i j}=0 \Rightarrow \sigma^{i j}=\sigma_{\mathrm{el}}^{i j}$ and $\tau_{\alpha}^{n}=0$. In particular we assume for the constitutive function of the entropy density $\rho \eta$ in Eq. (2.34) a quite simple form, for which we need, as we shall see, four alternative functional representations:

$$
\begin{align*}
\rho \eta & =\tilde{\mathcal{S}}\left(\rho \epsilon, n_{1}, \ldots, n_{\nu}, c^{i j}\right)=\hat{\mathcal{S}}\left(T, n_{1}, \ldots, n_{\nu}, c^{i j}\right) \\
& =\overline{\mathcal{S}}\left(T, y_{1}, \ldots, y_{\nu-1}, \rho, c^{i j}\right)=\hat{\mathcal{S}}\left(T, y_{1}, \ldots, y_{\nu-1}, C^{i j}\right) \tag{2.40}
\end{align*}
$$

$\rho \epsilon$ identifies the thermal variable whereas the symbols $n_{\alpha}, \alpha \in\{1, \ldots, \nu\}$, and $c^{i j}$ characterizes the composition and the deformation of the solid. Note that $c^{i j}$ only contains five independent elements due to the relation $\operatorname{det} c^{i j}=\left(J^{-2 / 3}\right)^{3} J^{2}=1$ whereas $C^{i j}$ in Eq. $(2.40)_{4}$ incorporates six independent elements. The set $\left\{\rho, c^{i j}\right\}$ can be used alternatively instead of $C^{i j}$, which is reasonable since $\rho$ and $C^{i j}$ are not independent due to the relation $\rho_{0} / \rho=J=\operatorname{det} F^{i j}=\operatorname{det} \sqrt{C^{i j}}$ (cf., Section 2.3.2).

The alternative representations of the Eqs. (2.40) $)_{1-4}$ give $\rho \eta$ by $\nu+6$ arguments and will be needed for different purposes. For instance we will see that the function $\tilde{\mathcal{S}}$ is extremely useful for the exploitation of the 2nd law whereas the sets of arguments in $\overline{\mathcal{S}}, \hat{\mathcal{S}}$ and $\mathcal{\mathcal { S }}$ can be used for the definition of the chemical potential $\mu_{\alpha}$ or for the calculation of the pressure $p$ and the stresses $t^{i j}$.

In what follows we write for the entropy balance in Eq. (2.35) ${ }_{1}$ by means of the product rule:

$$
\begin{equation*}
\underbrace{\frac{\partial \tilde{\mathcal{S}}}{\partial t}}_{\mathrm{A}}+v^{i} \underbrace{\frac{\partial \tilde{\mathcal{S}}}{\partial x^{i}}}_{\mathrm{B}}+\tilde{\mathcal{S}} \frac{\partial v^{i}}{\partial x^{i}}+\frac{\partial \phi^{i}}{\partial x^{i}}=\zeta . \tag{2.41}
\end{equation*}
$$

The expressions A and B can be re-written using Eq. (2.40) ${ }_{1}$ and the chain rule, viz.

$$
\begin{align*}
\frac{\partial \tilde{\mathcal{S}}}{\partial t} & =\frac{\partial \tilde{\mathcal{S}}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial t}+\sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial t}+\frac{\partial \tilde{\mathcal{S}}}{\partial c^{i j}} \frac{\partial c^{i j}}{\partial t}  \tag{2.42}\\
\frac{\partial \tilde{\mathcal{S}}}{\partial x^{i}} & =\frac{\partial \tilde{\mathcal{S}}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial x^{i}}+\sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x^{i}}+\frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}} \frac{\partial c^{k l}}{\partial x^{i}} \tag{2.43}
\end{align*}
$$

The terms $\partial \rho \epsilon / \partial t$ and $\partial n_{\alpha} / \partial t$ in Eq. (2.42) can be substituted by the right hand sides of the according balances, Eqs. (2.10) and (2.17). The resulting equation as well as the Eqs. (2.43) and (2.36) can be inserted into Eq. (2.41). It follows:

$$
\begin{align*}
\zeta= & \frac{1}{T}\left[-\frac{\partial}{\partial x^{j}}\left(\rho \epsilon v^{j}+q^{j}\right)+\sigma_{\mathrm{el}}^{i j} \frac{\partial v^{i}}{\partial x^{j}}\right]+\sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}\left[-\frac{\partial\left(n_{\alpha} v^{i}+j_{i}^{\alpha}\right)}{\partial x^{i}}\right]+ \\
& \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}} \underbrace{\left(\frac{\partial c^{k l}}{\partial t}+v^{i} \frac{\partial c^{k l}}{\partial x^{i}}\right)}_{=\mathrm{d} c^{k l} / \mathrm{d} t}+v^{i}\left(\frac{1}{T} \frac{\partial \rho \epsilon}{\partial x^{i}}+\sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x^{i}}\right)+\tilde{\mathcal{S}} \frac{\partial v^{i}}{\partial x^{i}}+\frac{\partial \phi^{i}}{\partial x^{i}} . \tag{2.44}
\end{align*}
$$

The expression under the brace, $\mathrm{d}_{t} c^{k l}=\dot{c}^{k l} \stackrel{(\text { def })}{=} \frac{\partial c^{k l}}{\partial t}+v^{i} \frac{\partial c^{k l}}{\partial x^{i}}$, stands for the total temporal derivative of $c^{k l}$ and can be replaced by the relation (cf., Appendix A.1):

$$
\begin{equation*}
\dot{c}^{k l}=-\frac{2}{3} J^{-2 / 3} \frac{\partial v^{i}}{\partial x^{i}} C^{k l}+J^{-2 / 3} \frac{\partial v^{i}}{\partial x^{j}}\left(F^{j k} F^{i l}+F^{j l} F^{i k}\right) . \tag{2.45}
\end{equation*}
$$

Rearrangement and reduction of the terms in Eq. (2.44) yield:

$$
\begin{align*}
\zeta= & \frac{\partial}{\partial x^{i}}\left(\phi^{i}-\frac{q^{i}}{T}-\sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}\right)+\underbrace{\sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}\right)+q^{i} \frac{\partial 1 / T}{\partial x^{i}}}_{Q}+ \\
& \frac{\partial v^{i}}{\partial x^{j}}\left[\frac{\sigma_{\mathrm{el}}^{i j}}{T}+J^{-2 / 3}\left(F^{j k} F^{i l}+F^{j l} F^{i k}\right) \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}}+\right. \\
& \left.\delta^{i j}\left(\tilde{\mathcal{S}}-\frac{\rho \epsilon}{T}-\sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}-\frac{2}{3} J^{-2 / 3} C^{k l} \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}}\right)\right] \geq 0 \tag{2.46}
\end{align*}
$$

in which the symbol $\delta^{i j}$ stands for the Kronecker symbol. Note that all terms that are linear in $v^{i}$ vanish, and, therefore, Eq. (2.46) is in agreement with the Principle of Objectivity formulated by Coleman and Noll, [27].

The arrangement of Eq.(2.46) presumes a priori knowledge on the entropy production $\zeta$ according to Statement 4 of Section 2.3.4. In particular we arrange the expression Q to be of the form $\sum F_{z} D_{z}$ and extract the terms linear in $\partial v^{i} / \partial x^{j}$ due to the arbitrary list elements in Eq. (2.39). Now we define the entropy flux $\phi^{i}$ as:

$$
\begin{equation*}
\phi^{i} \stackrel{(\text { def })}{=} \frac{q^{i}}{T}+\sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} . \tag{2.47}
\end{equation*}
$$

Thus the parenthesis of the first summand in Eq. (2.46) vanishes and we obtain the form:

$$
\begin{equation*}
P x+Q \geq 0 \quad, \quad \forall x \in \mathbb{R} \quad \Rightarrow \quad P=0 \quad \wedge \quad Q \geq 0 \tag{2.48}
\end{equation*}
$$

with the abbreviations $\mathrm{x}=\partial v^{i} / \partial x^{j}$ for the velocity gradient and $\mathrm{P}=[\ldots]$ for the bracket of the fourth term. The conclusion in Eq. (2.48) results since Eq. $(2.48)_{1}$ is linear in x , which can be arbitrarily chosen. Therefore we can violate the inequality except for the case $P=0 \wedge Q \geq 0$.

Finally the definition of the entropy flux in Eq. (2.47) remedied the aforementioned flaw within the works of Coleman and Noll and Green and Naghdi, [27, 57], in which the entropy flux is assumed to be $\phi^{i}=q^{i} / T$. The flux $\phi^{i}$ in Eq. (2.47) additionally incorporates diffusional contributions, which corresponds to the results of Müller, [87].

### 2.4.2 Selected Results

## a. Heat Flux and Diffusion Flux

As a consequence of Eq. (2.46) and (2.48) we conclude:

$$
\begin{equation*}
q^{i} \frac{\partial 1 / T}{\partial x^{i}}+\sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}\right) \geq 0 \tag{2.49}
\end{equation*}
$$

A further evaluation of Eqs. (2.49) requires the substitution of the experimentally unmanageable expression $\partial \tilde{\mathcal{S}} / \partial n_{\alpha}$ by a measurable physical value. For this reason we introduce the following functional representations for the Helmholtz free energy density $\rho \varphi$ according to Eq. (2.40):

$$
\begin{align*}
\rho \varphi & =\tilde{\mathcal{F}}\left(\rho \epsilon, n_{1}, \ldots, n_{\nu}, c^{i j}\right)=\hat{\mathcal{F}}\left(T, n_{1}, \ldots, n_{\nu}, c^{i j}\right) \\
& =\overline{\mathcal{F}}\left(T, y_{1}, \ldots, y_{\nu-1}, \rho, c^{i j}\right)=\hat{\mathcal{F}}\left(T, y_{1}, \ldots, y_{\nu-1}, C^{i j}\right) \tag{2.50}
\end{align*}
$$

and define the chemical potential $\mu_{\alpha}$ as:

$$
\begin{equation*}
\mu_{\alpha} \stackrel{(\text { def })}{=} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} \tag{2.51}
\end{equation*}
$$

Moreover, the Legendre transform as outlined in Appendix A. 2 yields:

$$
\begin{equation*}
\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}=-\frac{1}{T} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}}=-\frac{\mu_{\alpha}}{T} \tag{2.52}
\end{equation*}
$$

By additionally applying the mass conservation of Eq. (2.16) ${ }_{3}, j_{\nu}^{i}=-\sum_{\beta=1}^{\nu-1} \frac{m_{\beta}}{m_{\nu}} j_{\beta}^{i}$, the following form of Eq. (2.49) is obtained:

$$
\begin{align*}
& q^{i} \frac{\partial 1 / T}{\partial x^{i}}+\sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}\right)=q^{i} \frac{\partial 1 / T}{\partial x^{i}}+\sum_{\beta=1}^{\nu-1} j_{\beta}^{i} \frac{\partial\left(\frac{m_{\beta}}{m_{\nu}} \mu_{\nu}-\mu_{\beta}\right) / T}{\partial x^{i}}= \\
& =q^{i} \frac{\partial 1 / T}{\partial x^{i}}+\sum_{\beta=1}^{\nu-1} m_{\beta} j_{\beta}^{i} \frac{\partial\left(\frac{\mu_{\nu}}{m_{\nu}}-\frac{\mu_{\beta}}{m_{\beta}}\right) / T}{\partial x^{i}} \geq 0 . \tag{2.53}
\end{align*}
$$

The simplest way to achieve a non-negative expression for the right hand side of Eq. $(2.53)_{1,2}$ is to choose $q^{i}, \sigma_{\text {diss }}^{i j}, j_{\beta}^{i}$ or $J_{\beta}^{i}=m_{\beta} j_{\beta}^{i}$ such that quadratic expressions in $\frac{\partial 1 / T}{\partial x^{i}}, \frac{\partial\left(m_{\beta} \mu_{\nu} / m_{\nu}-\mu_{\beta}\right) / T}{\partial x^{i}}$ or $\frac{\partial\left(\mu_{\nu} / m_{\nu}-\mu_{\beta} / m_{\beta}\right) / T}{\partial x^{i}}$ with positive coefficients result. If thermodiffusion coupling (Ludwig-Soret and Dufour effect, cf., [31]) is neglected we put:

$$
\begin{align*}
j_{\beta}^{i} & =\sum_{\delta=1}^{\nu-1} M_{\beta \delta}^{i j} \frac{\partial\left(\frac{m_{\delta}}{m_{\nu}} \mu_{\nu}-\mu_{\delta}\right) / T}{\partial x^{j}}, \quad J_{\beta}^{i}=\sum_{\delta=1}^{\nu-1} B_{\beta \delta}^{i j} \frac{\partial\left(\mu_{\nu}^{*}-\mu_{\delta}^{*}\right) / T}{\partial x^{j}}, \\
q^{i} & =\kappa^{i j} \frac{\partial 1 / T}{\partial x^{j}}, \tag{2.54}
\end{align*}
$$

with the alternative definition $\mu_{\alpha}^{*} \stackrel{(\text { def })}{=} \mu_{\alpha} / m_{\alpha}$ and furthermore:

$$
\begin{equation*}
\mu_{\alpha}^{*}=\frac{\partial \hat{\mathcal{F}}\left(T, \rho_{1}, \ldots, \rho_{\nu}, c^{i j}\right)}{\partial \rho_{\alpha}}=\frac{1}{m_{\alpha}} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} \quad, \quad \alpha=\{1, \ldots, \nu\} . \tag{2.55}
\end{equation*}
$$

Note that the material-specific, positive definite diagonal matrices $M_{\beta \delta}^{i j}, B_{\beta \delta}^{i j}$ and $\kappa^{i j}$ in Eq. (2.54) are not necessarily constant and, in general, can depend on the same arguments used in the Eqs. $(2.40 / 2.50)$.

By means of the chain rule, viz. $\frac{\partial 1 / T}{\partial x^{j}}=-\frac{1}{T^{2}} \frac{\partial T}{\partial x^{j}}$, Eq. (2.54) ${ }_{3}$ changes to $q^{i}=$ $-\bar{\kappa}^{i j}(T) \frac{\partial T}{\partial x^{j}}$, with $\bar{\kappa}^{i j}(T)=\kappa^{i j} / T^{2}$. If $\bar{\kappa}^{i j}=$ const this equation is called Fourier's law of heat conduction in which the symbol $\bar{\kappa}^{i j}$ denotes the matrix of thermal conductivity. On the other side Eqs. $(2.54)_{1,2}$ reveals that the diffusion flux is proportional to the gradient of the difference of the chemical potentials $\mu_{\alpha}$ or $\mu_{\alpha}^{*}$. The matrices $M_{\beta \delta}^{i j}$ and $B_{\beta \delta}^{i j}$ are often called mobilities.

## b. Mechanical Constitutive Equations

In order to determine the pressure and the stress tensor we consider the condition $\mathrm{P}=0$ in Eq. (2.48). The trace of $\sigma^{i j}$ defines the pressure. One obtains from Eq. (2.46):

$$
\begin{align*}
p=-\frac{1}{3} \sigma^{k k}= & \frac{1}{3} J^{-2 / 3} T\left(F^{m k} F^{m l}+F^{m l} F^{m k}\right) \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}}+ \\
& +T\left(\rho \eta-\frac{\rho \epsilon}{T}-\sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}-\frac{2}{3} J^{-2 / 3} C^{k l} \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}}\right) . \tag{2.56}
\end{align*}
$$

Note that $C^{i j}$ and $c^{i j}$ are symmetric since $\mathbf{C}^{T}=\left(\mathbf{F}^{T} \mathbf{F}\right)^{T}=\mathbf{F}^{T} \mathbf{F} \wedge \mathbf{c}=$ const $\cdot \mathbf{C}$ holds. Therefore the terms containing $\partial \tilde{\mathcal{S}} / \partial c^{k l}$ vanish and it follows by means of Eqs. (A.10) and (A.16) $)_{2}$ in Appendix A. 2 and A.3:

$$
\begin{align*}
& p=-\rho \varphi-T \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} \stackrel{(\text { App.A.2) }}{=}-\rho \varphi+\sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} \\
&(\stackrel{\text { App.A.3) }}{=}-\rho \varphi+\sum_{\alpha=1}^{\nu} n_{\alpha} m_{\alpha} \frac{\partial \overline{\mathcal{F}}}{\partial \rho}+\underbrace{\sum_{\alpha=1}^{\nu} \sum_{\beta=1}^{\nu-1} y_{\alpha} \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}}\left(\delta^{\alpha \beta}-\frac{n_{\beta}}{n}\right)}_{=0}  \tag{2.57}\\
&=\quad-\rho \varphi+\rho \frac{\partial \overline{\mathcal{F}}}{\partial \rho}=\rho^{2} \frac{\partial \bar{\varphi}}{\partial \rho} . \tag{2.58}
\end{align*}
$$

The 2nd Piola-Kirchhoff stress tensor $t^{i j}$ can be also expressed by a partial derivative of the Helmholtz free energy. For this purpose we use the definition of $t^{i j}$ in

Section 2.2 and analyze the constraint $P=0$ with respect to Eq. (2.46):

$$
\begin{align*}
t^{i j}= & J\left(F^{i m}\right)^{-1} \sigma^{m n}\left(F^{j n}\right)^{-1} \\
= & -J^{1 / 3} T\left[\delta^{j k} \delta^{i l}+\delta^{j l} \delta^{i k}\right] \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}}- \\
& J T \underbrace{\left(F^{i n}\right)^{-1}\left(F^{j n}\right)^{-1}}_{=\left(C^{i j}\right)^{-1}}\left(\tilde{\mathcal{S}}-\frac{\rho \epsilon}{T}-\sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}-\frac{2}{3} J^{-2 / 3} C^{k l} \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}}\right) \\
= & -2 J^{1 / 3} T \frac{\partial \tilde{\mathcal{S}}}{\partial c^{i j}}+J\left(C^{i j}\right)^{-1}\left(\rho \varphi+T \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}+\frac{2}{3} J^{-2 / 3} T C^{k l} \frac{\partial \tilde{\mathcal{S}}}{\partial c^{k l}}\right) . \tag{2.59}
\end{align*}
$$

This equation can be further simplified by successively applying the LEGENDRE transforms of Appendix A.2, A. 3 and A.4. One obtains:

$$
\begin{align*}
& t^{i j} \stackrel{\text { App. A.2,A.3) }}{=} 2 J^{1 / 3} \frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}}+J\left(C^{i j}\right)^{-1}\left(\rho \varphi-\rho \frac{\overline{\mathcal{F}}}{\partial \rho}-\frac{2}{3} J^{-2 / 3} C^{k l} \frac{\partial \overline{\mathcal{F}}}{\partial c^{k l}}\right) \\
& \stackrel{\text { App. A.4) }}{=} 2 J^{1 / 3} \frac{\partial \dot{\mathcal{F}}}{\partial C^{k l}}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3}+J\left(C^{i j}\right)^{-1} \times \\
& \times\left(\rho \varphi+\frac{2}{3} J^{2 / 3} c^{k l} \frac{\partial \hat{\mathcal{F}}}{\partial C^{k l}}-\frac{2}{3} C^{k l} \frac{1}{2}\left(\delta^{m k} \delta^{n l}+\delta^{n k} \delta^{m l}\right) \frac{\partial \hat{\mathcal{F}}}{\partial C^{m n}}\right) \\
& =\quad 2 J \frac{\partial \dot{\mathcal{F}}}{\partial C^{i j}}+J\left(C^{i j}\right)^{-1}(\rho \varphi) \\
& =\quad 2 J \frac{\partial \rho}{\partial C^{i j}} \varphi+2 J \rho \frac{\partial \dot{\varphi}}{\partial C^{i j}}+J\left(C^{i j}\right)^{-1}(\rho \varphi) \\
& =\quad 2 J \rho \frac{\partial \dot{\varphi}}{\partial C^{i j}}=2 \rho_{0} \frac{\partial \dot{\varphi}}{\partial C^{i j}} . \tag{2.60}
\end{align*}
$$

For the last step in Eq. (2.60) we used the relation $\partial \rho / \partial C^{i j}=\frac{\partial}{\partial C^{i j}}\left(\frac{\rho_{0}}{(\operatorname{det} \mathbf{C})^{1 / 2}}\right)=$ $-\frac{\rho_{0}}{2}(\operatorname{det} \mathbf{C})^{-3 / 2} \frac{\partial}{\partial C^{i j}}(\operatorname{det} \mathbf{C})=-\frac{\rho_{0}}{2}(\operatorname{det} \mathbf{C})^{-1 / 2}\left(C^{i j}\right)^{-1}=-\frac{\rho}{2}\left(C^{i j}\right)^{-1}$.

## c. Gibbs-Duhem Relation and Gibbs Equation

In order to underline the power of the present entropy principle we additionally derive two important equations of thermodynamics, namely the GibBS-DuHEM relation and the GIBBS equation. The first one follows directly from Eq. $(2.57)_{2}$ :

$$
\begin{equation*}
\frac{p}{\rho}+\varphi=\frac{1}{\rho} \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}}=\frac{1}{\rho} \sum_{\alpha=1}^{\nu} n_{\alpha} \mu_{\alpha}, \quad \text { (GIBBS-DUHEM equation) } \tag{2.61}
\end{equation*}
$$

The latter one relates the Helmholtz free energy density to the entropy, stresses and chemical potential. Therefore we consider the total differential $\mathrm{d}(\rho \varphi)=\mathrm{d} \hat{\mathcal{F}}$ :

$$
\begin{equation*}
\mathrm{d}(\rho \varphi)=\frac{\partial \hat{\mathcal{F}}}{\partial T} \mathrm{~d} T+\sum_{\alpha=1}^{\nu} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \hat{\mathcal{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j} . \tag{2.62}
\end{equation*}
$$

For the coefficients $\partial \hat{\mathcal{F}} / \partial T$ and $\partial \hat{\mathcal{F}} / \partial c^{i j}$, and $\partial \hat{\mathcal{F}} / \partial n_{\alpha}$ we apply the LEGENDRE transforms of Appendices A.2, A. 3 and A.4; it follows:

$$
\begin{align*}
& \frac{\partial \hat{\mathcal{F}}}{\partial T}=\frac{\partial}{\partial T}(\hat{\mathcal{E}}-T \hat{S}) \stackrel{(\text { App.A.2) }}{=}-\rho \eta \quad, \quad \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}}=\mu_{\alpha},  \tag{2.63}\\
& \frac{\partial \hat{\mathcal{F}}}{\partial c^{i j}} \stackrel{\text { App.A.3) }}{=} \frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}}=\rho \frac{\partial \varphi}{\partial c^{i j}} \stackrel{(\text { App.A.4) }}{=} \rho J^{2 / 3} \frac{\partial \varphi}{\partial C^{i j}} \stackrel{(2.60)}{=} \frac{1}{2} J^{-1 / 3} t^{i j} . \tag{2.64}
\end{align*}
$$

In particular Eq. $(2.64)_{2}$ holds since $\rho$ and $c^{i j}$ are independent arguments within $\overline{\mathcal{F}}$. Thus we can finally write:

$$
\begin{equation*}
\mathrm{d}(\rho \varphi)=-\rho \eta \mathrm{d} T+\frac{1}{2} J^{-1 / 3} t^{i j} \mathrm{~d} c^{i j}+\sum_{\alpha=1}^{\nu} \mu_{\alpha} \mathrm{d} n_{\alpha}, \quad \text { (GIBBS equation). } \tag{2.65}
\end{equation*}
$$

Eq. (2.65) can be used for the direct identification of $\rho \eta$ and $\mu_{\alpha}$ but cannot be used for the calculation of $t^{i j}$ since the constraint $\operatorname{det} c^{i j}=1 \Leftrightarrow\left(c^{i j}\right)^{-1} \mathrm{~d} c^{i j}=0$ holds. For the identification of the pressure and the 2nd Piola-Kirchhoff tensor one needs the GibBS equation - according to Eqs. (2.58) and (2.60) - in terms of $\bar{\varphi}$ and $\dot{\varphi}$. Here a straightforward calculation yields the two alternative forms of the GibBS equation:

$$
\begin{align*}
\mathrm{d} \overline{\mathcal{F}} & =\rho \mathrm{d} \bar{\varphi}+\bar{\varphi} \mathrm{d} \rho=\frac{\partial \overline{\mathcal{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \overline{\mathcal{F}}}{\partial \rho} \mathrm{d} \rho+\frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j}+\sum_{\beta}^{\nu-1} \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta} \\
\Leftrightarrow \mathrm{d} \bar{\varphi} & =-\eta \mathrm{d} T+\frac{p}{\rho^{2}} \mathrm{~d} \rho+\frac{1}{\rho} \frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j}+\frac{1}{\rho} \sum_{\beta}^{\nu-1} \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}, \tag{2.66}
\end{align*}
$$

and

$$
\begin{align*}
\mathrm{d} \dot{\mathcal{F}} & =\rho \mathrm{d} \dot{\varphi}+\dot{\varphi} \mathrm{d} \rho=\frac{\partial \dot{\mathcal{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \dot{\mathcal{F}}}{\partial C^{i j}} \mathrm{~d} C^{i j}+\sum_{\beta}^{\nu-1} \frac{\partial \dot{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta} \\
\Leftrightarrow \mathrm{d} \dot{\varphi} & =-\eta \mathrm{d} T+\frac{1}{2 \rho_{0}} t^{i j} \mathrm{~d} C^{i j}+\frac{1}{\rho} \sum_{\beta}^{\nu-1} \frac{\partial \dot{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta} . \tag{2.67}
\end{align*}
$$

Eqs. (2.66) and (2.67) allow for a direct identification of $p$ and $t^{i j}$ as partial derivatives of $\bar{\varphi}$ or $\dot{\varphi}$, respectively. However, the prize we pay is loss of the closed form
for the chemical potential $\mu_{\alpha}$. Furthermore Eqs. $(2.65,2.66)$ can be used for the liquid matter, where for purely volumetric deformations $c^{i j}=\delta^{i j} \Leftrightarrow \mathrm{~d} c^{i j}=0$ holds. Consequently, one obtains from (2.65)

$$
\begin{equation*}
\mathrm{d}(\rho \varphi)=-\rho \eta \mathrm{d} T+\sum \mu_{\alpha} \mathrm{d} n_{\alpha} \quad \text { (GIBBS equation for liquid mixtures) } \tag{2.68}
\end{equation*}
$$

and from (2.66):

$$
\begin{equation*}
\mathrm{d} \varphi=-\eta \mathrm{d} T+\frac{p}{\rho^{2}} \mathrm{~d} \rho \quad \text { (GIBBS equation for pure liquids), } \tag{2.69}
\end{equation*}
$$

which matches the classical results of thermodynamics, [88].

## d. Splitting of the Free Energy into a Mechanical and a Chemical Part ${ }^{4}$

In order to study diffusion processes in thermo-elastic solid mixtures one needs an explicit expression for $\rho \varphi$ that allows to determine the chemical potentials $\mu_{\alpha}$ or $\mu_{\alpha}^{*}$ according to Eqs. (2.51,2.55), which are necessary during calculation of the diffusion fluxes $j_{\alpha}^{i}$ or $J_{\alpha}^{i}$ in Eq. $(2.54)_{1,2}$.
(I) Concept We start with the observation that the deformation of the solid results from two independent effects, viz.:

1) (inelastic) deformations, resulting from internal diffusion processes (e.g., misfits, which follow from the redistribution of the atoms) and from temperature changes (i.e., thermal expansion),
2) elastic deformations resulting from the change of the stress state according to the application of external loadings.

In order to distinguish between these processes we consider three different states, characterized by temperature, particle concentrations, and deformation gradient, namely $\left(T, y_{\beta}, F^{i j}\right)$ with $\beta=\{1,2, \ldots, \nu-1\}$. These states are specified by the settings indicated in Table 2.2.

Furthermore the following conditions for the Cauchy stresses, $\sigma^{i j}$, and for the deformation gradient, $F^{i j}$, are formulated for the transformations between the states, $c f$., Figure 2.1:

$$
\sigma^{i j}\left\{\begin{array}{ll}
=-\bar{p} \delta^{i j} \stackrel{!}{=} \text { const., } & \text { for } \mathrm{S}_{0} \rightarrow \mathrm{~S}_{*}  \tag{2.70}\\
\neq-\bar{p} \delta^{i j}, & \text { for } \mathrm{S}_{*} \rightarrow \mathrm{~S}
\end{array}, \quad F^{i j} \begin{cases}=F_{*}^{i j}, & \text { for } \mathrm{S}_{0} \rightarrow \mathrm{~S}_{*} \\
=F_{\mathrm{el}}^{i j}, & \text { for } \mathrm{S}_{*} \rightarrow \mathrm{~S}\end{cases}\right.
$$

[^8]Table 2.2: Specification of the three states required for the distinction between elastic and inelastic deformations in multi-component, thermo-elastic, diffusive solids.

|  | reference state $\mathbf{S}_{0}$ | intermediate <br> state $\mathbf{S}_{*}$ | current state $\mathbf{S}$ |
| ---: | :--- | :--- | :--- |
|  |  | $T_{*}=T$ | $T$ |
| temperature $T$ | $T_{0}$ | $y_{\beta}^{*}=y_{\beta}$ | $y_{\beta}$ |
| composition $y_{\beta}$ | $y_{\beta}^{0}$ | $F_{*}^{i j}$ | $F^{i j}$ |

in which $\bar{p}$ is the reference pressure.
In summary, the deformation gradient $F_{*}^{i j}$ represents the inelastic part of the deformation at constant reference stress, whereas $F_{\mathrm{el}}^{i j}$ contains the purely elastic deformation. Note that neither the concentration, i.e., the distribution of the constituents over the lattice sites, nor the temperature do change for $S_{*} \rightarrow S$, cf., Figure 2.1.

Finally we note that chemical experiments, especially phase equilibria measurements, typically refer to the state $S_{*}$ or, with other words, the process, which is observed during the experiment is given by the transformation $S_{0} \rightarrow S_{*}$.
(II) Mass densities, particle densities, concentrations, and Jacobians Now we calculate for the three different states $\mathrm{S}_{0}, \mathrm{~S}_{*}$, and S the mass densities $\rho_{0}, \rho_{*}$ and $\rho$, and the Jacobians $J_{*}, J_{\mathrm{el}}$ and $J$, in terms of concentrations and particle densities. For the mass densities we obtain (see also Section 2.2):

$$
\begin{equation*}
\rho_{0}=m_{H} \cdot n_{0} \cdot M\left(y_{\alpha}^{0}\right) \quad, \quad \rho_{*}=m_{H} \cdot n_{*} \cdot M\left(y_{\alpha}\right) \quad, \quad \rho=m_{H} \cdot n \cdot M\left(y_{\alpha}\right) \tag{2.71}
\end{equation*}
$$

and the calculations of the Jacobians yields:

$$
\begin{align*}
& J_{*} \stackrel{(\text { def) }}{=} \\
& \operatorname{det} F_{*}^{i j}=\frac{\rho_{0}}{\rho_{*}}= \frac{M\left(y_{\alpha}^{0}\right)}{M\left(y_{\alpha}\right)} \frac{n_{0}}{n_{*}} \quad, \quad J_{\mathrm{el}} \stackrel{(\text { def })}{=} \operatorname{det} F_{\mathrm{el}}^{i j}=\frac{\rho_{*}}{\rho}=\frac{n_{*}}{n},  \tag{2.72}\\
& J \stackrel{\text { (def) }}{=} \nu\left(y_{\beta}\right) \\
& \stackrel{\text { (def) }}{=} \operatorname{det} F^{i j}=\frac{\rho_{0}}{\rho}=\nu\left(y_{\beta}\right) \frac{n_{0}}{n} .
\end{align*}
$$

From Eq. (2.72) the multiplicative decomposition of the Jacobian $J$ directly follows:

$$
\begin{equation*}
J=J_{\mathrm{el}} J_{*} . \tag{2.73}
\end{equation*}
$$



Figure 2.1: Three states of a multi-component thermo-elastic solid. (a) The reference state $\mathrm{S}_{0}$ with the reference temperature $T$, the reference composition $y_{\beta}^{0}$, and the reference (undeformed) strain state described by $F_{0}^{i j}=\delta^{i j}$. (b) The intermediate state $\mathrm{S}_{*}$ with $T_{*}=T, y_{\beta}^{*}=y_{\beta}$, and $F_{*}^{i j}$. (c) The current state S with $T, y_{\beta}$, and with $F^{i j}$ for $\mathrm{S}_{0} \rightarrow \mathrm{~S}$ or with $F_{\mathrm{el}}^{i j}$ for $\mathrm{S}_{*} \rightarrow \mathrm{~S}$.
(III) Relations between the deformation gradients In addition to Eq. (2.73) there is a corresponding decomposition of the total deformation gradient. If the concept of the three introduced states $S_{0}, S_{*}$, and $S$ is accepted then we have

$$
\begin{equation*}
F^{i j}=F_{\mathrm{el}}^{i k} F_{*}^{k j} \tag{2.74}
\end{equation*}
$$

The proof of Eq. (2.74) directly follows from the three motions of the body (see Section 2.3.1):

$$
\begin{equation*}
x^{i}=\chi^{i}\left(t, X^{j}\right) \quad, \quad X_{*}^{i}=\chi_{*}^{i}\left(t, X^{j}\right) \quad, \quad x^{i}=\chi_{\mathrm{el}}^{i}\left(t, X_{*}^{j}\right) \tag{2.75}
\end{equation*}
$$

so that by virtue of the chain rule we may write

$$
\begin{equation*}
F^{i j}=\frac{\partial \chi^{i}}{\partial X^{j}}=\underbrace{\frac{\partial \chi_{\mathrm{el}}^{i}}{\partial X_{*}^{k}}}_{=F_{\mathrm{el}}^{i k}} \underbrace{\frac{\partial \chi_{*}^{k}}{\partial X^{j}}}_{=F_{*}^{k j}} . \tag{2.76}
\end{equation*}
$$

(IV) Example At this point we briefly consider an example to illustrate the deformation that might lead to the intermediate state, characterized by $F_{*}^{i j}$. At first we consider isotropic thermal expansion. Usually the thermal expansion coefficient is measured without considering any changes of the composition within the body, cf., [64], or [101]. In this case we may write

$$
\begin{equation*}
J_{*}=\underbrace{\nu\left(y_{\beta}\right)}_{=1} \frac{n_{0}}{n_{*}}=\frac{n_{0}}{n_{*}}=\frac{V_{*}}{V_{0}}=\left[1+\alpha\left(T-T_{0}\right)\right]^{3} \tag{2.77}
\end{equation*}
$$

where $\alpha$ denotes the linear thermal expansion coefficient. In other words, the change of the volume from $V_{0}$ to $V_{*}$ is measured.

If we now consider a process that incorporates thermal expansion and diffusion, then we have to use in the model

$$
\begin{equation*}
J_{*}=\nu\left(y_{\beta}\right) \frac{n_{0}}{n_{*}}=\nu\left(y_{\beta}\right) \frac{V_{*}}{V_{0}}=\operatorname{det} F_{*}^{i j}=\nu\left(y_{\beta}\right)\left[1+\alpha\left(T-T_{0}\right)\right]^{3} \tag{2.78}
\end{equation*}
$$

Next we investigate the case of anisotropic thermal expansion with diffusion. Instead of the volume of the body we now have to determine the deformation gradient experimentally, which relies, in analogy to the above equations, on the ansatz:

$$
\begin{equation*}
F_{*}^{i j}=\nu\left(y_{\beta}\right)^{1 / 3}\left[\delta^{i j}+\alpha^{i j}\left(T-T_{0}\right)\right] . \tag{2.79}
\end{equation*}
$$

(V) Second Piola-Kirchhoff \& Cauchy stress tensor According to Section 2.2 the Cauchy stress tensor can be written as:

$$
\begin{equation*}
\sigma^{i j}=\frac{1}{J} F^{i m} F^{j n} t^{m n} \quad, \quad \sigma^{i j}=\frac{1}{J_{\mathrm{el}}} F_{\mathrm{el}}^{i m} F_{\mathrm{el}}^{j n} z^{m n} \tag{2.80}
\end{equation*}
$$

where $t^{i j}$ refers to the reference state $\mathrm{S}_{0}$ and $z^{i j}$ to the intermediate state $\mathrm{S}_{*}$. A combination of Eq. (2.80) $)_{1,2}$ yields the relation:

$$
\begin{equation*}
t^{i j}=J_{*}\left(F_{*}^{-1}\right)^{i m}\left(F_{*}^{-1}\right)^{j n} z^{m n} . \tag{2.81}
\end{equation*}
$$

(VI) St. Venant-Kirchhoff law The St. Venant-Kirchhoff law relates a second Piola-Kirchifoff stress tensor to the elastic strains, cf., [108]. Since for the case illustrated in Figure 2.1 the elastic deformation starts at $S_{*}$ and ends in $S$, we have to formulate that law for $z^{i j}$. It reads:

$$
\begin{equation*}
z^{i j}=-\bar{p} J_{\mathrm{el}}\left(C_{\mathrm{el}}^{-1}\right)^{i j}+\frac{1}{2} \bar{K}^{i j k l}\left(T, y_{\beta}\right)\left(C_{\mathrm{el}}^{k l}-\delta^{k l}\right) \quad \text { with } \quad C_{\mathrm{el}}^{k l}=F_{\mathrm{el}}^{m k} F_{\mathrm{el}}^{m l} \tag{2.82}
\end{equation*}
$$

where the symbol $\bar{K}^{i j k l}=\bar{K}^{j i k l}=\bar{K}^{i j l k}=\bar{K}^{k l i j}$ stands for the stiffness matrix, which is generally assumed to be a function of $T$ and $y_{\beta}$.

However, in order to calculate the free energy density by means of the exploitation of the 2nd law, cf., Eq. (2.60), we also need to know the second Piola-Kirchhoff stress tensor $t^{i j}$. By inserting Eq. (2.82) into Eq. (2.81) we find after some rearrangements of the terms:

$$
\begin{equation*}
t^{i j}=-\bar{p} J\left(C^{-1}\right)^{i j}+\frac{1}{2} K^{i j k l}\left(T, y_{\beta}\right)\left(C^{k l}-C_{*}^{k l}\left(T, y_{\beta}\right)\right) \tag{2.83}
\end{equation*}
$$

with the relations:

$$
\begin{align*}
C_{*}^{k l} & =F_{*}^{m k} F_{*}^{m l} \quad, \quad C^{k l}=F^{m k} F^{m l} \quad \text { and } \\
K^{i j k l} & =J_{*}\left(F_{*}^{-1}\right)^{i m}\left(F_{*}^{-1}\right)^{j n}\left(F_{*}^{-1}\right)^{k p}\left(F_{*}^{-1}\right)^{l q} \bar{K}^{m n p q} \tag{2.84}
\end{align*}
$$

The Jacobian $J_{*}$ as well as the deformation gradient $F_{*}^{i j}$ depend on temperature $T$ and on the concentrations $y_{\beta}$, cf., Eqs. (2.79) $)_{2}$ and (2.78). Thus $C_{*}^{i j}=C_{*}^{i j}\left(T, y_{\beta}\right)$ and $K^{i j k l}=K^{i j k l}\left(T, y_{\beta}\right)$ depend on the same variables. The newly introduced quantity $C_{*}^{i j}$ is often called misfit strain or eigen-strain.
(VI) Chemical and mechanical part of the free energy According to the decomposition of the deformation gradient in Eq. (2.74) we now present a decomposition of the Helmholtz free energy. We assume that the Helmholtz free energy can be represented by two additive contributions:

$$
\begin{equation*}
\varphi=\varphi^{\mathrm{mech}}+\varphi^{\mathrm{chem}} \tag{2.85}
\end{equation*}
$$

namely a chemical part and a mechanical part, which, in this context, refers to the elastic deformations. The chemical part is exclusively subjected to the change of the concentration and the temperature, i.e., to diffusion and thermal expansion. Therefore $\varphi^{\text {chem }}$ represents the Helmholtz free energy of $S_{*}$, for which the stress state
$\sigma^{i j}=-\bar{p} \delta^{i j}$ and the strain state $C^{i j}=C_{*}^{i j}$ holds. Therefore we define analogously to Eqs. (2.40, 2.50):

$$
\begin{align*}
& \varphi^{\text {chem }} \stackrel{\text { def) }}{=} \dot{\varphi}\left(T, y_{1}, \ldots, y_{\nu-1}, C^{i j}=C_{*}^{i j}\right) \\
& \varphi^{\text {mech }} \stackrel{\text { (def) }}{=}  \tag{2.86}\\
& \varphi \\
&\left(T, y_{1}, \ldots, y_{\nu-1}, C^{i j}\right)-\varphi^{\text {chem }} .
\end{align*}
$$

The chemical part, $\varphi^{\text {chem }}$, is typically obtained from phase equilibrium measurements performed under the pressure $\bar{p}$ or by calculations within the settings of statistical mechanics. The mechanical part, $\varphi^{\text {mech }}$, which is exclusively related to the elastic deformations during the transformation $S_{*} \rightarrow \mathrm{~S}$, is calculated from a given stressstrain relation, e.g., from Eq. (2.60). To this end recall that Eq. (2.83) only depends on $\left\{T, y_{1}, \ldots, y_{\nu-1}, C^{i j}\right\}$ using the relation $J=\mathcal{J}^{\prime}\left(C^{k l}\right)=\sqrt{\operatorname{det} C_{k l}}$. Therefore we can insert Eq. (2.83) into Eq. (2.60) and integrate the result w.r.t. $C^{i j}$. We obtain:

$$
\begin{align*}
\dot{\varphi}\left(T, y_{\beta}, C^{i j}\right)= & \frac{K^{i j k l}\left(T, y_{\beta}\right)}{8 \rho_{0}}\left(C^{i j}-C_{*}^{i j}\right)\left(C^{k l}-C_{*}^{k l}\right)-\frac{\bar{p}}{\rho_{0}}\left[J_{*}\left(T, y_{\beta}\right)-\dot{J}\right] \\
& +\mathcal{K}\left(T, y_{\beta}\right) \tag{2.87}
\end{align*}
$$

in which $\mathcal{K}$ and $\bar{p} J_{*} / \rho_{0}$ denote integration "constants" because they depend exclusively on the variables $\left\{T, y_{1}, \ldots, y_{\nu-1}\right\}$. Furthermore we made use of the relation $\left(C^{-1}\right)^{i j}=\left(\operatorname{det} C^{k l}\right)^{-1} \partial_{C^{i j}}\left(\operatorname{det} C^{k l}\right)$.

Thus, one finds for the functional representation of $\rho \varphi$ :

$$
\begin{equation*}
\dot{\mathcal{F}}=\frac{K^{i j k l}\left(T, y_{\beta}\right)}{8 \dot{J}}\left(C^{i j}-C_{*}^{i j}\right)\left(C^{k l}-C_{*}^{k l}\right)-\bar{p}\left(\frac{J_{*}\left(T, y_{\beta}\right)}{\dot{J}}-1\right)+\dot{\rho} \mathcal{K}\left(T, y_{\beta}\right),( \tag{2.88}
\end{equation*}
$$

with $\rho=\dot{\rho}\left(C^{i j}\right)=\rho_{0} / J\left(C^{i j}\right)$. The mechanical part, $\rho \varphi^{\text {mech }}$, must vanish for the case $C^{i j}=C_{*}^{i j}$ and $J=J_{*}$. Thus we conclude:

$$
\begin{equation*}
\rho \varphi^{\text {mech }}=\dot{\mathcal{F}}^{\text {mech }}=\frac{K^{i j k l}\left(T, y_{\beta}\right)}{8 \dot{J}}\left(C^{i j}-C_{*}^{i j}\right)\left(C^{k l}-C_{*}^{k l}\right)-\bar{p}\left(\frac{J_{*}\left(T, y_{\beta}\right)}{\bar{J}}-1\right), \tag{2.89}
\end{equation*}
$$

$$
\begin{equation*}
\rho \varphi^{\text {chem }}=\dot{\mathcal{F}}^{\text {chem }}=\dot{\rho} \mathcal{K}\left(T, y_{\beta}\right) . \tag{2.90}
\end{equation*}
$$

In order to calculate the chemical potentials, $\mu_{\alpha}$, according to in Eq. (2.51) we have to rewrite $\mathcal{F}^{\text {mech } / \text { chem }}$ in terms of $\left\{T, n_{\alpha}, c^{i j}\right\}$ with $\alpha=\{1, \ldots, \nu\}$. By means of the relations:

$$
\begin{align*}
& \rho=\hat{\rho}\left(n_{\alpha}\right)=\sum_{\alpha} m_{\alpha} n_{\alpha}, \quad J=\hat{J}\left(n_{\alpha}\right)=\frac{\rho_{0}}{\sum_{\alpha} m_{\alpha} n_{\alpha}},  \tag{2.91}\\
& C^{i j}=\hat{J}^{2 / 3} c^{i j} \quad, \quad y_{\beta}=\hat{y}_{\beta}\left(n_{\alpha}\right)=\frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}} \tag{2.92}
\end{align*}
$$

we reformulate Eq. (2.88) as follows:

$$
\begin{align*}
\hat{\mathcal{F}}= & \hat{\mathcal{F}}^{\mathrm{mech}}+\hat{\mathcal{F}}^{\mathrm{chem}}= \\
= & \frac{K^{i j k l}\left(T, \hat{y}_{\beta}\right)}{8 \hat{J}}\left(\hat{J}^{2 / 3} c^{i j}-C_{*}^{i j}\left(T, \hat{y}_{\beta}\right)\right)\left(\hat{J}^{2 / 3} c^{k l}-C_{*}^{k l}\left(T, \hat{y}_{\beta}\right)\right) \\
& +\hat{\rho} \mathcal{K}\left(T, \hat{y}_{\beta}\right)-\bar{p}\left(\frac{J_{*}\left(T, \hat{y}_{\beta}\right)}{\hat{J}}-1\right), \tag{2.93}
\end{align*}
$$

which can be now differentiated w.r.t. $n_{\alpha}$. We find for the chemical potential:

$$
\begin{align*}
\mu_{\alpha} \stackrel{(\text { def })}{=} & \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}}=\frac{\left(K^{i j k l}\right)^{\prime}}{8 J} \frac{\partial \hat{y}_{\beta}}{n_{\alpha}}\left(C^{i j}-C_{*}^{i j}\right)\left(C^{k l}-C_{*}^{k l}\right) \\
& +\frac{K^{i j k l} m_{\alpha}}{8 \rho_{0}}\left(C^{i j}-C_{*}^{i j}\right)\left(C^{k l}-C_{*}^{k l}\right) \\
& +\frac{K^{i j k l}}{8 J}\left(-\frac{2}{3} \frac{m_{\alpha}}{\rho} C^{i j}-\left(C_{*}^{i j}\right)^{\prime} \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}}\right)\left(C^{k l}-C_{*}^{k l}\right) \\
& +\frac{K^{i j k l}}{8 J}\left(-\frac{2}{3} \frac{m_{\alpha}}{\rho} C^{k l}-\left(C_{*}^{k l}\right)^{\prime} \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}}\right)\left(C^{i j}-C_{*}^{i j}\right) \\
& -\bar{p}\left(\frac{J_{*}^{\prime}}{J} \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}}+J_{*} \frac{m_{\alpha}}{\rho_{0}}\right)+m_{\alpha} \mathcal{K}+\rho \mathcal{K}^{\prime} \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}}, \tag{2.94}
\end{align*}
$$

where the symbol $(\diamond)^{\prime}$ stands for the partial derivative $\partial \diamond / \partial y_{\beta}$. Furthermore holds: $\partial \hat{y}_{\beta} / \partial n_{\alpha}=\frac{1}{n}\left(\delta^{\alpha \beta}-y_{\beta}\right)$, which follows directly from Eq. (2.92) ${ }_{2}$.

### 2.4.3 Comparison with the Literature: Gibbs and Helmholtz Free Energy, Strain Energy, Complementary Strain Energy, and Theorems of Castigliano

Finally we compare some of the derived equations with the literature. To this end we specialize to pure substances and start with the corresponding alternative form of the Gibbs relation in Eq. (2.67):

$$
\begin{align*}
\mathrm{d} \varphi & =-\eta \mathrm{d} T+\frac{1}{2 \rho_{0}} t^{i j} \mathrm{~d} C^{i j}  \tag{2.95}\\
\Leftrightarrow \mathrm{~d} w^{\star} & =-\eta \mathrm{d} T-\frac{1}{2 \rho_{0}} C^{i j} \mathrm{~d} t^{i j} \quad \text { with } \quad w^{\star} \stackrel{(\text { def })}{=} \varphi-\frac{1}{2 \rho_{0}} t^{i j} C^{i j}, \tag{2.96}
\end{align*}
$$

where $\varphi=\tilde{\varphi}\left(T, C^{i j}\right)$ and $w^{\star}=\hat{w}^{\star}\left(T, t^{i j}\right)$.
Note that Eq. (2.96) - in which we temporarily call the introduced quantity $w^{\star}$ the strain potential - holds solely, if the stress strain relation, e.g., Eq. (2.83), is
invertible ${ }^{5}$. Furthermore Eq. (2.95) and (2.96) imply the following hyper-elastic relations for the stresses and strains:

$$
\begin{equation*}
2 \rho_{0} \frac{\partial \tilde{\varphi}}{\partial C^{i j}}=t^{i j} \quad, \quad 2 \rho_{0} \frac{\partial \hat{w}^{\star}}{\partial t^{i j}}=-C^{i j} \tag{2.97}
\end{equation*}
$$

Another version of the GibBS relations can be found by using the definition for the first Piola Kirchhoff stress tensor:

$$
\begin{equation*}
p^{i j} \stackrel{(\text { def })}{=} J \sigma^{i k}\left(F^{-1}\right)^{j k} \tag{2.98}
\end{equation*}
$$

and the differentiation rule $\mathrm{d} C^{i j}=\left(\mathrm{d} F^{k i}\right) F^{k j}+F^{k i} \mathrm{~d} F^{k j}$. Then one obtains from Eq. (2.95):

$$
\begin{align*}
\mathrm{d} \varphi & =-\eta \mathrm{d} T+\frac{1}{\rho_{0}} p^{i j} \mathrm{~d} F^{i j}  \tag{2.99}\\
\Leftrightarrow \mathrm{~d} w^{\star} & =-\eta \mathrm{d} T-\frac{1}{\rho_{0}} F^{i j} \mathrm{~d} p^{i j} \quad \text { with } \quad w^{\star} \tag{2.100}
\end{align*} \stackrel{\text { def) }}{=} \varphi-\frac{1}{\rho_{0}} p^{i j} F^{i j}, ~ \$
$$

where $\varphi=\bar{\varphi}\left(T, F^{i j}\right)$ and $w^{\star}=\widehat{w}{ }^{\star}\left(T, p^{i j}\right)$. Hence follows:

$$
\begin{equation*}
\rho_{0} \frac{\partial \bar{\varphi}}{\partial F^{i j}}=p^{i j} \quad, \quad \rho_{0} \frac{\partial \widehat{w}^{\star}}{\partial p^{i j}}=-F^{i j} . \tag{2.101}
\end{equation*}
$$

It is worth mentioning that $\bar{\varphi}\left(T, F^{i j}\right)$ cannot depend on all nine independent coefficients of $F^{i j}$ due to the Principle of Objectivity, [27]. In particular $\varphi$ only depend on six components following from symmetric combinations of $F^{i j}$, e.g., $\mathbf{C}=\mathbf{F}^{\mathrm{T}} \mathbf{F}$.

Landau and Lifschitz, [73], used a third form of the GibBS relations to be obtained with the linearization $\mathrm{d} C^{i j} \approx \mathrm{~d}\left(2 \varepsilon^{i j}+\delta^{i j}\right)=2 \mathrm{~d} \varepsilon^{i j}$ and $t^{i j}=\sigma^{i j}$ in Eq. (2.95). Consequently they found (in our notation):

$$
\begin{align*}
\mathrm{d} \varphi & =-\eta \mathrm{d} T+\frac{1}{\rho_{0}} \sigma^{i j} \mathrm{~d} \varepsilon^{i j}  \tag{2.102}\\
\Leftrightarrow \mathrm{~d} w^{\star} & =-\eta \mathrm{d} T-\frac{1}{\rho_{0}} \varepsilon^{i j} \mathrm{~d} \sigma^{i j} \quad \operatorname{with}^{6} \quad w^{\star} \stackrel{(\text { def })}{=} \varphi-\frac{1}{\rho_{0}} \sigma^{i j} \varepsilon^{i j}, \tag{2.103}
\end{align*}
$$

where $\varphi=\breve{\varphi}\left(T, \varepsilon^{i j}\right), w^{\star}=\hat{w}^{\star}\left(T, \sigma^{i j}\right)$ and furthermore

$$
\begin{equation*}
\rho_{0} \frac{\partial \breve{\varphi}}{\partial \varepsilon^{i j}}=\sigma^{i j} \quad, \quad \rho_{0} \frac{\partial \hat{w}^{\star}}{\partial \sigma^{i j}}=-\varepsilon^{i j} . \tag{2.104}
\end{equation*}
$$

[^9]The energetic formulations for the stresses and strains in Eqs. (2.97,2.101,2.104) are frequently found in literature, e.g., [109], and can be interpreted as the continuum mechanical version of the first and second theorem of Castigliano, [6]. The quantities $\varphi$ and $w^{\star}$ are typically called the (mass-) specific strain energy ${ }^{7}$ and the complementary specific strain energy.

In this context we point out that there is a considerable confusion about the meaning of $w^{\star}$ in the literature. So, for instance, Landau and Lifschitz, [73], Becker and Bürger, [6], and Truedsell and Toupin, [111], wrongly identify the complementary specific strain energy $w^{\star}$ with the GibBS free energy $\psi$. In turn, Landau and Lifschitz are puzzled in [73] that their definition of the GibBS free energy for solids does not agree with the "classical" ones, $\psi=\varphi+p / \rho$, used in fluid thermodynamics. This irritation is remedied within the present work, in which - for solids as well as for liquids - the same definition holds for the Gibbs free energy, viz.:

$$
\begin{equation*}
\psi=\varphi+\frac{p}{\rho} \quad \text { with } \quad p=-\frac{\sigma^{k k}}{3}=-\frac{1}{3 J} t^{i j} C^{i j}=-\frac{1}{3 J} p^{i j} F^{i j} \tag{2.105}
\end{equation*}
$$

Note that for the case of solids this form of the Gibbs free energy cannot be derived from the Legendre transforms performed in the Eqs. $(2.95,2.96)$, $(2.99,2.100)$ and (2.102,2.103).

### 2.5 Multiphase Mixtures

### 2.5.1 Exploitation of the 2nd Law by Considering Higher Gradients

In this section materials that consist of different phases are considered. First of all, one has to clarify of which nature the various occurring phases are and which physical quantity can be used for their characterization. Note that multi-phase materials are manifold. The phases can vary for instance in their compositions, e.g., Ag-rich $\alpha$ - or Cu -rich $\beta$-phases in eutectic Ag - Cu below the eutectic temperature, or in the lattice structures, e.g., ferrite ( $\alpha$-phase, BCT) and austenite ( $\gamma$-phase, FCC) in iron.

According to the Introduction we turn the attention to diffusion-induced phase transformations, such as spinodal decomposition, nucleation and subsequent coarsening in non-reacting, multi-component, elastically stressed solids ( $\tau_{\alpha}^{n}=0$ and $\left.\sigma^{i j}=\sigma_{\mathrm{el}}^{i j}\right)$. Consequently the occurring phases differ in its composition, i.e., in the partial particle densities $n_{1}, \ldots, n_{\nu}$. Therefore we must incorporate phase boundaries containing considerable gradients $\nabla_{i} n_{\alpha}, \nabla_{i j} n_{\alpha}, \ldots$ etc. $(\alpha=\{1, \ldots, \nu\})$, and we modify the

[^10]functional representation of $\rho \eta$ according to Eq. (2.40) as follows:
\[

$$
\begin{align*}
\rho \eta & =\tilde{\mathbb{S}}\left(\rho \epsilon, n_{\alpha}, \nabla_{i} n_{\alpha}, \nabla_{i j} n_{\alpha}, c^{i j}\right)=\hat{\mathbb{S}}\left(T, n_{\alpha}, \nabla_{i} n_{\alpha}, \nabla_{i j} n_{\alpha}, c^{i j}\right)= \\
& =\overline{\mathbb{S}}\left(T, y_{\beta}, \nabla_{i} y_{\beta}, \nabla_{i j} y_{\beta}, \nabla_{i} \rho, \nabla_{i j} \rho, \rho, c^{i j}\right)= \\
& =\mathbb{S}\left(T, y_{\beta}, \nabla_{i} y_{\beta}, \nabla_{i j} y_{\beta}, \nabla_{i} \rho, \nabla_{i j} \rho, C^{i j}\right) . \tag{2.106}
\end{align*}
$$
\]

The index $\alpha=\{1, \ldots, \nu\}$ and $\beta=\{1, \ldots, \nu-1\}$ were used as abbreviations. The expressions A and B of the dissipation inequality, Eq. (2.41), are now re-written analogously to Eqs. (2.42,2.43):

$$
\begin{gather*}
\frac{\partial \tilde{\mathbb{S}}}{\partial t}=\frac{\partial \tilde{\mathbb{S}}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial t}+\frac{\partial \tilde{\mathbb{S}}}{\partial c^{i j}} \frac{\partial c^{i j}}{\partial t}+\sum_{\alpha=1}^{\nu}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial t}+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i} n_{\alpha}} \frac{\partial \nabla_{i} n_{\alpha}}{\partial t}+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i j} n_{\alpha}} \frac{\partial \nabla_{i j} n_{\alpha}}{\partial t}\right)  \tag{2.107}\\
\frac{\partial \tilde{\mathbb{S}}}{\partial x^{i}}=\frac{\partial \tilde{\mathbb{S}}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial x^{i}}+\frac{\partial \tilde{\mathbb{S}}}{\partial c^{k l}} \frac{\partial c^{k l}}{\partial x^{i}}+\sum_{\alpha=1}^{\nu}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x^{i}}+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}} \frac{\partial \nabla_{k} n_{\alpha}}{\partial x^{i}}+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}} \frac{\partial \nabla_{k l} n_{\alpha}}{\partial x^{i}}\right) \tag{2.108}
\end{gather*}
$$

The terms $\partial \rho \epsilon / \partial t$ and $\partial n_{\alpha} / \partial t$ are substituted in the same manner as in Section 2.4.1, namely by the right hand sides of Eqs. (2.10,2.17). The additional terms $\partial \nabla_{i} n_{\alpha} / \partial t$ and $\partial \nabla_{i j} n_{\alpha} / \partial t$ are replaced by the right hand side of the differentiated partial particle balance, Eq. (2.17), viz.:

$$
\begin{align*}
\frac{\partial \nabla_{k} n_{\alpha}}{\partial t}= & -\frac{\partial}{\partial x^{k}}\left[v^{i} \frac{\partial n_{\alpha}}{\partial x^{i}}+n_{\alpha} \frac{\partial v^{i}}{\partial x^{i}}+\frac{\partial j_{\alpha}^{i}}{\partial x^{i}}\right] \\
= & -\frac{\partial v^{i}}{\partial x^{k}} \frac{\partial n_{\alpha}}{\partial x^{i}}-v^{i} \frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{k}}-\frac{\partial n_{\alpha}}{\partial x^{k}} \frac{\partial v^{i}}{\partial x^{i}}-n_{\alpha} \frac{\partial^{2} v^{i}}{\partial x^{i} \partial x^{k}}-\frac{\partial^{2} j_{\alpha}^{i}}{\partial x^{i} \partial x^{k}},  \tag{2.109}\\
\frac{\partial \nabla_{k l} n_{\alpha}}{\partial t}= & -\frac{\partial^{2} v^{i}}{\partial x^{k} \partial x^{l}} \frac{\partial n_{\alpha}}{\partial x^{i}}-2 \frac{\partial v^{i}}{\partial x^{k}} \frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{l}}-v^{i} \frac{\partial^{3} n_{\alpha}}{\partial x^{i} \partial x^{k} \partial x^{l}}-\frac{\partial^{2} n_{\alpha}}{\partial x^{k} \partial x^{l}} \frac{\partial v^{i}}{\partial x^{i}} \\
& -2 \frac{\partial n_{\alpha}}{\partial x^{k}} \frac{\partial^{2} v^{i}}{\partial x^{i} \partial x^{l}}-n_{\alpha} \frac{\partial^{3} v^{i}}{\partial x^{i} \partial x^{k} \partial x^{l}}-\frac{\partial^{3} j_{\alpha}^{i}}{\partial x^{i} \partial x^{k} \partial x^{l}} . \tag{2.110}
\end{align*}
$$

Note, that Eq. (2.107) gives directly rise, which balances and which differentiated balances must be considered during the exploitation of the 2nd law. Indeed, this fact remedies the aforementioned shortcoming of Liu's procedure, cf., Section 2.3.4. Here the occurring temporal derivatives of Eq. (2.107) occur due to Statement 1 of the Entropy Principle, proposed in Section 2.3.4, and depend on the choice of the arguments in Eq. (2.106) ${ }_{1}$.

By inserting Eqs. (2.10, 2.17, 2.109, 2.110) into Eq. (2.107) one obtains for the
entropy production $\zeta$ according to Eq. (2.41):

$$
\left.\begin{array}{rl}
\zeta= & \frac{\partial}{\partial x^{i}}\left[\phi^{i}-\frac{q^{i}}{T}-\sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}}\right]+q^{i} \frac{\partial 1 / T}{\partial x^{i}}+\sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}}\right) \\
& +\frac{\partial v^{i}}{\partial x^{j}}\left[\frac{\sigma_{\mathrm{el}}^{i j}}{T}+J^{-2 / 3}\left(F^{j k} F^{i l}+F^{i k} F^{j l}\right) \frac{\partial \tilde{\mathbb{S}}}{\partial c^{k l}}\right. \\
& \left.-\delta^{i j}\left(\frac{\rho \epsilon}{T}-\tilde{\mathbb{S}}+\sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}}+\frac{2}{3} J^{-2 / 3} C^{k l} \frac{\tilde{\mathbb{S}}}{\partial c^{k l}}\right)\right] \\
- & \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}}(\underbrace{\frac{\partial v^{i}}{\partial x^{k}} \frac{\partial n_{\alpha}}{\partial x^{i}}}_{=\mathrm{a}}+\frac{\partial n_{\alpha}}{\partial x^{k}} \frac{\partial v^{i}}{\partial x^{i}}+\underbrace{n_{\alpha} \frac{\partial^{2} v^{i}}{\partial x^{i} \partial x^{k}}}_{=\mathrm{b}}+\underbrace{\underbrace{}_{=\mathrm{s}}}_{=\mathrm{c}}+\underbrace{\partial x^{i} \partial x^{k}}_{=\mathrm{d}}
\end{array}\right) .
$$

The first four summands correspond to the result in Eq. (2.46). In what follows one has to include the HG-terms $\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}}(\mathrm{a}+\ldots+\mathrm{d})$ and $\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}(\mathrm{e}+\ldots+\mathrm{j})$ "suitably" into the first three rows of Eq. (2.111), which will later be used in order to define the entropy flux $\phi^{i}$, the diffusion flux $j_{\alpha}^{i}$, and the mechanical constitutive relations. For this reason we use the following strategy according to the previous section:
a) Rearrange the diffusion flux terms (d) and (j) such that terms linear in $j_{\alpha}^{i}$ and linear in the divergence operator $\partial / \partial x^{i}$ will result.
b) Transpose the velocity terms (a-c) and (e-i) in such a way that terms linear in $\partial v^{i} / \partial x^{i}$ and $\partial v^{i} / \partial x^{j}$ or terms linear in $\partial / \partial x^{i}$, respectively, will result.

From the first item one finds:

$$
-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}}(\mathrm{d})=\frac{\partial}{\partial x^{i}}\left[j_{\alpha}^{i} \frac{\partial}{\partial x^{k}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}}\right)-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i} n_{\alpha}} \frac{\partial j_{\alpha}^{k}}{\partial x^{k}}\right]-j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left[\frac{\partial}{\partial x^{k}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}}\right)\right]
$$

$-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}(\mathrm{j})=\frac{\partial}{\partial x^{i}}\left[-j_{\alpha}^{i} \frac{\partial^{2}}{\partial x^{k} \partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}\right)+\frac{\partial j_{\alpha}^{l}}{\partial x^{l}} \frac{\partial}{\partial x^{k}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k i} n_{\alpha}}\right)\right.$

$$
\begin{equation*}
\left.-\frac{\partial}{\partial x^{k}}\left(\frac{\partial j_{\alpha}^{l}}{\partial x^{l}}\right) \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k i} n_{\alpha}}\right]+j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left[\frac{\partial^{2}}{\partial x^{k} \partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}\right)\right] . \tag{2.113}
\end{equation*}
$$

According to the second "strategy point" we re-arrange as follows:

$$
\begin{align*}
&-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}}(\mathrm{a}+\mathrm{b}+\mathrm{c})= n_{\alpha} \frac{\partial v^{i}}{\partial x^{i}} \frac{\partial}{\partial x^{k}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}}\right)-\frac{\partial v^{i}}{\partial x^{k}} \frac{\partial n_{\alpha}}{\partial x^{i}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}} \\
&-\frac{\partial}{\partial x^{i}}\left[n_{\alpha} \frac{\partial v^{k}}{\partial x^{k}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i} n_{\alpha}}\right]  \tag{2.114}\\
&-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}(\mathrm{e}+\mathrm{f})=\frac{\partial v^{i}}{\partial x^{k}}\left[\frac{\partial n_{\alpha}}{\partial x^{i}} \frac{\partial}{\partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}\right)-\frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}\right] \\
&-\frac{\partial}{\partial x^{i}}\left(\frac{\partial v^{k}}{\partial x^{l}} \frac{\partial n_{\alpha}}{\partial x^{k}} \frac{\partial \tilde{\mathbb{S}}^{2}}{\partial \nabla_{l i} n_{\alpha}}\right),  \tag{2.115}\\
&-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}(\mathrm{g}+\mathrm{h}+\mathrm{i})= \frac{\partial}{\partial x^{i}}\left[n_{\alpha} \frac{\partial v^{k}}{\partial x^{k}} \frac{\partial}{\partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i l} n_{\alpha}}\right)-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k i} n_{\alpha}} \frac{\partial}{\partial x^{k}}\left(n_{\alpha} \frac{\partial v^{l}}{\partial x^{l}}\right)\right] \\
&-n_{\alpha} \frac{\partial v^{i}}{\partial x^{i}} \frac{\partial^{2}}{\partial x^{k} \partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k l} n_{\alpha}}\right) . \tag{2.116}
\end{align*}
$$

Eq. (2.112-2.116) can be substituted into Eq. (2.111). By means of the EulerLagrange derivative:

$$
\begin{equation*}
\frac{\delta \diamond}{\delta n_{\alpha}} \stackrel{(\text { def })}{=} \frac{\partial \diamond}{\partial n_{\alpha}}-\nabla_{k} \cdot \frac{\partial \diamond}{\partial \nabla_{k} n_{\alpha}}+\nabla_{k l} \cdot \frac{\partial \diamond}{\partial \nabla_{k l} n_{\alpha}} \tag{2.117}
\end{equation*}
$$

and the partial particle balance in the form:

$$
\begin{equation*}
\dot{n}_{\alpha} \stackrel{(\text { def })}{=} \frac{\partial n_{\alpha}}{\partial t}+v^{i} \frac{\partial n_{\alpha}}{\partial x^{i}} \stackrel{(2.17)}{=}-n_{\alpha} \frac{\partial v^{i}}{\partial x^{i}}-\frac{\partial j_{\alpha}^{i}}{\partial x^{i}} . \tag{2.118}
\end{equation*}
$$

one can finally write for the entropy production $\zeta$ :

$$
\begin{align*}
\zeta= & \frac{\partial}{\partial x^{i}}\left\{\phi^{i}-\frac{q^{i}}{T}-\sum_{\alpha}^{\nu} j_{\alpha}^{i} \frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}}+\sum_{\alpha}^{\nu} \dot{n}_{\alpha}\left[\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i} n_{\alpha}}-\frac{\partial}{\partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{l i} n_{\alpha}}\right)\right]\right. \\
& \left.+\sum_{\alpha}^{\nu} \frac{\partial \dot{n}_{\alpha}}{\partial x^{l}} \frac{\partial \tilde{\mathbb{S}}^{2}}{\partial \nabla_{l i} n_{\alpha}}-\sum_{\alpha}^{\nu} \frac{\partial v^{l}}{\partial x^{k}} \frac{\partial n_{\alpha}}{\partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k i} n_{\alpha}}\right\} \\
& +q^{i} \frac{\partial 1 / T}{\partial x^{i}}+\sum_{\alpha}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left(\frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}}\right) \\
& +\frac{\partial v^{i}}{\partial x^{j}}\left\{\frac{\sigma_{\mathrm{el}}^{i j}}{T}+J^{-2 / 3}\left(F^{j k} F^{i l}+F^{i k} F^{j l}\right) \frac{\partial \tilde{\mathbb{S}}}{\partial c^{k l}}\right. \\
& -\sum_{\alpha}^{\nu} \frac{\partial n_{\alpha}}{\partial x^{i}}\left[\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{j} n_{\alpha}}-\frac{\partial}{\partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{j l} n_{\alpha}}\right)\right]-\sum_{\alpha}^{\nu} \frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{j l} n_{\alpha}} \\
& \left.-\delta^{i j}\left[\frac{\rho \epsilon}{T}-\tilde{\mathbb{S}}+\sum_{\alpha}^{\nu} n_{\alpha} \frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}}+\frac{2}{3} J^{-2 / 3} C^{k l} \frac{\partial \tilde{\mathbb{S}}}{\partial c^{k l}}\right]\right\} \geq 0 . \tag{2.119}
\end{align*}
$$

Indeed, the calculations leading to Eqs. (2.112-2.116) are lengthy but easily reproducible. In particular the divergence term of Eq. (2.116) was arranged in this form because of the last two summands of the divergence term in Eq. (2.113) and keeping the partial particle balance of Eq. (2.118) in mind. In the same manner one can combine the last term of Eq. (2.114) and the second part of the divergence term in Eq. (2.112).

### 2.5.2 Entropy, Heat and Diffusion Flux and Mechanical Constitutive Equations

Eq. (2.119) can now be exploited in the same manner as in Section 2.4.1. First, we define the entropy flux such that the divergence term of the first two rows vanishes:
$\checkmark$ Entropy flux:

$$
\begin{align*}
\phi^{i}= & \frac{q^{i}}{T}+\sum_{\alpha}^{\nu} j_{\alpha}^{i} \frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}}-\sum_{\alpha}^{\nu} \dot{n}_{\alpha}\left[\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i} n_{\alpha}}-\frac{\partial}{\partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{l i} n_{\alpha}}\right)\right]- \\
& \sum_{\alpha}^{\nu} \frac{\partial \dot{n}_{\alpha}}{\partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{l i} n_{\alpha}}+\sum_{\alpha}^{\nu} \frac{\partial v^{l}}{\partial x^{k}} \frac{\partial n_{\alpha}}{\partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k i} n_{\alpha}} . \tag{2.120}
\end{align*}
$$

Consequently the remaining equation takes the form $\mathbf{P} \cdot \mathrm{x}+\mathrm{Q} \geq 0, \forall\left(\mathrm{x}=\nabla^{j} v^{i}\right)$; and it follows $\mathrm{P}=0$ and $\mathrm{Q} \geq 0$. In particular it holds that:

$$
\begin{align*}
& q^{i} \frac{\partial 1 / T}{\partial x^{i}}+ \sum_{\alpha}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}}\left(\frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}}\right) \geq 0  \tag{2.121}\\
&- \frac{\sigma_{\mathrm{el}}^{i j}}{T}= \\
& J^{-2 / 3}\left(F^{j k} F^{i l}+F^{i k} F^{j l}\right) \frac{\partial \tilde{\mathbb{S}}}{\partial c^{k l}}-\sum_{\alpha}^{\nu} \frac{\partial n_{\alpha}}{\partial x^{i}}\left[\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{j} n_{\alpha}}-\frac{\partial}{\partial x^{l}}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{j l} n_{\alpha}}\right)\right]-  \tag{2.122}\\
& \sum_{\alpha}^{\nu} \frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{j l} n_{\alpha}}-\delta^{i j}\left[\frac{\rho \epsilon}{T}-\tilde{\mathbb{S}}+\sum_{\alpha}^{\nu} n_{\alpha} \frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}}+\frac{2}{3} J^{-2 / 3} C^{k l} \frac{\partial \tilde{\mathbb{S}}}{\partial c^{k l}}\right]
\end{align*}
$$

Eq. (2.121) and (2.122) represent important results which allow to derive the constitutive equations for the heat flux, the diffusion flux and for the stresses in multicomponent, multi-phase solid mixtures. The partial derivatives of $\tilde{\mathbb{S}}$ must be substituted using the different functional representations of the Helmholtz free energy $(\alpha=1, \ldots, \nu$ and $\beta=1, \ldots, \nu-1)$ :

$$
\begin{align*}
\rho \varphi & =\tilde{\mathbb{F}}\left(\rho \epsilon, n_{\alpha}, \nabla_{i} n_{\alpha}, \nabla_{i j} n_{\alpha}, c^{i j}\right)=\hat{\mathbb{F}}\left(T, n_{\alpha}, \nabla_{i} n_{\alpha}, \nabla_{i j} n_{\alpha}, c^{i j}\right) \\
& =\overline{\mathbb{F}}\left(T, y_{\beta}, \nabla_{i} y_{\beta}, \nabla_{i j} y_{\beta}, \nabla_{i} \rho, \nabla_{i j} \rho, \rho, c^{i j}\right) \\
& =\tilde{\mathbb{F}}\left(T, y_{\beta}, \nabla_{i} y_{\beta}, \nabla_{i j} y_{\beta}, \nabla_{i} \rho, \nabla_{i j} \rho, C^{i j}\right) \tag{2.123}
\end{align*}
$$

and applying the LEGENDRE transforms of Appendix A.5-A.7.
As an example we consider the heat and the diffusion flux in Eq. (2.121). To this end we define the chemical potential $\mu_{\alpha}$ in multi-phase mixtures according to Eq. (2.51) and (2.55) as:

$$
\begin{equation*}
\frac{\mu_{\alpha}}{T} \quad \stackrel{\text { def) }}{=} \frac{\delta \hat{\mathbb{F}} / T}{\delta n_{\alpha}} \quad \text { or } \quad \frac{\mu_{\alpha}^{*}}{T} \stackrel{\text { (def) }}{=} \frac{\delta \widehat{\hat{\mathbb{F}}} / T}{\delta \rho_{\alpha}}=\frac{1}{m_{\alpha}} \frac{\delta \hat{\mathbb{F}} / T}{\delta n_{\alpha}} \tag{2.124}
\end{equation*}
$$

with the alternative functional representation of the Helmholtz free energy $\rho \varphi=$ $\widehat{\hat{\mathbb{F}}}\left(T, \rho_{\alpha}, \nabla_{i} \rho_{\alpha}, \nabla_{i j} \rho_{\alpha}, c^{i j}\right)$ and the Euler-Lagrange derivative introduced in Eq. (2.117).

In order to guarantee a non-negative entropy production in Eq. (2.121) we choose $j_{\alpha}^{i}$ and $q^{i}$ such that quadratic expressions result, cf., Section 2.4.2. The Legendre transform in Appendix A. 5 yields $\delta \tilde{\mathbb{S}} / \delta n_{\alpha}=-\delta(\hat{\mathbb{F}} / T) / \delta n_{\alpha}$. Therefore we find (without thermo-diffusion coupling):
$\diamond$ Diffusion flux:

$$
\begin{equation*}
j_{\beta}^{i}=\sum_{\delta=1}^{\nu-1} M_{\beta \delta}^{i j} \frac{\partial \frac{1}{T}\left(\frac{m_{\delta}}{m_{\nu}} \mu_{\nu}-\mu_{\delta}\right)}{\partial x^{j}} \quad \text { and } \quad J_{\beta}^{i}=\sum_{\delta=1}^{\nu-1} B_{\beta \delta}^{i j} \frac{\partial \frac{1}{T}\left(\mu_{\nu}^{*}-\mu_{\delta}^{*}\right)}{\partial x^{j}} \tag{2.125}
\end{equation*}
$$

$\diamond$ Heat flux:

$$
\begin{equation*}
q^{i}=\kappa^{i j} \frac{\partial 1 / T}{\partial x^{j}} \quad \text { (Fourier's law) } \tag{2.126}
\end{equation*}
$$

where the symbols $M_{\beta \delta}^{i j}, B_{\beta \delta}^{i j}$ and $\kappa^{i j}$ stand for the (positive definite) coefficients of the mobility and conductivity matrix. Moreover, the sums range from 1 to $\nu-1$, and the difference of the chemical potentials occurs due to the incorporation of the constraints $j_{\nu}^{i}=-\sum_{\beta=1}^{\nu-1} \frac{m_{\beta}}{m_{\nu}} j_{\beta}^{i}$ or $J_{\nu}^{i}=-\sum_{\beta=1}^{\nu-1} J_{\beta}^{i}$, respectively.

Note that the higher gradients do not enter the classical Fourier's law in Eq. (2.126) whereas the diffusion flux incorporates higher gradients due to the re-definition of the chemical potentials in terms of the Euler-Lagrange derivative according to Eq. (2.124).

The mechanical constitutive equations, e.g., for the pressure $p$ or the 2nd PiolaKirchioff tensor $t^{i j}$ follow in an analogous manner as illustrated in Section 2.4.2, i.e., from the exploitation of Eq. (2.122) and the Legendre transforms examined in the Appendices A.5-A.7.

### 2.5.3 Isothermal Diffusion in Binary Mixtures

## a. Preliminary Calculations on the Chemical Potential

As we shall see below it may be practical to express the chemical potential $\mu_{\alpha}$ or $\mu_{\alpha}^{*}$ in terms of $\delta \overline{\mathbb{F}} / \delta y_{\beta}$ or $\delta \overline{\bar{F}} / \delta c_{\beta}$, respectively. To this end we consider the LEGENDRE transform in Appendix A. 6 and write for the case of isothermal diffusion (i.e., $T=$ const):

$$
\begin{equation*}
\mu_{\alpha} \stackrel{(2.124)_{1}}{=} \frac{\delta \hat{\mathbb{F}}}{\delta n_{\alpha}} \stackrel{(\text { App.A.6) }}{=} m_{\alpha} \frac{\delta \overline{\mathbb{F}}}{\delta \rho}+\sum_{\lambda=1}^{\nu-1} \frac{\delta \overline{\mathbb{F}}}{\delta y_{\lambda}}\left(\frac{\delta_{\alpha \lambda}}{n}-\frac{n_{\lambda}}{n^{2}}\right) \tag{2.127}
\end{equation*}
$$

Thus one obtains for the difference term in Eq. (2.125) ${ }_{1}$ :

$$
\begin{equation*}
\frac{m_{\delta}}{m_{\nu}} \mu_{\nu}-\mu_{\delta}=\frac{m_{\delta}}{m_{\nu}} \sum_{\lambda=1}^{\nu-1} \frac{\delta \overline{\mathbb{F}}}{\delta y_{\lambda}}\left(\frac{\delta_{\nu \lambda}}{n}-\frac{n_{\lambda}}{n^{2}}\right)-\sum_{\lambda=1}^{\nu-1} \frac{\delta \overline{\mathbb{F}}}{\delta y_{\lambda}}\left(\frac{\delta_{\delta \lambda}}{n}-\frac{n_{\lambda}}{n^{2}}\right) . \tag{2.128}
\end{equation*}
$$

Note that the calculation of Eq. (2.127) $)_{2}$ directly follows by applying the relations of Eqs. (A.61-A.63) to the three summands of the Euler-Lagrange derivative defined in Eq. (2.117).

For the consideration of the alternative definition of the chemical potential $\mu_{\alpha}^{*}$ in Eq. $(2.124)_{2}$ one needs the LEGENDRE transform between the following functional representations of $\rho \varphi$ :

$$
\begin{equation*}
\rho \varphi=\widehat{\widehat{\mathbb{F}}}\left(T, \rho_{\alpha}, \nabla_{i} \rho_{\alpha}, \nabla_{i j} \rho_{\alpha}, c^{i j}\right)=\overline{\overline{\mathbb{F}}}\left(T, c_{\beta}, \nabla_{i} c_{\beta}, \nabla_{i j} c_{\beta}, \nabla_{i} \rho, \nabla_{i j} \rho, \rho, c^{i j}\right), \tag{2.129}
\end{equation*}
$$

where $\alpha=1, \ldots, \nu$ and $\beta=1, \ldots, \nu-1$. By means of the relations derived in Appendix A. 8 the following relations hold:

$$
\begin{equation*}
\mu_{\alpha}^{*} \stackrel{(2.124)_{2}}{=} \frac{\delta \widehat{\widehat{\mathbb{F}}}}{\delta \rho_{\alpha}} \stackrel{(\text { App.A. } 8)}{=} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta \rho}+\sum_{\lambda=1}^{\nu-1} \frac{\delta \overline{\mathbb{F}}}{\delta c_{\lambda}}\left(\frac{\delta_{\alpha \lambda}}{\rho}-\frac{\rho_{\lambda}}{\rho^{2}}\right), \tag{2.130}
\end{equation*}
$$

and for the difference term in Eq. $(2.125)_{2}$ :

$$
\begin{align*}
\mu_{\nu}^{*}-\mu_{\delta}^{*} & =\sum_{\lambda=1}^{\nu-1} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\lambda}}\left(\frac{\delta_{\nu \lambda}}{\rho}-\frac{\rho_{\lambda}}{\rho^{2}}\right)-\sum_{\lambda=1}^{\nu-1} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\lambda}}\left(\frac{\delta_{\delta \lambda}}{\rho}-\frac{\rho_{\lambda}}{\rho^{2}}\right) \\
& =-\sum_{\lambda=1}^{\nu-1} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\lambda}} \frac{\delta_{\delta \lambda}}{\rho}=-\frac{1}{\rho} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\delta}} . \tag{2.131}
\end{align*}
$$

Note that the variational derivatives $\delta \overline{\mathbb{F}} / \delta \rho$ and $\delta \overline{\bar{F}} / \delta \rho$ vanish in the difference of the chemical potentials in Eqs. $(2.128,2.131)$.

## b. Particle Diffusion Flux

In what follows we specify to a binary mixture A-B characterized by the following relations:

$$
\begin{equation*}
n=n_{\mathrm{A}}+n_{\mathrm{B}} \quad, \quad y_{\mathrm{B}}=1-y_{\mathrm{A}} \tag{2.132}
\end{equation*}
$$

For the case of isothermal diffusion as defined before, Eq. (2.125) ${ }_{1}$ reduces to:

$$
\begin{equation*}
j_{\mathrm{A}}^{i}=\frac{M_{\mathrm{AA}}^{i j}}{T} \frac{\partial\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \mu_{\mathrm{B}}-\mu_{\mathrm{A}}\right)}{\partial x^{j}} \text { and } j_{\mathrm{B}}^{i}=-\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} j_{\mathrm{A}}^{i} . \tag{2.133}
\end{equation*}
$$

The difference of the chemical potentials reads according to Eq. (2.128):

$$
\begin{align*}
\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \mu_{\mathrm{B}}-\mu_{\mathrm{A}} & =\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \frac{\delta \hat{\mathbb{F}}}{\delta n_{\mathrm{B}}}-\frac{\delta \hat{\mathbb{F}}}{\delta n_{\mathrm{A}}} \\
\stackrel{(2.128)}{=} & \frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \frac{\delta \overline{\mathbb{F}}}{\delta y_{\mathrm{A}}}(\underbrace{\frac{\delta_{\mathrm{BA}}}{n}}_{=0}-\frac{n_{\mathrm{A}}}{n^{2}})-\frac{\delta \overline{\mathbb{F}}}{\delta y_{\mathrm{A}}}\left(\frac{\delta_{\mathrm{AA}}}{n}-\frac{n_{\mathrm{A}}}{n^{2}}\right) \\
& =-\frac{1}{n} \frac{\delta \overline{\mathbb{F}}}{\delta y_{\mathrm{A}}}\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} y_{\mathrm{A}}+y_{\mathrm{B}}\right) . \tag{2.134}
\end{align*}
$$

Thus a combination of Eq. (2.134) and (2.133) $)_{1}$ yields for the particle diffusion flux of component A:

$$
\begin{align*}
j_{\mathrm{A}}^{i} & =-\frac{M_{\mathrm{AA}}^{i j}}{T} \nabla^{j}\left[\frac{1}{n} \frac{\delta \overline{\mathbb{F}}}{\delta y_{\mathrm{A}}}\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} y_{\mathrm{A}}+y_{\mathrm{B}}\right)\right] \\
& \stackrel{(\text { App.A. } 7)}{=}-\frac{M_{\mathrm{AA}}^{i j}}{T} \nabla^{j}\left[\frac{1}{n} \frac{\delta \mathbb{F}}{\delta y_{\mathrm{A}}}\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} y_{\mathrm{A}}+y_{\mathrm{B}}\right)\right], \tag{2.135}
\end{align*}
$$

in which the diffusion flux of component $\mathbf{B}$ is determined by the relation of Eq. $(2.133)_{2}$.

## c. Mass Diffusion Flux

Analogously to Eq. (2.132) and (2.133) we write for the total mass density, the mass concentrations and the mass diffusion flux of component $\mathbf{A}$ :

$$
\begin{equation*}
\rho=\rho_{\mathrm{A}}+\rho_{\mathrm{B}} \quad, \quad c_{\mathrm{A}}=1-c_{\mathrm{B}} \tag{2.136}
\end{equation*}
$$

and with Eq. $(2.125)_{2}$

$$
\begin{equation*}
J_{\mathrm{A}}^{i}=\frac{B_{\mathrm{AA}}^{i j}}{T} \frac{\partial\left(\mu_{\mathrm{B}}^{*}-\mu_{\mathrm{A}}^{*}\right)}{\partial x^{j}} \text { with } J_{\mathrm{B}}^{i}=-J_{\mathrm{A}}^{i} . \tag{2.137}
\end{equation*}
$$

By using the relation of Eq. (2.131) the difference of the chemical potentials reduces to:

$$
\begin{align*}
& \mu_{\mathrm{B}}^{*}-\mu_{\mathrm{A}}^{*}=\frac{\delta \widehat{\hat{\mathbb{F}}}}{\delta \rho_{\mathrm{B}}}-\frac{\delta \widehat{\widehat{\mathbb{F}}}}{\delta \rho_{\mathrm{A}}} \\
& \stackrel{(2.131)}{=} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\mathrm{A}}}(\underbrace{\frac{\delta \mathrm{BA}}{\rho}}_{=0}-\frac{\rho_{\mathrm{A}}}{\rho^{2}})-\frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\mathrm{A}}}\left(\frac{\delta_{\mathrm{AA}}}{\rho}-\frac{\rho_{\mathrm{A}}}{\rho^{2}}\right)=-\frac{1}{\rho} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\mathrm{A}}} . \tag{2.138}
\end{align*}
$$

Hence we finally obtain from Eq. (2.137) and (2.138) and the Legendre transforms in Appendix A. 7 and A.8:
in which the functional representation: $\rho \varphi=\stackrel{\ominus}{\mathbb{F}}\left(T, c_{\beta}, \nabla_{i} c_{\beta}, \nabla_{i j} c_{\beta}, \nabla_{i} \rho, \nabla_{i j} \rho, C^{i j}\right)$ was used.

Eq. (2.139) implies that, in contrast to the 'multiphase-field approach' of Eiken et al. in [44], the relation $\rho\left(\mu_{\mathrm{B}}^{*}-\mu_{\mathrm{A}}^{*}\right)=\delta \stackrel{\stackrel{\diamond}{\mathbb{F}} / \delta c_{\mathrm{B}}=-\delta \stackrel{\ominus}{\mathbb{F}} / \delta c_{\mathrm{A}} \text { holds exclusively, if the mass }}{ }$ concentration $c_{\beta}$ is used, otherwise the relations in Eq. (2.135) must be considered.

## d. Expansion of the Free Energy Density

In order to investigate Eq. (2.139) in more detail the question arise, how $\stackrel{\stackrel{1}{\mathbb{F}}}{ }$ depends on the higher gradients, e.g., $\nabla_{i} c_{\mathrm{B}}, \nabla_{i j} c_{\mathrm{B}}, \nabla_{i} \rho$, and $\nabla_{i j} \rho$. To this end we follow the strategy of Cahn and Hilliard in [24] and expand the Helmholtz free energy into a TAYLOR series around the homogeneous (i.e., no gradients) state ${ }^{8}$ :

$$
\begin{align*}
& \mathbb{F}=\mathbb{F}_{0}\left(T, c_{\mathrm{B}}, C^{i j}\right)+\underbrace{\frac{\partial \mathbb{F}_{0}}{\partial \nabla_{k} c_{\mathrm{B}}}}_{\left(\stackrel{\text { deff }}{=} l^{k}\right.} \cdot \nabla_{k} c_{\mathrm{B}}+\underbrace{\frac{\partial \mathbb{F}_{0}}{\partial \nabla_{k l} c_{\mathrm{B}}}}_{\left(\stackrel{\text { def) }}{=}-a^{k l}\right.} \cdot \nabla_{k l} c_{\mathrm{B}}+ \\
& \frac{1}{2} \underbrace{\frac{\partial^{2} \mathbb{F}_{0}}{\partial \nabla_{k} c_{\mathrm{B}} \partial \nabla_{l} c_{\mathrm{B}}}}_{\stackrel{(\text { deff }}{=} 2 b^{k l}} \cdot \nabla_{k} c_{\mathrm{B}} \cdot \nabla_{l} c_{\mathrm{B}}+\ldots, \tag{2.140}
\end{align*}
$$

where the introduced so-called Higher Gradient Coefficients (HGCs) depend on the temperature $T$, the (homogeneous) composition $c_{\mathrm{B}}$, and the strain tensor $C^{i j}$, i.e., $l^{k}=l^{k}\left(T, c_{\mathrm{B}}, C^{i j}\right), a^{k l}=a^{k l}\left(T, c_{\mathrm{B}}, C^{i j}\right)$, and $b^{k l}=b^{k l}\left(T, c_{\mathrm{B}}, C^{i j}\right)$. Furthermore we neglect in Eq. (2.140) the higher gradients $\nabla_{i} \rho$ and $\nabla_{i j} \rho$, since they do not enter the diffusion flux in Eq. (2.139).

The HGCs in Eq. (2.140) characterize the (smoothly) changing composition within the phase boundaries and are directly linked to the surface tensions between the different phases, cf., [39]. Moreover, they can be exactly determined by means of microscopic theories taking interatomic potentials into account, e.g., Lennard-Jones potentials, cf., [36], or Embedded-Atom-Method potentials as explained in Chapter

[^11]3. For instance it follows in the case of cubic lattices (due to the periodic arrangement of the crystal) that $l^{k}=0$ and in case of no lattice deformations that $a^{k l}=a \cdot \delta^{k l}$ and $b^{k l}=b \cdot \delta^{k l}$.

The Helmholtz free energy of the homogeneous state (e.g., of the melt), $\mathbb{F}_{0}$, consists of a pure chemical part and a pure mechanical part: $\mathbb{F}_{0}=\mathbb{F}_{0}^{\text {chem }}+\mathbb{F}_{0}^{\text {mech }}$, cf., Section 2.4.2(d.). The chemical part can be found from phase equilibrium data, typically provided by thermodynamical databases, e.g., MTdata, [83]. The mechanical part follows from the integration of the stress-strain relation as explained for the case of the St. Venant Kirchhoff law in Section 2.4.2(d.).

## e. Extended Diffusion Equation

For the investigation of the temporal and spatial evolution of the mass concentration field $c_{\mathrm{B}}=c\left(x^{i}, t\right)$ within a non-reacting elastic solid mixture we rewrite Eq. (2.14) by means of the relation $\rho_{\alpha}=c_{\alpha} \rho$ as follows:

$$
\begin{equation*}
\rho \frac{\mathrm{d} c}{\mathrm{~d} t}+\frac{\partial J^{i}}{\partial x^{i}}=0 \quad \text { (partial mass balance) } \tag{2.141}
\end{equation*}
$$

where we put $J_{\mathrm{B}}^{i}=J^{i}$ and used the total temporal derivative $\mathrm{d}_{t} c=\partial_{t} c+v^{i}\left(\nabla_{i} c\right)$. In order to calculate the Euler-Lagrange derivative $\delta \mathbb{F} / \delta c$ in Eq. (2.139) we obtain by means of Eq. (2.140) and $l^{k}=0$ :

$$
\begin{align*}
& \frac{\partial \mathbb{F}}{\partial c}=\frac{\partial \mathbb{F}_{0}}{\partial c}-\frac{\partial a^{k l}}{\partial c} \frac{\partial^{2} c}{\partial x^{k} \partial x^{l}}+\frac{\partial b^{k l}}{\partial c} \frac{\partial c}{\partial x^{k}} \frac{\partial c}{\partial x^{l}} \\
& \frac{\partial \mathbb{F}}{\partial\left(\partial c / \partial x^{m}\right)}=2 b^{m l} \frac{\partial c}{\partial x^{l}} \quad, \quad \frac{\partial \mathbb{F}}{\partial\left(\partial^{2} c / \partial x^{m} \partial x^{n}\right)}=-a^{k l} . \tag{2.142}
\end{align*}
$$

Thus it follows by virtue of the chain rule:

$$
\begin{gather*}
\frac{\partial}{\partial x^{m}}\left(\frac{\partial \mathbb{F}}{\partial\left(\partial c / \partial x^{m}\right)}\right)=2 \frac{\partial b^{m l}}{\partial c} \frac{\partial c}{\partial x^{m}} \frac{\partial c}{\partial x^{l}}+2 \frac{\partial b^{m l}}{\partial C^{r s}} \frac{\partial C^{r s}}{\partial x^{m}} \frac{\partial c}{\partial x^{l}}+2 b^{m l} \frac{\partial^{2} c}{\partial x^{m} \partial x^{l}},  \tag{2.143}\\
\frac{\partial^{2}}{\partial x^{m} \partial x^{n}}\left(\frac{\partial \mathbb{F}}{\partial\left(\partial^{2} c / \partial x^{m} \partial x^{n}\right)}\right)=-\frac{\partial^{2} a^{m n}}{\partial c^{2}} \frac{\partial c}{\partial x^{m}} \frac{\partial c}{\partial x^{n}}-\frac{\partial a^{m n}}{\partial c} \frac{\partial^{2} c}{\partial x^{m} \partial x^{n}}- \\
2 \frac{\partial^{2} a^{m n}}{\partial c \partial C^{r s}} \frac{\partial C^{r s}}{\partial x^{m}} \frac{\partial c}{\partial x^{n}}-\frac{\partial^{2} a^{m n}}{\partial C^{o p} C^{r s}} \frac{\partial C^{o p}}{\partial x^{m}} \frac{\partial C^{r s}}{\partial x^{n}}-\frac{\partial a^{m n}}{\partial C^{r s}} \frac{\partial^{2} C^{r s}}{\partial x^{m} \partial x^{n}} \tag{2.144}
\end{gather*}
$$

The relation $(2.142)_{1}-(2.143)+(2.144)$ defines the variational derivative $\delta \mathbb{F} / \delta c$. Consequently one obtains for the diffusion flux in Eq. $(2.139)_{2}$ by using the abbreviation

$$
\begin{align*}
A^{i j}=\frac{\partial a^{i j}}{\partial c}+ & b^{i j}: \\
J^{i}= & -\frac{B_{\mathrm{AA}}^{i j}}{T} \nabla^{j}\left[\frac { 1 } { \rho } \left(\frac{\partial \mathbb{F}_{0}}{\partial c}-2 A^{k l} \frac{\partial^{2} c}{\partial x^{k} \partial x^{l}}-\frac{\partial A^{k l}}{\partial c} \frac{\partial c}{\partial x^{k}} \frac{\partial c}{\partial x^{l}}\right.\right. \\
& \left.\left.-2 \frac{\partial A^{k l}}{\partial C^{m n}} \frac{\partial c}{\partial x^{k}} \frac{\partial C^{m n}}{\partial x^{l}}-\frac{\partial^{2} a^{k l}}{\partial C^{o p} C^{m n}} \frac{\partial C^{o p}}{\partial x^{k}} \frac{\partial C^{m n}}{\partial x^{l}}-\frac{\partial a^{k l}}{\partial C^{m n}} \frac{\partial^{2} C^{m n}}{\partial x^{k} \partial x^{l}}\right)\right] . \tag{2.145}
\end{align*}
$$

Eq. (2.141) and Eq. (2.145) represent the Extended Diffusion Equation (EDE). It is a non-linear Partial Differential Equation (PDE) of fourth order for the concentration field $c\left(x^{i}, t\right)$ and can be interpreted as the generalization of the Cahn-Hilliard equation ${ }^{9}$.

Note that the Eqs. (2.141) and (2.145) are formulated in Euler coordinates and refer to large deformations, which is indicated by the right Cauchy-Green tensor $C^{i j}$. In what follows we want to restrict to small deformations, i.e., to linear elastic deformations. Consequently, we use for the functional representations the linearized strains $\varepsilon^{i j}$ instead of the right Cauchy-Green strain tensor, i.e., $\mathbb{F}_{0}=\mathbb{F}_{0}\left(T, c, \varepsilon^{i j}\right)$, $a^{k l}=a^{k l}\left(T, c, \varepsilon^{i j}\right), b^{k l}=b^{k l}\left(T, c, \varepsilon^{i j}\right)$, and $A^{k l}=A^{k l}\left(T, c, \varepsilon^{i j}\right)$. For this case and by means of Lagrange coordinates (cf., Section 2.3.1) Dreyer and Müller derived in [37] an analogous version of the above EDE for the concentration field $c\left(X^{j}, t\right)$, namely:

$$
\begin{equation*}
\rho_{0} \frac{\mathrm{~d} c}{\mathrm{~d} t}+\frac{\partial J^{i}}{\partial X^{i}}=0 \quad \text { (partial mass balance) } \tag{2.146}
\end{equation*}
$$

and

$$
\begin{align*}
J^{i}= & -\rho_{0} \mathcal{M}^{i j}(T) \nabla^{j}\left[\frac{\partial \mathbb{F}_{0}}{\partial c}-2 A^{k l} \frac{\partial^{2} c}{\partial X^{k} \partial X^{l}}-\frac{\partial A^{k l}}{\partial c} \frac{\partial c}{\partial X^{k}} \frac{\partial c}{\partial X^{l}}\right. \\
& \left.-2 \frac{\partial A^{k l}}{\partial \varepsilon^{m n}} \frac{\partial c}{\partial X^{k}} \frac{\partial \varepsilon^{m n}}{\partial X^{l}}-\frac{\partial^{2} a^{k l}}{\partial \varepsilon^{o p} \varepsilon^{m n}} \frac{\partial \varepsilon^{o p}}{\partial X^{k}} \frac{\partial \varepsilon^{m n}}{\partial X^{l}}-\frac{\partial a^{k l}}{\partial \varepsilon^{m n}} \frac{\partial^{2} \varepsilon^{m n}}{\partial X^{k} \partial X^{l}}\right] . \tag{2.147}
\end{align*}
$$

Here the reference configuration is typically chosen to be the one of the melt, characterized by the homogeneous mass density $\rho_{0}=$ const., $\forall X^{i}$. Consequently, the different mobilities, $B^{i j}$ in Eq. (2.145) and $\mathcal{M}^{i j}(T)$ in Eq. (4.53), are connected by the relation $\rho_{0}^{2} \mathcal{M}^{i j}(T)=B_{\mathrm{AA}}^{i j} / T$ with the unit $\left[\mathcal{M}^{i j}\right]=\mathrm{m}^{5} /(\mathrm{Js})$.

In order to calculate the strains, $\varepsilon^{i j}$, the static momentum balance - which determines the displacements $U^{i}\left(X^{j}, t\right)$ - must be considered:

$$
\begin{equation*}
\frac{\partial p^{i j}}{\partial X^{j}}=0 \quad \text { (static momentum balance) } \tag{2.148}
\end{equation*}
$$

[^12]In the limit case of small deformations, in which the differences between the reference and the current configuration are neglected, both stress tensors, the first and the second Piola-Kirchhoff tensor, $p^{i j}$ and $t^{i j}$, respectively, are approximated by the Cauchy stresses $\sigma^{i j}$. Thus one can write by means of Eq. $(2.104)_{1}$ with $\rho_{0}=$ const.:

$$
\begin{equation*}
p^{i j} \approx \sigma^{i j} \approx \frac{\partial \mathbb{F}}{\partial \varepsilon^{i j}} \stackrel{(2.140)}{=} \underbrace{\frac{\partial \mathbb{F}_{0}}{\partial \varepsilon^{i j}}}_{=\sigma_{\text {local }}^{i j}}-\frac{\partial a^{k l}}{\partial \varepsilon^{i j}} \frac{\partial^{2} c}{\partial X^{k} \partial X^{l}}+\frac{\partial b^{k l}}{\partial \varepsilon^{i j}} \frac{\partial c}{\partial X^{k}} \frac{\partial c}{\partial X^{l}} . \tag{2.149}
\end{equation*}
$$

Here the local stresses $\sigma_{\text {local }}^{i j}$ can be calculated, e.g., by Hooke's law, viz. $\sigma_{\text {local }}^{i j}=$ $K^{i j k l}(T, c)\left(\varepsilon^{k l}-\alpha^{k l} \Delta T\right)$, where $a^{k l}=\alpha \cdot \delta^{k l}$ stands for the linear thermal expansion coefficient.

A quantitative predictions of the microstructural evolution, based on the numerical treatment of the EDE in the Eqs. $(2.141 / 2.145)$ or $(4.51 / 4.53)$, respectively, presumes reliable material data. In particular, the question about the exact determination of the HGCs arises. To this end a microscopic theory will be developed in the next Chapter, which is based on different atomic interactions and which allows for the calculation of the HGCs, namely as functions of the mass concentration and the strains.

## Chapter 3

## Calculation of Higher Gradient and Stiffness Coefficients by using the Embedded Atom Method ${ }^{1}$

### 3.1 Introductional Remarks

In the last Chapter an extended diffusion equation for binary alloys was derived, which represents a nonlinear PDE for the concentration field $c\left(X^{i}, t\right), c f$., Eqs. (4.51/4.53). Here the (extended) diffusion flux $J^{i}$ incorporates influences of concentration gradients, surface tensions along the phase boundaries, and local thermo-mechanical strains taking so-called higher gradients of the concentration into account, cf., Section 2.5.3(d.).

For a quantitative assessment of the diffusion process realistic material data are required, i.e., in particular the HGCs and the stiffness of the binary mixture $A^{k l}$, $a^{k l}$, $b^{k l}$ and $K^{i j k l}$ must be specified. Note that, for a prescribed external load, the stiffness constants, $K^{i j k l}$, are, in the simplest case, combined with the linearized strains, $\varepsilon^{k l}$, according to Hooke's law, cf., subsequent explanations w.r.t. Eq. (4.54).

To this end we consider in the present Chapter a binary alloy A-B below its critical temperature (melting point). Usually such systems consist of two or more phases, which differ in their composition, i.e., in the concentrations of the components, $c_{\mathrm{A}}$ or $c_{\mathrm{B}}=\left(1-c_{\mathrm{A}}\right)$, respectively. For instance in pure solid mixtures below the eutectic temperature two different phases can be observed, the $\alpha$-phase (A-rich) and the $\beta$ phase (B-rich) with equilibrium concentrations, $c_{\alpha}$ and $c_{\beta}$, respectively ( $c f$., Figure 1.3 (lower left)). Moreover, the EDE in Eq. (4.51/4.53) allows for a "smooth" change of the concentration within the interface between the $\alpha$ - and $\beta$-phases, which is typical for so-called phase field theories. Consequently, it is reasonable to concentrate on

[^13]the material data of, first, the $\alpha$-phase, second, the $\beta$-phase and, third, of the phase boundary.

The purpose of this Chapter is to provide a theoretical approach for the determination of the stiffness $K^{i j k l}$ and the higher gradient coefficients $a^{k l}, b^{k l}$ and $A^{k l}$ of the different phases in binary alloys. This is particularly useful in the case of the HGCs for which there is a considerable lack of data in the literature. The approach is based on the evaluation of interatomic potentials and allows for a quantitative calculation of these material data in order to perform computer simulations based on the equations (4.51/4.53). With respect to the material data within the phase boundary a linear interpolation

$$
\begin{equation*}
\Xi(c)=\Theta(c) \Xi_{\alpha}+(1-\Theta(c)) \Xi_{\beta} \quad, \quad \Theta(c)=\frac{c_{\beta}-c}{c_{\beta}-c_{\alpha}} \quad \text { (shape function) } \tag{3.1}
\end{equation*}
$$

between the material data $\Xi_{\alpha / \beta}=\left\{K_{\alpha / \beta}^{i j k l}, A_{\alpha / \beta}^{k l}, a_{\alpha / \beta}^{k l}, b_{\alpha / \beta}^{k l}\right\}$ of the equilibrium phases can be performed. Consequently it only remains to specify $\Xi_{\alpha / \beta}$. However, this linear approach is only a first approximation, and it is more desirable to find the general dependence $\Xi=\tilde{\Xi}(c)$. Then the interpolation of Eq. (3.1) becomes superfluous.

Atomistic arguments for the calculation of stiffness coefficients as well as higher gradient coefficients of Ag -Cu have already been presented by Dreyer and Müller in [36]. However, problems arose already during the prediction of the stiffness constants of the pure substances, $K_{\mathrm{Ag}}^{i j k l}$ and $K_{\mathrm{Cu}}^{i j k l}$, respectively. Due to the use of pair potentials (Lennard-Jones potentials) the Cauchy paradox $\left(K^{1122}=K^{2323}\right)$ could a priori not be avoided and, consequently, the deviation from experimental data was considerable. Moreover, for alloys showing a higher degree of anisotropy than cubic crystal structure (e.g., Sn-Pb, BCT-structure), negative shear moduli were obtained, [36].

Consequently the predicted HGCs seemed also questionable and alternative atomistic methods should be used that avoid the aforementioned shortcomings. The EmbeddedAtom Method (EAM) is such a technique. It is a powerful, semi-empirical approach that allows to capture the state of energy of an atomic system reasonably well. It was developed in the eighties by Daw and Baskes, [28] and [29], and considerably improves the quality of data when predicting physical properties of alloys, especially for those of the FCC type.

In the following a brief introduction to the general idea of EAM and to the underlying assumptions is given. After that we concentrate on the analytic EAM-model proposed by Johnson, [67], which holds for nearest neighbor interactions. It is shown how the expression for the energy can be evaluated for binary alloys to obtain atomistic relations for the stiffness and the higher gradient coefficients. After that the brazing binary alloy $\mathrm{Ag}-\mathrm{Cu}$ is considered, which has a simple FCC-structure. In particular, we illustrate the fitting procedure and present results for the elastic constants and the HGCs. Finally we construct the part of the phase diagram pertinent to the solid
in order to emphasize the trustworthiness of the predicted values.

### 3.2 Introduction to EAM

### 3.2.1 Basic Concepts

The principle of EAM is illustrated in Figure 3.1. If effects of lattice dynamics are ignored the energy of a solid is exclusively given by static atomic interactions. Unlike during the use of pair-potentials ${ }^{2}$ the mathematical key to EAM consists of introducing a nonlinear function $F_{\alpha}=\tilde{F}_{\alpha}\left(\bar{\rho}_{\alpha}\right)$ in the energy expression for atom $\alpha$, in addition to the pairwise-interaction term:

$$
\begin{equation*}
E_{\alpha}=\frac{1}{2} \sum_{\substack{\beta \\(\beta \neq \alpha)}} \phi_{\alpha \beta}\left(r_{\alpha \beta}\right)+F_{\alpha}\left(\bar{\rho}_{\alpha}\right) \quad \text { where } \quad \bar{\rho}_{\alpha}=\sum_{\substack{\beta \\(\beta \neq \alpha)}} \rho_{\beta}\left(r_{\alpha \beta}\right) \tag{3.2}
\end{equation*}
$$

$F_{\alpha}$ is known as the embedding function and $\bar{\rho}_{\alpha}$ is the (constant) electron density at the position $r_{\alpha}^{i}$ of atom $\alpha$ due to all neighbors $\beta$. The first term in (3.2) ${ }_{1}$ refers to interactions between the nuclei and the second to atom-electron interactions. This type of separation was proposed by Daw and Baskes and can be justified by arguments from quantum mechanics, $[28,29]$. The contribution to the electron density by the neighbor $\beta, \rho_{\beta}$, is a function of the scalar distance $r_{\alpha \beta}$ between atom $\alpha$ and the nucleus of $\beta$. Summation of the contributions from all neighbors yields $\bar{\rho}_{\alpha}$, which can be interpreted as a constant background electron density of a homogeneous electron gas. Thus $\bar{\rho}_{\alpha}$ denotes the resulting electron density, which is "felt" by atom $\alpha$ due to the presence of its neighbors $\beta$.

The embedding function, $F_{\alpha}\left(\bar{\rho}_{\alpha}\right)$, can be interpreted as the energy required to incorporate an atom $\alpha$ in a homogeneous electron gas with the constant electron density $\bar{\rho}_{\alpha}$. Note that the functional form of $F_{\alpha}$ depends only on the type of the (embedded) atom $\alpha$ and the argument of $F_{\alpha}$ refers to the electron density of the medium in which atom $\alpha$ is embedded.
$\phi_{\alpha \beta}=\tilde{\phi}_{\alpha \beta}\left(r_{\alpha \beta}\right)$ characterizes the (purely repulsive) interactions between the nuclei of atom $\alpha$ and $\beta$. It depends on the scalar distance $r_{\alpha \beta}$ between $\alpha$ and $\beta$ and is, according to [67], a positive, monotonically decreasing function.

In summary we may say that in order to determine the energy $E_{\alpha}$ of a particle $\alpha$ in a binary alloy A-B it is required to know the following quantities: $F_{\mathrm{A}}, F_{\mathrm{B}}, \rho_{\mathrm{A}}, \rho_{\mathrm{B}}$,

[^14]

Figure 3.1: The general principle of EAM as proposed by Daw and Baskes, [28], [29].
$\phi_{\mathrm{AA}}, \phi_{\mathrm{BB}}$, and $\phi_{\mathrm{AB}}$. With the exception of $\phi_{\mathrm{AB}}$ all of these functions can easily be related to (macroscopic) mechanical and calorimetric data of the pure substances A and B . In order to obtain $\phi_{\mathrm{AB}}$ a model will be used that relates this quantity to the interactions $\phi_{\mathrm{AA}}$ and $\phi_{\mathrm{BB}}$ of the pure substances.

In the following sections it is assumed that every atom in the solid interacts only with its nearest neighbors (first shell). This assumption leads to a special modification of EAM introduced by Johnson in [67].

### 3.2.2 Johnson's Analytic Nearest-Neighbor Model

Consider Figure 3.2 and recall that in an FCC-lattice an arbitrary atom $\alpha$ is surrounded by exactly twelve nearest neighbors from which it is separated by the distance $r_{\alpha \beta} \equiv r=a / \sqrt{2}$ (or, in equilibrium, $R=a_{\mathrm{e}} / \sqrt{2}$ ), where $a$ denotes the lattice parameter.


Figure 3.2: The nearest neighbors for an arbitrary atom $\alpha$ in a FCC-lattice.

In order to obtain $E_{\alpha}$ in Eq. (3.2) it is necessary to specify $\phi_{\alpha \beta}, F_{\alpha}$ and $\rho_{\beta}\left(\Rightarrow \bar{\rho}_{\alpha}\right)$. More specifically we have to choose a suitable functional form. In particular for a binary alloy A-B the functions $F_{\mathrm{A}}, F_{\mathrm{B}}, \rho_{\mathrm{A}}, \rho_{\mathrm{B}}, \phi_{\mathrm{AA}}, \phi_{\mathrm{BB}}$, and $\phi_{\mathrm{AB}}$ must be specified. For that reason Johnson proposed in [67] to use the following form ${ }^{3}$ for $\rho_{\mathrm{A} / \mathrm{B}}$ and $\phi_{\mathrm{AA} / \mathrm{BB}}$ (where the indices A and B of the two atom species have been omitted for simplicity):

$$
\begin{equation*}
\rho(r)=\rho_{\mathrm{e}} \exp \left[-\beta\left(\frac{r}{R}-1\right)\right] \quad, \quad \phi(r)=\phi_{\mathrm{e}} \exp \left[-\gamma\left(\frac{r}{R}-1\right)\right] . \tag{3.3}
\end{equation*}
$$

[^15]The four parameters $\rho_{\mathrm{e}}, \phi_{\mathrm{e}}, \beta$, and $\gamma$ depend on the type of the atom and will be determined using information from both pure substances, A and B. Furthermore the nearest neighbor distance $R$ must be known or calculated from the lattice parameter $a_{\mathrm{e}}$ as indicated before.

For the interaction $\phi_{\mathrm{AB}}$ between nuclei of different atom types Johnson used the following form:

$$
\begin{equation*}
\phi_{\mathrm{AB}}(r)=\frac{1}{2}\left[\frac{\rho_{\mathrm{B}}(r)}{\rho_{\mathrm{A}}(r)} \phi_{\mathrm{AA}}(r)+\frac{\rho_{\mathrm{A}}(r)}{\rho_{\mathrm{B}}(r)} \phi_{\mathrm{BB}}(r)\right] . \tag{3.4}
\end{equation*}
$$

This relation can easily be quantified using data for the pure substances A and B.
Finally it remains to specify $F_{\mathrm{A}}$ and $F_{\mathrm{B}}$. For this purpose a universal function of state is used as suggested by Rose et al. in [103]. According to them the particle-specific energy for a broad range of materials can be approximated by:

$$
\begin{equation*}
E(a)=-E_{\mathrm{sub}}\left[1+a^{*}(a)\right] e^{-a^{*}(a)} \quad, \quad a^{*}(a)=\left(\frac{a}{a_{\mathrm{e}}}-1\right)\left(\frac{E_{\mathrm{sub}}}{9 \kappa \Omega_{0}}\right)^{-\frac{1}{2}} \tag{3.5}
\end{equation*}
$$

where $E_{\text {sub }}$ denotes the sublimation energy per atom of the material, $\kappa$ is the incompressibility (bulk modulus) and $\Omega_{0}$ is the volume occupied by an atom in the lattice at equilibrium. Hence $\Omega_{0}$ is a function of $a_{\mathrm{e}}$ and, for an FCC-lattice, can be obtained from

$$
\begin{equation*}
\Omega_{0}=\frac{a_{\mathrm{e}}^{3}}{4} \tag{3.6}
\end{equation*}
$$

since there are four atoms in the unit cell $\left(8 \times \frac{1}{8}\right.$ atoms in the corner; $6 \times \frac{1}{2}$ atoms on the faces). All quantities in Eq. (3.5) can be found in the literature or databases, e.g., [119].

By combining the relation $E(a)=E_{\alpha}$ with Eq. (3.2) and substituting $a=r \sqrt{2}$ and $a_{\mathrm{e}}=R \sqrt{2}$ by the inverse relation resulting from Eq. (3.3), namely:

$$
\begin{equation*}
\ln \frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}=-\beta\left(\frac{r}{R}-1\right) \quad, \quad \frac{\phi}{\phi_{\mathrm{e}}}=\left(\frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}\right)^{\frac{\gamma}{\beta}} \tag{3.7}
\end{equation*}
$$

the following form is obtained for $F$ :

$$
\begin{equation*}
F(\bar{\rho})=-E_{\text {sub }}\left[1-\frac{\alpha}{\beta} \ln \left(\frac{\bar{\rho}}{\overline{\rho_{\mathrm{e}}}}\right)\right]\left(\frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}\right)^{\frac{\alpha}{\beta}}-6 \phi_{\mathrm{e}}\left(\frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}\right)^{\frac{\gamma}{\beta}} \text { with } \alpha=3\left(\frac{\kappa \Omega_{0}}{E_{\text {sub }}}\right)^{\frac{1}{2}} \tag{3.8}
\end{equation*}
$$

For this result the relations:

$$
\begin{equation*}
\bar{\rho}(r)=\sum_{\beta} \rho(r)=12 \rho(r) \quad, \quad \frac{1}{2} \sum_{\beta} \phi(r)=\frac{1}{2} 12 \phi(r)=6 \phi(r) \tag{3.9}
\end{equation*}
$$

were used which hold for FCC crystals and nearest neighbor interactions. Note that the explicit form of $F=\tilde{F}(\bar{\rho})$ only arises because of the special functional forms in Eq. (3.3), which allow an inversion from $r$ to $\bar{\rho}$.

In order to determine all relevant functions for a binary alloy in Eq. (3.2) it is necessary to know the various material parameters introduced in Eqs. (3.3) and (3.8), namely $\alpha, \beta, \gamma, \phi_{\mathrm{e}}$, and $\bar{\rho}_{\mathrm{e}}=12 \rho_{\mathrm{e}}$ for the pure substances A and B. How to obtain these quantities through a fitting procedure will be explained in one of the following sections.

### 3.3 Evaluation of the EAM Energy Expression

### 3.3.1 Lattice Deformation and Strain Measures

We consider an arbitrary lattice for which the equilibrium state is given by the undeformed (reference) configuration. In this case the position of an arbitrary atom $\alpha$ is given by its reference position vector $X_{\alpha}^{i}$. Analogously the atom of the deformed lattice configuration outside of equilibrium is characterized by the current position vector $x_{\alpha}^{i}=X_{\alpha}^{i}+\xi_{\alpha}^{i}$, where $\xi_{\alpha}^{i}$ denotes the displacement of atom $\alpha$ from its reference position. In the same manner all lattice atoms $\beta, \gamma, \delta, \ldots$ are characterized, i.e., the conglomerate of all reference positions ( $X_{\alpha}^{i}, X_{\beta}^{i}, X_{\gamma}^{i}, \ldots$ ) and current positions $\left(x_{\alpha}^{i}, x_{\beta}^{i}, x_{\gamma}^{i}, \ldots\right)$ contains the whole information on the undeformed and deformed lattice, respectively. Moreover, the distance between two arbitrary atoms $\alpha$ and $\beta$ is written as $R_{\alpha \beta}^{i} \equiv X_{\beta}^{i}-X_{\alpha}^{i}$ or $r_{\alpha \beta}^{i} \equiv x_{\beta}^{i}-x_{\alpha}^{i}$ (also note Figure 3.3 for an illustration of the situation). Consequently the following relations can easily be obtained:

$$
\begin{align*}
x_{\alpha}^{i} & =X_{\alpha}^{i}+\xi_{\alpha}^{i} \quad, \quad x_{\beta}^{i}=X_{\beta}^{i}+\xi_{\beta}^{i},  \tag{3.10}\\
r_{\alpha \beta}^{i} & =x_{\beta}^{i}-x_{\alpha}^{i}=X_{\beta}^{i}-X_{\alpha}^{i}+\xi_{\beta}^{i}-\xi_{\alpha}^{i}=R_{\alpha \beta}^{i}+\xi_{\beta}^{i}-\xi_{\alpha}^{i} . \tag{3.11}
\end{align*}
$$

By performing the so-called mean field limit, i.e., by introducing a continuous displacement function $U^{i}=\tilde{U}^{i}\left(X_{\alpha}^{j}\right)$ instead of the discrete displacements $\xi_{\alpha}^{i}$, a TAYLOR


Figure 3.3: The different lattice vectors and their notation.
expansion, [36], yields:

$$
\begin{align*}
\xi_{\alpha}^{i} & =U^{i}\left(X_{\alpha}^{j}\right) \equiv U^{i}\left(X^{j}\right)  \tag{3.12}\\
\xi_{\beta}^{i} & =U^{i}\left(X_{\beta}^{j}\right)=U^{i}\left(X_{\alpha}^{j}+R_{\alpha \beta}^{j}\right)=U^{i}\left(X^{j}\right)+\frac{\partial U^{i}}{\partial X^{j}} R_{\alpha \beta}^{j}+\ldots,  \tag{3.13}\\
\Rightarrow r_{\alpha \beta}^{i} & =R_{\alpha \beta}^{i}+\frac{\partial U^{i}}{\partial X^{j}} R_{\alpha \beta}^{j}=\left(\delta^{i j}+H^{i j}\right) R_{\alpha \beta}^{j} \equiv F^{i j} R_{\alpha \beta}^{j} \tag{3.14}
\end{align*}
$$

Here $F^{i j}=\delta^{i j}+H^{i j}$ denotes the coefficients of the deformation gradient and $H^{i j}=$ $\frac{\partial U^{i}}{\partial X^{j}}$ stands for coefficients of the displacement gradient.

In order to identify the elastic constants in atomistic theories numerous publications based on interatomic interactions (e.g., two-body atom-atom interactions) can be found, e.g., $[65,66]$. Usually the authors consider the total energy of the $N$ (deformed) lattice bonds, $\Phi\left(r_{1}^{i}, \ldots, r_{N}^{i}\right)$, as a function of the current distance vector between the atoms and expand the energy in a TAYLOR series as follows, [65]:

$$
\begin{align*}
& \Phi\left(r_{1}^{i}, \ldots, r_{N}^{i}\right)=\Phi\left(R_{1}^{i}+H^{i j} R_{1}^{j}, \ldots, R_{N}^{i}+H^{i j} R_{N}^{j}\right)= \\
& =\Phi\left(R_{1}^{i}, \ldots, R_{N}^{i}\right)+\left.\sum_{b} \frac{\partial \Phi}{\partial r_{b}^{j}}\right|_{R_{b}^{j}} \vartheta_{b}^{j}+\left.\frac{1}{2} \sum_{b} \frac{\partial^{2} \Phi}{\partial r_{b}^{k} \partial r_{b}^{l}}\right|_{R_{b}^{k}, R_{b}^{l}} \vartheta_{b}^{k} \vartheta_{b}^{l}+\ldots \tag{3.15}
\end{align*}
$$

In this equation the index $b$ identifies the bond between the different atoms $\alpha$ and $\beta$ and the symbol $\vartheta_{b}^{i}$ denotes the coefficients of the difference vector between the displacements of $\alpha$ and $\beta$, namely $\xi_{\beta}^{i}-\xi_{\alpha}^{i} \approx \frac{\partial U^{i}}{\partial X^{j}} R_{\alpha \beta}^{j}$ according to $\vartheta_{\alpha \beta}^{i}$ in Figure 3.3. Thus Eq. (3.15) can be recast as follows:

$$
\begin{align*}
& \Phi\left(r_{1}^{i}, \ldots, r_{N}^{i}\right)=\Phi\left(R_{1}^{i}, \ldots, R_{N}^{i}\right)+ \\
& +\left.H^{i j} \sum_{b} \frac{\partial \Phi}{\partial r_{\alpha \beta}^{i}}\right|_{R_{\alpha \beta}^{i}} R_{\alpha \beta}^{j}+\left.\frac{1}{2} H^{i j} H^{k l} \sum_{b} \frac{\partial^{2} \Phi}{\partial r_{\alpha \beta}^{j} \partial r_{\alpha \beta}^{l}}\right|_{R_{\alpha \beta}^{j}, R_{\alpha \beta}^{l}} R_{\alpha \beta}^{i} R_{\alpha \beta}^{k} \tag{3.16}
\end{align*}
$$

The first derivatives of $\Phi$ vanish at equilibrium. Therefore the total elastic energy of the lattice is represented in Eq. (3.16) by the term with second-derivatives. Substituting $H^{i j}$ by its symmetric part (i.e., the coefficients of the strain tensor $\varepsilon^{i j}$ ) this term can be linked to the stiffness coefficients $K^{i j k l}$, [66].

Unfortunately I could not find a completely convincing argument to justify the substitution $H^{i j} \rightarrow \varepsilon^{i j}$ and, consequently, we want to use another strain measure in order to avoid further irritations and misunderstandings. For this purpose we consider the square of Eq. (3.14):

$$
\begin{align*}
r_{\alpha \beta}^{2} & =r_{\alpha \beta}^{i} r_{\alpha \beta}^{i}=F^{i j} F^{i k} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k}=C^{j k} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k}=R_{\alpha \beta}^{2}+\left(C^{j k}-\delta^{j k}\right) R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} \\
& =R_{\alpha \beta}^{2}+2 G^{j k} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k}, \tag{3.17}
\end{align*}
$$

where $C^{j k}=F^{i j} F^{i k} \equiv \mathbf{F}^{T} \cdot \mathbf{F}$ stands for the right Cauchy-Green tensor and $G^{j k}=\frac{1}{2}\left(C^{j k}-\delta^{j k}\right) \equiv \frac{1}{2}(\mathbf{C}-\mathbf{I})$ for Green's strain tensor. By means of $G^{j k}$ we can write for the energy of a lattice:

$$
\begin{align*}
\Phi\left(r_{\alpha \beta}^{2}\right)= & \Phi\left(R_{\alpha \beta}^{2}+2 G^{j k} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k}\right)=\Phi\left(R_{\alpha \beta}^{2}\right)+ \\
& +\left.2 G^{i j} \sum_{b} \frac{\partial \Phi}{\partial r_{\alpha \beta}^{2}}\right|_{R_{\alpha \beta}^{2}} R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}+ \\
& +\left.\frac{4}{2} G^{i j} G^{k l} \sum_{b} \frac{\partial^{2} \Phi}{\partial r_{\alpha \beta}^{2} \partial r_{\alpha \beta}^{2}}\right|_{R_{\alpha \beta}^{2}} R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l}+\ldots \tag{3.18}
\end{align*}
$$

This equation can be linked to the stiffness coefficients without any further substitutions. However, the underlying interatomic potentials have to be reformulated in terms of $r_{\alpha \beta}^{2}$.

### 3.3.2 Equilibrium Condition and Stiffness Coefficients

According to Section 3.2 the EAM energy expression of the whole system is given by the sum of the energies of all atoms in the system, $E_{\text {tot }}=\sum_{\alpha} E_{\alpha}$, where $E_{\alpha}$ is given by Eq. (3.2). Since $\phi_{\alpha \beta}, \rho_{\beta}$ and $\bar{\rho}_{\alpha}$ depend only on the scalar distance $r_{\alpha \beta}$ between $\alpha$ and $\beta$ it is also possible to use $r_{\alpha \beta}^{2}$ in the argument. The corresponding functions are $\hat{\phi}=\tilde{\hat{\phi}}\left(r_{\alpha \beta}^{2}\right)$ and $\hat{\rho}_{\beta}=\tilde{\hat{\rho}}_{\beta}\left(r_{\alpha \beta}^{2}\right)$ and one can write:

$$
\begin{equation*}
E_{\text {tot }}=\sum_{\alpha} E_{\alpha}=\frac{1}{2} \sum_{\substack{\alpha, \beta \\(\beta \neq \alpha)}} \hat{\phi}_{\alpha \beta}\left(r_{\alpha \beta}^{2}\right)+\sum_{\alpha} \hat{F}_{\alpha}\left(\hat{\bar{\rho}}_{\alpha}\right) \quad \text { and } \quad \hat{\bar{\rho}}_{\alpha}=\sum_{\substack{\beta \\(\beta \neq \alpha)}} \hat{\rho}_{\beta}\left(r_{\alpha \beta}^{2}\right) \tag{3.2a}
\end{equation*}
$$

For convenience we will omit the circumflexes ^ in the following sections. $\phi_{\alpha \beta}, \rho_{\beta}$ and $\bar{\rho}_{\alpha}$ implicitly refer to the argument $r_{\alpha \beta}^{2}$. The individual energy contributions of Eq.
(3.2a) can be expanded in a Taylor series at equilibrium (undeformed state). The following steps seem worth mentioning:

$$
\begin{align*}
& \phi_{\alpha \beta}\left(r_{\alpha \beta}^{2}\right)=\phi_{\alpha \beta}\left(R_{\alpha \beta}^{2}+2 G^{i j} R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}\right)= \\
& =\phi_{\alpha \beta}\left(R_{\alpha \beta}^{2}\right)+2 \phi_{\alpha \beta}^{\prime}\left(R_{\alpha \beta}^{2}\right) G^{i j} R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}+2 \phi_{\alpha \beta}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) G^{i j} G^{k l} R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l} . \tag{3.19}
\end{align*}
$$

In an analogous manner one obtains:

$$
\begin{align*}
& \rho_{\beta}\left(r^{\alpha \beta^{2}}\right)= \\
& =\rho_{\beta}\left(R^{\alpha \beta^{2}}\right)+2 \rho_{\beta}^{\prime}\left(R^{\alpha \beta^{2}}\right) G_{i j} R_{j}^{\alpha \beta} R_{j}^{\alpha \beta}+2 \rho_{\beta}^{\prime \prime}\left(R^{\alpha \beta^{2}}\right) G_{i j} G_{k l} R_{i}^{\alpha \beta} R_{j}^{\alpha \beta} R_{k}^{\alpha \beta} R_{l}^{\alpha \beta} \tag{3.20}
\end{align*}
$$

Here the abbreviations $(\diamond)^{\prime}\left(R_{\alpha \beta}^{2}\right)$ and $(\diamond)^{\prime \prime}\left(R_{\alpha \beta}^{2}\right)$ represent the derivatives of $(\diamond)$ with respect to its argument $r_{\alpha \beta}^{2}$ evaluated at $R_{\alpha \beta}^{2}$. Furthermore Eq. (3.20) is of the form $\rho_{\beta}\left(r_{\alpha \beta}^{2}\right)=\mathcal{A}_{\beta}+\mathcal{B}_{\beta} \mathcal{X}_{\alpha \beta}+\frac{1}{2} \mathcal{C}_{\beta} \mathcal{X}_{\alpha \beta}^{2}$ with $\mathcal{A}_{\beta}=\rho_{\beta}\left(R_{\alpha \beta}^{2}\right), \mathcal{B}_{\beta}=\rho_{\beta}^{\prime}\left(R_{\alpha \beta}^{2}\right), \mathcal{C}_{\beta}=\rho_{\beta}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right)$ and $\mathcal{X}_{\alpha \beta}=2 G^{i j} R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}$. Consequently a TAYLOR expansion of $F_{\alpha}\left(\bar{\rho}_{\alpha}\right)$ at $\mathcal{A}_{\beta}$ can be performed as follows:

$$
\begin{align*}
& F_{\alpha}\left(\sum_{\beta} \rho_{\beta}\left(r^{\alpha \beta^{2}}\right)\right)=F_{\alpha}\left(\sum_{\beta}\left[\mathcal{A}_{\beta}+\mathcal{B}_{\beta} \mathcal{X}_{\alpha \beta}+\frac{1}{2} \mathcal{C}_{\beta} \mathcal{X}_{\alpha \beta}^{2}\right]\right)= \\
& =F_{\alpha}\left(\sum_{\beta} \mathcal{A}_{\beta}\right)+\left.\sum_{\beta} \frac{\partial F_{\alpha}}{\partial \mathcal{X}_{\alpha \beta}}\right|_{\mathcal{X}_{\alpha \beta}=0} \mathcal{X}_{\alpha \beta}+\left.\frac{1}{2} \sum_{\beta, \gamma} \frac{\partial^{2} F_{\alpha}}{\partial \mathcal{X}_{\alpha \beta} \partial \mathcal{X}_{\alpha \gamma}}\right|_{\mathcal{X}_{\alpha \beta}=\mathcal{X}_{\alpha \gamma}=0} \mathcal{X}_{\alpha \beta} \mathcal{X}_{\alpha \gamma} . \tag{3.21}
\end{align*}
$$

By introducing

$$
\begin{array}{ll}
A_{\alpha}^{i j}=\sum_{\beta} \phi_{\alpha \beta}^{\prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} \quad, \quad B_{\alpha}^{i j k l}=\sum_{\beta} \phi_{\alpha \beta}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l}, \\
V_{\alpha}^{i j}=\sum_{\beta} \rho_{\beta}^{\prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}, & W_{\alpha}^{i j k l}=\sum_{\beta} \rho_{\beta}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l} \tag{3.23}
\end{array}
$$

one can find the following important relation for the energy of an arbitrary atom $\alpha$ :

$$
\begin{align*}
E_{\alpha}= & \frac{1}{2} \sum_{\beta} \phi_{\alpha \beta}\left(R_{\alpha \beta}^{2}\right)+F_{\alpha}\left(\bar{\rho}_{\alpha}^{0}\right)+G^{i j}\left[A_{\alpha}^{i j}+2 F_{\alpha}^{\prime}\left(\bar{\rho}_{\alpha}^{0}\right) V_{\alpha}^{i j}\right]+ \\
& +G^{i j} G^{k l}\left[B_{\alpha}^{i j k l}+2 F_{\alpha}^{\prime}\left(\bar{\rho}_{\alpha}^{0}\right) W_{\alpha}^{i j k l}+2 F_{\alpha}^{\prime \prime}\left(\bar{\rho}_{\alpha}^{0}\right) V_{\alpha}^{i j} V_{\alpha}^{k l}\right] \tag{3.24}
\end{align*}
$$

where $F_{\alpha}^{\prime}\left(\bar{\rho}_{\alpha}^{0}\right)$ and $F_{\alpha}^{\prime \prime}\left(\bar{\rho}_{\alpha}^{0}\right)$ refer the derivatives with respect to the argument at $\bar{\rho}_{\alpha}^{0}=$ $\sum_{\beta} \mathcal{A}_{\beta}=\sum_{\beta} \rho_{\beta}\left(R_{\alpha \beta}^{2}\right)$. Note that in order to derive Eq. (3.24) the chain rule was
applied as follows:

$$
\begin{align*}
& \left.\frac{\partial F_{\alpha}}{\partial \mathcal{X}_{\alpha \beta}}\right|_{\mathcal{X}_{\alpha \beta}=0}=F_{\alpha}^{\prime}\left(\sum_{\beta} \mathcal{A}_{\beta}\right) \cdot \sum_{\beta} \mathcal{B}_{\beta}  \tag{3.25}\\
& \left.\frac{\partial^{2} F_{\alpha}}{\partial \mathcal{X}_{\alpha \beta} \partial \mathcal{X}_{\alpha \gamma}}\right|_{\mathcal{X}_{\alpha \beta}=\mathcal{X}_{\alpha \gamma}=0}=F_{\alpha}^{\prime \prime}\left(\sum_{\beta} \mathcal{A}_{\beta}\right) \cdot \sum_{\beta, \gamma} \mathcal{B}_{\beta} \mathcal{B}_{\gamma}+F_{\alpha}^{\prime}\left(\sum_{\beta} \mathcal{A}_{\beta}\right) \cdot \sum_{\beta} \mathcal{C}_{\beta} \tag{3.26}
\end{align*}
$$

Eq. (3.24) represents an important relation for the energy of atom $\alpha$. It is valid in pure substances as well as in solid mixtures. In the case of solid mixtures one can find different types of atoms in the lattice, and we have to specify the type of $\alpha$ and of its neighbors $\beta$ in more detail.

Moreover, if thermal expansion is neglected, it is reasonable to postulate that $E_{\alpha}$ assumes a minimum at equilibrium. Thus in Eq. (3.24) the first bracket on the right hand side must vanish and we find for the equilibrium condition:

$$
\begin{equation*}
A_{\alpha}^{i j}+2 F_{\alpha}^{\prime}\left(\bar{\rho}_{\alpha}^{0}\right) V_{\alpha}^{i j}=0 . \tag{3.27}
\end{equation*}
$$

Furthermore it holds that $E_{\text {elast }} / V=\frac{1}{2} G^{i j} K^{i j k l} G^{k l}$ (law of St.-VEnAnt-Kirchhoff), [40]. Defining $\Omega_{0}^{\alpha}$ as the volume occupied by an atom $\alpha$ we obtain for the stiffness coefficients from Eq. (3.24):

$$
\begin{equation*}
K_{\alpha}^{i j k l}=\frac{1}{\Omega_{0}^{\alpha}}\left[2 B_{\alpha}^{i j k l}+4 F_{\alpha}^{\prime}\left(\bar{\rho}_{\alpha}^{0}\right) W_{\alpha}^{i j k l}+4 F_{\alpha}^{\prime \prime}\left(\bar{\rho}_{\alpha}^{0}\right) V_{\alpha}^{i j} V_{\alpha}^{k l}\right] . \tag{3.28}
\end{equation*}
$$

It should be pointed out that the underlying potentials of Eqs. (3.27,3.28) depend on the argument $R_{\alpha \beta}^{2}$. Taking into account the chain rule and, in particular, the relations $\hat{\phi}_{\alpha \beta}^{\prime}\left(R_{\alpha \beta}^{2}\right)=\frac{\phi_{\alpha \beta}^{\prime}\left(R_{\alpha \beta}\right)}{2 R_{\alpha \beta}}, \hat{\rho}_{\beta}^{\prime}\left(R_{\alpha \beta}^{2}\right)=\frac{\rho_{\beta}^{\prime}\left(R_{\alpha \beta}\right)}{2 R_{\alpha \beta}}, \hat{\phi}_{\alpha \beta}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right)=\frac{1}{4}\left(\frac{\phi_{\alpha \beta}^{\prime \prime}\left(R_{\alpha \beta}\right)}{R_{\alpha \beta}^{2}}-\frac{\phi_{\alpha \beta}^{\prime}\left(R_{\alpha \beta}\right)}{R_{\alpha \beta}^{3}}\right)$, and $\hat{\rho}_{\beta}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right)=\frac{1}{4}\left(\frac{\rho_{\beta}^{\prime \prime}\left(R_{\alpha \beta}\right)}{R_{\alpha \beta}^{2}}-\frac{\rho_{\beta}^{\prime}\left(R_{\alpha \beta}\right)}{R_{\alpha \beta}^{3}}\right)$, Eqs. $(3.27,3.28)$ are in agreement with the accepted results communicated by Daw and Baskes in [29].

We already indicated the importance of Eqs. (3.24,3.27,3.28) for solid mixtures. More specifically the question arises, how to specify these equations for different types of atoms. In the next section we want to turn the attention to binary alloys and present a procedure yielding all corresponding equations for binary mixtures.

### 3.4 EAM for Binary Alloys

### 3.4.1 Specification of the Energy-Expression: DPC Operator and Higher Gradients

In context with Eq. (3.24) the question arises of how to exploit this energy expression for binary alloys or, in other words, how additional information on the different types of atoms can be incorporated in this equation. In the case of a binary alloy A-B three different forms of interactions can be distinguished: $A \leftrightarrow A, B \leftrightarrow B$ and $A \leftrightarrow B$. In order to include these interaction terms in Eq. (3.24) one can use a so-called Discrete Particle Concentration (DPC) operator, introduced for example by de Fontaine, [30].

$$
\hat{y}_{\gamma}=\left\{\begin{array}{ll}
0, & \gamma=\mathrm{A}  \tag{3.29}\\
1, & \gamma=\mathrm{B}
\end{array} .\right.
$$

We now have to specify the following expressions of Eq. (3.24): $\phi_{\alpha \beta}, \bar{\rho}_{\alpha}^{0}, F_{\alpha}, A_{\alpha}^{i j}$, $B_{\alpha}^{i j k l}, F_{\alpha}^{\prime} V_{\alpha}^{i j}, F_{\alpha}^{\prime \prime} V_{\alpha}^{i j} V_{\alpha}^{k l}$ and $F_{\alpha}^{\prime} W_{\alpha}^{i j k l}$. For this purpose we begin the analysis with the decomposition of $\phi_{\alpha \beta}$ and $\bar{\rho}_{\alpha}^{0}$ in the following manner:

$$
\begin{align*}
\phi_{\alpha \beta} & =\left(1-\hat{y}_{\alpha}\right)\left(1-\hat{y}_{\beta}\right) \phi_{\mathrm{AA}}+\hat{y}_{\alpha} \hat{y}_{\beta} \phi_{\mathrm{BB}}+\left[\left(1-\hat{y}_{\alpha}\right) \hat{y}_{\beta}+\left(1-\hat{y}_{\beta}\right) \hat{y}_{\alpha}\right] \phi_{\mathrm{AB}} \\
& =\phi_{\mathrm{AA}}+\left[\hat{y}_{\alpha}+\left(1-2 \hat{y}_{\alpha}\right) \hat{y}_{\beta}\right] \phi+\left(\hat{y}_{\alpha}+\hat{y}_{\beta}\right) \tilde{\phi},  \tag{3.30}\\
\bar{\rho}_{\alpha}^{0} & =\sum_{\beta}\left[\left(1-\hat{y}_{\beta}\right) \rho_{\mathrm{A}}+\hat{y}_{\beta} \rho_{\mathrm{B}}\right]=\sum_{\beta}\left[\hat{y}_{\beta}\left(\rho_{\mathrm{B}}-\rho_{\mathrm{A}}\right)+\rho_{\mathrm{A}}\right] \tag{3.31}
\end{align*}
$$

with the definitions $\phi=\phi_{\mathrm{AB}}-\frac{1}{2}\left(\phi_{\mathrm{AA}}+\phi_{\mathrm{BB}}\right)$ and $\tilde{\phi}=\frac{1}{2}\left(\phi_{\mathrm{BB}}-\phi_{\mathrm{AA}}\right)$. Obviously the DCP operator acts as a "selector" and "chooses" the corresponding interaction depending on which types of atoms are considered. If for example $\alpha$ and $\beta$ are two A-atoms, $\hat{y}_{\alpha}$ as well as $\hat{y}_{\beta}$ are zero and only the terms $\phi_{\mathrm{AA}}$ and $\bar{\rho}_{\mathrm{A}}^{0}=\sum_{\beta} \rho_{\mathrm{A}}$ remain in Eq. (3.30) and (3.31). In the same manner one can obtain $\phi_{\mathrm{BB}}, \phi_{\mathrm{AB}}$ and $\bar{\rho}_{\mathrm{B}}^{0}$.

Moreover the DCP operator can be replaced by its continuous counterpart if the mean field limit is applied. Thus a Taylor expansion results in:

$$
\begin{align*}
\hat{y}_{\alpha} & =y\left(X_{i}^{\alpha}\right) \equiv y\left(X_{i}\right),  \tag{3.32}\\
\hat{y}_{\beta} & =y\left(X_{i}^{\beta}\right)=y\left(X_{i}+R_{i}^{\alpha \beta}\right)= \\
& =y\left(X_{i}\right)+\underbrace{\frac{\partial y}{\partial X_{i}}}_{=\nabla_{i} y} R_{i}^{\alpha \beta}+\frac{1}{2} \underbrace{\frac{\partial^{2} y}{\partial X_{i} \partial X_{j}}}_{=\nabla_{i j}^{2} y} R_{i}^{\alpha \beta} R_{j}^{\alpha \beta}+\ldots . \tag{3.33}
\end{align*}
$$

The symbols $\nabla_{i} y$ and $\nabla_{i j}^{2} y$ are referred to as higher gradients and are characteristic of phase field theories. After a straightforward calculation we find:

$$
\begin{align*}
\phi_{\alpha \beta}= & \phi_{\mathrm{AA}}+2 y(1-y) \phi+2 y \tilde{\phi}+\nabla_{i} y[(1-2 y) \phi+\tilde{\phi}] R_{\alpha \beta}^{i}+ \\
& \frac{1}{2} \nabla_{i j}^{2} y[(1-2 y) \phi+\tilde{\phi}] R_{\alpha \beta}^{i} R_{\alpha \beta}^{j},  \tag{3.34}\\
\bar{\rho}_{\alpha}^{0}= & \sum_{\beta} \rho_{\mathrm{A}}+y \sum_{\beta}\left(\rho_{\mathrm{B}}-\rho_{\mathrm{A}}\right)+\nabla_{i} y \sum_{\beta}\left(\rho_{\mathrm{B}}-\rho_{\mathrm{A}}\right) R_{\alpha \beta}^{i}+ \\
& \frac{1}{2} \nabla_{i j}^{2} y \sum_{\beta}\left(\rho_{\mathrm{B}}-\rho_{\mathrm{A}}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}  \tag{3.35}\\
= & \bar{\rho}_{\mathrm{A}}+y \bar{\rho}_{\triangle}+\left(\nabla_{i} y\right) \bar{\rho}_{\triangle}^{i}+\frac{1}{2}\left(\nabla_{i j}^{2} y\right) \bar{\rho}_{\triangle}^{i j} \tag{3.36}
\end{align*}
$$

with the definitions $\bar{\rho}_{\mathrm{A}}=\sum_{\beta} \rho_{\mathrm{A}} ; \bar{\rho}_{\Delta}=\sum_{\beta}\left(\rho_{\mathrm{B}}-\rho_{\mathrm{A}}\right) ; \bar{\rho}_{\triangle}^{i}=\sum_{\beta}\left(\rho_{\mathrm{B}}-\rho_{\mathrm{A}}\right) R_{\alpha \beta}^{i}$ and $\bar{\rho}_{\Delta}^{i j}=\sum_{\beta}\left(\rho_{\mathrm{B}}-\rho_{\mathrm{A}}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}$. At this point it is important to mention that for any scalar function $f\left(R_{\alpha \beta}\right)$ depending only on the radial distance $R_{\alpha \beta}$ between atom $\alpha$ and $\beta$ the following sum vanishes:

$$
\begin{equation*}
\sum_{\beta} f\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i_{1}} \ldots R_{\alpha \beta}^{i_{N}}=0 \quad, \quad(\forall N=\text { odd number }) . \tag{3.37}
\end{equation*}
$$

This relation stems from the fact that in an arbitrary lattice, due to its periodic arrangement, for all vectors $R_{\alpha \beta}^{i}$ a vector $-R_{\alpha \beta}^{i}$ in opposite direction can be found (if boundary effects are neglected). Thus Eqs. $(3.34,3.36)$ result in:

$$
\begin{align*}
\phi_{\alpha \beta} & =\phi_{\mathrm{AA}}+2 y(1-y) \phi+2 y \tilde{\phi}+\frac{1}{2} \nabla_{i j}^{2} y[(1-2 y) \phi+\tilde{\phi}] R_{\alpha \beta}^{i} R_{\alpha \beta}^{j},  \tag{3.38}\\
\bar{\rho}_{\alpha}^{0} & =\bar{\rho}_{\mathrm{A}}+y \bar{\rho}_{\triangle}+\frac{1}{2}\left(\nabla_{i j}^{2} y\right) \bar{\rho}_{\triangle}^{i j} . \tag{3.39}
\end{align*}
$$

Using Eq. (3.36) the embedding function $F_{\alpha}\left(\bar{\rho}_{\alpha}^{0}\right)$ can be also expanded into a TAYLOR series evaluated at a weighted average electron density $\bar{\rho}_{a v}=\bar{\rho}_{\mathrm{A}}+y \bar{\rho}_{\triangle}=(1-y) \bar{\rho}_{\mathrm{A}}+$ $y \bar{\rho}_{\mathrm{B}}$ :

$$
\begin{equation*}
F_{\alpha}\left(\bar{\rho}_{\alpha}^{0}\right)=F_{\alpha}(\underbrace{\bar{\rho}_{A}+y \bar{\rho}_{\Delta}}_{=\bar{\rho}_{a v}}+\frac{1}{2}\left(\nabla_{i j}^{2} y\right) \bar{\rho}_{\Delta}^{i j})=F_{\alpha}\left(\bar{\rho}_{a v}\right)+\frac{1}{2} F_{\alpha}^{\prime}\left(\bar{\rho}_{a v}\right) \bar{\rho}_{\Delta}^{i j}\left(\nabla_{i j}^{2} y\right)+\ldots \tag{3.40}
\end{equation*}
$$

Note that gradient terms of higher than second order were assumed not to contribute to the energy of the system. Moreover $F_{\alpha}$ itself is also decomposed analogously to

Eq. (3.31) and we write:

$$
\begin{align*}
F_{\alpha}\left(\bar{\rho}_{\alpha}^{0}\right) & =(1-y) F_{\mathrm{A}}+y F_{\mathrm{B}},  \tag{3.41}\\
F_{\mathrm{A}} & =F_{\mathrm{A}}\left(\bar{\rho}_{a v}\right)+\frac{1}{2} F_{\mathrm{A}}^{\prime}\left(\bar{\rho}_{a v}\right) \bar{\rho}_{i j}^{\triangle}\left(\nabla_{i j}^{2} y\right) \ldots, \\
F_{\mathrm{B}} & =F_{\mathrm{B}}\left(\bar{\rho}_{a v}\right)+\frac{1}{2} F_{\mathrm{B}}^{\prime}\left(\bar{\rho}_{a v}\right) \bar{\rho}_{i j}^{\triangle}\left(\nabla_{i j}^{2} y\right) \ldots . \tag{3.42}
\end{align*}
$$

Thus the first two terms of the right hand side of Eq. (3.24) are specified in terms of concentration gradients by Eqs. (3.34) and (3.41-3.42).

In what follows we want to investigate the symbols $A_{\alpha}^{i j}, B_{\alpha}^{i j k l}, F_{\alpha}^{\prime} V_{\alpha}^{i j}, F_{\alpha}^{\prime \prime} V_{\alpha}^{i j} V_{\alpha}^{k l}$ and $F_{\alpha}^{\prime} W_{\alpha}^{i j k l}$ of Eq. (3.24). Here it is worth mentioning that the products of the last three expressions $F_{\alpha}^{\prime} V_{\alpha}^{i j}, F_{\alpha}^{\prime \prime} V_{\alpha}^{i j} V_{\alpha}^{k l}$ and $F_{\alpha}^{\prime} W_{\alpha}^{i j k l}$ cannot be separated and evaluated separately since they are coupled by the same index $\alpha$. Hence the decomposition by means of the DCP-operator must be applied to the complete product.

The first two abbreviations, $A_{\alpha}^{i j}$ and $B_{\alpha}^{i j k l}$, can be written in the same manner as in Eq. (3.34):

$$
\begin{align*}
& A_{\alpha}^{i j}=A_{\mathrm{A}}^{i j}+2 y(1-y) A_{\phi}^{i j}+2 y A_{\tilde{\phi}}^{i j}+\frac{1}{2} \nabla_{k l}^{2} y\left[(1-2 y) A_{\phi}^{i j k l}+A_{\tilde{\phi}}^{i j k l}\right]  \tag{3.43}\\
& B_{\alpha}^{i j k l}=B_{\mathrm{A}}^{i j k l}+2 y(1-y) B_{\phi}^{i j k l}+2 y B_{\tilde{\phi}}^{i j k l}+\frac{1}{2} \nabla_{m n}^{2} y\left[(1-2 y) B_{\phi}^{i j k l m n}+B_{\tilde{\phi}}^{i j k l m n}\right] \tag{3.44}
\end{align*}
$$

with the definitions:

$$
\begin{align*}
& A_{\mathrm{A}}^{i j}=\sum_{\beta} \phi_{\mathrm{AA}}^{\prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}, \quad A_{\phi}^{i j k l}=\sum_{\beta} \phi^{\prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l},  \tag{3.45}\\
& A_{\tilde{\phi}}^{i j k l}=\sum_{\beta} \tilde{\phi}^{\prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l}, \quad B_{\mathrm{A}}^{i j k l}=\sum_{\beta} \phi_{\mathrm{AA}}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l},  \tag{3.46}\\
& B_{\phi}^{i j k l m n}=\sum_{\beta} \phi^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} \ldots R_{\alpha \beta}^{n}, \quad B_{\dot{\phi}}^{i j k l m n}=\sum_{\beta} \tilde{\phi}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} \ldots R_{\alpha \beta}^{n}, \tag{3.47}
\end{align*}
$$

Analogously to Eq. (3.41) the following relations hold:

$$
\begin{align*}
& F_{\alpha}^{\prime}\left(\bar{\rho}_{\alpha}^{0}\right) V_{\alpha}^{i j}=\left.(1-y) F_{\mathrm{A}}^{\prime} V_{\alpha}^{i j}\right|_{\alpha=\mathrm{A}}+\left.y F_{\mathrm{B}}^{\prime} V_{\alpha}^{i j}\right|_{\alpha=\mathrm{B}}  \tag{3.48}\\
& F_{\alpha}^{\prime}\left(\bar{\rho}_{\alpha}^{0}\right) W_{\alpha}^{i j k l}=\left.(1-y) F_{\mathrm{A}}^{\prime} W_{\alpha}^{i j k l}\right|_{\alpha=\mathrm{A}}+\left.y F_{\mathrm{B}}^{\prime} W_{\alpha}^{i j k l}\right|_{\alpha=\mathrm{B}},  \tag{3.49}\\
& F_{\alpha}^{\prime \prime}\left(\bar{\rho}_{\alpha}^{0}\right) V_{\alpha}^{i j} V_{\alpha}^{k l}=\left.(1-y) F_{\mathrm{A}}^{\prime \prime} V_{\alpha}^{i j} V_{\alpha}^{k l}\right|_{\alpha=\mathrm{A}}+\left.y F_{\mathrm{B}}^{\prime \prime} V_{\alpha}^{i j} V_{\alpha}^{k l}\right|_{\alpha=\mathrm{B}} \tag{3.50}
\end{align*}
$$

The derivatives $F_{\alpha}^{\prime}$ and $F_{\alpha}^{\prime \prime}$ can be calculated analogously to Eqs. (3.42). We increase the order of derivatives in these equations consistently:

$$
\begin{align*}
F_{\mathrm{A} / \mathrm{B}}^{\prime} & =F_{\mathrm{A} / \mathrm{B}}^{\prime}\left(\bar{\rho}_{a v}\right)+\frac{1}{2} F_{\mathrm{A} / \mathrm{B}}^{\prime \prime}\left(\bar{\rho}_{a v}\right) \bar{\rho}_{\Delta}^{i j}\left(\nabla_{i j}^{2} y\right),  \tag{3.51}\\
F_{\mathrm{A} / \mathrm{B}}^{\prime \prime} & =F_{\mathrm{A} / \mathrm{B}}^{\prime \prime}\left(\bar{\rho}_{a v}\right)+\frac{1}{2} F_{\mathrm{A} / \mathrm{B}}^{\prime \prime \prime}\left(\bar{\rho}_{a v}\right) \bar{\rho}_{\Delta}^{i j}\left(\nabla_{i j}^{2} y\right) . \tag{3.52}
\end{align*}
$$

By combination of Eqs. (3.23) and (3.39) we finally find ( $\alpha=\{\mathrm{A}, \mathrm{B}\}$ ):

$$
\begin{align*}
V_{\alpha}^{i j} & =V_{\mathrm{A}}^{i j}+y V_{\Delta}^{i j}+\frac{1}{2}\left(\nabla_{k l}^{2} y\right) V_{\Delta}^{i j k l}  \tag{3.53}\\
W_{\alpha}^{i j k l} & =W_{\mathrm{A}}^{i j k l}+y W_{\Delta}^{i j k l}+\frac{1}{2}\left(\nabla_{m n}^{2} y\right) W_{\Delta}^{i j k l m n} \tag{3.54}
\end{align*}
$$

with the abbreviations:

$$
\begin{align*}
& V_{\mathrm{A}}^{i j}=\sum_{\beta} \rho_{\mathrm{A}}^{\prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}, \quad V_{\triangle}^{i_{1}, \ldots, i_{n}}=\sum_{\beta}\left[\rho_{\mathrm{B}}^{\prime}\left(R_{\alpha \beta}^{2}\right)-\rho_{\mathrm{A}}^{\prime}\left(R_{\alpha \beta}^{2}\right)\right] R_{\alpha \beta}^{i_{1}} \ldots R_{\alpha \beta}^{i_{n}},  \tag{3.55}\\
& W_{\mathrm{A}}^{i j k l}=\sum_{\beta} \rho_{\mathrm{A}}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} \ldots R_{\alpha \beta}^{l}, \quad W_{\triangle}^{i_{1}, \ldots, i_{n}}=\sum_{\beta}\left[\rho_{\mathrm{B}}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right)-\rho_{\mathrm{A}}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right)\right] R_{\alpha \beta}^{i_{1}} \ldots R_{\alpha \beta}^{i_{n}} \tag{3.56}
\end{align*}
$$

and all terms of Eq. (3.24) are now specified for a binary alloy A-B. In the following section it is shown how these cumbersome equations can be structured in order to obtain information regarding the equilibrium condition, the stiffness and the HGCs.

### 3.4.2 Equilibrium Condition, Stiffness and Higher Gradient Coefficients

By combination of Eq. (3.24) with Eqs. (3.38, 3.41, 3.42, 3.43, 3.44, 3.48-3.54) and by means of the definitions:

$$
\begin{align*}
& g_{\mathrm{AA}}=\sum_{\beta} \phi_{\mathrm{AA}} \quad, \quad g_{\phi}=\sum_{\beta} \phi \quad, \quad g_{\tilde{\phi}}=\sum_{\beta} \tilde{\phi},  \tag{3.57}\\
& g_{\phi}^{i j}=\sum_{\beta} \phi R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}, \quad g_{\tilde{\phi}}^{i j}=\sum_{\beta} \tilde{\phi} R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} . \tag{3.58}
\end{align*}
$$

we obtain for the energy of atom $\alpha$ :

$$
\begin{align*}
E_{\alpha} & =\frac{1}{2} g_{\mathrm{AA}}+y(1-y) g_{\phi}+y g_{\tilde{\phi}}+\frac{1}{4}\left(\nabla_{i j}^{2} y\right)\left[(1-2 y) g_{\phi}^{i j}+g_{\tilde{\phi}}^{i j}\right] \\
+ & F_{\mathrm{A}}+y\left(F_{\mathrm{B}}-F_{\mathrm{A}}\right)+\frac{1}{2}\left(\nabla_{i j}^{2} y\right) \bar{\rho}_{\Delta}^{i j}\left[F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right] \\
+ & G^{i j}\left\{A_{\mathrm{A}}^{i j}+2 y(1-y) A_{\phi}^{i j}+2 y A_{\tilde{\phi}}^{i j}+\frac{1}{2}\left(\nabla_{k l}^{2} y\right)\left[(1-2 y) A_{\phi}^{i j k l}+A_{\tilde{\phi}}^{i j k l}\right]\right. \\
& +2\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right) \\
& \left.+\left(\nabla_{k l}^{2} y\right)\left[V_{\triangle}^{i j k l}\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)+\bar{\rho}_{\triangle}^{k l}\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right]\right\} \\
+ & \frac{1}{2} G^{i j} G^{k l}\left\{2 B_{\mathrm{A}}^{i j k l}+4 y(1-y) B_{\phi}^{i j k l}+4 y B_{\dot{\phi}}^{i j k l}+\left(\nabla_{m n}^{2} y\right)\left[(1-2 y) B_{\phi}^{i j k l m n}+B_{\bar{\phi}}^{i j k l m n}\right]\right. \\
& +4\left(W_{\mathrm{A}}^{i j k l}+y W_{\triangle}^{i j k l}\right)\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right) \\
& +2\left(\nabla_{m n}^{2} y\right)\left[W_{\triangle}^{i j k l m n}\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)+\bar{\rho}_{\triangle}^{m n}\left(W_{\mathrm{A}}^{i j k l}+y W_{\triangle}^{i j k l}\right) \times\right. \\
& \left.\times\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right]+4\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right) \\
& +2\left(\nabla_{m n}^{2} y\right)\left[V_{\triangle}^{k l m n}\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)+V_{\triangle}^{i j m n}\left(V_{\mathrm{A}}^{k l}+y V_{\triangle}^{k l}\right) \times\right. \\
& \left.\left.\times\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)+\bar{\rho}_{\triangle}^{m n}\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y V_{\Delta}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime \prime}-F_{\mathrm{A}}^{\prime \prime \prime}\right)\right)\right]\right\} \tag{3.59}
\end{align*}
$$

where $F_{\mathrm{A} / \mathrm{B}}$ and all derivatives of $F_{\mathrm{A} / \mathrm{B}}$ depend on the argument $\bar{\rho}_{a v}$.

Following Cahn and Hilliard in [24] and Dreyer and Müller in [37, 39] (see also Section 2.5.3(d.)) the Helmholtz free energy density $\mathbb{F}$ of a two-component system with an inhomogeneous mass-concentration profile $c\left(x^{i}, t\right)$ can be characterized by the equation (without eigenstrains and thermal expansion):

$$
\begin{equation*}
\mathbb{F}=\mathbb{F}_{0}\left(c, G^{i j}\right)-a^{k l}\left(c, G^{i j}\right) \nabla_{k l}^{2} c+b^{k l}\left(c, G^{i j}\right)\left(\nabla_{k} c\right)\left(\nabla_{l} c\right) \tag{3.60}
\end{equation*}
$$

The first term, $\mathbb{F}_{0}\left(c, G^{i j}\right)$, represents the Helmholtz free energy density of the corresponding system with a homogeneous concentration profile. It also includes a mechanical energy term, $\mathbb{F}_{0}^{\text {mech }}$, as reflected by the strains $G^{k l}$. Therefore one can split
$\mathbb{F}_{0}$ into two parts (here for pure elastic deformations):

$$
\begin{equation*}
\mathbb{F}_{0}\left(c, G^{i j}\right)=\mathbb{F}_{0}^{\text {chem }}(c)+\underbrace{\frac{1}{2} G^{i j} K^{i j k l}(c) G^{k l}}_{=\mathbb{F}_{0}^{\text {mech }}}, \tag{3.61}
\end{equation*}
$$

where the first part stands for the energy density without elastic energy contributions. Moreover it is important to mention that $\mathbb{F}_{0}^{\text {mech }}$ does not contain higher gradients and, consequently, it is reasonable to rearrange Eq. (3.59) as follows:

$$
\begin{align*}
E_{\alpha} & =\frac{1}{2} g_{\mathrm{AA}}+y(1-y) g_{\phi}+y g_{\tilde{\phi}}+F_{\mathrm{A}}+y\left(F_{\mathrm{B}}-F_{\mathrm{A}}\right) \\
+ & \frac{1}{2} G^{i j} G^{k l}\left\{2 B_{\mathrm{A}}^{i j k l}+4 y(1-y) B_{\phi}^{i j k l}+4 y B_{\tilde{\phi}}^{i j k l}+4\left(W_{\mathrm{A}}^{i j k l}+y W_{\triangle}^{i j k l}\right) \times\right. \\
& \left.\times\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)+4\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right\} \\
+ & \left(\nabla_{m n}^{2} y\right)\left\{\frac{1}{4}\left((1-2 y) g_{\phi}^{m n}+g_{\tilde{\phi}}^{m n}\right)+\frac{1}{2} \bar{\rho}_{\triangle}^{m n}\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)\right. \\
& +\frac{1}{2} G^{i j}\left[(1-2 y) A_{\phi}^{i j m n}+A_{\tilde{\phi}}^{i j m n}+2 V_{\triangle}^{i j m n}\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)\right. \\
& \left.+2 \bar{\rho}_{\triangle}^{m n}\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right] \\
& +\frac{1}{2} G^{i j} G^{k l}\left[(1-2 y) B_{\phi}^{i j k l m n}+B_{\tilde{\phi}}^{i j k l m n}\right. \\
& +2 W_{\triangle}^{i j k l m n}\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)+2 \bar{\rho}_{\triangle}^{m n}\left(W_{\mathrm{A}}^{i j k l}+y W_{\triangle}^{i j k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right) \\
& +2 V_{\triangle}^{k l m n}\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime \prime}\right)\right)+2 V_{\triangle}^{i j m n}\left(V_{\mathrm{A}}^{k l}+y V_{\triangle}^{k l}\right) \times \\
& \left.\left.\times\left(F_{\mathrm{A}}^{\prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)+2 \bar{\rho}_{\triangle}^{m n}\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime \prime}+y\left(F_{\mathrm{B}}^{\prime \prime \prime}-F_{\mathrm{A}}^{\prime \prime \prime}\right)\right)\right]\right\} \\
+ & G^{i j}\left\{A_{\mathrm{A}}^{i j}+2 y(1-y) A_{\phi}^{i j}+2 y A_{\tilde{\phi}}^{i j}+2\left(V_{\mathrm{A}}^{i j}+y V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)\right\} . \tag{3.62}
\end{align*}
$$

Equation (3.62) consists of four parts ( $1^{\text {st }}$ row; $2^{\text {nd }}$ and $3^{\text {rd }}$ row; $4^{\text {th }}-10^{\text {th }}$ row; last row).

- The first part represents the energy of an atom $\alpha$ in an undeformed, homogeneous (i.e., without concentration gradients) solid, according to $\mathbb{F}_{0}^{\text {chem }}$ in Eq. (3.61).
- The second part denotes the elastic energy $\mathbb{F}_{0}^{\text {mech }}$ of a mixture with particle concentration $y$.
- The third part can be related to the HGCs. Note that in Eq. (3.62) only derivatives $\nabla_{k l}^{2} y$ occur. A substitution to $\nabla_{k l}^{2} c$ will later allow the identification of $a^{k l}$ and $b^{k l}$ of Eq. (3.60).
- The last part stands for the equilibrium condition of a binary mixture A-B (minimum of energy), namely $\partial E_{\alpha} /\left.\partial G^{i j}\right|_{G^{i j}=0, y=y^{\text {eq }}}=0 \Rightarrow A_{\mathrm{A}}^{i j}+2 y(1-y) A_{\phi}^{i j}+$ $2 y A_{\tilde{\phi}}^{i j}+2\left(V_{\mathrm{A}}^{i j}+y V_{\Delta}^{i j}\right)\left(F_{\mathrm{A}}^{\prime}+y\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)=0$. By knowing the equilibrium concentration $y^{\text {eq }}$ this condition can be used to obtain the equilibrium nearest neighbor distance $R$ in the different equilibrium phases.

At this point it should be mentioned that all atomistic considerations are performed with respect to the particle concentration $y$. In order to identify the quantities in the EDE, cf., Eq. (2.145/4.53), we have to switch to mass concentrations c. Following the arguments of Appendix B. 1 we finally find:
$\diamond$ equilibrium condition:

$$
\begin{equation*}
A_{\mathrm{A}}^{i j}+2 y(c)(1-y(c)) A_{\phi}^{i j}+2 y(c) A_{\tilde{\phi}}^{i j}+2\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)=0 \tag{3.63}
\end{equation*}
$$

$\diamond$ Stiffness coefficients:

$$
\begin{align*}
K^{i j k l}(c)= & \frac{1}{\Omega_{0}^{\alpha}}\left[2 B_{\mathrm{A}}^{i j k l}+4 y(c)(1-y(c)) B_{\phi}^{i j k l}+4 y(c) B_{\dot{\phi}}^{i j k l}\right. \\
& +4\left(W_{\mathrm{A}}^{i j k l}+y(c) W_{\triangle}^{i j k l}\right)\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right) \\
& \left.+4\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y(c) V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right] \tag{3.64}
\end{align*}
$$

$\diamond$ Higher gradient coefficients:

$$
\begin{align*}
a^{m n}\left(c, G^{p q}\right) & =-\delta(c) \mathrm{M}^{(2)}(c) \mathbb{H}^{m n}\left(c, G^{p q}\right)  \tag{3.65}\\
b^{m n}\left(c, G^{p q}\right) & =\delta(c) \mathrm{M}^{(1)}(c) \mathbb{H}^{m n}\left(c, G^{p q}\right)  \tag{3.66}\\
A^{m n}\left(c, G^{p q}\right) & =\frac{\partial a^{m n}\left(c, G^{p q}\right)}{\partial c}+b^{m n}\left(c, G^{p q}\right) \tag{3.67}
\end{align*}
$$

with

$$
\begin{align*}
& \delta(c)=\frac{\rho_{0}}{m_{H} M(c)}, \\
& \mathrm{M}^{(1)}(c)=\frac{2 M_{\mathrm{A}} M_{\mathrm{B}}\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right)}{\left[M_{\mathrm{B}}-\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right) c\right]^{3}}, \quad \mathrm{M}^{(2)}(c)=\frac{M_{\mathrm{A}} M_{\mathrm{B}}}{\left[M_{\mathrm{B}}-\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right) c\right]^{2}},  \tag{3.68}\\
& \mathbb{H}^{m n}\left(c, G^{p q}\right)=\frac{1}{4}\left((1-2 y(c)) g_{\phi}^{m n}+g_{\tilde{\phi}}^{m n}\right)+\frac{1}{2} \bar{\rho}_{\triangle}^{m n}\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right) \\
& +\frac{1}{2} G^{i j}\left[(1-2 y(c)) A_{\phi}^{i j m n}+A_{\tilde{\phi}}^{i j m n}+2 V_{\triangle}^{i j m n}\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)\right. \\
& \left.\quad+2 \bar{\rho}_{\triangle}^{m n}\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right] \\
& +\frac{1}{2} G^{i j} G^{k l}\left[(1-2 y(c)) B_{\phi}^{i j k l m n}+B_{\tilde{\phi}}^{i j k l m n}\right. \\
& \quad+2 W_{\triangle}^{i j k l m n}\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)+2 \bar{\rho}_{\triangle}^{m n}\left(W_{\mathrm{A}}^{i j k l}+y(c) W_{\triangle}^{i j k l}\right) \times \\
& \quad \times\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)+2 V_{\triangle}^{k l m n}\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right) \\
& \quad+2 V_{\triangle}^{i j m n}\left(V_{\mathrm{A}}^{k l}+y(c) V_{\Delta}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right) \\
& \left.\quad+2 \bar{\rho}_{\triangle}^{m n}\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y(c) V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime \prime}-F_{\mathrm{A}}^{\prime \prime \prime}\right)\right)\right] \tag{3.69}
\end{align*}
$$

Recall that all atomistic quantities refer to arguments $R_{\alpha \beta}^{2}$ and $\bar{\rho}_{a v}$, respectively. In the following section we consider the specific binary alloy $\mathrm{Ag}-\mathrm{Cu}$ and will explicitly determine the stiffness and the higher gradient coefficients.

### 3.5 Application to the Ag-Cu System

In what follows we choose $y \equiv y_{\mathrm{Cu}}\left(c \equiv c_{\mathrm{Cu}}\right)$ and consider the solid eutectic binary alloy Ag-Cu at 1000 Kelvin ( $y_{\text {eut }}=0.41, c_{\text {eut }}=0.29, T_{\text {eut }} \approx 1052$ Kelvin $)$ which, from a technological point of view, serves as a brazing material. Two different equilibrium phases are observed, the $\alpha$ - and the $\beta$-phase, with the equilibrium concentrations $c_{\alpha}$ and $c_{\beta}$, respectively ( $c f$., Fig. 1.3 (lower left)). Fig. 3.4 shows the Helmholtz free energy density curve ${ }^{4},(\rho \varphi)(c)$, at 1000 Kelvin. It was obtained from a commercial database, [83]. By means of the common tangent rule construction the following

[^16]equilibrium concentrations $c_{\alpha / \beta}$ were determined:
\[

$$
\begin{align*}
& c_{\alpha}=0.063 \quad \Leftrightarrow \quad y_{\alpha}=0.102,  \tag{3.70}\\
& c_{\beta}=0.945 \quad \Leftrightarrow \quad y_{\beta}=0.967 . \tag{3.71}
\end{align*}
$$
\]

Moreover both species Ag and Cu as well as the random alloy $\mathrm{Ag}-\mathrm{Cu}$ form a simple Face-Centered-Cubic (FCC) lattice so that this material is particularly suited for our atomistic investigations performed at the two equilibrium concentrations, $c_{\alpha / \beta}$. Before we turn to the fitting procedure some remarks, assumptions, and interpretations in context with Eq. (3.62) will be made which are required for further investigations:

- $E_{\alpha}$ stands for the energy of an atom $\alpha$ in a binary lattice where two types of atoms (A and B) and three types of interactions (A-A, B-B, A-B) are possible.
- Independently of these different interactions and atom-types it is assumed that only one equilibrium distance $R$ to the nearest neighbors can be found in the lattice ${ }^{5}$. Indeed, this fact represents a serious assumption and is put up for discussion.
- All quantities of the right hand side of Eq. (3.62): $g_{\mathrm{AA} / \phi / \tilde{\phi}}, B_{\mathrm{A} / \phi / \tilde{\phi}}^{i j k l}, F_{\mathrm{A} / \mathrm{B}}, F_{\mathrm{A} / \mathrm{B}}^{\prime}$, $F_{\mathrm{A} / \mathrm{B}}^{\prime \prime}, F_{\mathrm{A} / \mathrm{B}}^{\prime \prime \prime}, V_{\mathrm{A} / \Delta}^{i j}, W_{\mathrm{A} / \Delta}^{i j k l}$, etc., can be calculated from the pure substances A and B. The "combination" of these quantities according to Eq. (3.62) in terms of $y,(1-y), \nabla_{m n}^{2} y$, etc. is interpreted as a suitable average describing the energy of an arbitrary particle in the mixture A-B.

The second bullet point gives rise to the question of how to find the equilibrium nearest neighbor distance of a given phase (mixture) with the equilibrium concentration $c^{\text {eq }}$. In this context we can revert to the equilibrium condition given by Eq. (3.63), provided that $c^{\text {eq }}$ is known (e.g., from experiments).

For the sake of transparency I will now give an overview of all procedures required to obtain the different EAM potentials, the stiffness and the higher gradient coefficients: (1) The EAM potentials for the pure substances


Figure 3.4: Helmholtz free energy density $\mathbb{F}_{0}^{\text {chem }}(c)$ for $\mathrm{Ag}-\mathrm{Cu}$ at 1000 Kelvin. Ag and Cu are fitted in terms of $R_{\alpha \beta}^{2}$. (2) We calculate the stiffness coefficients for the pure substances and compare them with experimental results (for the purpose of checking). (3) An exploitation of the equilibrium condition is performed in order to determine the nearest neighbor distances of

[^17]the $\alpha$ - and $\beta$-phase in Ag - Cu at 1000 K . (4) The stiffness coefficients of the different phases $K_{\alpha / \beta}^{i j k l}$ are determined and the pure-substance-limit (i.e., for Ag : $\lim c^{\alpha / \beta}=0$ and for $\mathrm{Cu}: \lim c^{\alpha / \beta}=1$ ) is performed. (5) The HGCs in the $\alpha$ - and $\beta$-phases and as functions of the concentration are calculated. (6) The phase-diagram of $\mathrm{Ag}-\mathrm{Cu}$ is constructed and the results are compared with measurements in order to emphasize the "quality" of the predicted HGCs.

### 3.5.1 The Fitting Procedure for Ag and Cu

Recall the advantages of the use of potentials in terms of $r_{\alpha \beta}^{2}$ or $R_{\alpha \beta}^{2}$, respectively as outlined in Section 3.3.1 For this reason we modify Johnson's functional representation from Eq. (3.3) as follows:

$$
\begin{equation*}
\rho\left(r^{2}\right)=\rho_{\mathrm{e}} \exp \left[-\beta\left(\frac{r^{2}}{R^{2}}-1\right)\right] \quad, \quad \phi\left(r^{2}\right)=\phi_{\mathrm{e}} \exp \left[-\gamma\left(\frac{r^{2}}{R^{2}}-1\right)\right] \tag{3.72}
\end{equation*}
$$

The symbols $r$ and $R$ denote the nearest neighbor distance in the deformed and in the undeformed lattice and, in an FCC ensemble, are given by $a / \sqrt{2}$ or $a_{\mathrm{e}} / \sqrt{2}(c f$., Fig. 3.2). Moreover the following relations hold:

$$
\begin{equation*}
\bar{\rho}\left(r^{2}\right)=12 \rho\left(r^{2}\right), \quad \bar{\rho}_{\mathrm{e}}=12 \rho_{\mathrm{e}} \quad, \quad \frac{1}{2} \sum_{\beta} \phi\left(r^{2}\right)=6 \phi\left(r^{2}\right), \quad 6 \phi_{\mathrm{e}} \equiv \Phi_{\mathrm{e}} \tag{3.73}
\end{equation*}
$$

In order to arrive at an explicit relation for the embedding function $F(\bar{\rho})$ analogously to Eq. (3.8) we follow the strategy explained in Section 3.2.2 and use the following inversions:

$$
\begin{equation*}
\frac{r}{R}=\sqrt{1-\frac{1}{\beta} \ln \frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}} \quad, \quad \frac{\phi}{\phi_{\mathrm{e}}}=\left(\frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}\right)^{\frac{\gamma}{\beta}} . \tag{3.74}
\end{equation*}
$$

By means of the universal function of state $E(a)$ from Section 3.2.2 and Eq. (3.74) the following result is obtained:

$$
\begin{align*}
F(\bar{\rho})= & -E_{\text {sub }}\left[1+\alpha\left(\sqrt{1-\frac{1}{\beta} \ln \frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}}-1\right)\right] \times \\
& \times \exp \left[-\alpha\left(\sqrt{1-\frac{1}{\beta} \ln \frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}}-1\right)\right]-\Phi_{\mathrm{e}}\left(\frac{\bar{\rho}}{\bar{\rho}_{\mathrm{e}}}\right)^{\frac{\gamma}{\beta}} \tag{3.75}
\end{align*}
$$

with $\alpha=3 \sqrt{\frac{\kappa \Omega_{0}}{E_{\text {sub }}}}$.

In what follows we focus on the pure substances Ag and Cu as well as on the binary alloy $\mathrm{Ag}-\mathrm{Cu}$ (silver-copper). In the case of the pure materials the following functions must be determined: $\phi_{\mathrm{AgAg}}, \phi_{\mathrm{CuCu}}, \rho_{\mathrm{Ag}}\left(=1 / 12 \bar{\rho}_{\mathrm{Ag}}\right), \rho_{\mathrm{Cu}}\left(=1 / 12 \bar{\rho}_{\mathrm{Cu}}\right), F_{\mathrm{Ag}}\left(\bar{\rho}_{\mathrm{Ag}}\right)$, and $F_{\mathrm{Cu}}\left(\bar{\rho}_{\mathrm{Cu}}\right)$. Thus for both pure components five parameters must be adjusted, namely $\alpha, \beta, \gamma, \phi_{\mathrm{e}}, \rho_{\mathrm{e}}$. Consequently ten parameters are unknown. Note that the interaction between an Ag and a Cu nucleus, i.e., $\phi_{\mathrm{AgCu}}$, follows directly from considering the pure species Ag and Cu (cf., Eq. (3.4)). For the fitting procedure the following ten experimental parameters of both substances are used:

1. Voigt average of the shear modulus $G$
2. bulk modulus $\kappa$
3. sublimation energy $E_{\text {sub }}$ (with respect to one particle)
4. (unrelaxed) vacancy formation energy $E_{\text {uvf }}$
5. (equilibrium) lattice parameter $a_{\mathrm{e}}$
$\alpha$ is already given by Eq. $(3.8)_{2}$, i.e., it only remains to determine $\beta, \gamma, \phi_{\mathrm{e}}$, and $\rho_{\mathrm{e}}$.

## a. Determination of $\phi_{\mathrm{e}}$ and $\rho_{\mathrm{e}}$

Following Johnson in [68] the sublimation energy per atom (i.e., the cohesive energy) of an arbitrary atom is represented by the nuclei-nuclei interactions with its neighbors: $E_{\text {sub }}=\frac{1}{2} \cdot 12 \cdot \phi\left(r^{2}\right)$. Hence it follows for equilibrium:

$$
\begin{equation*}
\phi_{\mathrm{e}}=\frac{E_{\text {sub }}}{6} . \tag{3.76}
\end{equation*}
$$

From the physical point of view it is plausible to establish that $\rho_{\mathrm{e}} \propto 1 / \Omega_{0}$ and $\rho_{\mathrm{e}} \propto E_{\text {sub }}$ and, consequently, we simply write:

$$
\begin{equation*}
\rho_{\mathrm{e}}=\frac{E_{\mathrm{sub}}}{\Omega_{0}} . \tag{3.77}
\end{equation*}
$$

The last two equations represent two relations for the unknown material parameters $\phi_{\mathrm{e}}$ und $\rho_{\mathrm{e}}$.

## b. Determination of $\beta$ and $\gamma$

The starting point to obtain these quantities are the equations for the unrelaxed vacancy formation energy $E_{\text {uvf }}$ and the Voigt average of the shear modulus $G$ :

$$
\begin{align*}
E_{\mathrm{uvf}} & =-\frac{1}{2} \sum_{\beta=1}^{12} \phi\left(r^{2}\right)-\sum_{\beta=1}^{12} F\left[12 \rho\left(r^{2}\right)\right]+\sum_{\beta=1}^{12} F\left[11 \rho\left(r^{2}\right)\right]  \tag{3.78}\\
G & =\frac{1}{5}\left(3 K^{2323}+2 K^{*}\right) \quad, \quad K^{*}=\frac{1}{2}\left(K^{1111}-K^{1122}\right) \tag{3.79}
\end{align*}
$$

where $K^{1111}, K^{1122}$, and $K^{2323}$ denote the elastic constants of the forth order stiffness matrix. These constants are characterized by derivatives of the energy expression of a solid (Eq. (3.2)). Recall that for the stiffness $K^{i j k l}$ of a pure substance A (cf., Eq. (3.28)) we have:

$$
\begin{equation*}
K_{\mathrm{A}}^{i j k l}=\frac{1}{\Omega_{0}^{\mathrm{A}}}\left[2 B_{\mathrm{AA}}^{i j k l}+4 F_{\mathrm{A}}^{\prime}\left(\bar{\rho}_{\mathrm{A}}^{0}\right) W_{\mathrm{A}}^{i j k l}+4 F_{\mathrm{A}}^{\prime \prime}\left(\bar{\rho}_{\mathrm{A}}^{0}\right) V_{\mathrm{A}}^{i j} V_{\mathrm{A}}^{k l}\right] \tag{3.28a}
\end{equation*}
$$

with the definitions:

$$
\begin{align*}
\bar{\rho}_{\mathrm{A}}^{0} & =\sum_{\beta} \rho_{\mathrm{A}}\left(R_{\alpha \beta}^{2}\right) \quad, \quad B_{\mathrm{AA}}^{i j k l}=\sum_{\beta} \phi_{\mathrm{AA}}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l},  \tag{3.80}\\
V_{\mathrm{A}}^{i j} & =\sum_{\beta} \rho_{\mathrm{A}}^{\prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j}, \quad W_{\mathrm{A}}^{i j k l}=\sum_{\beta} \rho_{\mathrm{A}}^{\prime \prime}\left(R_{\alpha \beta}^{2}\right) R_{\alpha \beta}^{i} R_{\alpha \beta}^{j} R_{\alpha \beta}^{k} R_{\alpha \beta}^{l},  \tag{3.81}\\
F_{\mathrm{A}}^{\prime} & =\left.\frac{\partial F_{\mathrm{A}}}{\partial \bar{\rho}_{\mathrm{A}}}\right|_{\bar{\rho}_{\mathrm{A}}=\bar{\rho}_{\mathrm{A}}^{0}}, \quad F_{\mathrm{A}}^{\prime \prime}=\left.\frac{\partial^{2} F_{\mathrm{A}}}{\partial \bar{\rho}_{\mathrm{A}}^{2}}\right|_{\bar{\rho}_{\mathrm{A}}=\bar{\rho}_{\mathrm{A}}^{0}}, \quad \phi_{\mathrm{AA}}^{\prime \prime}=\left.\frac{\partial^{2} \phi_{\mathrm{AA}}}{\partial\left(r_{\alpha \beta}^{2}\right)^{2}}\right|_{r_{\alpha \beta}^{2}=R_{\alpha \beta}^{2}},  \tag{3.82}\\
\rho_{\mathrm{A}}^{\prime} & =\left.\frac{\partial \rho_{\mathrm{A}}}{\partial r_{\alpha \beta}^{2}}\right|_{r_{\alpha \beta}^{2}=R_{\alpha \beta}^{2}}, \quad \rho_{\mathrm{A}}^{\prime \prime}=\left.\frac{\partial^{2} \rho_{\mathrm{A}}}{\partial\left(r_{\alpha \beta}^{2}\right)^{2}}\right|_{r_{\alpha \beta}^{2}=R_{\alpha \beta}^{2}}, \tag{3.83}
\end{align*}
$$

where $r_{\alpha \beta}^{2}$ or $R_{\alpha \beta}^{2}$ represent the distance between the atoms $\alpha$ and $\beta$ and can be identified with $r^{2}$ or $R^{2}$ in the nearest neighbor model.

Relation (3.28a) for the elastic constants can be used in Eq. (3.79) 1,2 . Then together with the parameterizations (3.72,3.73,3.75) it follows that (cf., Appendix B.2):

$$
\begin{equation*}
G=\frac{8}{5} \frac{\phi_{\mathrm{e}} \gamma(\gamma-\beta)}{\Omega_{0}} \tag{3.84}
\end{equation*}
$$

In a similar manner it is possible to approximate the unrelaxed vacancy formation energy $E_{\text {uvf }}$ in Eq. (3.78) by (cf., Appendix B.2):

$$
\begin{equation*}
E_{\mathrm{uvf}} \approx \frac{15}{4} \frac{G \Omega_{0}}{\gamma \beta}=6 \phi_{\mathrm{e}} \frac{\gamma-\beta}{\beta} \tag{3.85}
\end{equation*}
$$

The last two relations represent two equations for $\beta$ and $\gamma$. As input we use the Voigt average of the shear modulus and the unrelaxed vacancy formation energy. Using now Eqs. (3.8) $)_{2}$, (3.76), (3.77), (3.84), and (3.85), we can determine all parameters for Ag and Cu . The experimental data required during this procedure are compiled in Table 3.1, [68]:

Table 3.1: Experimental data for Ag and Cu .

| type of <br> atom | $\Omega_{0}$ in $\AA^{3}$ | $E_{\text {sub }}$ in eV | Input <br> $E_{\text {uvf }}$ in eV | $\Omega_{0} \kappa$ in eV | $\Omega_{0} G$ in eV |
| :---: | :--- | :--- | :--- | :--- | :--- |
| Ag | 17.10 | 2.85 | 1.10 | 11.10 | 3.61 |
| Cu | 11.81 | 3.54 | 1.30 | 10.17 | 4.05 |

In particular the following values can be used to obtain the second column of Table 3.1:

$$
\begin{array}{lll}
a_{\mathrm{Ag}}=4.09 \AA, & R_{\mathrm{Ag}}=2.89 \AA \quad, & R_{\mathrm{Ag}}^{2}=8.36 \AA^{2} \\
a_{\mathrm{Cu}}=3.61 \AA, & R_{\mathrm{Cu}}=2.56 \AA, & R_{\mathrm{Cu}}^{2}=6.53 \AA^{2} \tag{3.87}
\end{array}
$$

From this data the parameters and corresponding functions shown in Table 3.2 and in Figure 3.5 were obtained.

Table 3.2: Parameters for Ag and Cu calculated.

| type of atom | $\alpha$ | $\beta$ | $\gamma$ | $\phi_{\mathrm{e}}$ in eV | $\rho_{\mathrm{e}}$ in $\mathrm{eV} / \AA^{3}$ | $\bar{\rho}_{\mathrm{e}}$ in $\mathrm{eV} / \AA^{3}$ |
| :---: | :--- | :--- | :--- | :--- | :--- | :--- |
| Ag | 5.9205 | 2.9799 | 4.1300 | 0.4750 | 0.1672 | 2.0064 |
| Cu | 5.0849 | 2.9232 | 3.9966 | 0.5900 | 0.2998 | 3.5971 |

### 3.5.2 The Elastic Constants of Ag and Cu

With the fitted and illustrated functions from the last section it becomes possible to calculate the elastic constants for pure Ag and Cu according to Eq. (3.28a). The results are compiled in Table 3.3.

In comparison with the results obtained by means of pair potentials, [36], the discrepancy between experimental data and theoretically predicted values is visibly reduced and the agreement is reasonably good, the error ranging between $4.1 \%\left(K_{\mathrm{Ag}}^{1122}\right)$ and $9.4 \%\left(K_{\mathrm{Cu}}^{1111}\right)$. Moreover the Cauchy-Paradox ( $K^{1122}=K^{2323}$ ) no longer exists which is a considerable improvement.

nucleus-nulceus interactions between atoms of the same type

atomic electron-density for a silver and a copper atom

atomic energy for a silver and a copper atom in an FCC crystal as a function of $r^{2}$

Figure 3.5: Various functions relevant in Eq. $(3.72,3.75)$ and the resulting atomic energy $E_{\alpha}$ for Ag and Cu . Note that in the upper right picture $\phi_{\mathrm{AgCu}}=\phi_{\mathrm{CuAg}}$.

Table 3.3: Elastic constants for Ag and Cu in GPa. The values in parentheses stem from experiments, [71].

| $\underset{i j}{K_{\mathrm{Ag}}^{i j k l}} k l$ | 11 | 22 | 33 | 23 | 31 | 12 | $\underset{{ }_{i j}}{K_{\mathrm{Cu}}^{i j k l} k l}$ | 11 | 22 | 33 | 23 | 31 | 12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 11 | $\begin{aligned} & 132.6 \\ & (124) \end{aligned}$ | $\begin{gathered} 90.2 \\ (94) \end{gathered}$ | $\begin{aligned} & 90.2 \\ & (94) \end{aligned}$ | 0 | 0 | 0 | 11 | $\begin{aligned} & 183.7 \\ & (168) \end{aligned}$ | $\begin{aligned} & 115.1 \\ & (121) \end{aligned}$ | $\begin{aligned} & 115.1 \\ & (121) \end{aligned}$ | 0 | 0 | 0 |
| 22 | $\begin{aligned} & 90.2 \\ & (94) \end{aligned}$ | $\begin{aligned} & 132.6 \\ & (124) \end{aligned}$ | $\begin{aligned} & 90.2 \\ & (94) \end{aligned}$ | 0 | 0 | 0 | 22 | $\begin{aligned} & 115.1 \\ & (121) \end{aligned}$ | $\begin{aligned} & 183.7 \\ & (168) \end{aligned}$ | $\begin{aligned} & 115.1 \\ & (121) \end{aligned}$ | 0 | 0 | 0 |
| 33 | $\begin{aligned} & 90.2 \\ & (94) \end{aligned}$ | $\begin{aligned} & 90.2 \\ & (94) \end{aligned}$ | $\begin{aligned} & 132.6 \\ & (124) \end{aligned}$ |  | 0 | 0 | 33 | $\begin{aligned} & 115.1 \\ & (121) \end{aligned}$ | $\begin{aligned} & 115.1 \\ & (121) \end{aligned}$ | $\begin{aligned} & 183.7 \\ & (168) \end{aligned}$ | 0 | 0 | 0 |
| 23 | 0 | 0 | 0 | $\begin{aligned} & 42.4 \\ & (46) \end{aligned}$ | 0 | 0 | 23 | 0 | 0 | 0 | $\begin{aligned} & 68.7 \\ & (75) \end{aligned}$ | 0 | 0 |
| 31 | 0 | 0 | 0 | 0 | $\begin{aligned} & 42.4 \\ & (46) \end{aligned}$ | 0 | 31 | 0 | 0 | 0 | 0 | $\begin{aligned} & 68.7 \\ & (75) \end{aligned}$ | 0 |
| 12 | 0 | 0 | 0 | 0 | 0 | $\begin{aligned} & 42.4 \\ & (46) \end{aligned}$ | 12 | 0 | 0 | 0 | 0 | 0 | $\begin{aligned} & 68.7 \\ & (75) \end{aligned}$ |

### 3.5.3 The Alloy Ag-Cu I: Evaluation of the Equilibrium Condition

In this section we investigate the equilibrium condition shown in Eq. (3.63). We choose $\mathrm{A}=\mathrm{Ag}$ and $\mathrm{B}=\mathrm{Cu}$ and the corresponding equilibrium concentrations $c_{\alpha}=$ 0.063 and $c_{\beta}=0.945$ at 1000 K . Eq. (3.63) has a non-trivial solution only for the index-pair $i=j$ since in an FCC lattice the following relation holds for an arbitrary scalar function $f: \sum f\left(R^{2}\right) R^{i} R^{j}=0,(i \neq j)$ and $\sum f\left(R^{2}\right) R^{i} R^{i}=$ const, $(\forall i, j=$ $\{1,2,3\}$ ). Consequently we may plot the left side (for the index 11) of Eq. (3.63) as shown in Figure 3.6 (Left). The point of intersection with the abscissa defines the nearest neighbor distances in equilibrium of a crystal consisting of $\alpha$ or $\beta$ phase, respectively.

On the other side it is possible to vary the concentration in the equilibrium condition (3.63) and determine the nearest neighbor distance in equilibrium as a function of the concentration $c$. The corresponding points of intersection were determined for various discrete concentrations $c=0,0.05,0.10, \ldots, 0.90,0.95,1$, cf., Figure 3.6 (Right). As one can see the obtained values of $R$ are in good agreement with the weighed average $R=(1-c) R_{\mathrm{Ag}}+c R_{\mathrm{Cu}}$ which is represented by the continuous line in Figure 3.6 (Right). Especially for the $\alpha-$ and $\beta$-phase we can conclude:

$$
\begin{array}{lll}
R_{\alpha}=\sqrt{8.202} \AA=2.864 \AA \quad, & \Omega_{0}^{\alpha}=16.61 \AA^{3}, \\
R_{\beta}=\sqrt{6.631} \AA=2.575 \AA \quad, \quad \Omega_{0}^{\beta}=12.07 \AA^{3} . \tag{3.89}
\end{array}
$$



Figure 3.6: Illustration of different results following from the exploitation of the equilibrium condition (3.63).

### 3.5.4 The Alloy Ag-Cu II: The Stiffness Coefficients

Equation (3.64) allows us to obtain the stiffness coefficients as a function of the mass concentration $c$. Note that for every value of $c$ one must first evaluate the equilibrium condition in order to find the nearest neighbor distance $R$ in equilibrium. If $R$ is determined for a certain value of $c$ the unit cell volume $\Omega_{0}^{\alpha}$ occupied by an atom $\alpha$ as well as all quantities in (3.64) can be calculated. In order to investigate the stiffness of the different phases in $\mathrm{Ag}-\mathrm{Cu}$ we consider the equilibrium concentrations $c_{\alpha}$ and $c_{\beta}$ and analyze Eq. (3.64) at the distances $R_{\alpha}$ and $R_{\beta}$ presented in the previous section. The results are compiled in Table 3.4.

Table 3.4: Elastic constants in GPa predicted for the $\alpha$ - and $\beta$-phases in an Ag - Cu system at 1000 K .

| $K_{\alpha}^{i j k l}$ <br> $k j$ | 11 | 22 | 33 | 23 | 31 | 12 | $K_{\beta}^{i j k l}{ }_{i j}$ | 11 | 22 | 33 | 23 | 31 | 12 |
| :---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 11 | 135.3 | 92.2 | 92.2 | 0 | 0 | 0 | 11 | 181.3 | 115.2 | 115.2 | 0 | 0 | 0 |
| 22 | 92.2 | 135.3 | 92.2 | 0 | 0 | 0 | 22 | 115.2 | 181.3 | 115.2 | 0 | 0 | 0 |
| 33 | 92.2 | 92.2 | 135.3 | 0 | 0 | 0 | 33 | 115.2 | 115.2 | 181.3 | 0 | 0 | 0 |
| 23 | 0 | 0 | 0 | 43.1 | 0 | 0 | 23 | 0 | 0 | 0 | 66.0 | 0 | 0 |
| 31 | 0 | 0 | 0 | 0 | 43.1 | 0 | 31 | 0 | 0 | 0 | 0 | 66.0 | 0 |
| 12 | 0 | 0 | 0 | 0 | 0 | 43.1 | 12 | 0 | 0 | 0 | 0 | 0 | 66.0 |

On the other hand it is of interest to determine the stiffness of the alloy with an arbitrary mass concentration $c$. This problem is equivalent to a somewhat hypothetical experiment in which the atoms of a pure Ag lattice are successively replaced by Cu atoms. For this purpose we use the calculated equilibrium distances $R$ illustrated in

Figure 3.6, right, and the corresponding concentrations values. The (discrete) values of the calculated stiffness coefficients are shown as bullets in Figure 3.7. Obviously


Figure 3.7: Calculated elastic constants for $\mathrm{Ag}-\mathrm{Cu}$ as a function of the mass concentration $c$. The continuous line represents the linear interpolation between the values of pure Ag and Cu .
the pure-substance-limit is exactly fulfilled, i.e., the elastic constants lead to $K_{\text {Ag }}^{i j k l}$ and $K_{\mathrm{Cu}}^{i j k l}$ for $c=0$ or $c=1$, respectively.

### 3.5.5 The Alloy Ag-Cu III: The Higher Gradient Coefficients

In order to calculate the higher gradient coefficients for the strain-free case ( $\mathbf{G}=\mathbf{0}$, for simplicity) we use the reduced form of Eq. (3.69):

$$
\begin{equation*}
\mathbb{H}^{m n}\left(c, G^{i j}=0\right)=\frac{1}{4}\left[(1-2 y(c)) g_{\phi}^{m n}+g_{\grave{\phi}}^{m n}\right]+\frac{1}{2} \bar{\rho}_{\Delta}^{m n}\left[F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right] . \tag{3.90}
\end{equation*}
$$

Furthermore the following data can be compiled for eutectic $\mathrm{Ag}-\mathrm{Cu}$ :

$$
\begin{equation*}
\rho_{\mathrm{Ag}}=10490 \frac{\mathrm{~kg}}{\mathrm{~m}^{3}}, \quad \rho_{\mathrm{Cu}}=8920 \frac{\mathrm{~kg}}{\mathrm{~m}^{3}}, \quad \rho_{0}=9980.57 \frac{\mathrm{~kg}}{\mathrm{~m}^{3}}, \quad \delta(c)=\frac{\rho_{0}}{m_{H} M(c)} . \tag{3.91}
\end{equation*}
$$

By applying $c_{\alpha / \beta}$ and $R_{\alpha / \beta}$ in Eqs. $\left(3.65,3.66,3.90,3.91_{4}\right)$ one can determine the higher gradient coefficients $a^{i j}$ and $b^{i j}$ for the $\alpha$ - and $\beta$-phase (cf., Table 3.5). Moreover, together with the calculated nearest neighbor distances in equilibrium which depend on $c$ (Figure 3.6, Right) we calculate $a^{i j}(c)$ and $b^{i j}(c)$ (cf., Figure 3.8). Note that for an (undeformed) FCC crystal we have $a^{i j}=b^{i j}=0$ for $i \neq j$ and $a^{11}=a^{22}=a^{33}$ or $b^{11}=b^{22}=b^{33}$, respectively.

Table 3.5: Calculated higher gradient coefficients for the different $\alpha$ - and $\beta$-phases in eutectic Ag-Cu.

| phase | $a^{11}$ in N | $b^{11}$ in N | $A^{11}$ in N | $\partial A^{11} / \partial c$ in N |
| :---: | :--- | :--- | :--- | :--- |
| $\alpha$ | $4.59 \cdot 10^{-11}$ | $6.14 \cdot 10^{-11}$ | $1.55 \cdot 10^{-10}$ | $7.34 \cdot 10^{-11}$ |
| $\beta$ | $1.23 \cdot 10^{-10}$ | $1.03 \cdot 10^{-10}$ | $1.88 \cdot 10^{-10}$ | $2.86 \cdot 10^{-11}$ |

For the determination of $A_{\alpha / \beta}^{i j}$ or (more generally) $A^{i j}(c)$ and the corresponding derivative one has to find a closed form expression for the equilibrium distances $R_{\alpha / \beta}=R\left(c_{\alpha / \beta}\right)$ or $R=R(c)$ first. Note that the derivatives $\partial a^{i j} / \partial c, \partial^{2} a^{i j} / \partial c^{2}$ and $\partial b^{i j} / \partial c$ must be calculated and evaluated at the equilibrium distances $R$ which also depend on $c$. Here we want to use the numerically obtained results from Section 3.5.3, i.e.,

$$
\begin{equation*}
R(c) \approx(1-c) R_{\mathrm{Ag}}+c R_{\mathrm{Cu}} \tag{3.92}
\end{equation*}
$$

Now we can evaluate $A_{\alpha / \beta}^{i j}$ (cf., Table 3.5) as well as $A^{i j}(c)$ and the corresponding derivatives with respect to $c(c f$., Figure 3.8). Analogously we have for FCC crystals $A^{i j}=0$ for $i \neq j$ and $A^{11}=A^{22}=A^{33}$ for $i=j$.

Eqs. (3.65-3.69) also allow the calculation of the HGCs as functions of the mass concentration $c$ and of the six independent coefficients of the strain tensor $G^{i j}=G^{j i}$. However, for a graphical illustration of these dependencies we consider the following two strain states:
i) isotropic strains, i.e.:

$$
\begin{equation*}
G^{i j} \simeq \varepsilon^{i j}=\varepsilon \cdot \delta^{i j} \tag{3.93}
\end{equation*}
$$

In this case the calculated HGCs have the following isotropic form (for FCC structures):

$$
\Xi^{i j}=\left(\begin{array}{ccc}
\Xi^{11} & 0 & 0  \tag{3.94}\\
0 & \Xi^{11} & 0 \\
0 & 0 & \Xi^{11}
\end{array}\right) \quad \text { with } \quad \Xi=\{a, b, A\}
$$



Figure 3.8: Higher gradient coefficients calculated for $\mathrm{Ag}-\mathrm{Cu}$ as a function of the mass concentration $c$ (strain free case).
ii) so-called "line" strains, i.e.:

$$
G^{i j} \simeq \varepsilon^{i j}=\varepsilon \cdot \delta^{i 1} \delta^{j 1} \delta^{i j}=\left(\begin{array}{ccc}
\varepsilon & 0 & 0  \tag{3.95}\\
0 & 0 & 0 \\
0 & 0 & 0
\end{array}\right)
$$

As we will see in the next Chapter the assumption of such a strain state is very convenient for the investigation of the EDE in one dimension. In particular we will see, that the restriction on "line" strains allows to find a closed expression for the strain field $\varepsilon\left(X^{i}, t\right)$ within the multiphase material.
In contrast to item (i) the calculated HGCs are of the following non-isotropic form:

$$
\Xi^{i j}=\left(\begin{array}{ccc}
\Xi^{11} & 0 & 0  \tag{3.96}\\
0 & \Xi^{22} & 0 \\
0 & 0 & \Xi^{22}
\end{array}\right) \quad \text { with } \quad \Xi=\{a, b, A\}
$$

Figure 3.9 shows the calculated HGCs w.r.t. the isotropic strain state in item (i). Here we calculated the HGCs for the discrete values of $\varepsilon=0.2,0.15,0.1,0.05,0.0$, $-0.05,-0.1,-0.15$, and -0.2 and as continuous functions of the mass concentration $c$. Figure 3.10 illustrates the according curves for the line strain state of item (ii).


Figure 3.9: Higher gradient coefficients calculated for $\mathrm{Ag}-\mathrm{Cu}$ as a function of the mass concentration $c$ and of the strains $\varepsilon^{i j}=\varepsilon \cdot \delta^{i j}$ (isotropic strains).

Obviously, the HGCs are not symmetric w.r.t. positive (i.e., tensile loading) and negative (i.e., pressure loading) strains. This asymmetry directly influent the EDE and, consequently, it is possible to separately investigate the impact of positive and negative loading regimes on the phase evolution process.

Furthermore it is worth mentioning that the range $\varepsilon=-0.2, \ldots,+0.2$ was chosen ad hoc, in order to illustrate the strain-dependency of the HGCs. Here the "middle curves" for $\varepsilon=0$ in Figure 3.9 and 3.10 agree with the corresponding curves in Figure 3.8. However, the atomistic calculations leading the graphs in Figures 3.8-3.10 are extremely time-consuming. Therefore it is reasonable - in particular under the background of the numerical simulation of the EDE - to perform a polynomial fit of the HGC functions (cf., next Chapter). However, in order to distinguish between tensile and pressure loading within the simulations the fit procedure must be performed separately for positive and negative strains.


Figure 3.10: Higher gradient coefficients calculated for $\mathrm{Ag}-\mathrm{Cu}$ as a function of the mass concentration $c$ and of the strains $\varepsilon^{i j}=\varepsilon \cdot \delta^{i 1} \delta^{j 1} \delta^{i j}$ (line strains).

### 3.6 Construction of the Phase Diagram

In order to point out the reliability of the predicted stiffness coefficients and the HGCs we want to calculate finally the equilibrium particle concentrations $y_{\alpha / \beta}$ for different temperatures using the EAM and compare them with experimental data. The resulting phase diagram represents the coexisting phases in the binary alloy at different temperatures.

In principle, Eq. (2.127) and the atomistic energy expression in Eq. (3.62) allow for the calculation of the chemical potentials, which incorporate a local thermomechanical stress field. By means of the jump conditions at the interface between the $\alpha$ - and $\beta$-phase, [34], the equilibrium concentrations $y_{\alpha / \beta}$ can be calculated. However, for convenience we want to neglect in the following considerations any mechanical contributions to the chemical potentials $\mu_{\mathrm{Ag} / \mathrm{Cu}}$. Consequently, the subsequent formalism relies on the following jump conditions: $\left[\left[\mu_{\mathrm{Ag} / \mathrm{Cu}}\right]\right]=0$ and $\left[\left[\mu_{\mathrm{Cu}}-\mu_{\mathrm{Ag}}\right]\right]=0$ with $[[\diamond]]=\diamond^{\beta}-\diamond^{\alpha},[39]$.

From (phenomenological) thermodynamics of mixtures it is well-known that the equilibrium concentrations of a binary mixture can be constructed from the GibBS free energy $g(y, T)$, (pressure $p=$ const) for a given temperature by applying the Maxwell tangent construction. In this technique the derivatives of the $g(y, T)$-curve at the equilibrium concentrations $y_{\alpha / \beta}$ must be identical to the slope of the common tangent.

Starting from the atomistic point-of-view the GibBS free energy $g(y, T)$ per atom can be identified according to Eq. (3.62) as follows:

$$
\begin{align*}
g(y, T) \equiv & E_{\alpha}-T s=\frac{1}{2} g_{\mathrm{AA}}+y(1-y) g_{\phi}+y g_{\tilde{\phi}}+F_{\mathrm{A}}+y\left(F_{\mathrm{B}}-F_{\mathrm{A}}\right)-T s \\
= & (1-y)\left(6 \phi_{\mathrm{AA}}\left(R^{2}\right)+F_{\mathrm{A}}\left(\bar{\rho}_{a v}\left(R^{2}\right)\right)\right)+y\left(6 \phi_{\mathrm{BB}}\left(R^{2}\right)+F_{\mathrm{B}}\left(\bar{\rho}_{a v}\left(R^{2}\right)\right)\right) \\
& +12 y(1-y) g_{\phi}\left(R^{2}\right)+k_{\mathrm{B}} T(y \ln y+(1-y) \ln (1-y)) \tag{3.97}
\end{align*}
$$

In this expression the temperature-dependence of $g(y, T)$ is only characterized by the entropic part, namely by $-T s$. Moreover the Maxwell tangent construction reads:

$$
\begin{equation*}
\left.\frac{\partial g(y, T)}{\partial y}\right|_{y=y_{\alpha}}=\left.\frac{\partial g(y, T)}{\partial y}\right|_{y=y_{\beta}}=\frac{g\left(y_{\beta}, T\right)-g\left(y_{\alpha}, T\right)}{y_{\beta}-y_{\alpha}} \tag{3.98}
\end{equation*}
$$

Note that in Eq. (3.97) all terms, i.e., $g_{\mathrm{AA}}, g_{\phi}, g_{\tilde{\phi}}$ and $F_{\mathrm{A} / \mathrm{B}}$ depend on the equilibrium nearest neighbor distance $R^{2}$ which is a function of the mass concentration $c(c f$. , Eq. (3.92)). In order to find $R=R(y)$ one can use the inverse relation $c=c(y)$ of Eq. (B.3):

$$
\begin{equation*}
c_{\mathrm{Cu}} \equiv c=\frac{m_{\mathrm{Cu}}}{m_{\mathrm{Cu}}+m_{\mathrm{Ag}}}=\frac{y M_{\mathrm{Cu}}}{y M_{\mathrm{Cu}}+(1-y) M_{\mathrm{Ag}}} . \tag{3.99}
\end{equation*}
$$

In the same manner one can analyze the GibBS free energy density $(\rho \psi)(c, T)=$ $g(y(c), T) / \delta(c)$ as a function of the mass concentration $c$. Then the resulting equilibrium concentrations are represented by $c_{\alpha / \beta}$ in the phase diagram. Both approaches are equivalent and $y$ can be transferred to $c$ through Eq. (3.99). At this point we want to investigate $g(y, T)$ and calculate the equilibrium concentrations $y_{\alpha / \beta}$ as well as the corresponding phase diagram in order to allow for a better comparison with experimental and literature data.

Figure 3.11 shows the particle-specific GibBs free energy for the temperature 1000 Kelvin following from Eq. (3.97) and the corresponding $\rho \psi$-curve ( $1^{\text {st }}$ row) as well as the relation $R(y)$ ( $2^{\text {nd }}$ row). Note that the $\rho \psi$-curves of Figure 3.4 and Figure


Figure 3.11: 1st row: Theoretical curves of $g(y, T)$ and $(\rho \psi)(c, T)$ for 1000 Kelvin including Maxwell's tangent (dashed line) and the constructed equilibrium points (dots). 2nd row: The nearest-neighbor-distance $R(y)$ for equilibrium and its deviation from linear interpolation (Vegard's law, dashed line).
3.11 can not directly be compared due to different zero points on the energy scale. Furthermore one can find a considerable deviation between $R(y)$ and Vegard's law. A transformation to $R(c)$ can remedy this shortcoming.

Evaluating Eq. (3.97) for different temperatures, in particular for 700, 800, 900, and 1000 Kelvin yields the curves illustrated in Figure 3.12 (1 $1^{\text {st }}$ row). In this viewgraph Maxwell's tangent was subtracted from the values of $g$. Thus the minima of these functions represent the equilibrium concentrations for the corresponding temperature.

Note that there are also minima on the right hand side of the curve, as emphasized in the close-up shown in the second picture. Furthermore the calculated and experimental equilibrium concentrations $y_{\alpha / \beta}$ and $c_{\alpha / \beta}$ are juxtaposed in Table 3.6. The resulting (theoretically determined) phase diagram is shown in Figure 3.12 ( $2^{\text {nd }}$ row, left). The full diagram on the right hand side is the one obtained from MTdata ${ }^{\mathrm{TM}}$, [83]. A comparison of the values in Table 3.6 as well as the theoretical and experimental phase diagram shows that the theoretically predicted equilibrium concentrations have qualitatively the same tendency as the experimental ones. Furthermore the absolute values of the $\alpha$-phase (left part of the phase diagram) are in good agreement but, nevertheless, the values of the $\beta$-phase are poorly reproduced.

Table 3.6: Calculated and experimental equilibrium concentrations for $\mathrm{Ag}-\mathrm{Cu}$ at different temperatures. The experimental data for 700, 800, 900 Kelvin stem from [94] and for 1000 Kelvin from [119].

| Temp. | predicted by EAM |  |  |  |  |  |  |  |
| :---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| in K | $y_{\alpha}$ | $y_{\beta}$ | $c_{\alpha}$ | $c_{\beta}$ | $y_{\alpha}$ | $y_{\beta}$ | $c_{\alpha}$ | $c_{\beta}$ |
| 700 | 0.024 | 0.999999 | 0.014 | 0.999999 | 0.015 | 0.993 | 0.0089 | 0.9882 |
| 800 | 0.039 | 0.999996 | 0.023 | 0.999994 | 0.033 | 0.986 | 0.0197 | 0.9765 |
| 900 | 0.056 | 0.999986 | 0.033 | 0.999976 | 0.063 | 0.976 | 0.0381 | 0.9599 |
| 1000 | 0.075 | 0.999957 | 0.045 | 0.999928 | 0.102 | 0.967 | 0.0627 | 0.9452 |

Let us abbreviate the difference of GibBS free energy $g(y, T)$ and Maxwells's tangent with $g^{*}(y, T)\left(c f\right.$., Figure 3.12, $1^{\text {st }}$ row) and the corresponding values of $(\rho \psi)(c, T)$ with $(\rho \psi)^{*}(c, T)$. In order to investigate the reason for the difference between the experimental and calculated equilibrium concentrations one can now compare $g^{*}(y, T=$ $1000 \mathrm{~K})$ as well as $(\rho \psi)^{*}(c, T=1000 \mathrm{~K})$ following from the atomistic calculations and from MTdata ${ }^{\mathrm{TM}}$. Moreover it is also possible to calculate the so-called excess enthalpy $g^{\text {ex }}$, the non-ideal heat of mixing, which can be obtained from the following relation:

$$
\begin{align*}
g(y, T)= & y g(y=0, T)+(1-y) g(y=1, T) \\
& +k_{\mathrm{B}} T(y \ln y+(1-y) \ln (1-y))+g^{\mathrm{ex}}(y, T) \tag{3.100}
\end{align*}
$$

Figure 3.13 shows the corresponding curves for 1000 Kelvin. Obviously the crucial value that determines the quality of the calculated phase diagram is the excess enthalpy $g^{\text {ex }}$. In particular, its asymmetry is the source of the asymmetry in the phase diagram related to the solid state and its absolute values compete with the entropic part -Ts and determine the horizontal position of the minima of $g^{\text {mix }}$. Thus values of $g^{\text {ex }}$ that are too large lead to a shift of the minima (and, consequently, of the equilibrium concentrations) in the vicinity of $y=0$ or $y=1$, respectively. This fact


Figure 3.12: 1 st row: The calculated GibBS free energy $g^{*}(y, T)$ for different temperatures $700,800,900,1000$ Kelvin. 2nd row, left: Calculated phase diagram of the solid phases in $\mathrm{Ag}-\mathrm{Cu}$ (filled and joined dots) vs. experimental data (unfilled dots). Right: The phase diagram generated by MTdata ${ }^{\mathrm{TM}}$.
is observable in our theoretical calculations where the calculated $g^{\text {ex }}$ is considerably larger than the experimental curve but, nevertheless, have the same magnitude and the same functional characteristics (asymmetry) as the other curves. The source of the deviation of $g^{\text {ex }}$ is due to the use of the calculated nearest neighbor distance $R$ in equilibrium, a measure for the relaxation of the lattice caused by different atom-types. This value can only be as realistic as the (fitted) EAM potentials because they enter the equilibrium condition used to find $R$. In spite of these shortcomings our phase diagram calculations qualitatively reproduce the experimental values and are of the same magnitude as literature data.


Figure 3.13: A comparison of the calculated functions $g^{*}(y, T=1000 \mathrm{~K}),(\rho \psi)^{*}(c, T=$ 1000 K ), and $g^{\mathrm{ex}}(y, T=1000 \mathrm{~K})$ with the corresponding functions from MTdata ${ }^{\mathrm{TM}}$ (dashed line).

### 3.7 Some Concluding Remarks about this Chapter

In this Chapter a microscopic theory was presented which allows for an atomistic identification of mechanical, thermodynamical, as well as thermo-mechanical material parameters in binary alloys. It is based on EAM potentials and results in an energy expression for an arbitrary atom $\alpha$, given by Eq. (3.62). Undoubtedly this equation represents the central element in the outlined procedure and is generally valid, i.e., it does not depend on the functional form of the EAM-functions.

By considering a binary (multiphase) mixture, here $\mathrm{Ag}-\mathrm{Cu}$, the equilibrium (atomic) nearest neighbor distance $R$, the stiffness coefficients, the higher gradient coefficients, and the (temperature-depending) equilibrium concentrations of the different phases can easily be calculated. Moreover it is also possible to determine these quantities as (continuous) functions of mass or particle concentrations, $c$ and $y$, respectively. Furthermore the equilibrium condition following from Eq. (3.62) represents the energy-minimization-principle and provides a theoretical tool for an estimate of lattice relaxations due to different atom-types in the lattice.

However, the main focus of this Chapter was the theoretical description of the HGCs, since so far the communicated data is mostly estimated or its origin is unclear. This
is why the existing data is questionable. In order to substantiate the reliability of the predicted HGCs we also determined the stiffness coefficients and constructed the phase diagram for the solid phases. Especially we chose the binary alloy $\mathrm{Ag}-\mathrm{Cu}$ to illustrate how the aforementioned parameters can be determined theoretically.

For the whole investigation the nearest neighbor model as proposed by Johnson, [67], was used. In this approach a very simple functional dependence for the EAM functions is considered by assuming only nearest neighbor interactions and s-orbitals for the electron densities. Nevertheless, the determined quantities, for instance the stiffness coefficients, are in good agreement with the experimental data. Only some of the calculated equilibrium concentrations in the phase diagram reproduce the experimental values inaccurately. It seems that the underlying assumptions, namely the neglect of lattice dynamics (vibrations), Johnson's parametrization, and the consideration of one equilibrium nearest neighbor distance, only allow a qualitative calculation of phase diagram data. For further improvement one could use other functional forms for the potentials, extensions of Johnson's model and/or one could consider lattice vibrations, [94]. One possibility is to consider more than just nearest-neighbor-interaction as suggested by Daw and Baskes in [29].

Moreover new modifications of EAM were developed in the last years in order to apply this method to other than FCC lattices, [5, 77]. As an example the Modified Embedded-Atom Method (MEAM) allows the investigation of BCC-metals, for instance Fe. HCP structures were also investigated successfully using EAM, [98]. Therefore, in principle, it is possible to determine the HGCs of more complex lattice structures using EAM/MEAM. Other applications of EAM, which could be interesting in the future, are simulations and investigations of fracture, plasticity behavior, impurities, surfaces, or grain boundaries.

In summary one can say that the predicted HGCs originated from a microscopic theory based on interatomic interactions are reliable as indicated by the quality of the stiffness coefficients and (despite of some deviations) by the phase diagram construction. Indeed, the value of $A^{i j}$ is close to those found in literature (e.g., [72], $A^{i j}=2 \cdot 10^{-10} \delta^{i j} \mathrm{~N}$ ), and it is considerably smaller than the corresponding results following from pairwise interactions, [36]. An investigation of the influence of the calculated HGCs on phase separation and the coarsening processes in binary alloys according to Eqs. $(2.145 / 4.53)$ will be given in the next Chapter.

## Chapter 4

## Numerical Simulations

The extended diffusion equation, Eq. (4.51/4.53), derived in Chapter 2 represents a nonlinear Partial Differential Equation (PDE) of fourth order for the concentration field $c\left(X^{i}, t\right)$, which generally reads, [15]:

$$
\begin{equation*}
F\left(c\left(X^{i}, t\right), \frac{\partial c\left(X^{i}, t\right)}{\partial t}, \frac{\partial^{m} c\left(X^{i}, t\right)}{\left(\partial X^{j}\right)^{m}}\right)=0 \quad, \quad m=\{1,2,3,4\} . \tag{4.1}
\end{equation*}
$$

In order to simulate the development of the concentration field within the multi-phase material one needs suitable numerical methods, especially for the numerical treatment of the spatial and time derivatives. To this end we apply in this work the method of Discrete Fourier Transforms (DFT) in combination with Finite Differences (FD), which allow to substitute the spatial derivatives by an algebraic expression, cf., [37]. The resulting (first order) Ordinary Differential Equation (ODE), viz.

$$
\begin{equation*}
\frac{\mathrm{d} \hat{c}}{\mathrm{~d} t}=f(\hat{c}, t) \quad, \quad(\text { general form }) \tag{4.2}
\end{equation*}
$$

can be solved by means of, e.g., One-Step-Time-Integration (OSTI) methods, such as an explicit Euler procedure. In the following some mathematical background of the required numerical methods will be presented.

### 4.1 Some Elements of Numerical Mathematics

### 4.1.1 Discrete Fourier Transforms and Spatial Discretization

We start with the introduction of the concept of the so-called Representative Volume Element (RVE), the side length of which, $2 \pi L$, must be chosen sufficiently large so


Figure 4.1: Left: Discretization of the representative volume element in the twodimensional case $(N=6)$. Right: Characterization of the microstructure by periodic continuation of RVE's.
that it contains sufficient information about the microstructure of the material. On the other hand it must also be sufficiently small in order to reproduce the different forms of the phases realistically after discretization of the RVE. Moreover, we postulate, that the microstructure of the material is characterized by the periodic continuation of the RVE's, cf., Figure 4.1 (Right).

Now we consider a discretization of the RVE by $N \in \mathbb{Z}$ (one dimension), $N \times N$ (two dimensions) or $N \times N \times N$ (three dimensions) equidistant grid points, cf., Figure 4.1 (Left). Consequently, the position vector, $X^{i}$, of an arbitrary material point within the RVE reads:

$$
X^{i}=\frac{2 \pi L}{N} \alpha^{i} \quad \text { with } \quad \alpha^{i} \stackrel{(3 \mathrm{D})}{=}\left(\begin{array}{c}
\alpha^{1}  \tag{4.3}\\
\alpha^{2} \\
\alpha^{3}
\end{array}\right) \wedge \quad \alpha^{1 / 2 / 3} \in\{0,1,2, \ldots, N-1\},
$$

where the grid point vector $\alpha^{i}$ identifies the position of an arbitrary grid point within the discrete grid-point-array, [91].

For a scalar function :

$$
\begin{align*}
c:\{0,1,2, \ldots, N-1\}^{3} & \rightarrow \mathbb{R} \\
\alpha^{i} & \mapsto c\left(\alpha^{i}\right) \tag{4.4}
\end{align*}
$$

with the following periodicity property:

$$
c\left(\alpha^{i}\right)=c\left(\alpha^{i}+N r^{i}\right) \quad \text { and } \quad r^{i} \stackrel{(3 \mathrm{D})}{=}\left(\begin{array}{l}
r^{1}  \tag{4.5}\\
r^{2} \\
r^{3}
\end{array}\right) \quad \wedge \quad r^{1 / 2 / 3} \in \mathbb{Z}
$$

the discrete Fourier transform $\hat{c}\left(k^{j}\right)=\mathfrak{F}\left[c\left(\alpha^{j}\right)\right]$ and the according inverse transform $c\left(\alpha^{j}\right)=\mathfrak{F}^{-1}\left[\hat{c}\left(k^{j}\right)\right]$ are defined as, [16, 91]:

$$
\begin{align*}
& \mathfrak{F}\left[c\left(\alpha^{j}\right)\right] \equiv \hat{c}\left(k^{j}\right) \stackrel{(\text { def })}{=} \frac{1}{N^{d / 2}} \sum_{\alpha^{1}=0}^{N-1} \ldots \sum_{\alpha^{d}=0}^{N-1} c\left(\alpha^{j}\right) \exp \left[\mathrm{i} \frac{2 \pi L}{N} k^{l} \alpha^{l}\right],  \tag{4.6}\\
& \mathfrak{F}^{-1}\left[\hat{c}\left(k^{j}\right)\right] \stackrel{(\text { def })}{=} \frac{1}{N^{d / 2}} \sum_{\alpha^{1}=0}^{N-1} \ldots \sum_{\alpha^{d}=0}^{N-1} \hat{c}\left(k^{j}\right) \exp \left[-\mathrm{i} \frac{2 \pi L}{N} k^{l} \alpha^{l}\right] \tag{4.7}
\end{align*}
$$

where $j \in\{1, \ldots, d\}$ and $d$ stands for the dimension, i.e., $d=1$ (one dimension), $d=2$ (two dimensions), or $d=3$ (three dimensions). Furthermore the symbol $k^{j}$ denotes analogously to $\alpha^{j}$ in real space - the discrete position vector in Fourier space and is often called the wave vector. For the one-dimensional case Eqs. (4.6) and (4.7) reduce to the following form:

$$
\begin{align*}
& \mathfrak{F}[c(\alpha)] \stackrel{(\text { def })}{=} \frac{1}{N^{1 / 2}} \sum_{\alpha=0}^{N-1} c(\alpha) \exp \left[\mathrm{i} \frac{2 \pi L}{N} k \alpha\right],  \tag{4.8}\\
& \mathfrak{F}^{-1}[\hat{c}(k)] \stackrel{(\text { def })}{=} \frac{1}{N^{1 / 2}} \sum_{\alpha=0}^{N-1} \hat{c}(k) \exp \left[-\mathrm{i} \frac{2 \pi L}{N} k \alpha\right] . \tag{4.9}
\end{align*}
$$

Following from the definition of the DFT the shift theorem holds:

$$
\begin{equation*}
\mathfrak{F}\left[c\left(\alpha^{j}+\beta^{j}\right)\right]=\exp \left[-\mathrm{i} \frac{2 \pi L}{N} \beta^{j} k^{j}\right] \cdot \mathfrak{F}\left[c\left(\alpha^{(j)}\right)\right] \tag{4.10}
\end{equation*}
$$

and for the one-dimensional case:

$$
\begin{equation*}
\mathfrak{F}[c(\alpha+\beta)]=\exp \left[-\mathrm{i} \frac{2 \pi L}{N} \beta k\right] \cdot \mathfrak{F}[c(\alpha)] \tag{4.11}
\end{equation*}
$$

which can be easily shown by means of Eqs. $(4.6,4.7),(4.8,4.9)$ and the constraint of periodicity in Eq. (4.5), [91].

For the numerical treatment of spatial derivatives of the scalar function $c\left(X^{i}, t\right)$ occurring in the EDE we replace the spatial derivatives by finite differences defined on an arbitrary discrete grid-point $\left(\alpha^{1}, \alpha^{2}, \alpha^{3}\right)=(k, l, m)$ :

$$
\begin{align*}
& \frac{\partial c\left(X^{i}\right)}{\partial X^{1}} \simeq \frac{\Delta c\left(\alpha^{i}\right)}{\Delta \alpha^{1}} \stackrel{(\text { def })}{=} \frac{c(k+1, l, m)-c(k-1, l, m)}{2 h} \\
& \frac{\partial c\left(X^{i}\right)}{\partial X^{2}} \simeq \frac{\Delta c\left(\alpha^{i}\right)}{\Delta \alpha^{2}} \stackrel{(\text { def })}{=} \frac{c(k, l+1, m)-c(k, l-1, m)}{2 h} \\
& \frac{\partial c\left(X^{i}\right)}{\partial X^{3}} \simeq \frac{\Delta c\left(\alpha^{i}\right)}{\Delta \alpha^{3}} \stackrel{(\text { def) }}{=} \frac{c(k, l, m+1)-c(k, l, m-1)}{2 h} \tag{4.12}
\end{align*}
$$

with $h=2 \pi L / N$. For the second derivatives the following finite differences approximation is used ${ }^{1}$ [17, 91]:

$$
\begin{align*}
& \frac{\partial^{2} c\left(X^{i}\right)}{\partial\left(X^{1}\right)^{2}} \simeq \frac{\Delta^{2} c\left(\alpha^{i}\right)}{\Delta\left(\alpha^{1}\right)^{2}} \stackrel{(\text { def })}{=} \frac{c(k+1, l, m)+c(k-1, l, m)-2 c(k, l, m)}{h^{2}} \\
& \frac{\partial^{2} c\left(X^{i}\right)}{\partial\left(X^{2}\right)^{2}} \simeq \frac{\Delta^{2} c\left(\alpha^{i}\right)}{\Delta\left(\alpha^{2}\right)^{2}} \stackrel{(\text { def })}{=} \frac{c(k, l+1, m)+c(k, l-1, m)-2 c(k, l, m)}{h^{2}} \\
& \frac{\partial^{2} c\left(X^{i}\right)}{\partial\left(X^{3}\right)^{2}} \simeq \frac{\Delta^{2} c\left(\alpha^{i}\right)}{\Delta\left(\alpha^{3}\right)^{2}} \stackrel{\text { (def) }}{=} \frac{c(k, l, m+1)+c(k, l, m-1)-2 c(k, l, m)}{h^{2}} \tag{4.13}
\end{align*}
$$

A transformation of the finite differences schemes in Eqs. (4.12) $)_{1,2,3}$ and (4.13) $)_{1,2,3}$ into Fourier space by means of the definitions in the Eqs. (4.6-4.9) yields the following algebraic relations for the spatial derivatives:

$$
\begin{align*}
\mathfrak{F}\left[\frac{\Delta c\left(\alpha^{i}\right)}{\Delta \alpha^{j}}\right] & =\mathfrak{F}\left[c\left(\alpha^{i}\right)\right] \cdot \xi_{j}^{(1)} \quad, \quad \xi_{j}^{(1)}=-\frac{\mathrm{i}}{h} \sin \left(\frac{2 \pi L}{N} k^{j}\right),  \tag{4.14}\\
\mathfrak{F}\left[\frac{\Delta^{2} c\left(\alpha^{i}\right)}{\Delta\left(\alpha^{j}\right)^{2}}\right] & =\mathfrak{F}\left[c\left(\alpha^{i}\right)\right] \cdot \xi_{j}^{(2)} \quad, \quad \xi_{j}^{(2)}=\frac{2}{h^{2}}\left[\cos \left(\frac{2 \pi L}{N} k^{j}\right)-1\right] . \tag{4.15}
\end{align*}
$$

The corresponding relations in one dimension read:

$$
\begin{align*}
\mathfrak{F}\left[\frac{\Delta c(\alpha)}{\Delta \alpha}\right] & =\mathfrak{F}[c(\alpha)] \cdot \xi^{(1)} \quad, \quad \xi^{(1)}=-\frac{i}{h} \sin \left(\frac{2 \pi L}{N} k\right)  \tag{4.16}\\
\mathfrak{F}\left[\frac{\Delta^{2} c(\alpha)}{\Delta \alpha^{2}}\right] & =\mathfrak{F}[c(\alpha)] \cdot \xi^{(2)} \quad, \quad \xi^{(2)}=\frac{2}{h^{2}}\left[\cos \left(\frac{2 \pi L}{N} k\right)-1\right] . \tag{4.17}
\end{align*}
$$

[^18]Eqs. (4.14-4.17) can be easily verified by applying the shift theorem of Eq. (4.10) for $\beta^{j}= \pm 1$ and by using Euler's relation $\exp [\mathrm{i} \alpha]=\cos \alpha+\mathrm{i} \sin \alpha$, [91].

As a consequence of these considerations one may conclude that it is useful to transform the EDE into Fourier space, in which the spatial derivatives of $c\left(X^{i}, t\right)$ in Eq. (4.53) can be approximate by the algebraic relations presented in Eqs. (4.14-4.17). Consequently the resulting EDE in Fourier space represents an ODE of the form:

$$
\begin{equation*}
\frac{\mathrm{d} \hat{c}^{j}(t)}{\mathrm{d} t}=f\left(\hat{c}^{j}(t)\right) \quad \text { with } \quad \hat{c}^{j}=\hat{c}\left(k^{j}\right)=\mathfrak{F}\left[c\left(\alpha^{j}\right)\right] \tag{4.18}
\end{equation*}
$$

which can be numerically solved by means of OSTI methods, [17].
However, it is worth mentioning, that the application of the Fourier transform in combination with the shift theorem presumes periodic boundary conditions for the concentration field $c\left(X^{i}, t\right)$ within the RVE. This assumptions is necessary due to the use of the relation (4.5) in order to establish the shift theorem and is in agreement with the periodic continuation of RVE's as illustrated in Figure 4.1 (Right).

### 4.1.2 One-Step-Time-Integration Methods

In order to explain the numerical solution of the ODE in Eq. (4.18) we consider the autonomous, one-dimensional form ${ }^{2}$ [18]:

$$
\begin{equation*}
\frac{\mathrm{d} \hat{c}}{\mathrm{~d} t}=f(\hat{c}) \tag{4.19}
\end{equation*}
$$

in which - according to the EDE - the time $t$ does not explicitly occur in the function $f$ on the right hand side.

The aim of OSTI methods is to successively construct the solution $\hat{c}\left(t_{i}+\Delta t\right)$ by starting from a known initial value $\hat{c}_{i}=\hat{c}\left(t_{i}\right)$ and applying the discrete time step $\Delta t$. To this end various procedures with different orders of accuracy exist. The most popular ones will be briefly explained in what follows.

## a. Explicit Methods

Euler Method In order to find a numerical solution of Eq. (4.19) we consider the initial condition $\hat{c}\left(t=t_{0}\right)=\hat{c}_{0}$ and discretize the time $t$ by $t_{k}=t_{0}+k \cdot \Delta t(k=$

[^19]


Figure 4.2: Left: Illustration of the explicit Euler approximation. Right: Correction of the slope according to the $v$. Heun procedure.
$1,2,3, \ldots$ ) using the equidistant time intervals $\Delta t$. The ODE is now approximated by finite differences as follows:

$$
\begin{equation*}
f(\hat{c})=\frac{\hat{c}(t+\Delta t)-\hat{c}(t)}{\Delta t} \quad \text { or } \quad \hat{c}(t+\Delta t)=\hat{c}(t)+\Delta t \cdot f(\hat{c}) \tag{4.20}
\end{equation*}
$$

Furthermore the approximation of the solution $\hat{c}_{i}=\hat{c}\left(t_{i}\right)$ is defined by $\eta_{i}$ with $\eta_{0} \stackrel{\text { deff }}{=}$ $\hat{c}_{0}$. Then the explicit Euler method is given by the formulae, [106]:

$$
\begin{equation*}
\eta_{i+1}=\eta_{i}+\Delta t \cdot f\left(\eta_{i}\right) \quad \text { and } \quad t_{i+1}=t_{i}+\Delta t \tag{4.21}
\end{equation*}
$$

or in a more general way:

$$
\eta_{i+1}=\eta_{i}+\Delta t \cdot \Gamma\left(\hat{c}_{i}, \Delta t\right) \quad \text { with }
$$

$$
\begin{equation*}
\text { EULER : } \Gamma\left(\hat{c}_{i}, \Delta t\right)=f\left(\hat{c}_{i}\right)=\mathrm{d} \hat{c}\left(t_{i}\right) / \mathrm{d} t \tag{4.22}
\end{equation*}
$$

i.e., in case of the Euler method the function $\Gamma$ is independent from $\Delta t$. Figure 4.2 (Left) illustrates the principle of this methods for the case of an arbitrary nonlinear monoton increasing function $\hat{c}(t)$.

The order of accuracy is typically quantified by the local error of discretization $\tau$. For this reason we define the difference quotient of the exact solution by:

$$
\boldsymbol{\Delta}(\hat{c}, \Delta t)=\left\{\begin{array}{cl}
\frac{\hat{c}(t+\Delta t)-\hat{c}(t)}{\Delta t} & \text { if } \Delta t \neq 0  \tag{4.23}\\
f(\hat{c}) & \text { if } \Delta t=0
\end{array}\right.
$$

From Eq. $(4.22)_{1}$ one finds the the corresponding difference quotient of the approximated solution, namely:

$$
\begin{equation*}
\Gamma\left(\hat{c}_{i}, \Delta t\right)=\frac{\eta_{i+1}-\eta_{i}}{\Delta t} . \tag{4.24}
\end{equation*}
$$

The derivation $\tau\left(\hat{c}_{i}, \Delta t\right)=\Delta\left(\hat{c}_{i}, \Delta t\right)-\Gamma\left(\hat{c}_{i}, \Delta t\right)$ (local error of discretization) characterizes the quality of the approximation between $\hat{c}_{i}$ and $\eta_{i}$. If, in addition

$$
\begin{equation*}
\lim _{\Delta t \rightarrow 0} \tau=0 \tag{4.25}
\end{equation*}
$$

holds, then the method is called consistent, [81]. Obviously it follows by means of Eq. $(4.22)_{2}$, that the Euler method is consistent. Moreover, in order to predict the order of which $\tau$ converges to 0 for $\Delta t \rightarrow 0$, we assume $f$ to be sufficiently smooth (differentiable). The TAYLor series of $\hat{c}$ reads:

$$
\begin{equation*}
\hat{c}(t+\Delta t)=\hat{c}(t)+\Delta t \cdot f(\hat{c})+\frac{(\Delta t)^{2}}{2} \cdot f^{\prime}(\hat{c})+\ldots+\frac{(\Delta t)^{p}}{p!} \cdot f^{(p-1)}(\hat{c}) \tag{4.26}
\end{equation*}
$$

and by means of the relations $\tau(\hat{c}, \Delta t)=\boldsymbol{\Delta}(\hat{c}, \Delta t)-\Gamma(\hat{c}, \Delta t)$ and $\Gamma(\hat{c}, \Delta t) \stackrel{(\text { Euler })}{=} f(\hat{c})$ it follows from Eq. (4.26):

$$
\begin{equation*}
\tau(\hat{c}, \Delta t)=\frac{\Delta t}{2} \cdot f^{\prime}(\hat{c})+\ldots=\mathcal{O}(\Delta t) . \tag{4.27}
\end{equation*}
$$

In general a method is called to be of convergence-order $p$, if $\tau=\mathcal{O}\left[(\Delta t)^{p}\right]$. Consequently the Euler method is of the convergence-order 1, [106].
v. Heun Approximation Typically, the convergence-order of the Euler method is not sufficiently large and, consequently, alternative methods may be used (at least for comparison). In order to find a method of higher order the strategy is to use an alternative/better slope $\Gamma\left(\hat{c}_{i}, \Delta t\right)$ in Eq. (4.22) 1,2 such, that after the TAYLor expansion in Eq. (4.26) and after the calculation of $\tau$ in Eq. (4.27) higher order terms of $\Delta t$ remain.

The simplest correction of the slope in Eq. (4.22) is given by:

$$
\begin{align*}
\eta_{i+1} & =\eta_{i}+\Delta t \cdot \Gamma\left(\hat{c}_{i}, \Delta t\right) \quad \text { with } \\
\text { V. HEUN }: \Gamma\left(\hat{c}_{i}, \Delta t\right) & =\frac{1}{2}\left[f\left(\hat{c}_{i}\right)+f\left(\hat{c}_{i}+\Delta t \cdot f\left(\hat{c}_{i}\right)\right)\right] \tag{4.28}
\end{align*}
$$

which can be understood as the average between the slope of $\hat{c}_{i}$ and $\hat{c}_{i+1}, c f$., Figure 4.2 (Right). This method is called the V. Heun approximation and its convergenceorder is 2, [106].

Runge-Kutta Methods An algorithm of the convergence-order $n$ is provided by the general Runge-Kutta method, which reads:

$$
\begin{align*}
\eta_{i+1} & =\eta_{i}+\Delta t \cdot \Gamma\left(\hat{c}_{i}, \Delta t\right) \quad \text { with } \\
n \text {-th-order R.-K. : } \Gamma\left(\hat{c}_{i}, \Delta t\right) & =\gamma_{1} k_{1}+\gamma_{2} k_{2}+\gamma_{3} k_{3}+\ldots+\gamma_{n} k_{n} . \tag{4.29}
\end{align*}
$$

The different $k_{i}$ 's $(i=1,2,3, \ldots, n)$ can be calculated by the following relations, [82]:

$$
\begin{align*}
k_{1} & =f\left(\hat{c}_{i}\right) \\
k_{2} & =f\left(\hat{c}_{i}+\Delta t \cdot \beta_{21} \cdot k_{1}\right) \\
k_{3} & =f\left(\hat{c}_{i}+\Delta t \cdot\left[\beta_{31} \cdot k_{1}+\beta_{32} \cdot k_{2}\right]\right) \\
\vdots &  \tag{4.30}\\
k_{n} & =f\left(\hat{c}_{i}+\Delta t \cdot\left[\beta_{n 1} \cdot k_{1}+\beta_{n 2} \cdot k_{2}+\ldots+\beta_{n(n-1)} \cdot k_{n-1}\right]\right) .
\end{align*}
$$

The coefficients $\beta_{k l}$ and $\gamma_{k}(k=, 1,2,3, \ldots, n$ and $l=1,2,3, \ldots,(n-1))$ are constant and can be found from the so-called Butcher-diagram, [82], which has the form:

$$
\begin{array}{c|cccc}
0 & & & & \\
\alpha_{2} & \beta_{21} & & & \\
\alpha_{3} & \beta_{31} & \ddots & & \\
\vdots & \vdots & & & \\
\alpha_{n} & \beta_{n 1} & \ldots & \beta_{n(n-1)} & \\
\hline & \gamma_{1} & \ldots & \gamma_{n-1} & \gamma_{n}
\end{array}
$$

Table 4.1: General form of the Butcher-diagram.

Note that the coefficients $\alpha_{k}$ are not included into the above formalism. They refer to the corresponding algorithm for non-autonomous ODE's, in which the time $t$ explicitly occurs on the right hand side of Eq. (4.19), [18]. They are reported here, but for the numerical solution of the EDE they are not required.

Finally two popular Runge-Kutta methods, namely the classical Runge-Kutta method (4th-order) and the Simpson rule (KutTa method, 3rd-order) are mentioned. In these cases the Butcher-diagrams illustrated in Table 4.2 hold, cf., [42].

Consequently, the following relations are derived according to the formalism in the Eqs. (4.29, 4.30):


Table 4.2: Left: Butcher-diagram for the classical Runge-Kutta method. Right: Butcherdiagram for the Simpson rule.
$\diamond$ classical Runge-Kutta method (4th order):

$$
\begin{align*}
\eta_{i+1} & =\eta_{i}+\Delta t \cdot \Gamma\left(\hat{c}_{i}, \Delta t\right) \quad \text { with } \\
\Gamma\left(\hat{c}_{i}, \Delta t\right) & =\frac{1}{6}\left[k_{1}+2 \cdot k_{2}+2 \cdot k_{3}+k_{4}\right] \quad \text { and }  \tag{4.31}\\
k_{1} & =f\left(\hat{c}_{i}\right)  \tag{4.32}\\
k_{2} & =f\left(\hat{c}_{i}+\frac{1}{2} \cdot \Delta t \cdot k_{1}\right)  \tag{4.33}\\
k_{3} & =f\left(\hat{c}_{i}+\frac{1}{2} \cdot \Delta t \cdot k_{2}\right)  \tag{4.34}\\
k_{4} & =f\left(\hat{c}_{i}+\Delta t \cdot k_{3}\right) \tag{4.35}
\end{align*}
$$

$\diamond$ Kutta method / Simpson rule (3th order):

$$
\begin{align*}
\eta_{i+1} & =\eta_{i}+\Delta t \cdot \Gamma\left(\hat{c}_{i}, \Delta t\right) \quad \text { with } \\
\Gamma\left(\hat{c}_{i}, \Delta t\right) & =\frac{1}{6}\left[k_{1}+4 \cdot k_{2}+k_{3}\right] \quad \text { and }  \tag{4.36}\\
k_{1} & =f\left(\hat{c}_{i}\right)  \tag{4.37}\\
k_{2} & =f\left(\hat{c}_{i}+\frac{1}{2} \cdot \Delta t \cdot k_{1}\right),  \tag{4.38}\\
k_{3} & =f\left(\hat{c}_{i}+\Delta t \cdot\left[-k_{1}+2 \cdot k_{2}\right]\right) \tag{4.39}
\end{align*}
$$

## b. (Semi-)Implicit Methods

For various problems (for example for ODE's with exponentially decreasing solutions, e.g., $\mathrm{d}_{t} c(t)=\lambda \cdot c(t), c(0)=1$ and $\left.\lambda<0, c f .,[19]\right)$ the numerical solution calculated by explicit methods tend to considerably oscillate around the exact solution. In such cases one says, that the numerical solution is unstable. Such behavior is also observable for so-called stiff ODE's. Stiffness typically occurs if a set of two or more

ODE's would be considered, in which the independent variables change by different scales, [102].

In order to numerically treat such (sets of) differential equations one has to use socalled (semi-)implicit methods. During the following explanations we will restrict ourselves to the (semi-)implicit Euler method. Corresponding higher order algorithms are frequently explained in the literature, e.g., in [82].

We start with the investigation of the following $N$ dimensional initial value problem, with $f^{i}: \mathbb{R}^{N} \rightarrow \mathbb{R}$ :

$$
\begin{equation*}
\frac{\mathrm{d} \hat{c}^{i}}{\mathrm{~d} t}=f^{i}\left(\hat{c}^{j}\right) \quad, \quad \hat{c}^{i}\left(t_{0}\right)=\hat{c}_{0}^{i} \quad, \quad(i, j=1,2,3, \ldots, N) \tag{4.40}
\end{equation*}
$$

We denote the approximation of the exact solution, $\hat{c}_{n}=\hat{c}\left(t_{n}\right) \wedge t_{n+1}=t_{n}+\Delta t$, according to the previous paragraph, by $\eta_{n}$. Then the implicit Euler scheme ${ }^{3}$ is defined by the recursive equation, [19]:

$$
\begin{equation*}
\eta_{n+1}^{i}=\eta_{n}^{i}+\Delta t \cdot f^{i}\left(\eta_{n+1}^{j}\right) \quad, \quad \eta_{0}^{i} \stackrel{(\text { def })}{=} \hat{c}_{0}^{i} \quad(\mathrm{impl} . \text { EuLER sheme }) \tag{4.41}
\end{equation*}
$$

For known variables $\eta_{n}^{i}$ in Eq. (4.41) generally represents a (most cumbersome) nonlinear, algebraic system of equations of the form:

$$
\begin{equation*}
g^{i}\left(\eta_{n+1}^{j}\right)=0 \tag{4.42}
\end{equation*}
$$

for the unknown variables $\eta_{n+1}^{j}$, which must be solved numerically. One possibility is to perform a Newton iteration, which follows from a TAYLOR expansion by starting from an initial value $\eta_{n+1,(0)}^{j}$ in the vicinity of the root $\bar{\eta}_{n+1}^{j}$ :

$$
\begin{equation*}
0=g^{i}\left(\bar{\eta}_{n+1}^{j}\right)=g^{i}\left(\eta_{n+1,(0)}^{j}\right)+\left.\frac{\partial g^{i}}{\partial \eta_{n+1}^{j}}\right|_{\eta_{n+1,(0)}^{j}} \cdot\left(\bar{\eta}_{n+1}^{j}-\eta_{n+1,(0)}^{j}\right)+\ldots \tag{4.43}
\end{equation*}
$$

By means of Eq. (4.43) the following iteration rule can be established, [20]:

$$
\begin{equation*}
\eta_{n+1,(k+1)}^{j}=\eta_{n+1,(k)}^{j}-\frac{g^{i}\left(\eta_{n+1,(k)}^{j}\right)}{[\mathcal{D} g]^{i j}\left(\eta_{n+1,(k)}^{j}\right)} \quad \text { (NEWTON iteration) } \tag{4.44}
\end{equation*}
$$

where $[\mathcal{D} g]^{i j}$ stands for the so-called JACOBI matrix $\left.\frac{\partial g^{i}}{\partial \eta_{n+1}^{j}}\right|_{\eta_{n+1,(k)}^{j}}$. Note that Eq. (4.44) contains three independent indices: $j$ for the vector components of $\eta, n$ for the

[^20]

Figure 4.3: Illustration of the NEWTON iteration in order to find the root of the nonlinear function $g\left(\eta_{n+1}\right)$.
time integration, and $k$ for the Newton iteration. The principle of the Newton iteration is finally illustrated in Figure 4.3 for the one-dimensional case of $g\left(\eta_{n+1}\right)=0$.

For many cases only one Newton iteration yields a sufficiently good approximation of the root. For such cases, we can linearize the function $f^{i}$ by means of a Taylor expansion, as performed analogously in Eq. (4.43), and insert the result into the implicit scheme of Eq. (4.41). One obtains:

$$
\begin{equation*}
\eta_{n+1}^{i}=\eta_{n}^{i}+\Delta t \cdot\left[f^{i}\left(\eta_{n}^{j}\right)+\frac{\partial f^{i}\left(\eta_{n}^{j}\right)}{\partial \eta_{n}^{j}} \cdot\left(\eta_{n+1}^{j}-\eta_{n}^{j}\right)+\ldots\right] \tag{4.45}
\end{equation*}
$$

and by rearrangement:

$$
\begin{equation*}
\eta_{n+1}^{j}=\eta_{n}^{j}+\Delta t \cdot \underbrace{\left[\delta^{i j}-\Delta t \cdot \frac{\partial f^{i}\left(\eta_{n}^{j}\right)}{\partial \eta_{n}^{j}}\right]^{-1}}_{=[\mathbf{1}-\Delta t \cdot \mathbf{D f}]^{-1}} \cdot f^{i}\left(\eta_{n}^{j}\right), \quad \text { (semi-impl. EULER) } \tag{4.46}
\end{equation*}
$$

The resulting algorithm, Eq. (4.46), following from the linearization of $f^{i}$ in Eq. (4.45), i.e., by performing only one Newton iteration, is called the semi-implicit Euler method. Here one has to invert at each time step the matrix $[\mathbf{1}-\Delta t \cdot \mathbf{D} \mathbf{f}]$ containing the Jacobi matrix $\mathbf{D f} \in \mathbb{R}^{N \times N}$.

Usually semi-implicit methods yield - in comparison with explicit methods - a sufficient improvement w.r.t the stability of the numerical solution. However, in the majority of cases the inversion of the matrix above the brace in Eq. (4.46) is extremely time and memory-capacity consuming, in particular for large values of $N$.

Thus it may be advantageous to compare different methods, for instance the explicit Euler scheme with very small time steps and the semi-implicit Euler method with moderate time steps, in order to find the best compromise between accuracy, stability and computational efforts.

## c. Time Adaptation

An additional tool that allows to optimize the computational time during the numerical solution of ODE's is given by the time adaption. Here the idea is to compare the numerical solutions of two methods with different converge orders, $p$ and $q$, with $q>p \wedge p, q \in \mathbb{N}_{\backslash\{0\}}$, and to adjust the time step such that the derivation between the different solutions goes below a critical (user specific) tolerance value $\varepsilon$.

Without loss of generality we explain the strategy in the following for two explicit methods with the convergence-order $p$ and $q$. The different numerical solutions read:

Furthermore we consider an arbitrary tolerance value $\varepsilon>0$ and define a scalar measure, $z$, for the derivation between $\stackrel{(p)}{\eta}{ }_{n+1}$ and $\stackrel{(q)}{\eta}_{n+1}$, for instance:

$$
\begin{equation*}
z=\max _{i}\left|\stackrel{(q)}{\eta}_{i}{ }_{n+1}-\stackrel{(p)}{\eta}_{i}{ }_{n+1}\right| \quad \text { or } \quad z=\sqrt{\sum_{i=1}^{N}\left(\stackrel{(q)}{\eta}_{n+1}-\stackrel{(p)}{\eta}_{n+1}\right)^{2}} \tag{4.48}
\end{equation*}
$$

Hence the time adaption can be realized by the following programming rule, [82]:

## IF THE RELATION

$$
\begin{equation*}
\frac{\varepsilon}{10} \leq z<\varepsilon \quad, \quad(\varepsilon>0) \tag{4.49}
\end{equation*}
$$

holds, THEN KEEP $\Delta t$ and GO TO THE NEXT TIME ITERATION, ELSE REPEAT THE ITERATION WITH

$$
\begin{equation*}
(\Delta t)_{\mathrm{new}}=\Delta t \cdot \sqrt[p]{\alpha \frac{\varepsilon}{z}} \quad, \quad p=(2,3, \ldots) \quad, \quad \alpha \stackrel{e . g .}{=} \frac{9}{10} . \tag{4.50}
\end{equation*}
$$

It is easily to show, that the algorithm in Eq. $(4.50)_{1}$ reduces the time step $(\Delta t)_{\text {new }}$, if $z$ is larger than $\varepsilon$ and increases the time step for values $z>\varepsilon$. Furthermore $p$ and $\alpha$ are constants, which must be individually adjusted in order to optimize the time adaption. Moreover, it is worth mentioning that the use of the maximum norm in Eq. $(4.48)_{1}$ is stricter than the average quadratic deviation in Eq. (4.48) ${ }_{2}$. However, which norm is used depends on the considered problem and, partially, on the programmer's preference.

A typically methods, which is frequently found in literature represents the Runge-Kutta-Fehlberg 4(5) procedure, see, e.g., [21]. Here a 4th-order Runge-Kutta method is used for the time integration, whereas a 5th-order Runge-Kutta method is performed in order to evaluate the "4th-order solution," which is required for time adaptation. The outstanding advantage of this procedure is that one can refer to the calculated $k_{i}$ 's obtained from the 4th-order method in order to calculate the " 5 thorder solution," a fact, that saves much computational time, [21].

### 4.2 Simulation of Phase Separation and Coarsening in $\mathrm{Ag}-\mathrm{Cu}$

### 4.2.1 Restrictions and Assumptions

In order to reduce the computational efforts during the simulations we restrict ourselves in what follows to linear elastic loading regimes, as explained at the end of Section 2.5.3(e.). Consequently, the primary variables - in Lagrange coordinates are the concentration field $c\left(X^{j}, t\right)$ and the displacements $U^{i}\left(X^{j}, t\right)$, which are determined by the following balances:

$$
\begin{align*}
\rho_{0} \frac{\mathrm{~d} c}{\mathrm{~d} t}+\frac{\partial J^{i}}{\partial X^{i}} & =0 \quad(\text { partial mass balance })  \tag{4.51}\\
\frac{\partial p^{i j}}{\partial X^{j}} & =0 \quad \text { (static momentum balance) } \tag{4.52}
\end{align*}
$$

The required constitutive relations for the diffusion flux and for the stresses read:

$$
\begin{align*}
J^{i}= & -\rho_{0} \mathcal{M}^{i j}(T) \nabla^{j}\left[\frac{\partial\left(\mathbb{F}_{0}^{\text {chem }}+\mathbb{F}_{0}^{\text {mech }}\right)}{\partial c}-2 A^{k l} \frac{\partial^{2} c}{\partial X^{k} \partial X^{l}}-\frac{\partial A^{k l}}{\partial c} \frac{\partial c}{\partial X^{k}} \frac{\partial c}{\partial X^{l}}\right. \\
& \left.-2 \frac{\partial A^{k l}}{\partial \varepsilon^{m n}} \frac{\partial c}{\partial X^{k}} \frac{\partial \varepsilon^{m n}}{\partial X^{l}}-\frac{\partial^{2} a^{k l}}{\partial \varepsilon^{o p} \varepsilon^{m n}} \frac{\partial \varepsilon^{o p}}{\partial X^{k}} \frac{\partial \varepsilon^{m n}}{\partial X^{l}}-\frac{\partial a^{k l}}{\partial \varepsilon^{m n}} \frac{\partial^{2} \varepsilon^{m n}}{\partial X^{k} \partial X^{l}}\right]  \tag{4.53}\\
p^{i j} \approx & \sigma^{i j} \approx \frac{\partial \mathbb{F}}{\partial \varepsilon^{i j}}=\sigma_{\text {local }}^{i j}-\frac{\partial a^{k l}}{\partial \varepsilon^{i j}} \frac{\partial^{2} c}{\partial X^{k} \partial X^{l}}+\frac{\partial b^{k l}}{\partial \varepsilon^{i j}} \frac{\partial c}{\partial X^{k}} \frac{\partial c}{\partial X^{l}}, \tag{4.54}
\end{align*}
$$

in which the following dependencies exist: $\rho_{0}=$ const., $\mathbb{F}_{0}=\mathbb{F}_{0}\left(T, c, \varepsilon^{i j}\right)$, $a^{k l}=$ $a^{k l}\left(T, c, \varepsilon^{i j}\right), b^{k l}=b^{k l}\left(T, c, \varepsilon^{i j}\right)$, and $A^{k l}=A^{k l}\left(T, c, \varepsilon^{i j}\right)$. By considering Eq. (4.54) we assume that $\sigma_{\text {local }}^{i j}$ represents the leading term, and, therefore, we neglect in the following the last two terms on the right hand side of Eq. (4.54). The local thermomechanical stresses, $\sigma_{\text {local }}^{i j}$, can be calculated from Hooke's law, i.e.,

$$
\begin{align*}
\sigma_{\text {local }}^{i j} & =K^{i j k l}(T, c)\left(\varepsilon^{k l}-\alpha^{k l} \Delta T\right) \quad, \quad \mathbb{F}_{0}^{\text {mech }}=\frac{1}{2} \sigma^{i j}\left(\varepsilon^{i j}-\alpha^{i j} \Delta T\right)  \tag{4.55}\\
\varepsilon^{i j} & =\frac{1}{2}\left(\frac{\partial U^{i}}{\partial X^{j}}+\frac{\partial U^{j}}{\partial X^{i}}\right) \quad, \quad \alpha^{i j}=\alpha \delta^{i j} \quad \text { (therm. expan. coeff.) } \tag{4.56}
\end{align*}
$$

Eq. (4.54) implies that we do not distinguish between the CAUCHY stresses and the first Piola-Kirchhoff stress tensor, which is characteristic for small deformations since the differences between the reference and the current configuration are neglected.

In order to solve the PDE system (4.51-4.54) for the unknown variables $c$ and $U^{i}$ numerically we restrict ourselves to three cases:
(a) 1D simulations without local thermo-mechanical strains, i.e., $\varepsilon_{\text {elast }}^{k l}=\varepsilon^{k l}-$ $\alpha^{k l} \Delta T=0, \forall\{k, l\}$.
(b) 1D simulations under the presence of one-dimensional local thermo-mechanical strains $^{4}$ ("line strains"), i.e., $\varepsilon_{\text {elast }}^{11}=\varepsilon_{\text {elast }} \neq 0 \wedge \varepsilon_{\text {elast }}^{k l}=0, \forall\{k, l\}=\{k, l \mid k \cdot l>$ $0\}$.
(c) 2D simulations without local thermo-mechanical strains.

The restriction to line strains according to Case (b) requires overestimated stresses to be applied in order to avoid deformations in the second and third dimension. However, this 1D-case enables us to find a closed expression for the strains $\varepsilon_{\text {elast }}=$ $\varepsilon_{\text {elast }}(X, t)$ with $X \equiv X^{1}$. To this end we assume linearity for the stiffness $K^{i j k l}$ and for the thermal expansion coefficient $\alpha^{k l}$ within the smoothly changing phase boundary between the two equilibrium phase $\alpha$ and $\beta$, viz.:

$$
\begin{align*}
& \Xi(c)=\Theta(c) \Xi_{\alpha}+(1-\Theta(c)) \Xi_{\beta} \quad, \quad \Xi_{\alpha / \beta}=\left\{K_{\alpha / \beta}^{i j k l}, \alpha_{\alpha / \beta}^{k l}\right\} \\
& \Theta(c)=\frac{c_{\beta}-c(X, t)}{c_{\beta}-c_{\alpha}} \quad \text { (shape function) } \tag{4.57}
\end{align*}
$$

For cubic lattice structures (as given for $\mathrm{Ag}, \mathrm{Cu}$ and $\mathrm{Ag}-\mathrm{Cu}$ ) all elements of the stiffness matrix vanish except of $K^{11}=K^{22}=K^{33}, K^{12}=K^{13}=K^{23}$, and $K^{44}=$

[^21]$K^{55}=K^{66}$ (Voigt notation), cf., Table 3.3. By assuming in Eq. (4.54) $\sigma_{\text {local }}^{i j}$ to be the leading term one obtains from Hooke's law:
\[

$$
\begin{align*}
\sigma^{11} & =\left[K_{\beta}^{11}-\Theta(c)\left(K_{\beta}^{11}-K_{\alpha}^{11}\right)\right]\left(\varepsilon^{11}-\alpha^{11} \Delta T\right),  \tag{4.58}\\
\sigma^{22} & =\left[K_{\beta}^{12}-\Theta(c)\left(K_{\beta}^{12}-K_{\alpha}^{12}\right)\right]\left(\varepsilon^{11}-\alpha^{11} \Delta T\right),  \tag{4.59}\\
\sigma^{33} & =\left[K_{\beta}^{13}-\Theta(c)\left(K_{\beta}^{13}-K_{\alpha}^{13}\right)\right]\left(\varepsilon^{11}-\alpha^{11} \Delta T\right),  \tag{4.60}\\
\sigma^{12} & =\sigma^{13}=\sigma^{23}=0 . \tag{4.61}
\end{align*}
$$
\]

From the static balance of momentum in the form $\partial \sigma^{i j} / \partial X^{j}=0$ and with the dependencies $\sigma^{11}=\sigma^{11}(X), \sigma^{22}=\sigma^{22}(X)$, and $\sigma^{33}=\sigma^{33}(X)$ one obtains the only non-trivial solution:

$$
\begin{equation*}
\frac{\mathrm{d} \sigma^{11}}{\mathrm{~d} X}=0 \quad \Rightarrow \quad \sigma^{11}=\sigma_{0}=\text { const. } \tag{4.62}
\end{equation*}
$$

and consequently for the elastic strains, cf., Eq. (4.58) and for the mechanical part of the Helmholtz free energy:

$$
\begin{align*}
\varepsilon_{\text {elast }}^{11} & =\frac{\sigma_{0}}{K_{\beta}^{11}-\frac{c_{\beta}-c(X, t)}{c_{\beta}-c_{\alpha}}\left(K_{\beta}^{11}-K_{\alpha}^{11}\right)}  \tag{4.63}\\
\mathbb{F}_{0}^{\text {mech }} & =\frac{1}{2} \frac{\sigma_{0}^{2}}{K_{\beta}^{11}-\frac{c^{\beta}-c(X, t)}{c_{\beta}-c_{\alpha}}\left(K_{\beta}^{11}-K_{\alpha}^{11}\right)} \tag{4.64}
\end{align*}
$$

Eqs. $(4.63,4.64)$ can be directly used in order to substitute the $\mathbb{F}_{0}^{\text {mech }}$-term as well as the $\varepsilon^{i j}$-term in Eq. (4.53). In order to solve the resulting EDE one needs reliable material data, in particular for
(i) the chemical part of the Helmholiz free energy $\mathbb{F}_{0}^{\text {chem }}$,
(ii) the stiffness matrix $K_{\alpha / \beta}^{11}$ and the thermal expansion coefficients $\alpha^{11}$,
(iii) the mobility $\mathcal{M}^{i j}$, and
(iv) the HGCs $a^{k l}$, $b^{k l}$, and $A^{k l}$.

For this reason we consider the eutectic binary alloy $\mathrm{Ag}-\mathrm{Cu}$ at 1000 Kelvin and put $\mathrm{A} \equiv \mathrm{Ag}, \mathrm{B} \equiv \mathrm{Cu}$, and $c \equiv c_{\mathrm{Cu}}$.

### 4.2.2 Compilation of Materials Data

## a. Chemical Part of the Free Energy

In order to determine $\mathbb{F}_{0}^{\text {chem }}$ we use the commercial MTdata ${ }^{T M}$ database ${ }^{5}$ [83], which provides a field of discrete values $\mathbb{F}_{0}^{\text {chem }}\left(c_{i}\right), c_{i}=\{0,0.01,0.02, \ldots, 0.99,1\}$ from phase equilibrium measurements. In order to obtain a closed functional form of this data required for the numerical computation and the coding we simply perform a polynomial fit according to the Margules-ansatz

$$
\begin{align*}
\mathbb{F}_{0}^{\text {chem }}(c)= & (1-c) g_{\mathrm{a}}+c g_{\mathrm{b}}+g_{\mathrm{c}} R T[c \ln c+(1-c) \ln (1-c)]+ \\
& c(1-c)\left[\chi_{\mathrm{I}} c+\chi_{\mathrm{II}}(1-c)\right], \tag{4.65}
\end{align*}
$$

where $R=8.314[\mathrm{~J} /(\mathrm{mol} \mathrm{K})]$ stands for the universal gas constant. The introduced fit parameters $g_{a}, g_{b}, g_{c}, \chi_{I}$, and $\chi_{I I}$ have no physical meaning and are compiled in Table 4.3, together with the resulting equilibrium concentrations, $c_{\alpha / \beta}$, following from the common tangent rule and the spinodal concentrations, $c_{1 / 2}^{\mathrm{sp}}$, resulting from the roots of $\partial^{2} \mathbb{F}_{0}^{\text {chem }} / \partial c^{2}$. The corresponding curves are displayed in Figure 4.4.

Table 4.3: Fit parameters according to the MARGULES-ansatz and characteristic concentrations.

| $g_{\mathrm{a}}\left[\frac{\mathrm{GJ}}{\mathrm{m}^{3}}\right]$ | $g_{\mathrm{b}}\left[\frac{\mathrm{GJ}}{\mathrm{m}^{3}}\right]$ | $g_{\mathrm{c}}\left[\frac{\mathrm{mole}}{\mathrm{m}^{3}}\right]$ | $\chi_{\mathrm{I}}\left[\frac{\mathrm{GJ}}{\mathrm{m}^{3}}\right]$ | $\chi_{\mathrm{II}}\left[\frac{\mathrm{GJ}}{\mathrm{m}^{3}}\right]$ | $c_{\text {eut }}$ | $c_{\alpha}$ | $c_{\beta}$ | $c_{1}^{\text {sp }}$ | $c_{2}^{\text {sp }}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| -5.20 | -7.27 | $1.11 \cdot 10^{5}$ | 2.97 | 3.01 | 0.29 | 0.063 | 0.945 | 0.19 | 0.79 |



Figure 4.4: Free energy density and its second derivative as functions of the mass concentration for $\mathrm{Ag}-\mathrm{Cu}$ at $T=1000$ Kelvin.

[^22]
## b. Mobility, Stiffness, and Thermal Expansion Coefficient

By comparison of the first and second Fick's law, i.e., $\mathrm{d}_{t} c=-\partial J^{i} / \partial X^{i}$ with $J^{i}=$ $-D^{i j}\left(\partial c / \partial X^{j}\right)$ with the EDE for the limit case of classical Fickian diffusion (no mechanical and HGC terms) one obtains the following relations between the diffusion coefficients $D^{i j}$ and the mobility $\mathcal{M}^{i j}$ :

$$
\begin{equation*}
D^{i j}=\mathcal{M}^{i j} \frac{\partial^{2} \mathbb{F}_{0}^{\text {chem }}}{\partial c^{2}} \Rightarrow \mathcal{M}_{\alpha / \beta}^{i j}=\left.\frac{D_{\alpha / \beta}^{i j}}{\frac{\partial^{2} \mathbb{F}_{0}^{\mathrm{chem}}}{\partial c^{2}}}\right|_{c=c_{\alpha / \beta}} \tag{4.66}
\end{equation*}
$$

The diffusion coefficients for the pure substances $D_{\mathrm{Ag} / \mathrm{Cu}}^{i j}=D_{\mathrm{Ag} / \mathrm{Cu}} \delta^{i j}$ can be easily found in the literature, e.g., [13], where they are measured by means of tracer experiments w.r.t Cu in Ag and vice versa. Obviously the sign of the mobility depends on the curvature of $\mathbb{F}_{0}^{\text {chem }}$, which is positive outside the spinodal area (enclosed by the spinodal concentrations) and negative for $c_{1}^{\mathrm{sp}}<c<c_{2}^{\mathrm{sp}}$. In particular a negative mobility gives rise for "uphill" diffusion (e.g., spinodal decomposition), during which concentrations gradients are amplified.

As indicated by the equilibrium concentrations, $c_{\alpha / \beta}$, cf., Table 4.3, the equilibrium $\alpha$ - and $\beta$-phases are extremely Ag - or Cu -containing. Therefore it is reasonable to approximate for the equilibrium phases:

$$
\begin{equation*}
\Xi_{\alpha} \approx \Xi_{\mathrm{Ag}} \quad \text { and } \quad \Xi_{\beta} \approx \Xi_{\mathrm{Cu}} \quad \text { with } \quad \Xi=\left\{K^{11}, \alpha^{11}, \mathcal{M}^{i j}\right\} \tag{4.67}
\end{equation*}
$$

In order to determine the corresponding values within the phase boundaries we assume a linear dependence according to Eq. (4.57). Table 4.4 and 4.5 finally shows the according quantities used during the simulations.

Table 4.4: Stiffness matrix of pure silver and copper in GPa and in Voigt notation, Source: [71].

| $\left.K_{i j}^{k l}\right\|_{\mathrm{Ag}}$ | 11 | 22 | 33 | 23 | 31 | 12 | $\left.K_{i j}^{k l}\right\|_{\mathrm{Cu}}$ | 11 | 22 | 33 | 23 | 31 | 12 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 11 | 168 | 121 | 121 | 0 | 0 | 0 | 11 | 124 | 94 | 94 | 0 | 0 | 0 |
| 22 | 121 | 168 | 121 | 0 | 0 | 0 | 22 | 94 | 124 | 94 | 0 | 0 | 0 |
| 33 | 121 | 121 | 168 | 0 | 0 | 0 | 33 | 94 | 94 | 124 | 0 | 0 | 0 |
| 23 | 0 | 0 | 0 | 75 | 0 | 0 | 23 | 0 | 0 | 0 | 46 | 0 | 0 |
| 31 | 0 | 0 | 0 | 0 | 75 | 0 | 31 | 0 | 0 | 0 | 0 | 46 | 0 |
| 12 | 0 | 0 | 0 | 0 | 0 | 75 | 12 | 0 | 0 | 0 | 0 | 0 | 46 |

Table 4.5: Diffusion, mobility, and thermal expansion coefficients for the pure substances Ag and Cu Source: [13], [119].

| $D_{\alpha}\left[\mathrm{m}^{2} / \mathrm{s}\right]$ | $D_{\beta}\left[\mathrm{m}^{2} / \mathrm{s}\right]$ | $M_{\alpha}\left[\mathrm{m}^{5} / \mathrm{Js}\right]$ | $M_{\beta}\left[\mathrm{m}^{5} / \mathrm{Js}\right]$ | $\alpha_{\alpha}^{11}\left[10^{6} / \mathrm{K}\right]$ | $\alpha_{\beta}^{11}\left[10^{6} / \mathrm{K}\right]$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $1.01 \times 10^{-14}$ | $4.09 \times 10^{-15}$ | $7.25 \times 10^{-25}$ | $3.65 \times 10^{-25}$ | 18.9 | 16.5 |

## c. Interpolation of the HGCs

The HGCs represent the crucial data that determines the coarsening rate of the Ostwald ripening process in the two-phase system. In particular HGC values which are too high lead to overestimated coarsening and vice versa. Unfortunately the HGCs are extremely poorly documented, and, even if found, they are frequently ad hoc estimates the source of which is not clear. Furthermore we could only find constant HGCs so that Eq. (4.53) would reduce to the first two terms within the brackets, [72, 78, 113].

Because of these shortcomings an atomistic theory was developed in Chapter 3, which allows for the exact calculation of the HGCs as functions of the mass concentration $c$ and of the strains $\varepsilon^{k l}$, cf., Section 3.4.2 and 3.5.5. According to Eqs. (3.65-3.69) the following compact form holds for the HGCs:

$$
\begin{align*}
& a^{k l}\left(c, \varepsilon^{i j}\right)=-\delta(c) \frac{\partial \tilde{y}(c)}{\partial c} \cdot \mathbb{H}^{k l}\left(c, \varepsilon^{i j}\right), \quad b^{k l}\left(c, \varepsilon^{i j}\right)=\delta(c) \frac{\partial^{2} \tilde{y}(c)}{\partial c^{2}} \cdot \mathbb{H}^{k l}\left(c, \varepsilon^{i j}\right),  \tag{4.68}\\
& A^{k l} \stackrel{(\text { def })}{=} \frac{\partial a^{k l}}{\partial c}+b^{k l}, \quad \tilde{y}(c)=\frac{c M_{\mathrm{A}}}{M_{\mathrm{B}}-c\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right)}, \quad \text { and }  \tag{4.69}\\
& \mathbb{H}^{k l}\left(c, \varepsilon^{i j}\right)=\mathbb{H}_{0}^{k l}(c)+\varepsilon^{m n} \mathbb{H}_{1}^{m n k l}(c)+\varepsilon^{m n} \varepsilon^{p q} \mathbb{H}_{2}^{m n p q k l}(c) . \tag{4.70}
\end{align*}
$$

The functions $\mathbb{H}_{0}^{k l}\left(c f\right.$. , first row of Eq. (3.69)), $\mathbb{H}_{1}^{m n k l}(c f$. , second and third row of Eq. (3.69)), and $\mathbb{H}_{2}^{\text {mnpqqk }}$ (cf., last five rows of Eq. (3.69)), introduced as abbreviations, represent combinations of the different contributions to the interatomic potentials and depend explicitly and implicitly (via the equilibrium lattice parameter $R=R(c)$ ) on c. Obviously, $\mathbb{H}^{k l}$ contains a linear term w.r.t. $\varepsilon^{i j}$, and, consequently, the HGCs are not symmetric with respect to positive or negative strains. Therefore we can distinct between the effects of compressive and tensile loadings during the diffusion simulations.

Recalling the restrictions on the simulations ( $\mathbf{a - c}$ ) introduced in Section 4.2.1 we exclusively investigate the interpolation of $a^{11}, b^{11}$, and $A^{11}$ in the following. This is reasonable, because for the 1D simulations ( $X^{i}=X^{1}=X$ ) only the index combinations -11- is of interest, whereas the relation $\Xi^{k l}=\Xi^{11} \delta^{k l}$ with $\Xi=\{a, b, A\}$ holds for the (strain-free) 2D simulations. Hence the values resulting from the curves illustrated in Figure 3.10 (first column) and in Figure 3.8 (first row) must be used during
the simulations. Here it is worth mentioning that the curves displayed in Figure 3.8 (first row) represent the curve for $\varepsilon=0$ in Figure 3.10 (first column).

Note that - due to the micromorphological evolution - the local mass concentration as well as the local strains continuously change during the simulations. Thus, the values of the HGCs must be updated for each time step $\Delta t$ and for each material point, $X^{i}$, of the simulated RVE. However, the atomistic calculations underlying the graphs of the Figures $3.8-3.10$ are extremely time-consuming and, consequently, it is reasonable to perform a polynomial fit for the corresponding curves in order to save computational times. Here we apply a bilinear interpolation of the form:

$$
\begin{equation*}
\Xi(c, \varepsilon)=k_{\varepsilon}^{\Xi} \cdot \varepsilon+k_{c}^{\Xi} \cdot c+k_{c \varepsilon}^{\Xi} \cdot \varepsilon \cdot c+k_{0}^{\Xi} \quad \text { with } \quad \Xi=\left\{a^{11}, b^{11}, A^{11}\right\}, \tag{4.71}
\end{equation*}
$$

in which the fitting procedure must be performed separately for positive and negative strains. Therefore one needs four data points in order to determine the fit parameters $k_{\varepsilon}^{\Xi}, k_{c}^{\Xi}, k_{c \varepsilon}^{\Xi}$, and $k_{0}^{\Xi}$. For this reason the HGC values following from the curves in Figure 3.10 (first column) with the ad hoc chosen arguments

$$
\begin{equation*}
(c, \varepsilon)=\left\{\left(c_{\alpha}, 0\right),\left(c_{\beta}, 0\right),\left(c_{\alpha}, \pm 0.2\right),\left(c_{\beta}, \pm 0.2\right)\right\} \tag{4.72}
\end{equation*}
$$

are used. Table 4.6 shows the fit parameters following form the interpolation. The corresponding bilinear functions are illustrated in Figure 4.5.

Table 4.6: Interpolated coefficients for the HGCs as bilinear functions of $c$ and $\varepsilon$.

| $\Xi$ | $k_{\varepsilon}^{\Xi}$ in N | $k_{c}^{\Xi}$ in N | $k_{c \varepsilon}^{\Xi}$ in N | $k_{0}^{\Xi}$ in N |
| :--- | :--- | :--- | :--- | :--- |
| $\varepsilon>0$ (tensile loading) |  |  |  |  |
| $a^{11}$ | $-3.79 \cdot 10^{-10}$ | $8.74 \cdot 10^{-11}$ | $-6.40 \cdot 10^{-11}$ | $4.04 \cdot 10^{-11}$ |
| $b^{11}$ | $-5.22 \cdot 10^{-10}$ | $4.72 \cdot 10^{-11}$ | $1.64 \cdot 10^{-10}$ | $5.84 \cdot 10^{-11}$ |
| $A^{11}$ | $-5.74 \cdot 10^{-10}$ | $3.74 \cdot 10^{-11}$ | $1.50 \cdot 10^{-10}$ | $1.53 \cdot 10^{-10}$ |
| $\varepsilon<0$ (compres. loading) |  |  |  |  |
| $a^{11}$ | $-1.11 \cdot 10^{-9}$ | $8.74 \cdot 10^{-11}$ | $1.91 \cdot 10^{-10}$ | $4.04 \cdot 10^{-11}$ |
| $b^{11}$ | $-1.52 \cdot 10^{-9}$ | $4.72 \cdot 10^{-11}$ | $7.77 \cdot 10^{-10}$ | $5.84 \cdot 10^{-11}$ |
| $A^{11}$ | $-1.10 \cdot 10^{-9}$ | $3.74 \cdot 10^{-11}$ | $3.80 \cdot 10^{-10}$ | $1.53 \cdot 10^{-10}$ |

The values $a^{11}, b^{11}$, and $A^{11}$ for the strain free case follow directly from the interpolation by putting $k_{\varepsilon}^{\Xi}=k_{c \varepsilon}^{\Xi}=0$. The resulting linear functions $a^{11}(c), b^{11}(c)$, and $A^{11}(c)$ are given by the lines along the "kink" in Figure 4.5.


Figure 4.5: Interpolated HGCs as bilinear functions of the mass concentration and the strains.

### 4.2.3 Remarks on the Numerical Realization

For the numerical treatment we, first, transform the EDE to a dimensionless form by replacing $X^{i}, \mathbb{F}_{0}$, and $t$ by the dimensionless quantities $\tilde{X}^{i}, \tilde{\mathbb{F}}_{0}$, and $\tilde{t}$ using the relations, cf., [78]:

$$
\begin{equation*}
\tilde{X}^{i}=\frac{X^{i}}{L} \quad, \quad \tilde{\mathbb{F}}_{0}=\frac{\mathbb{F}_{0}}{\Psi_{0}} \quad, \quad \tilde{t}=\frac{\Psi_{0} M_{\beta}}{L^{2}\left(c_{\beta}-c_{\alpha}\right)}=\frac{t}{t_{0}} \tag{4.73}
\end{equation*}
$$

in which the factors $L, \Psi_{0}$, and $t_{0}$ must be "appropriately" chosen. Table 4.7 shows the corresponding values, which were used during the simulations. ${ }^{6}$

The resulting dimensionless EDE is implemented in a FORTRAN 90 program. Furthermore the spatial derivatives are discretized by finite differences (with $N$ grid points in 1D and $N \times N$ grid points in 2D, cf., Table 4.7) and replaced by an algebraic expression in Fourier space, cf., [37, 12]. For the required discrete Fourier transforms we use the free available FFTPACK5 package, [104]. The time integration is performed by means of an explicit Euler method with the constant time step $\Delta \tilde{t}$

[^23]Table 4.7: Numerical parameters used during the simulations.

| Simulations | $\Psi_{0}$ in $\frac{\mathrm{GJ}}{\mathrm{m}^{3}}$ | $2 \pi L$ in $\mu \mathrm{m}$ | $t_{0}$ in s | $N(N \times N)$ | $\Delta \tilde{t}$ |
| ---: | :---: | :---: | :---: | :---: | :---: |
| 1D (strain-free) | 0.1 | 0.06 | 2.105 | 256 | $0.4 \cdot 10^{-6}$ |
| 1D (5000 MPa) | 0.1 | 0.06 | 2.105 | 256 | $0.4 \cdot 10^{-6}$ |
| 1D (-5000 MPa) | 0.1 | 0.06 | 2.105 | 256 | $0.2 \cdot 10^{-6}$ |
| 2D (EuLER, 1 fluc.) | 0.1 | 0.05 | 1.462 | $128 \times 128$ | $0.1 \cdot 10^{-5}$ |
| 2D (EULER, 16 fluc.) | 0.1 | 0.05 | 1.462 | $128 \times 128$ | $0.1 \cdot 10^{-5}$ |
| 2D (RADAU) | 0.1 | 0.05 | 1.462 | $128 \times 128$ | - |

and, partially, by an implicit and time adaptive Runge-Kutta procedure using the free available RADAU package, [60].

In the case of one dimension, the dimensionless ODE following from the spatial discretization of the EDE ( $X \rightarrow \alpha$, cf., Section 4.1.1) and the subsequent transformation into the Fourier space reads:

$$
\begin{align*}
\frac{\mathrm{d} \hat{c}}{\mathrm{~d} \tilde{t}} & =\frac{\mathrm{d} \mathfrak{F}[c]}{\mathrm{d} \tilde{t}}= \\
& =\left(\frac{c^{\beta} M^{\beta}}{M^{\alpha}}-c^{\alpha}\right) \tilde{\xi}^{(2)}(s) \mathfrak{F}[\Upsilon]+\left(1-\frac{M^{\alpha}}{M^{\beta}}\right)\left\{\mathfrak{F}\left[\frac{\Delta c}{\Delta \alpha} \frac{\Delta \Upsilon}{\Delta \alpha}\right]+\mathfrak{F}\left[c \frac{\Delta^{2} \Upsilon}{\Delta \alpha^{2}}\right]\right\} \tag{4.74}
\end{align*}
$$

with the definition for the symbol $\Upsilon$ :

$$
\begin{align*}
\Upsilon= & \frac{\partial \tilde{\mathbb{F}}_{0}}{\partial c}-\frac{2}{\Psi_{0} L^{2}}\left(k_{0}^{A}+k_{c}^{A} c+k_{\varepsilon}^{A} \varepsilon_{\text {elast }}+k_{c \varepsilon}^{A} \varepsilon_{\text {elast }} \cdot c\right) \frac{\Delta^{2} c}{\Delta \alpha^{2}} \\
& -\frac{1}{\Psi_{0} L^{2}}\left(k_{c}^{A}+k_{c \varepsilon}^{A} \varepsilon_{\text {elast }}\right)\left(\frac{\Delta c}{\Delta \alpha}\right)^{2}-\frac{2}{\Psi_{0} L^{2}}\left(k_{\epsilon}^{A}+k_{c \epsilon}^{A} c\right)\left(\frac{\partial \varepsilon_{\text {elast }}}{\partial c}\right)\left(\frac{\Delta c}{\Delta \alpha}\right)^{2} \\
& -\frac{1}{\Psi_{0} L^{2}}\left(k_{\epsilon}^{a}+k_{c \epsilon}^{a} c\right)\left[\left(\frac{\partial^{2} \varepsilon_{\text {elast }}}{\partial c^{2}}\right)\left(\frac{\Delta c}{\Delta \alpha}\right)^{2}+\left(\frac{\partial \varepsilon_{\text {elast }}}{\partial c}\right)\left(\frac{\Delta^{2} c}{\Delta \alpha^{2}}\right)\right] . \tag{4.75}
\end{align*}
$$

Here, analogously to the Eqs. (4.16, 4.17), the dimensionless relations:

$$
\begin{align*}
\mathfrak{F}\left[\frac{\Delta c(\alpha)}{\Delta \alpha}\right] & =\mathfrak{F}[c(\alpha)] \cdot \tilde{\xi}^{(1)} \quad, \quad \tilde{\xi}^{(1)}(s)=-\frac{\mathrm{i}}{\tilde{h}} \sin \left(\frac{2 \pi s}{N}\right),  \tag{4.76}\\
\mathfrak{F}\left[\frac{\Delta^{2} c(\alpha)}{\Delta \alpha^{2}}\right] & =\mathfrak{F}[c(\alpha)] \cdot \tilde{\xi}^{(2)} \quad, \quad \tilde{\xi}^{(2)}(s)=\frac{2}{\tilde{h}^{2}}\left[\cos \left(\frac{2 \pi s}{N}\right)-1\right] . \tag{4.77}
\end{align*}
$$

hold, in which the symbol $s=L \cdot k=0,0,2, \ldots, N-1$ denotes the position vector in Fourier space, and $\tilde{h}=\frac{2 \pi}{N}$ represents the dimensionless distance between the $N$ grid points in real space.

Note that in Eq. (4.74) and (4.75) the (discretized) spatial derivatives $\frac{\Delta c}{\Delta \alpha}$ and $\frac{\Delta^{2} c}{\Delta \alpha^{2}}$ occur as a matter of a better readability. They must be substituted by the algebraic expressions following from the stepwise application of the forward and backward Fourier transform, $\mathfrak{F}$ and $\mathfrak{F}^{-1}$. For instance, the full expression, which is implemented for the first summand within the parenthesis $\{\ldots\}$ of Eq. (4.74), reads:

$$
\begin{equation*}
\mathfrak{F}\left[\Delta_{\alpha} c \cdot \Delta_{\alpha} \Upsilon\right]=\mathfrak{F}\left\{\mathfrak{F}^{-1}\left[\tilde{\xi}^{(1)} \cdot \hat{c}\right] \cdot \mathfrak{F}^{-1}\left[\tilde{\xi}^{(1)} \cdot \mathfrak{F}(\Upsilon)\right]\right\} \tag{4.78}
\end{equation*}
$$

Furthermore the quantities $\mathbb{F}_{0}=\mathbb{F}_{0}^{\text {chem }}+\mathbb{F}_{0}^{\text {mech }}$ and $\varepsilon_{\text {elast }}$ are determined by the relations in Eqs. (4.63), (4.64), and (4.65), and, consequently, the corresponding derivatives in Eq. (4.75) can be directly calculated.

Eq. (4.74) as well as the two dimensional counterpart, which can be derived in the same manner, [14], must be numerically solved by means of OSTI methods. A final inverse Fourier transform, $\mathfrak{F}^{-1}$, of the resulting discretized concentration field, $\hat{c}_{i}(s)$, yields the concentration field in real space, $c_{i}(\alpha)$, which characterizes the temporal phase evolution within the binary alloy $\mathrm{Ag}-\mathrm{Cu}$.

### 4.2.4 One-Dimensional Simulations ${ }^{7}$

First, we investigate the one dimensional case according to Eq. (4.74). Figures 4.64.8 display the spinodal decomposition and coarsening process along a "line" in AgCu at 1000 Kelvin. Here we started with an eutectic homogeneous concentration profile ( $c_{\text {eut }}=0.29$ ), which is disturbed by a slight fluctuation in order to enforce the unstable state to decompose. The outermost dashed lines represent the corresponding equilibrium concentrations of the $\alpha$ - and $\beta$-phase, whereas the innermost lines identify the spinodal concentrations, cf., Table 4.3. Obviously, the system immediately begins to decompose after starting the simulations. When the whole mixture reaches the equilibrium concentrations coarsening proceeds such that the bigger phases grow at the expense of the smaller ones.

At this point it is worth mentioning that the total simulation times are in the range of some minutes, which is notedly short w.r.t. the experimental observations of these phenomena, cf., next Chapter or [93]. The reason for that are the extremely small HGCs used during the simulations. In fact, typical values found in literature are much larger, cf., [113], ${ }^{8}$ which is more convenient to have from the numerical point of view since it results in bigger time steps $\Delta \tilde{t}$. However, in some rare cases there are also similarly small HGC values in the literature, cf., [72], ${ }^{9}$ in which the simulation

[^24]

Figure 4.6: One-dimensional simulation of spinodal decomposition and coarsening in AgCu at 1000 Kelvin (strain-free case).


Figure 4.7: One-dimensional simulation of spinodal decomposition and coarsening in AgCu at 1000 Kelvin (tensile loading of $\sigma_{0}=5000 \mathrm{MPa}$ ).


Figure 4.8: One-dimensional simulation of spinodal decomposition and coarsening in AgCu at 1000 Kelvin (pressure loading of $\sigma_{0}=-5000 \mathrm{MPa}$ ).
times are also extremely short.
Moreover, smaller HGCs result in a sharper width of the phase boundary and, consequently, the discretization $N$ must be chosen sufficiently large, whereas the simulated volume element $2 \pi L$ must be chosen small in order to model the interface boundary realistically, ${ }^{10} c f$., Table 4.7. In particular, the discretization of $N=256$ yields approximately nine grid points within the phase boundary as illustrated in Figure 4.9 (second row, left). From this fact we calculate:

$$
\begin{equation*}
256 \text { grid points }=0.06 \mu \mathrm{~m} \quad \Leftrightarrow \quad 9 \text { grid points }=2.1 \mathrm{~nm}=21 \AA \tag{4.79}
\end{equation*}
$$

which corresponds to approximately seven atomic distances $\left(r_{\mathrm{Ag}}=2.88 ~ \AA\right)$ and underscores a realistically sharp interface boundary.

The impact of the HGCs on the interface width is illustrated in Figure 4.9 (second row), in which we varied the magnitude of $A^{11}$ under the constraint of $\partial A^{11} / \partial c=$ constant. The corresponding coarsening behavior is displayed in Figure 4.9 (first row), in which the larger interfaces widths result in faster coarsening rates. From the phenomenological point-of-view this fact is clear since sharper interfaces increase the separation of the different phases and, thus, decrease their interaction and, in turn, their coarsening behavior.


Figure 4.9: The impact of the magnitude of the HGCs on the phase boundary width and on the coarsening rate. First Row: Coarsening stages after 20000 loops (strain-free case) using a HGC of $A^{11}=A_{\text {EAM }}^{11}, A^{11}=2 \cdot A_{\text {EAM }}^{11}$, and $A^{11}=4 \cdot A_{\text {EAM }}^{11}$. Second Row: According zoomed interface areas.

[^25]Finally the application of very large loading regimes during the simulations illustrated in the Figure 4.7 and 4.8 is noticeable. This was done in order to investigate the effect of thermo-mechanical stresses within manageable computational times. However, although the applied stresses of $\sigma_{0}= \pm 5000 \mathrm{MPa}$ are extremely large, the resulting strains are moderate, as indicated in Figure 4.10. Indeed, tensile and pressure stresses increase the coarsening rate. In particular it seems that pressure loading has a stronger influence on coarsening than tensile loading.


Figure 4.10: The inhomogeneous strain field following from the phase evolution exemplarily calculated for a discretization of $N=128$. First Row: tensile loading. Second Row: pressure loading.

### 4.2.5 Two-Dimensional Simulations ${ }^{11}$

For the two-dimensional simulations we start with a eutectic homogeneous concentration profile disturbed by one, two and 18 fluctuations, as indicated in Figure 4.11. Furthermore we use a spatial discretization of $N \times N=128 \times 128$ so that approximately $4-5$ grid points are within the phase boundary. Figures 4.12 and 4.13 display the obtained micrographs and the decomposition and coarsening process, in which the white areas belong to the Cu -rich $\beta$-phase. In particular, we performed - as already used for the one-dimensional simulations - an explicit Euler method for the time integration.

Note that the 2D-simulations are extremely time-consuming and, consequently we searched for optimization possibilities. To this end we realized the time integration by means of a time-adaptive Implicit Runge-Kutta (IRK) method provided by the

[^26]

Figure 4.11: Initial concentration profiles used for the two-dimensional simulations.

RADAU routine, [60]. The corresponding simulations are illustrated in Figure 4.14. Unfortunately the complex IRK procedure considerably increases the computational time, which cannot be compensated by the larger adaptive time steps $\Delta \tilde{t}$. Therefore the investigated coarsening stages are much smaller than the corresponding ones in Figures 4.12 and 4.13. In particular, the final stage in Figure 4.14 approximately corresponds to the right graph of the middle row in Figure 4.12 and to the left graph of the middle row in Figure 4.13. Finally, Figure 4.15 illustrates the resolution of the interface width between the different phases following from the discretization of $N \times N=128 \times 128$. Here the different shades of gray indicate the phase boundary, $c f$., marked dashed square in the zoomed picture of Figure 4.15 (Right). Thus one may say, that approximately $4-5$ grid points are situated within the interface.

### 4.2.6 Quantification of the Coarsening Rate

At the end of this chapter we investigate the coarsening rate of the precipitated $\beta$ phase resulting from the 1D- and 2D-simulations. For this reason we restrict the analysis, on the one hand side, to the no-loading case and consider the 1D simulation in Figure 4.6 and the 2D simulations in Figure 4.12 and 4.14. On the other hand side, we analyze the coarsening behavior under tensile and pressure loading, cf., Figure 4.7 and 4.8 , in order to predict their impact on the phase evolution.


Figure 4.12: Two dimensional simulation of spinodal decomposition and coarsening in AgCu at 1000 Kelvin without thermo-mechanical loading by using the explicit Euler method (one initial fluctuation). From upper left to lower right: after $\tilde{t}=0.005 ; 0.01 ; 0.015 ; 0.035$; $0.1 ; 0.4 ; 1 ; 2.1 ; 4.9$.


Figure 4.13: Two dimensional simulation of spinodal decomposition and coarsening in AgCu at 1000 Kelvin without thermo-mechanical loading by using the explicit Euler method (18 initial fluctuation). From upper left to lower right: after $\tilde{t}=0.004 ; 0.006 ; 0.015 ; 0.04$; $0.06 ; 0.1 ; 0.6 ; 1.5 ; 4.3$.


Figure 4.14: Two dimensional simulation of spinodal decomposition and coarsening in AgCu at 1000 Kelvin without thermo-mechanical loading by using the time adaptive implicit Runge-Kutta method provided by the RADAU routine (two initial fluctuation). From upper left to lower right: after $\tilde{t}=0.0038 ; 0.0077 ; 0.0088 ; 0.0131 ; 0.0163 ; 0.0217 ; 0.0307$; 0.0354; 0.0486 .


Figure 4.15: On the resolution of the interface width for the two dimensional case with $N=128$ (the dashed square marks the interface).
(i) 1D-analysis In order to determine the coarsening rate following from the 1D simulation one has, first, to eliminate the continuous phase boundaries. For this reason the $c$-profiles are modified to a step function, which"jumps" between the equilibrium values $c_{\alpha / \beta}$. Here the interface boundary is eliminated by the formula:

$$
c=\left\{\begin{array}{ll}
c_{\alpha} & \text { if } c \leq c^{\mathrm{crit}}  \tag{4.80}\\
c_{\beta} & \text { if } c \geq c^{\mathrm{crit}}
\end{array} \quad \text { with } \quad c^{\mathrm{crit}}=\frac{c_{\alpha}+c_{\beta}}{2} .\right.
$$

Furthermore note that the left and right boundary phases of the simulated RVE's in Figures $4.6-4.8$ belong to the same phase because of the periodic continuative structure of the material.

According to these considerations Figure 4.16 exemplarily documents the stepwise modification of the $c$-profiles taken from Figure 4.6 for the times $t=8.42 \mathrm{~s}(10000000$ loops) and $t=151.6 \mathrm{~s}$ ( 180000000 loops). Each row represents a separate coarsening stage. In particular, the first column contains the originally simulated micromorphology, the second row contains the corresponding step functions after the elimination of the phase boundary, and the third row shows the $c$-profiles, in which the left phase is eliminated and added to the right phase.

The right graphs of Figure 4.16 can be analyzed by means the program Mathematica ${ }^{\mathrm{TM}}$ in order to determine the total intercept length, $l^{\beta}$, as well as the total number, $N$, of the $\beta$-phases. From these values we calculate the mean intercept length, $\bar{l}^{\beta}=l^{\beta} / N$, which can be used to derive the mean phase radius, cf., Table 4.8. At this point we emphasize that the exploitation of the $c$-profiles in Figure 4.6-4.8 represents a 1D-analysis of a (by nature) 3D-problem, cf., the explanations in Section 5.2 on page 135 ff .. Analogously to the Eqs. $(5.4,5.5)$ one can use the following relations to calculate a $3 D$-equivalent mean phase radius (see [114] for a detailed derivation of the


Figure 4.16: Modification of the 1D concentration profiles exemplarily for two coarsening stages. First Column: original profiles. Second column: after the elimination of the phase boundary. Third row: after the merging of the left and right phases.
relations):

$$
\begin{align*}
\bar{r}^{\beta} & =\frac{3}{4} \cdot \bar{l}^{\beta} \quad(\text { spherical phases })  \tag{4.81}\\
\bar{a}^{\beta} & \left.=\frac{1}{1.278} \cdot \bar{l}^{\beta} \quad \text { (oblate spheroids with } b / a=0.5, c f ., \text { Figure } 5.3\right) \tag{4.82}
\end{align*}
$$

where we assumed the phases to be spherical with the mean phase radius $\bar{r}^{\beta}$ or oblatespheroid with $\bar{a}^{\beta}$, respectively.

The calculated values are compiled in Table 4.8. The resulting coarsening behavior is illustrated in Figure 4.17, which shows the development of the mean phase radii for the strain-free case. Recalling the proportionality $\bar{r} \propto t^{1 / 3}$ or $\bar{a} \propto t^{1 / 3}$, respectively, which is well-known from the LSW-theory, [115], we fit the curves of Figure 4.17 (right) and obtain:

$$
\begin{equation*}
\bar{r}^{\beta}=0.00082 \cdot t^{1 / 3} \quad \text { and } \quad \bar{a}^{\beta}=0.00086 \cdot t^{1 / 3} \quad(1 \mathrm{D}, \text { strain-free case }) . \tag{4.83}
\end{equation*}
$$

Finally, we consider the coarsening behavior under tensile and pressure loading ( $\pm 5000$ MPa), cf., Figure 4.7 and 4.8. The corresponding curves are displayed in Figure 4.18. Two characteristics are worth mentioning. First, the relation $\bar{r}^{\beta} \propto t^{1 / 3}$ is violated, which results from the application of mechanical loadings. Second, the "guess" mentioned in Section 4.2.4, namely pressure loading leading to faster coarsening than tensile loading, is verified by comparison of Figures 4.18 (left) and (right).

Table 4.8: Coarsening values obtained from the analysis of the simulated 1D-micrographs in Figure 4.6-4.8.

| $\tilde{t}$ in sec | $\bar{l}^{\beta}$ in $\mu \mathrm{m}$ | $\bar{r}^{\beta}$ in $\mu \mathrm{m}$ | $\bar{a}^{\beta}$ in $\mu \mathrm{m}$ |
| :--- | :--- | :--- | :--- |
| strain-free |  |  |  |
| 0.019 | 0.0018 | 0.0014 | 0.0014 |
| 0.053 | 0.0027 | 0.0020 | 0.0021 |
| 8.422 | 0.0032 | 0.0024 | 0.0025 |
| 50.53 | 0.0040 | 0.0030 | 0.0031 |
| 151.6 | 0.0053 | 0.0040 | 0.0041 |
| tensile loading |  |  |  |
| 0.035 | 0.0026 | 0.0020 | 0.0020 |
| 1.600 | 0.0040 | 0.0030 | 0.0031 |
| 16.84 | 0.0040 | 0.0030 | 0.0031 |
| 25.27 | 0.0053 | 0.0040 | 0.0041 |
| 151.6 | 0.0081 | 0.0061 | 0.0063 |
| 235.8 | 0.0162 | 0.0122 | 0.0127 |
| pressure loading |  |  |  |
| 0.011 | 0.0023 | 0.0017 | 0.0018 |
| 0.019 | 0.0031 | 0.0023 | 0.0024 |
| 1.432 | 0.0052 | 0.0039 | 0.0041 |
| 50.53 | 0.0081 | 0.0061 | 0.0063 |
| 105.3 | 0.0162 | 0.0122 | 0.0127 |



Figure 4.17: The temporal development of the mean phase radius $\bar{r}^{\beta}$ and $\bar{a}^{\beta}$ in eutectic $\mathrm{Ag}-\mathrm{Cu}$ at $\approx 1000$ Kelvin obtained from the strain-free 1D simulations.


Figure 4.18: The temporal development of the mean phase radius $\bar{r}^{\beta}$ and $\bar{a}^{\beta}$ in eutectic $\mathrm{Ag}-\mathrm{Cu}$ at $\approx 1000$ Kelvin obtained from the 1D simulations. Left: tensile loading of 5000 MPa. Right: pressure loading of -5000 MPa .
(ii) 2D-analysis For the quantification of the coarsening rate following from the 2D-simulations we exemplarily investigate the micrographs of Figures 4.12 and 4.14. In particular, we examined the pictures by means of the metallurgical image analysis software package $\mathrm{DHS}{ }^{\circledR}$, which yields the total number, $N$, as well as the total intercept area, $A^{\beta}$, of the $\beta$-phases. Following the considerations in Section 5.2 on page 135 ff . we calculate the mean radii $\bar{r}^{\beta}$ (for spherical shapes) and $\bar{a}^{\beta}$ (for oblatespheroid shapes) of the $\beta$-phase. The obtained values are shown in Table 4.9 and 4.10 for the different coarsening stages.

The resulting curves are displayed in Figure 4.19 and 4.20, where the right graphs can be fitted to the $t^{1 / 3}$-law. We obtain for the Euler method:

$$
\begin{equation*}
\bar{r}^{\beta}=0.0071 \cdot t^{1 / 3} \quad, \quad \bar{a}^{\beta}=0.0092 \cdot t^{1 / 3} \quad(2 \mathrm{D}, \text { strain-free, EULER }), \tag{4.84}
\end{equation*}
$$

and for the RADAU solver:

$$
\begin{equation*}
\bar{r}^{\beta}=0.0098 \cdot t^{1 / 3} \quad, \quad \bar{a}^{\beta}=0.013 \cdot t^{1 / 3} \quad(2 \mathrm{D}, \text { strain-free, RADAU }) . \tag{4.85}
\end{equation*}
$$

Obviously, the 2D-simulations lead to much larger coarsening rates than the (strainfree) 1D simulations, cp., Eq. (4.83) and (4.84/4.85). In particular the fit of proportionality between $\bar{r}$ and $t^{1 / 3}$ approximately deviates by $\approx 11$. Thus there is a considerable effect of the dimension during the simulations and we expect that 3Dsimulations lead to a further increase of the coarsening rate.

Table 4.9: Different values obtained from the digital image analysis of the simulated 2D micrographs in Figure 4.12.

| $\tilde{t} \cdot t_{0}$ in sec | $N$ | $\bar{A}^{\beta}$ in $\mu \mathrm{m}^{2}$ | $\bar{r}^{\beta}$ in $\mu \mathrm{m}$ | $\bar{a}^{\beta}$ in $\mu \mathrm{m}$ |
| :--- | :--- | :--- | :--- | :--- |
| $0.015 \cdot 1.462$ | 101 | $9.2300 \cdot 10^{-6}$ | $2.09929 \cdot 10^{-3}$ | $2.73380 \cdot 10^{-3}$ |
| $0.035 \cdot 1.462$ | 37 | $22.710 \cdot 10^{-6}$ | $3.29291 \cdot 10^{-3}$ | $4.28820 \cdot 10^{-3}$ |
| $0.10 \cdot 1.462$ | 12 | $58.500 \cdot 10^{-6}$ | $5.28504 \cdot 10^{-3}$ | $6.88247 \cdot 10^{-3}$ |
| $0.40 \cdot 1.462$ | 9 | $78.440 \cdot 10^{-6}$ | $6.11983 \cdot 10^{-3}$ | $7.96958 \cdot 10^{-3}$ |
| $1.0 \cdot 1.462$ | 4 | $123.08 \cdot 10^{-6}$ | $7.66593 \cdot 10^{-3}$ | $9.98298 \cdot 10^{-3}$ |
| $2.1 \cdot 1.462$ | 2 | $197.17 \cdot 10^{-6}$ | $9.70267 \cdot 10^{-3}$ | $12.63534 \cdot 10^{-3}$ |

Table 4.10: Different values obtained from the digital image analysis of the simulated 2D micrographs in Figure 4.14.

| $\tilde{t} \cdot t_{0}$ in sec | $N$ | $\bar{A}^{\beta}$ in $\mu \mathrm{m}^{2}$ | $\bar{r}^{\beta}$ in $\mu \mathrm{m}$ | $\bar{a}^{\beta}$ in $\mu \mathrm{m}$ |
| :--- | :--- | :--- | :--- | :--- |
| $0.0088 \cdot 1.462$ | 99 | $9.2500 \cdot 10^{-6}$ | $2.1016 \cdot 10^{-3}$ | $2.7368 \cdot 10^{-3}$ |
| $0.0131 \cdot 1.462$ | 80 | $12.020 \cdot 10^{-6}$ | $2.3957 \cdot 10^{-3}$ | $3.1197 \cdot 10^{-3}$ |
| $0.0163 \cdot 1.462$ | 71 | $13.790 \cdot 10^{-6}$ | $2.5660 \cdot 10^{-3}$ | $3.3416 \cdot 10^{-3}$ |
| $0.0217 \cdot 1.462$ | 51 | $19.350 \cdot 10^{-6}$ | $3.0396 \cdot 10^{-3}$ | $3.9583 \cdot 10^{-3}$ |
| $0.0307 \cdot 1.462$ | 36 | $27.740 \cdot 10^{-6}$ | $3.6394 \cdot 10^{-3}$ | $4.7394 \cdot 10^{-3}$ |
| $0.0354 \cdot 1.462$ | 30 | $31.420 \cdot 10^{-6}$ | $3.8732 \cdot 10^{-3}$ | $5.0439 \cdot 10^{-3}$ |
| $0.0486 \cdot 1.462$ | 26 | $37.020 \cdot 10^{-6}$ | $4.2043 \cdot 10^{-3}$ | $5.4750 \cdot 10^{-3}$ |



Figure 4.19: The temporal development of the mean phase radius $\bar{r}^{\beta}$ and $\bar{a}^{\beta}$ in eutectic $\mathrm{Ag}-\mathrm{Cu}$ at $\approx 1000$ Kelvin obtained from the 2D simulations in Figure 4.12.


Figure 4.20: The temporal development of the mean phase radius $\bar{r}^{\beta}$ and $\bar{a}^{\beta}$ in eutectic $\mathrm{Ag}-\mathrm{Cu}$ at $\approx 1000$ Kelvin obtained from the 2D simulations in Figure 4.14.

## Chapter 5

## Experimental Investigations

In this section the eutectic, binary brazing alloy $\mathrm{Ag}-\mathrm{Cu}$ is considered in order to verify and document the phase separation and coarsening process resulting from spinodal decomposition, nucleation and subsequent Ostwald ripening. The aim is to provide experimental reference data, which can be used to analyze and assess the results theoretically obtained from the simulations.

### 5.1 Methodology and Realization

According to the schematically illustrated different procedures of Figure 5.1 one can distinct between four tasks/steps:

1. The making of eutectic $\mathrm{Ag}-\mathrm{Cu}$ (i.e., $71 \mathrm{wt} \% \mathrm{Ag}$ and $29 \mathrm{wt} \% \mathrm{Cu}$ ).
2. Metallographic surface preparation of the specimen, viz. sawing, embedding, grinding, polishing, etching (if necessary).
3. Microscopic investigation and documentation followed by digital analysis of the micrographs..
4. Heat treatment (before: deflasking) of the material, during which the microstructural development within the bulk is initiated and proceeds, using a fixed temperature and different time intervals.

Now these items are explained in more detail.


Figure 5.1: Schematic procedures performed during the experimental investigations of $\mathrm{Ag}-\mathrm{Cu}$.

### 5.1.1 Purchase of the Material and Making of the Specimen

In cooperation with Dr.-Ing. Klaus Müller from the company Neue Materialien Bayreuth GmbH (provision of Ag and Cu ) and Dr.-Ing. Rainer Völkl from the Chair of Metallic Materials, University Bayreuth (melting and casting of Ag and $\mathrm{Cu}^{1}$ ) a "splodge- or button-like" sample of eutectic $\mathrm{Ag}-\mathrm{Cu}$ was produced (diameter: $\approx 40$

[^27]$\mathrm{mm})$. In order to prepare the surface of the sample one needs to bring the specimen into a suitable form. For that reason the sample is cut into various cubes (cf., Figure 5.2 ), which can be easily embedded into especially fabricated epoxy cylinders (cf., Figure $5.1 A, B$ ). Note, that, subsequently to the preparation and the microscopic investigations, the analyzed material will be aged in a furnace. Therefore it is important to perform the embedding procedure reversibly so, that the specimen can easily be deflasked ( $c f$., Figure $5.1 A, B$ ).


Figure 5.2: Illustration of making the rectangular specimen from the "buttton-like" sample.

### 5.1.2 Metallographic Preparation

For an optical visualization of the different phases within the material its surface must be suitably prepared. This can be done, in a first step, by means of multiple grinding and successively finer grained polishing. The number, time and intensity (pressure) of each routine depends on the material (cf., Figure 5.1 C, D and Table 5.1). Note, that these steps are extremely time-consuming. However, they are necessary for the subsequent microscopy in order to eliminate the various scratches usually found at the surface.

After this procedure the different phases are still planar at the surface, and, consequently, they cannot be distinct by means of optical microscopy. Therefore one of the components (i.e., Ag or Cu ) must be (selectively) etched resulting in vertical differences at the surface, which, in turn, are observable under the microscope. According to [100] the following silver-etching solution were used:

- distilled $\mathrm{H}_{2} \mathrm{O}$ : five drops,

Table 5.1: Performed grinding and polishing steps for eutectic Ag-Cu.

| GRINDING |  |  |  |
| :--- | :--- | :--- | :--- |
| step | graining (grain diameter in $\mu \mathrm{m})$ | press capacity | time |
| 01. | $220 \quad(66)$ | 10 N | 15 s |
| 02. | $500 \quad(30)$ | 20 N | 60 s |
| 03. | $1000(18)$ | 20 N | 60 s |
| 04. | 1000 | 10 N | 60 s |
| 05. | $4000 \quad(4)$ | 30 N | 60 s |
| 06. | 4000 | 10 N | 120 s |
| 07. | 4000 | 5 N | 60 s |
|  | POLISHING |  |  |
| step | polishing agent | press capacity | time |
| 08. | DiaDuo Diamant-Polish (Struers corp.) | 20 N | 180 s |
| 09. | OP-S Suspension (Struers corp.) | 20 N | 120 s |
| 10. | OP-S Suspension (Struers corp.) | 10 N | 60 s |

- diluted ammoniac, (25\%): five drops,
- diluted hydrogen peroxide $\left(30 \%, \mathrm{H}_{2} \mathrm{O}_{2}\right)$ : ten drops,
which corresponds to a ratio of 1:1:2. It is worthwhile mentioning that the specimen should be in contact with the above solution only for a fraction of seconds (max. 1 s ) and subsequently be cleaned with distilled water and ethanol, otherwise the surface of the $\mathrm{Ag}-\mathrm{Cu}$ sample is "burned" and the preparation must be repeated.


### 5.1.3 Optical Microscopy and Digital Image Analysis

As a consequence of the etching procedure the Ag-rich ( $\alpha$ ) phase is vertically lower situated at the surface of the material, which results in optical contrasts allowing for the visualization of the different phases during microscopy.

In the following the observed and saved micrographs can be analyzed using (commercial) Digital Imaging Analysis software, cf., Figure 5.1 F, G. On the basis of the different colors of the photos it is possible to identify the different phases, to assess their number and to measure the surface area. Under the assumption of spherical phases (or similar shapes) one can calculate an equivalent phase radius for each phase and, considering all phases, an average phase radius. The latter quantity characterizes the coarsening progress for the investigated aging stage and is suitable to quantify the temporal development of the microstructure.

### 5.1.4 Heat Treatment

After the microscopic examinations the solder cubes are heat-treated for a predefined period (e.g., 5 h), cf., Figure 5.1 E. In order to observe the diffusion-induced micromorphological changes within manageable times a temperature considerably above the homologeous temperature $T_{\text {hom }} \stackrel{\text { (def) }}{=} T / T_{\text {melt }}=0.5$ is required. For eutectic $\mathrm{Ag}-\mathrm{Cu}$ the following working temperature is chosen in these experiments:

$$
\begin{equation*}
T=700^{\circ} \mathrm{C}=973.15 \mathrm{~K} \quad \Rightarrow \quad T_{\mathrm{hom}}=\frac{T}{T_{\mathrm{eut}}}=0.899 \tag{5.1}
\end{equation*}
$$

After the heat treatment the "experimental cycle" is finished and one can repeat the procedure starting from the embedding of the specimen, surface preparation, etching, microscopy, heat treatment, etc. . Hence the aging time increases, and, consequently, the temporal change of the microstructure, in particular the coarsening process, can be observed and documented.

During the experiments explained in this work the coarsening stage after 0 h (i.e., after the solidification), $2 \mathrm{~h}, 5 \mathrm{~h}, 10 \mathrm{~h}, 20 \mathrm{~h}$, and 40 h were examined. As a result microphotos with a scaling factor of 1:200, 1:500 and 1:1000 were obtained, cp., Section 5.3. Furthermore one finds that after a sufficient long aging-time the coarsening state is so advanced that the different phases are observable without preliminary etching. That means for the current case, that additional micro-photos with un-etched surfaces were documented for heat treatment times $t \geq 5 \mathrm{~h}$.

### 5.2 On the Quantification of Coarsening

In order to determine the coarsening rate of the precipitated Cu -rich $(\beta)$ phase quantitatively one must preliminarily clarify two questions:

1. Which parameter is suitable for the quantification of microstructural changes?
2. How can one determine this parameter?

Regarding the first point two quantities can be found: (a) the surface area $A$ of the precipitated phase or (b) the phase perimeter $U$. For the analysis in the work (see Section 5.3) the surface area $A$ of the precipitated $\beta$-phase is chosen. The reason for this is simply that the image analysis software available at the institute supports the determination of this quantity.

Concerning the second question it is worth mentioning the the exploitation of the micro-graphs presented in Section 5.3 denotes a 2D-analysis of a 3D problem. In
particular the software only allows the investigation of the different $\beta$-phases for a fixed intercept area. Consequently the observed amount of $\beta$-precipitations can vary for different intercept areas (cf., Figure 5.3).


Figure 5.3: 1st row: On the dependence of the total surface area of the observed phases on the intercept area. 2nd row: Particle shapes to be considered in the analysis.

This "shortcoming" can be remedied by means of statistical averaging in two ways:

- The investigation of an sufficient large area of intersection $l \times l$ containing many precipitated phases.
- The analysis of various microphotos at the same coarsening stage representing different intercept areas.

For the analysis that was performed here, six pictures for each coarsening stage are investigated, three photos with a scale factor 1:500 (i.e., many precipitates) and three photos with a scale factor $1: 1000$. For better readability the following notation required in the subsequent analysis is introduced:
$A_{i}^{\beta}$ : surface area of a single $\beta$-phase,
$A^{\beta}$ : averaged surface area of a $\beta$-phase of an individual photo (i.e., for a fixed intercept area),
$\bar{A}^{\beta}$ : averaged surface area of a $\beta$-phase of the coarsening stage (results from all photos of a fixed stage),
$N$ : number of $\beta$-phases of one photo/intercept area,
$\bar{r}^{\beta}$ : mean phase radius using the assumption of spherical phase shapes,
$\bar{a}^{\beta}:$ mean phase radius using the assumption of oblate spheroids.

Thus the following relations can be formulated:

$$
\begin{align*}
& A^{\beta}=\frac{1}{N} \sum_{i=1}^{N} A_{i}^{\beta} \quad \text { (for the individual photos) }  \tag{5.2}\\
& \bar{A}^{\beta}=\frac{1}{6} \sum_{\text {photos }} A^{\beta} \quad \text { (for the individual stages) } \tag{5.3}
\end{align*}
$$

Additionally one can also calculate the mean phase radius $\bar{r}$ and $\bar{a}$. Here it holds with [114]:

$$
\left.\begin{array}{rl}
\bar{r}^{\beta} & =\sqrt{\frac{3 \bar{A}^{\beta}}{2 \pi}} \\
\bar{a}^{\beta} & =\sqrt{\frac{\bar{A}^{\beta}}{1.235}} \tag{5.5}
\end{array} \text { (spherical phases) }, ~ \text { oblate spheroids with } b / a=0.5\right) .
$$

Note that the volume of the oblate spheroid is given by $V=\frac{4}{3} \pi a^{2} b$ for $a=b$ ( $c f$., Figure 5.3, second row).

### 5.3 Selected Results

In the following some selected results are presented and we restrict ourselves only to the most important ones. For instance, as a consequence of the performed experimental investigations, more than 50 microphotos were obtained, which document the different stages of coarsening in eutectic $\mathrm{Ag}-\mathrm{Cu}$ at $\approx 1000 \mathrm{~K}$. Obviously, a presentation of all these pictures goes beyond the scope of this work and will unnecessarily "strain" the reader's concentration.

### 5.3.1 Micrographs

In what follows various micrographs with a scale factor of 1:200, 1:500 and 1:1000 are shown. The light areas represent the Ag-rich $\alpha$-matrix ( $c^{\alpha}=0.063$ ), whereas the dark areas denote the Cu -rich $\beta$-phase $\left(c^{\beta}=0.945\right)$.


Figure 5.4: Un-etched photos of the temporal development of the micromorphology in Ag -Cu. From upper left to lower right: after $10 \mathrm{~h}, 20 \mathrm{~h}, 40 \mathrm{~h}$ (scale factor 1:200).

The pictures illustrated in Figures 5.4-5.8 clearly show the the different phases and the corresponding coarsening process. In particular one can see that Ostwald ripening proceeds in such a way that the bigger phases grow at the expense of the smaller ones, i.e., the number of precipitates decreases whereas the surface area of the remaining $\beta$-phases increases.

Furthermore it is worth mentioning that some of the pictures contain unusually "dark areas", cf., e.g., Figure 5.6, (lower-right) or Figure 5.8 (middle-right). These (nonphysical) regions simply results from the etching process, which were performed slightly too long, so that the surface of the specimen is a little "burned", cf., explanations in Section 5.1.2. Furthermore the (oversized) light spherical areas in Figure 5.6 (upper-right) and Figure 5.8 (upper-right) denote water stains remained from the etching and the subsequent cleaning procedure.


Figure 5.5: Un-Etched photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after $5 \mathrm{~h}, 10 \mathrm{~h}, 20 \mathrm{~h}, 40 \mathrm{~h}$ (scale factor 1:500).


Figure 5.6: Etched photos of the temporal development of the micromorphology in $\mathrm{Ag}-\mathrm{Cu}$. From upper left to lower right: after solidification, $2 \mathrm{~h}, 5 \mathrm{~h}, 10 \mathrm{~h}, 20 \mathrm{~h}, 40 \mathrm{~h}$ (scale factor 1:500).


Figure 5.7: Un-Etched photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after $5 \mathrm{~h}, 10 \mathrm{~h}, 20 \mathrm{~h}, 40 \mathrm{~h}$ (scale factor 1:1000).


Figure 5.8: Etched photos of the temporal development of the micromorphology in $\mathrm{Ag}-\mathrm{Cu}$. From upper left to lower right: after solidification, $2 \mathrm{~h}, 5 \mathrm{~h}, 10 \mathrm{~h}, 20 \mathrm{~h}, 40 \mathrm{~h}$ (scale factor 1:1000).

### 5.3.2 Determination of the Mean Phase Radius

In the following the microphotos were quantitatively analyzed by means of digital image analyzing in order to find the mean phase radius $\bar{r}$ or $\bar{a}$, respectively. For this reason one has to extract a representative area from the micrographs preferably such that no imperfections are included. Otherwise the analysis software will identify them as one of the phases, which distorts the results. Furthermore the domains used for the analysis should approximately have similar volume fractions $V^{\beta} / V^{\text {total }}$ w.r.t. the $\beta$-phase. Hence it is guaranteed that differences in the spatial distribution of the phases do not influence the experimentally determined coarsening rates.


Figure 5.9: Analyzed microphotos after $2 h$ heat treatment with a scaling factor of 1:500 (first row) and 1:1000 (second row). Left: Selected area used for the exploitation. Right: Corresponding B-W picture required for the digital image analysis.

The Figures 5.9-5.13 explain the procedure applied for digital image analysis. They show exemplarily one of three analyzed photos with a scaling factor of 1:500 and

1:1000, respectively, used in order to quantify the coarsening stage after $2 \mathrm{~h}, 5 \mathrm{~h}, 10$ h, 20 h , and 40 h .

Note that the transformation to the B-W (Black and White) pictures is required by the underlying algorithm of the analysis software, which yields the number of dark phases as well as their surface areas. The best results are achieved if the pictures are transformed to B-W format.


Figure 5.10: Analyzed microphotos after $5 h$ heat treatment with a scaling factor of 1:500 (first row) and 1:1000 (second row). Left: Selected area used for the exploitation. Right: Corresponding B-W picture required for the digital image analysis.

Hence the analysis software calculated the following values for $A_{\beta}$ and $N$ illustrated, exemplarily for the displayed photos, in Table 5.2. The software ignored all regions with a value of $A_{\beta}^{i}=0 \mu \mathrm{~m}^{2}$ (e.g. small dark points), which are assumed to be imperfections ${ }^{2}$ (e.g., due to uncleanliness).

[^28]

Figure 5.11: Analyzed microphotos after 10 h heat treatment with a scaling factor of 1:500 (first row) and 1:1000 (second row). Left: Selected area used for the exploitation. Right: Corresponding B-W picture required for the digital image analysis.

Note that these values only denote one of six statistical series used for the calculations of the averaged surface area $\bar{A}_{\beta}$ according to Eq. (5.3). Furthermore one must emphasize that the number of phases $N$ specified in Table 5.2 cannot be used for the determination of an empirical law for the temporal development of the precipitate number since the total areas used for the analysis are not uniform for all coarsening stages, cf., Figure 5.9-5.13 (left).

Analyzing the six microphotos for each aging stage and applying the formulae of Eq. $(5.4,5.5)$ yields the mean phase radii $\bar{r}$ and $\bar{a}$ as illustrated in Table 5.3. The declared error boundaries denote the maximal deviation between the mean phase radius of the coarsening stage (including six photos) and the corresponding values resulting from

[^29]

Figure 5.12: Analyzed microphotos after 20 h heat treatment with a scaling factor of 1:500 (first row) and 1:1000 (second row). Left: Selected area used for the exploitation. Right: Corresponding B-W picture required for the digital image analysis.
the individually analyzed photos.
Figure 5.14 illustrates the temporal development of the mean phase radius following from Table 5.3. Obviously the assumption of oblate spheroid-shaped phases results in faster coarsening rates, which already follows by a comparison of Eq. (5.4) and (5.5). Furthermore it holds that $\bar{r} \propto t^{1 / 3}$ or $\bar{a} \propto t^{1 / 3}$ (with the exception of the 2 h data), respectively. In particular one can finally write the following empirical laws by means of a fit procedure:

$$
\begin{equation*}
\bar{r}^{\beta}=0.024 \cdot t^{1 / 3} \quad \text { and } \quad \bar{a}^{\beta}=0.032 \cdot t^{1 / 3} . \tag{5.6}
\end{equation*}
$$

Indeed, Eq. (5.6) 1,2 is noteworthy. The $t^{1 / 3}$ dependence is well-known from socalled LSW-theories, labeled to the authors of the seminal works in the area of the


Figure 5.13: Analyzed microphotos after 40 h heat treatment with a scaling factor of 1:500 (first row) and 1:1000 (second row). Left: Selected area used for the exploitation. Right: Corresponding B-W picture required for the digital image analysis.
theoretical description of precipitate's growth in a (supersaturated) matrix, cf., [79, 116], which describe the surface-energy-minimization process - so-called OstwaLdripening, [96] - by means of the GibBS-Thomson effect.

Table 5.2: Values calculated by the image analysis software, exemplarily for the illustrated Figures 5.9-5.13.

| Time | Scaling factor | $A_{\beta}$ in $\mu \mathrm{m}^{2}$ | No. of phases | Vol. fraction $V^{\beta} / V^{\text {total }}$ |
| ---: | :--- | :--- | :--- | :--- |
| 2 h | $1: 500$ | 3.07 | 675 | 0.46 |
|  | $1: 1000$ | 2.43 | 131 | 0.45 |
| 5 h | $1: 500$ | 1.59 | 154 | 0.61 |
|  | $1: 1000$ | 0.75 | 262 | 0.61 |
| 10 h | $1: 500$ | 2.72 | 179 | 0.20 |
|  | $1: 1000$ | 1.29 | 95 | 0.41 |
| 20 h | $1: 500$ | 3.57 | 67 | 0.45 |
|  | $1: 1000$ | 6.52 | 65 | 0.46 |
| 40 h | $1: 500$ | 5.86 | 393 | 0.45 |
|  | $1: 1000$ | 2.52 | 193 | 0.41 |

Table 5.3: Mean phase radii for different coarsening stages and different types of phase shapes (assumed).

| time | spherical shaped <br> $\bar{r}^{\beta}$ in $\mu \mathrm{m}$ | oblate spheroid shaped |
| :--- | :--- | :--- |
|  | $0.76 \pm 0.28$ | $\bar{a}^{\beta}$ in $\mu \mathrm{m}$ |
| 2 h | $0.61 \pm 0.18$ | $0.99 \pm 0.37$ |
| 5 h | $0.82 \pm 0.33$ | $0.79 \pm 0.23$ |
| 10 h | $1.04 \pm 0.48$ | $1.07 \pm 0.43$ |
| 20 h | $1.24 \pm 0.30$ | $1.36 \pm 0.63$ |
| 40 h | $1.62 \pm 0.39$ |  |




Figure 5.14: The temporal development of the mean phase radius $\bar{r}^{\beta}$ and $\bar{a}^{\beta}$ in eutectic $\mathrm{Ag}-\mathrm{Cu}$ at $\approx 1000$ Kelvin observed in experiments. Dashed line: spherical phase shape. Continuous line: oblate spheroid-shaped phase.

## Chapter 6

## Résumé

### 6.1 Theory vs. Experiment

At the end of this work we will discuss the agreement between the simulations and the experimental investigations. To this end we compare the obtained coarsening rate of the 1D strain-free simulation in Eq. (4.83) with the rates following from the 2D-simulations, cf., Eqs. $(4.84,4.85)$ and the coarsening rates resulting from the experiments in Eq. (5.6). Table 6.1 compiles the fitted results, and the corresponding curves are shown in Figure 6.1. Three characteristics are worth mentioning:

Table 6.1: Comparison of the different coarsening rates following from the simulations and the experiment.

| source | $k_{s}\left(\right.$ sphere, $\left.\bar{r}^{\beta}=k_{s} \cdot t^{1 / 3}\right)$ | $k_{o}\left(\right.$ oblate-spheroids, $\bar{a}^{\beta}=k_{o} \cdot$ <br> $\left.t^{1 / 3}\right)$ |
| ---: | :--- | :--- |
| 1D Sim. | 0.00082 | 0.00086 |
| 2D Sim. (EULER) | 0.00710 | 0.00920 |
| 2D Sim. (RADAU) | 0.00980 | 0.01300 |
| Experiment | 0.02400 | 0.03200 |

- The factors $k_{s}$ and $k_{o}$ (factor of proportionality between $\bar{r}^{\beta}$ or $\bar{a}^{\beta}$ and $t^{1 / 3}$ ) found from the 1D simulations are much smaller (approximately 30-37 times smaller) than the corresponding factors obtained from the experiment.
- The factors $k_{s}$ and $k_{o}$ following from the 2D-simulations are approximately $2.4-$ 3.4 times smaller than the experimentally obtained factors, i.e., in comparison to the 1D-simulations the deviation is considerably reduced.
- The 2D-simulations performed by means of the RADAU routine yields the best agreement with the experimental coarsening rates.

As a consequence of these observations one may expect that 3D-simulations presumably lead to a further reduction of the deviation between theory and experiment. This is reasonable since the coarsening process observed during the experiments represents a three-dimensional process, although the documented and analyzed micrographs are in 2 D .

However, there are also a few, obvious shortcomings accompanying with the above comparison. On the one hand side, some of the analyzed micrographs are here and there slightly burned (extra dark areas), which results from the (too long) etching procedure. This "uncleanliness" within the pictures lead to a overestimation of the coarsening rate during digital image analysis. On the other hand side, the underlying analysis presumes spherical or oblate-spheroid phase shapes, which - obviously - do not match the situation for early coarsening stages, in which a net-like structure dominates, $c f$., Figure 5.10. Finally note that the total simulation time ranges within some minutes whereas the experimental aging was performed for 2-40 h. Consequently, a comparison of the results is only possible if the theoretically obtained coarsening rates would be strongly extrapolated.

Nevertheless, the theoretical results, in particular the 2D simulations, show an a priori unexpected, good agreement with the experiments. In this context it should be mentioned, that all parameters used during the simulations (e.g., mobilities, HGCs, elastic constants) are taken from the literature or determined from microscopic theories. No parameter was fitted to aging experiments! This fact denotes a distinctive difference to various simulations in the literature, cf., e.g., [113], in which, e.g., the mobility is adjusted to experiments in order to ensure agreement between theory and the really observed aging process.


Figure 6.1: Comparison of the coarsening behavior predicted from the (strain-free) simulations and from the experiment.

### 6.2 Conclusion and Outlook

In this work we investigated the process of phase separation and coarsening in multiphase alloys from a theoretical as well as experimental point-of-view. We concentrated on the brazing material $\mathrm{Ag}-\mathrm{Cu}$ representative for lead-free solder materials, which are currently favored for microelectronic solder joints. We started with an overview about the different technological and environmental tendencies in microelectronics and pointed out the relevance of the lead-free legalization in this sector. Due to these tendencies we turned the attention to lead-free solder materials and briefly gave an introduction into the various microstructural phenomena and their impact on microelectronic reliability.

In Chapter 2 a thermodynamically consistent phase field theory was developed, which allows modeling of the diffusion-induced phase evolution in multicomponent materials, especially under the presence of local thermo-mechanical strains. After a historical overview of the development of diffusion theories for solids we discussed existing shortcomings and open questions within the models and approaches. Four statements for an entropy principle were formulated, which allow to deduce the constitutive equations required for the theoretical description of spinodal decomposition and Ostwald ripening in solid mixtures. We, first, considered a single phase, which corresponds to the case of classical mixtures, and derived the established results for the entropy, heat, and diffusion flux as well as for the pressure and the second Piola-Kirchhoff stress tensor. Moreover, we also deduced the Gibbs-Duhem equation as well as various Gibbs relations. Furthermore an additive decomposition of the Helmholtz free energy $\varphi=\varphi^{\text {mech }}+\varphi^{\text {chem }}$ into a mechanical and into a chemical part was introduced, which allows to distinguish between elastic deformations and deformations due to eigen-strains. Second, we exploited the entropy principle for multi-phase mixtures by incorporating so-called higher gradients. In particular, we turned the attention to the diffusion flux and derived, after the restriction to binary alloys, an extended diffusion equation, which represents - in combination with the partial mass balance - a generalization of the well-established Cahn-Hilliard equation. This generalization relies on the fact that the HGCs depend on the concentration and on the local thermo-mechanical strains, which lead to additional contributions to the diffusion flux.

Subsequently, we developed in Chapter 3 an atomistic theory to determine the material parameters, such as the elastic constants and the HGCs, which are required for a quantitative investigation of the extended diffusion equation derived in Chapter 2. The obtained equations are based on the embedded-atom-method, [29], and allow to calculate the stiffness matrix as well as the higher gradient coefficients as functions of the concentration and the strains. Regarding the considerations in Chapter 1 we turned the attention to $\mathrm{Ag}-\mathrm{Cu}$ and, first, calculated the elastic constants of the pure substances, Ag and Cu , which show a good agreement with (experimentally obtained) literature values. Second, we calculated the corresponding values for $\mathrm{Ag}-\mathrm{Cu}$ as well
as the HGCs. In order to stress the reliability of the determined material data we finally performed phase equilibria calculations and constructed the solid part of the $\mathrm{Ag}-\mathrm{Cu}$ phase diagram by means of the EAM potentials.

The equations obtained in Chapter 2 in combination with the calculated materials data of Chapter 3 allow for quantitative simulations of the spinodal decomposition and coarsening process in $\mathrm{Ag}-\mathrm{Cu}$, as performed in Chapter 4. We begun with a brief explanation of the numerical methods required for the solution of the extended diffusion equation, which represents a nonlinear partial differential equations for the concentration field. In particular we used Discrete Fourier Transforms for the spatial discretization and one-step time integration methods (such as the Euler or the Runge-Kutta method) for the time discretization. Various simulated micromorphologies of $\mathrm{Ag}-\mathrm{Cu}$ in 1 D and 2 D were presented, and the results were discussed in view of the numerical efforts. During the 1D simulations special attention was paid to the impact of positive and negative strains on the phase evolution process. This distinction became possible for a first time due to the theoretically predicted HGCs followed from the considerations in Section 3. Chapter 4 ends with the quantification of the different coarsening rates of the simulations, which show considerable deviations between the 1D- and 2D-simulations.

In Section 6 experimental investigations w.r.t. Ag-Cu were performed. After a detailed explanation of the experimental methods (i.e., the metallographic preparation process, the microscopy, and the aging of the material by heat treatment) we presented selected micrographs for the different coarsening stages, which documented the phase evolution by Ostwald ripening. The chapter was ended with the quantification of the coarsening rates by means of digital image analysis, allowing for a direct comparison between the theoretical and the experimental results.

However, the present Ph.D. thesis, in particular the developed theoretical framework as well as the obtained results gives rise to further investigations. More specifically, the theoretical approach of Chapter 2 allows to (1) incorporate chemical reactions $\left(\tau_{\alpha}^{\rho / n} \neq 0\right)$ as required for the description of the formation of intermetallic compounds (IMCs). Furthermore investigations of (2) the impact of large deformations as well as dissipative effects $\left(\sigma_{\text {diss }}^{i j} \neq 0\right)$ are conceivable for future studies. Nevertheless, questions regarding (3) the microstructural evolution in ternary systems, such as $\mathrm{Sn}-\mathrm{Ag}-\mathrm{Cu}$, still remain open which, in principle, can be also investigated within the presented framework. On the other hand, (4) alternative numerical methods can be performed, such as finite element techniques, cf., [113, 52], in order to optimize the numerical efforts and to (eventually) increase convergence and stability of the numerical solution of the extended diffusion equation. In this context, this work has shown that (5) 3D-simulations are desirable for a further reduction of the deviation between the coarsening rates following from the simulations and the experiments, $c f$., the previous section. If the microstructural evolution can be reliably simulated, then (6) questions about the effective material properties and their impact on strength and lifetime will occur. Homogenization methods, [26], can be used in this context to
predict the behavior of the heterogeneous material. Finally the investigation should be extended to (7) alternative solders, such as $\mathrm{Sn}-\mathrm{Ag}$ or $\mathrm{Sn}-\mathrm{Cu}$. These alloys show a more complex lattice structure due to the anisotropy of Sn , which has a BCTstructure. Here the modified-embedded-atom-method, cf., [77], can be used to predict the required materials data, such as the elastic constants or the HGCs.

## Appendix A

## Additional Calculations required for Chapter 2

## A. 1 Proof of Equation (2.45)

The following relation holds between the derivatives of the reduced right CauchyGreen tensor $c^{k l}$ and the Cauchy-Green tensor $C^{k l}$ according to Section 2.2:

$$
\begin{equation*}
\dot{c}^{k l}=\frac{\mathrm{d}}{\mathrm{~d} t}\left(J^{-2 / 3} C^{k l}\right)=-\frac{2}{3} J^{-5 / 3} \dot{J} C^{k l}+J^{-2 / 3} \dot{C}^{k l} \tag{A.1}
\end{equation*}
$$

Moreover we have the identity:

$$
\begin{equation*}
\dot{J}=\frac{\mathrm{d}}{\mathrm{~d} t}\left(\operatorname{det} F^{i j}\right)=\left[\frac{\partial}{\partial F^{k l}}\left(\operatorname{det} F^{i j}\right)\right] \dot{F}^{k l}=\left[\left(\operatorname{det} F^{i j}\right)\left(F^{-1}\right)^{l k}\right] \frac{\partial v^{k}}{\partial X^{l}}=J \frac{\partial v^{k}}{\partial x^{k}} \tag{A.2}
\end{equation*}
$$

and

$$
\begin{align*}
\dot{C}^{k l} & =\frac{\mathrm{d}}{\mathrm{~d} t}\left(F^{m k} F^{m l}\right)=\dot{F}^{m k} F^{m l}+F^{m k} \dot{F}^{m l}=\frac{\partial v^{m}}{\partial X^{k}} F^{m l}+\frac{\partial v^{m}}{\partial X^{l}} F^{m k} \\
& =\frac{\partial v^{m}}{\partial x^{s}} \frac{\partial x^{s}}{\partial X^{k}} F^{m l}+\frac{\partial v^{m}}{\partial x^{s}} \frac{\partial x^{s}}{\partial X^{l}} F^{m k}=\frac{\partial v^{i}}{\partial x^{j}}\left(F^{j k} F^{i l}+F^{j l} F^{i k}\right) . \tag{A.3}
\end{align*}
$$

The result of Eqs. (A.3) and (A.2) can be inserted into Eq. (A.1). We finally find:

$$
\begin{equation*}
\dot{c}^{k l}=-\frac{2}{3} J^{-2 / 3} \frac{\partial v^{i}}{\partial x^{i}} C^{k l}+J^{-2 / 3} \frac{\partial v^{i}}{\partial x^{j}}\left(F^{j k} F^{i l}+F^{j l} F^{i k}\right) . \tag{A.4}
\end{equation*}
$$

## A. 2 Legendre Transform between $\tilde{\mathcal{S}}$ and $\hat{\mathcal{S}}$

We start with the functional representation $\tilde{\mathcal{S}}$ of the entropy density $\rho \eta$ and write for the total differential:

$$
\begin{align*}
\mathrm{d}(\rho \eta) & =\mathrm{d} \tilde{\mathcal{S}}=\frac{\partial \tilde{\mathcal{S}}}{\partial \rho \epsilon} \mathrm{d}(\rho \epsilon)+\sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \tilde{\mathcal{S}}}{\partial c^{i j}} \mathrm{~d} c^{i j}  \tag{A.5}\\
& =\mathrm{d} \hat{\mathcal{S}}=\frac{\partial \hat{\mathcal{S}}}{\partial T} \mathrm{~d} T+\sum_{\alpha=1}^{\nu} \frac{\partial \hat{\mathcal{S}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \hat{\mathcal{S}}}{\partial c^{i j}} \mathrm{~d} c^{i j} \tag{A.6}
\end{align*}
$$

with $\frac{\partial \tilde{S}}{\partial \rho \epsilon}=1 / T$. Furthermore it holds with $\rho \epsilon=\hat{\mathcal{E}}\left(T, n_{1}, \ldots, n_{\nu}, c^{i j}\right)$ :

$$
\begin{equation*}
\mathrm{d}(\rho \epsilon)=\mathrm{d} \hat{\mathcal{E}}=\frac{\partial \hat{\mathcal{E}}}{\partial T} \mathrm{~d} T+\sum_{\alpha=1}^{\nu} \frac{\partial \hat{\mathcal{E}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \hat{\mathcal{E}}}{\partial c^{i j}} \mathrm{~d} c^{i j} . \tag{A.7}
\end{equation*}
$$

The term $\mathrm{d}(\rho \epsilon)$ in Eq. (A.5) can now be substituted by the left hand side of Eq. (A.7). By means of the definition of the absolute temperature, Eq. (2.36), one obtains:

$$
\begin{equation*}
\mathrm{d}(\rho \eta)=\underbrace{\frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial T}}_{=\frac{\partial \hat{S}}{\partial T}} \mathrm{~d} T+\sum_{\alpha=1}^{\nu} \underbrace{\left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}+\frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial n_{\alpha}}\right)}_{=\frac{\partial \hat{\mathcal{S}}}{\partial n_{\alpha}}} \mathrm{d} n_{\alpha}+\underbrace{\left(\frac{\partial \tilde{\mathcal{S}}}{\partial c^{i j}}+\frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial c^{i j}}\right)}_{=\frac{\partial \hat{\mathcal{i}}}{\partial c^{i j}}} \mathrm{~d} c^{i j} \tag{A.8}
\end{equation*}
$$

and we identify with $\mathrm{d}(\rho \eta)=\mathrm{d} \hat{\mathcal{S}}$ :

$$
\begin{equation*}
\frac{\partial \hat{\mathcal{S}}}{\partial T}=\frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial T} \quad, \quad \frac{\partial \hat{\mathcal{S}}}{\partial n_{\alpha}}=\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}+\frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial n_{\alpha}} \quad, \quad \frac{\partial \hat{\mathcal{S}}}{\partial c^{i j}}=\frac{\partial \tilde{\mathcal{S}}}{\partial c^{i j}}+\frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial c^{i j}} \tag{A.9}
\end{equation*}
$$

Since the variables $T$ and $n_{\alpha}$ are independent within the domain of $\hat{\mathcal{S}}$ one can, in particular, find from Eq. (A.9) ${ }_{2}$ the relation $(\beta \neq \alpha)$ :

$$
\begin{equation*}
\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}=-\frac{1}{T}\left(\frac{\partial \hat{\mathcal{E}}}{\partial n_{\alpha}}-T \frac{\partial \hat{\mathcal{S}}}{\partial n_{\alpha}}\right)=-\frac{1}{T} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}}=-\left.\frac{1}{T} \frac{\partial(\rho \varphi)}{\partial n_{\alpha}}\right|_{T, n_{\beta}, c^{i j}} \tag{A.10}
\end{equation*}
$$

## A. 3 Legendre Transform between $\hat{\mathcal{F}}$ and $\overline{\mathcal{F}}$

Recall the functional representations shown in Eq. $(2.50)_{2,3}$. Consequently we can write:

$$
\begin{align*}
\mathrm{d}(\rho \varphi) & =\mathrm{d} \hat{\mathcal{F}}=\frac{\partial \hat{\mathcal{F}}}{\partial T} \mathrm{~d} T+\sum_{\alpha=1}^{\nu} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \hat{\mathcal{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j},  \tag{A.11}\\
& =\mathrm{d} \overline{\mathcal{F}}=\frac{\partial \overline{\mathcal{F}}}{\partial T} \mathrm{~d} T+\sum_{\beta=1}^{\nu-1} \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}+\frac{\partial \overline{\mathcal{F}}}{\partial \rho} \mathrm{d} \rho+\frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j} . \tag{A.12}
\end{align*}
$$

Obviously the transfer from $\overline{\mathcal{F}}$ to $\hat{\mathcal{F}}$ requires the substitution of $\mathrm{d} y_{\beta}$ and $\mathrm{d} \rho$ by $\mathrm{d} n_{\alpha}$. For this reason we calculate:

$$
\begin{align*}
& \rho\left(n_{1}, \ldots, n_{\nu}\right)=\sum_{\alpha=1}^{\nu} m_{\alpha} n_{\alpha} \Rightarrow \mathrm{d} \rho=\sum_{\alpha=1}^{\nu} \frac{\partial \rho}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}=\sum_{\alpha=1}^{\nu} m_{\alpha} \mathrm{d} n_{\alpha}  \tag{A.13}\\
& y_{\beta}\left(n_{1}, \ldots, n_{\nu}\right)=\frac{n_{\beta}}{\sum_{\alpha=1}^{\nu} n_{\alpha}} \Rightarrow \mathrm{d} y_{\beta}=\sum_{\alpha=1}^{\nu} \frac{\partial y_{\beta}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}=\sum_{\alpha=1}^{\nu}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \mathrm{d} n_{\alpha} . \tag{A.14}
\end{align*}
$$

Eqs. (A.13) and (A.14) can be inserted into Eq. (A.12). We obtain:

$$
\begin{equation*}
\mathrm{d}(\rho \varphi)=\frac{\partial \overline{\mathcal{F}}}{\partial T} \mathrm{~d} T+\sum_{\alpha=1}^{\nu}\left[m_{\alpha} \frac{\partial \overline{\mathcal{F}}}{\partial \rho}+\sum_{\beta=1}^{\nu-1} \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)\right] \mathrm{d} n_{\alpha}+\frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j} \tag{A.15}
\end{equation*}
$$

By comparing the coefficients between Eqs. (A.11) and (A.15) results:

$$
\begin{equation*}
\frac{\partial \hat{\mathcal{F}}}{\partial T}=\frac{\partial \overline{\mathcal{F}}}{\partial T}, \quad \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}}=m_{\alpha} \frac{\partial \overline{\mathcal{F}}}{\partial \rho}+\sum_{\beta=1}^{\nu-1} \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \quad, \quad \frac{\partial \hat{\mathcal{F}}}{\partial c^{i j}}=\frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}} \tag{A.16}
\end{equation*}
$$

## A. 4 Legendre Transform between $\overline{\mathcal{F}}$ and $\mathcal{\mathcal { F }}$

According to Eq. $(2.50)_{3,4}$ we write:

$$
\begin{align*}
\mathrm{d}(\rho \varphi) & =\mathrm{d} \overline{\mathcal{F}}=\frac{\partial \overline{\mathcal{F}}}{\partial T} \mathrm{~d} T+\sum_{\beta=1}^{\nu-1} \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}+\frac{\partial \overline{\mathcal{F}}}{\partial \rho} \mathrm{d} \rho+\frac{\partial \overline{\mathcal{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j}  \tag{A.12}\\
& =\mathrm{d} \dot{\mathcal{F}}=\frac{\partial \dot{\mathcal{F}}}{\partial T} \mathrm{~d} T+\sum_{\beta=1}^{\nu-1} \frac{\partial \dot{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}++\frac{\partial \dot{\mathcal{F}}}{\partial C^{i j}} \mathrm{~d} C^{i j} . \tag{A.17}
\end{align*}
$$

Hence we have to substitute $\mathrm{d} \rho$ and $\mathrm{d} c^{i j}$ by means of $\mathrm{d} C^{i j}$. For this reason we find:

$$
\begin{align*}
& C^{i j}\left(c^{i j}, \rho\right)=J^{2 / 3} c^{i j}=c^{i j}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3} \Rightarrow \mathrm{~d} C^{i j}=\frac{\partial C^{i j}}{\partial c^{k l}} \mathrm{~d} c^{k l}+\frac{\partial C^{i j}}{\partial \rho} \mathrm{~d} \rho,  \tag{A.18}\\
& \text { with } \frac{\partial C^{i j}}{\partial c^{k l}} \stackrel{\left(C^{i j}=C^{j i}\right)}{=} \frac{1}{2} \frac{\partial}{\partial c^{k l}}\left(C^{i j}+C^{j i}\right)=\frac{1}{2}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3}\left(\delta^{i k} \delta^{j l}+\delta^{j k} \delta^{i l}\right)  \tag{A.19}\\
& \text { and } \frac{\partial C^{i j}}{\partial \rho}=-\frac{2}{3} \frac{c^{i j}}{\rho}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3} . \tag{A.20}
\end{align*}
$$

Insertion of Eqs. (A.18) ${ }_{2}$, (A.19) and (A.20) into Eq. (A.17) results in:

$$
\begin{align*}
\mathrm{d}(\rho \varphi)= & \frac{\partial \dot{\mathcal{F}}}{\partial T} \mathrm{~d} T+\sum_{\beta=1}^{\nu-1} \frac{\partial \hat{\mathcal{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}+ \\
& \frac{\partial \dot{\mathcal{F}}}{\partial C^{i j}}\left[\frac{1}{2}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3}\left(\delta^{i k} \delta^{j l}+\delta^{j k} \delta^{i l}\right) \mathrm{d} c^{k l}-\frac{2}{3} \frac{c^{i j}}{\rho}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3} \mathrm{~d} \rho\right] . \tag{A.21}
\end{align*}
$$

Comparison of Eqs. (A.12) and (A.21) yields for the coefficients:

$$
\begin{align*}
\frac{\partial \overline{\mathcal{F}}}{\partial T} & =\frac{\partial \dot{\mathcal{F}}}{\partial T} \quad, \quad \frac{\partial \overline{\mathcal{F}}}{\partial y_{\beta}}=\frac{\partial \dot{\mathcal{F}}}{\partial y_{\beta}} \quad, \quad \frac{\partial \overline{\mathcal{F}}}{\partial \rho}=-\frac{2}{3} \frac{c^{i j}}{\rho}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3} \frac{\partial \dot{\mathcal{F}}}{\partial C^{i j}} \\
\frac{\partial \overline{\mathcal{F}}}{\partial c^{k l}} & =\frac{1}{2} \frac{\partial \dot{\mathcal{F}}}{\partial C^{i j}}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3}\left(\delta^{i k} \delta^{j l}+\delta^{j k} \delta^{i l}\right) . \tag{A.22}
\end{align*}
$$

## A. 5 Legendre Transform between $\widetilde{\mathbb{S}}$ and $\hat{\mathbb{S}}$

According to the functional representations in Eq. $(2.106)_{1,2}$ the following total differentials are formulated $(\alpha=1, \ldots, \nu)$ :

$$
\begin{align*}
\mathrm{d}(\rho \eta) & =\mathrm{d} \tilde{\mathbb{S}}=\frac{\partial \tilde{\mathbb{S}}}{\partial \rho \epsilon} \mathrm{d}(\rho \epsilon)+\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{i} n_{\alpha}} \mathrm{d}\left(\nabla^{i} n_{\alpha}\right)+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{i j} n_{\alpha}} \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right)+\frac{\partial \tilde{\mathbb{S}}}{\partial c^{i j}} \mathrm{~d} c^{i j}  \tag{A.23}\\
& =\mathrm{d} \hat{\mathbb{S}}=\frac{\partial \hat{\mathbb{S}}}{\partial T} \mathrm{~d} T+\frac{\partial \hat{\mathbb{S}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \hat{\mathbb{S}}}{\partial \nabla^{i} n_{\alpha}} \mathrm{d}\left(\nabla^{i} n_{\alpha}\right)+\frac{\partial \hat{\mathbb{S}}}{\partial \nabla^{i j} n_{\alpha}} \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right)+\frac{\partial \hat{\mathbb{S}}}{\partial c^{i j}} \mathrm{~d} c^{i j}, \tag{A.24}
\end{align*}
$$

with the definition of the absolute temperature $\frac{\partial \tilde{\mathcal{S}}}{\partial \rho \epsilon}=1 / T$. The total differential of the internal energy density $\rho \epsilon=\hat{\mathbb{E}}\left(T, n_{\alpha}, \nabla^{i} n_{\alpha}, \nabla^{i j} n_{\alpha}, c^{i j}\right)$ in Eq. (A.23) can be
replaced by means of:

$$
\begin{equation*}
\mathrm{d}(\rho \epsilon)=\mathrm{d} \hat{\mathbb{E}}=\frac{\partial \hat{\mathbb{E}}}{\partial T} \mathrm{~d} T+\frac{\partial \hat{\mathbb{E}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \hat{\mathbb{E}}}{\partial \nabla^{i} n_{\alpha}} \mathrm{d}\left(\nabla^{i} n_{\alpha}\right)+\frac{\partial \hat{\mathbb{E}}}{\partial \nabla^{i j} n_{\alpha}} \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right)+\frac{\partial \hat{\mathbb{E}}}{\partial c^{i j}} \mathrm{~d} c^{i j} \tag{A.25}
\end{equation*}
$$

Hence it follows from Eq. (A.23):

$$
\begin{align*}
\mathrm{d} \tilde{\mathbb{S}}= & \frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial T} \mathrm{~d} T+\left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial n_{\alpha}}+\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}}\right) \mathrm{d} n_{\alpha}+\left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial \nabla^{i} n_{\alpha}}+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{i} n_{\alpha}}\right) \mathrm{d}\left(\nabla^{i} n_{\alpha}\right) \\
& +\left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial \nabla^{i j} n_{\alpha}}+\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{i j} n_{\alpha}}\right) \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right)+\left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial c^{i j}}+\frac{\partial \tilde{\mathbb{S}}}{\partial c^{i j}}\right) \mathrm{d} c^{i j} . \tag{A.26}
\end{align*}
$$

Since $T$ and $n_{\alpha}$ are independent arguments within the functional representations $\hat{\mathbb{E}}$ and $\hat{\mathbb{S}}$ we identify:

$$
\begin{align*}
\frac{\partial \hat{\mathbb{S}}}{\partial T} & =\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial T} \quad, \quad-T \frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}}=\frac{\partial \hat{\mathbb{F}}}{\partial n_{\alpha}}, \quad-T \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{i} n_{\alpha}}=\frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{i} n_{\alpha}} \\
-T \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{i j} n_{\alpha}} & =\frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{i j} n_{\alpha}}, \quad-T \frac{\partial \tilde{\mathbb{S}}}{\partial c^{i j}}=\frac{\partial \hat{\mathbb{F}}}{\partial c^{i j}}, \tag{A.27}
\end{align*}
$$

where $\hat{\mathbb{F}}\left(T, n_{\alpha}, \nabla^{i} n_{\alpha}, \nabla^{i j} n_{\alpha}, c^{i j}\right)$ is the functional representation of the Helmholtz free energy density $\rho \varphi$.

## A. 6 Legendre Transform between $\hat{\mathbb{F}}$ and $\overline{\mathbb{F}}$

Using the representations in Eq. (2.123) we find the following total differentials $(\alpha=1, \ldots, \nu$ and $\beta=1, \ldots, \nu-1)$ :

$$
\begin{align*}
& d(\rho \varphi)= \mathrm{d} \hat{\mathbb{F}}=  \tag{A.28}\\
& \frac{\partial \hat{\mathbb{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \hat{\mathbb{F}}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{i} n_{\alpha}} \mathrm{d}\left(\nabla^{i} n_{\alpha}\right)+\frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{i j} n_{\alpha}} \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right)+\frac{\partial \hat{\mathbb{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j} \\
&=\mathrm{d} \overline{\mathbb{F}}= \frac{\partial \overline{\mathbb{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \overline{\mathbb{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}} \mathrm{d}\left(\nabla^{i} y_{\beta}\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}} \mathrm{d}\left(\nabla^{i j} y_{\beta}\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \rho} \mathrm{d} \rho  \tag{A.29}\\
&+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} \rho} \mathrm{~d}\left(\nabla^{i} \rho\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} \rho} \mathrm{~d}\left(\nabla^{i j} \rho\right)+\frac{\partial \overline{\mathbb{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j} .
\end{align*}
$$

Now the terms with brackets must be "suitably" replaced by expressions of $\mathrm{d} n_{\alpha}$, $\mathrm{d}\left(\nabla^{i} n_{\alpha}\right)$ and $\mathrm{d}\left(\nabla^{i j} n_{\alpha}\right)$. For this reason we write as follows:

$$
\begin{align*}
\rho & =\sum_{\alpha} m_{\alpha} n_{\alpha} \Rightarrow \mathrm{d} \rho=\sum_{\alpha} m_{\alpha} \mathrm{d} n_{\alpha},  \tag{A.30}\\
\nabla^{i} \rho & =\sum_{\alpha} m_{\alpha} \nabla^{i} n_{\alpha} \Rightarrow \mathrm{d}\left(\nabla^{i} \rho\right)=\sum_{\alpha} m_{\alpha} \mathrm{d}\left(\nabla^{i} n_{\alpha}\right),  \tag{A.31}\\
\nabla^{i j} \rho & =\sum_{\alpha} m_{\alpha} \nabla^{i j} n_{\alpha} \Rightarrow \mathrm{d}\left(\nabla^{i j} \rho\right)=\sum_{\alpha} m_{\alpha} \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right) . \tag{A.32}
\end{align*}
$$

Furthermore holds:

$$
\begin{align*}
y_{\beta} & =\frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}} \Rightarrow y_{\beta}=\hat{\mathbb{Y}}_{\beta}\left(n_{\alpha}\right),  \tag{A.33}\\
\nabla^{i} y_{\beta} & =\nabla^{i}\left(\frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}}\right) \Rightarrow \nabla^{i} y_{\beta}=\hat{\mathbb{Y}}_{\beta}^{i}\left(n_{\alpha}, \nabla^{i} n_{\alpha}\right),  \tag{A.34}\\
\nabla^{i j} y_{\beta} & =\nabla^{i j}\left(\frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}}\right) \Rightarrow \nabla^{i j} y_{\beta}=\hat{\mathbb{Y}}_{\beta}^{i j}\left(n_{\alpha}, \nabla^{i} n_{\alpha}, \nabla^{i j} n_{\alpha}\right) \tag{A.35}
\end{align*}
$$

and after a straightforward calculation:

$$
\begin{align*}
\mathrm{d} y_{\beta}= & \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}=\sum_{\alpha}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \mathrm{d} n_{\alpha}  \tag{A.36}\\
\mathrm{d}\left(\nabla^{i} y_{\beta}\right)= & \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{i}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{i}}{\partial \nabla^{i} n_{\alpha}} \mathrm{d}\left(\nabla^{i} n_{\alpha}\right) \\
= & \sum_{\alpha} \nabla^{i}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \mathrm{d} n_{\alpha}+\sum_{\alpha}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \mathrm{d}\left(\nabla^{i} n_{\alpha}\right)  \tag{A.37}\\
\mathrm{d}\left(\nabla^{i j} y_{\beta}\right)= & \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{i j}}{\partial n_{\alpha}} \mathrm{d} n_{\alpha}+\sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{i j}}{\partial \nabla^{k} n_{\alpha}} \mathrm{d}\left(\nabla^{k} n_{\alpha}\right)+\sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{i j}}{\partial \nabla^{k l} n_{\alpha}} \mathrm{d}\left(\nabla^{k l} n_{\alpha}\right) \\
= & \sum_{\alpha} \nabla^{i j}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \mathrm{d} n_{\alpha}+2 \sum_{\alpha} \nabla^{j}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \mathrm{d}\left(\nabla^{i} n_{\alpha}\right) \\
& +\sum_{\alpha}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right) \tag{A.38}
\end{align*}
$$

Substituting the underbracket terms in Eq. (A.29) by the results in Eqs. (A.30-A.32) and (A.36-A.38) yields:

$$
\begin{align*}
\mathrm{d} \overline{\mathbb{F}}= & \frac{\partial \overline{\mathbb{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \overline{\mathbb{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j}+ \\
+ & \sum_{\alpha}\left\{m_{\alpha} \frac{\partial \overline{\mathbb{F}}}{\partial \rho}+\sum_{\beta}\left[\frac{\partial \overline{\mathbb{F}}}{\partial y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)+\right.\right. \\
& \left.\left.\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}} \nabla^{i}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}} \nabla^{i j}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)\right]\right\} \mathrm{d} n_{\alpha} \\
+ & \sum_{\alpha}\left\{m_{\alpha} \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} \rho}+\sum_{\beta}\left[\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)+\right.\right. \\
& \left.\left.2 \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}} \nabla^{j}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)\right]\right\} \mathrm{d}\left(\nabla^{i} n_{\alpha}\right) \\
+ & \sum_{\alpha}\left\{m_{\alpha} \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} \rho}+\sum_{\beta} \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)\right\} \mathrm{d}\left(\nabla^{i j} n_{\alpha}\right) . \tag{A.39}
\end{align*}
$$

and we identify with $d \overline{\mathbb{F}}=d \hat{\mathbb{F}}$ :

$$
\begin{align*}
\frac{\partial \hat{\mathbb{F}}}{\partial T}= & \frac{\partial \overline{\mathbb{F}}}{\partial T}, \quad \frac{\partial \hat{\mathbb{F}}}{\partial c^{i j}}=\frac{\partial \overline{\mathbb{F}}}{\partial c^{i j}},  \tag{A.40}\\
\frac{\partial \hat{\mathbb{F}}}{\partial n_{\alpha}}= & m_{\alpha} \frac{\partial \overline{\mathbb{F}}}{\partial \rho}+\sum_{\beta}\left[\frac{\partial \overline{\mathbb{F}}}{\partial y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}} \nabla^{i}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)+\right. \\
& \left.\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}} \nabla^{i j}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)\right]  \tag{A.41}\\
\frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{i} n_{\alpha}}= & m_{\alpha} \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} \rho}+\sum_{\beta}\left[\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right)+\right. \\
\frac{2 \hat{\mathbb{F}}}{\partial \nabla^{i j} n_{\alpha}}= & m_{\alpha} \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} \rho}+\sum_{\beta} \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}}\left(\frac{\delta^{\alpha \beta}}{n}-\frac{n_{\beta}}{n^{2}}\right) \tag{A.42}
\end{align*}
$$

## A. 7 Legendre Transform between $\overline{\mathbb{F}}$ and $\mathbb{F}$

This calculation is similar to that one of Appendix A.4. We start with the total differentials for $\overline{\mathbb{F}}$ and $\mathbb{F}$, viz:

$$
\begin{align*}
d(\rho \varphi)= & \mathrm{d} \overline{\mathbb{F}}=\mathrm{d} \mathbb{\mathbb { F }}= \\
= & \frac{\partial \overline{\mathbb{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \overline{\mathbb{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}} \mathrm{d}\left(\nabla^{i} y_{\beta}\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}} \mathrm{d}\left(\nabla^{i j} y_{\beta}\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \rho} \mathrm{d} \rho \\
& +\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} \rho} \mathrm{~d}\left(\nabla^{i} \rho\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} \rho} \mathrm{~d}\left(\nabla^{i j} \rho\right)+\frac{\partial \overline{\mathbb{F}}}{\partial c^{i j}} \mathrm{~d} c^{i j}  \tag{A.44}\\
= & \frac{\partial \overline{\mathbb{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \overline{\mathbb{F}}}{\partial y_{\beta}} \mathrm{d} y_{\beta}+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}} \mathrm{d}\left(\nabla^{i} y_{\beta}\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} y_{\beta}} \mathrm{d}\left(\nabla^{i j} y_{\beta}\right) \\
& +\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} \rho} \mathrm{~d}\left(\nabla^{i} \rho\right)+\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i j} \rho} \mathrm{~d}\left(\nabla^{i j} \rho\right)+\frac{\partial \overline{\mathbb{F}}}{\partial C^{i j}} \mathrm{~d} C^{i j} . \tag{A.45}
\end{align*}
$$

The term with the bracket, i.e., $\mathrm{d} C^{i j}$, can be substituted by the relation

$$
\begin{equation*}
\mathrm{d} C^{i j}=\frac{1}{2}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3}\left(\delta^{i k} \delta^{j l}+\delta^{j k} \delta^{i l}\right) \mathrm{d} c^{k l}-\frac{2}{3} \frac{c^{i j}}{\rho}\left(\frac{\rho_{0}}{\rho}\right)^{2 / 3} \mathrm{~d} \rho \tag{A.46}
\end{equation*}
$$

following the calculations shown in Eqs. (A.18-A.20). The resulting total differential for $\mathrm{d} \overline{\mathbb{F}}$ can be used to identify the coefficients $\partial \overline{\mathbb{F}} / \partial T, \ldots, \partial \overline{\mathbb{F}} / \partial c^{i j}$. In particular it follows that:

$$
\begin{equation*}
\frac{\partial \overline{\mathbb{F}}}{\partial \Xi}=\frac{\partial \mathbb{F}}{\partial \Xi} \quad, \quad \Xi=\left\{T, y_{\beta}, \nabla^{i} y_{\beta}, \nabla^{i j} y_{\beta}, \nabla^{i} \rho, \nabla^{i j} \rho\right\} \tag{A.47}
\end{equation*}
$$

and

$$
\begin{equation*}
\frac{\partial \overline{\mathbb{F}}}{\partial \rho}=-\frac{2}{3} \frac{C^{i j}}{\rho} \frac{\partial \mathbb{F}}{\partial C^{i j}} \quad, \quad \frac{\partial \overline{\mathbb{F}}}{\partial c^{k l}}=\frac{1}{2}\left(\frac{\rho_{0}}{\rho}\right)^{\frac{2}{3}}\left(\delta^{i k} \delta^{j l}+\delta^{i l} \delta^{k j}\right) \frac{\partial \mathbb{F}}{\partial C^{i j}} \tag{A.48}
\end{equation*}
$$

## A. 8 Legendre Transform between $\widehat{\widehat{\mathbb{F}}}$ and $\overline{\overline{\mathbb{F}}}$

According to the functional representations introduced in Eq. (2.129) we write for the total differentials of $\rho \varphi(\alpha=1, \ldots, \nu$ and $\beta=1, \ldots, \nu-1)$ :

$$
\begin{align*}
& d(\rho \varphi)= \mathrm{d} \widehat{\widehat{\mathbb{F}}}= \\
& \frac{\partial \widehat{\mathbb{F}}}{\partial T} \mathrm{~d} T+\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \rho_{\alpha}} \mathrm{d} \rho_{\alpha}+\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \nabla^{i} \rho_{\alpha}} \mathrm{d}\left(\nabla^{i} \rho_{\alpha}\right)+\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \nabla^{i j} \rho_{\alpha}} \mathrm{d}\left(\nabla^{i j} \rho_{\alpha}\right)+\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial c^{i j}} \mathrm{~d} c^{i j}  \tag{A.49}\\
&=\mathrm{d} \overline{\overline{\mathbb{F}}}= \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial T} \mathrm{~d} T+\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c_{\beta}} \mathrm{d} c_{\beta}+\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i} c_{\beta}} \mathrm{d}\left(\nabla^{i} c_{\beta}\right)+\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i j} c_{\beta}} \mathrm{d}\left(\nabla^{i j} c_{\beta}\right)  \tag{A.50}\\
&+\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i} \rho} \mathrm{~d}\left(\nabla^{i} \rho\right)+\frac{\partial \overline{\bar{F}}^{i j}}{\partial \nabla^{i j} \rho} \mathrm{~d}\left(\nabla^{i j} \rho\right)+\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \rho} \mathrm{d} \rho+\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c^{i j}} \mathrm{~d} c^{i j} .
\end{align*}
$$

The highlighted terms must be substituted by the expressions $\mathrm{d} \rho_{\alpha}, \mathrm{d}\left(\nabla^{i} \rho_{\alpha}\right)$ and $\mathrm{d}\left(\nabla^{i j} \rho_{\alpha}\right)$. Analogously to the Eqs. (A.30-A.32) and (A.33-A.35) one finds:

$$
\begin{align*}
\rho & =\sum_{\alpha} \rho_{\alpha} \Rightarrow \mathrm{d} \rho=\sum_{\alpha} \mathrm{d} \rho_{\alpha}  \tag{A.51}\\
\nabla^{i} \rho & =\sum_{\alpha} \nabla^{i} \rho_{\alpha} \Rightarrow \mathrm{d}\left(\nabla^{i} \rho\right)=\sum_{\alpha} \mathrm{d}\left(\nabla^{i} \rho_{\alpha}\right),  \tag{A.52}\\
\nabla^{i j} \rho & =\sum_{\alpha} m_{\alpha} \nabla^{i j} n_{\alpha} \Rightarrow \mathrm{d}\left(\nabla^{i} \rho\right)=\sum_{\alpha} \mathrm{d}\left(\nabla^{i j} \rho_{\alpha}\right), \tag{A.53}
\end{align*}
$$

and

$$
\begin{align*}
c_{\beta} & =\frac{\rho_{\beta}}{\sum_{\alpha} \rho_{\alpha}} \Rightarrow c_{\beta}=\widehat{\widehat{\mathbb{C}}}_{\beta}\left(\rho_{\alpha}\right),  \tag{A.54}\\
\nabla^{i} c_{\beta} & =\nabla^{i}\left(\frac{\rho_{\beta}}{\sum_{\alpha} \rho_{\alpha}}\right) \Rightarrow \nabla^{i} c_{\beta}=\widehat{\widehat{\mathbb{C}}}_{\beta}^{i}\left(\rho_{\alpha}, \nabla^{i} \rho_{\alpha}\right),  \tag{A.55}\\
\nabla^{i j} c_{\beta} & =\nabla^{i j}\left(\frac{\rho_{\beta}}{\sum_{\alpha} \rho_{\alpha}}\right) \Rightarrow \nabla^{i j} c_{\beta}=\widehat{\widehat{\mathbb{C}}}_{\beta}^{i j}\left(\rho_{\alpha}, \nabla^{i} \rho_{\alpha}, \nabla^{i j} \rho_{\alpha}\right) . \tag{A.56}
\end{align*}
$$

Thus we derive in the same manner as in the Eqs. (A.36-A.38):

$$
\begin{equation*}
\mathrm{d} c_{\beta}=\sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}}{\partial \rho_{\alpha}} \mathrm{d} \rho_{\alpha}=\sum_{\alpha}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right) \mathrm{d} \rho_{\alpha}, \tag{A.57}
\end{equation*}
$$

$$
\begin{align*}
\mathrm{d}\left(\nabla^{i} c_{\beta}\right)= & \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{i}}{\partial \rho_{\alpha}} \mathrm{d} \rho_{\alpha}+\sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{i}}{\partial \nabla^{i} \rho_{\alpha}} \mathrm{d}\left(\nabla^{i} \rho_{\alpha}\right) \\
= & \sum_{\alpha} \nabla^{i}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right) \mathrm{d} \rho_{\alpha}+\sum_{\alpha}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right) \mathrm{d}\left(\nabla^{i} \rho_{\alpha}\right),  \tag{A.58}\\
\mathrm{d}\left(\nabla^{i j} c_{\beta}\right)= & \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{i j}}{\partial \rho_{\alpha}} \mathrm{d} \rho_{\alpha}+\sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{i j}}{\partial \nabla^{k} \rho_{\alpha}} \mathrm{d}\left(\nabla^{k} \rho_{\alpha}\right)+\sum_{\alpha} \frac{\partial \widehat{\mathbb{C}}_{\beta}^{i j}}{\partial \nabla^{k l} \rho_{\alpha}} \mathrm{d}\left(\nabla^{k l} \rho_{\alpha}\right) \\
= & \sum_{\alpha} \nabla^{i j}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right) \mathrm{d} \rho_{\alpha}+2 \sum_{\alpha} \nabla^{j}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right) \mathrm{d}\left(\nabla^{i} \rho_{\alpha}\right)+ \\
& \sum_{\alpha}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right) \mathrm{d}\left(\nabla^{i j} \rho_{\alpha}\right) . \tag{A.59}
\end{align*}
$$

Eqs. (A.51-A.59) can be inserted into Eq. (A.50). A following comparison of the coefficients between the Eqs. (A.49) and (A.50) allows to identify the final relations:

$$
\begin{align*}
& \frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial T}=\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial T} \quad, \quad \frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial c^{i j}}=\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c^{i j}},  \tag{A.60}\\
& \frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \rho_{\alpha}}=\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \rho}+\sum_{\beta}\left[\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c_{\beta}}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right)+\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i} c_{\beta}} \nabla^{i}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right)+\right. \\
& \left.\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i j} c_{\beta}} \nabla^{i j}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right)\right],  \tag{A.61}\\
& \frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \nabla^{i} \rho_{\alpha}}=\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i} \rho}+\sum_{\beta}\left[\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i} c_{\beta}}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right)+2 \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i j} c_{\beta}} \nabla^{j}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right)\right], \\
& \frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \nabla^{i j} \rho_{\alpha}}=\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i j} \rho}+\sum_{\beta} \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i j} c_{\beta}}\left(\frac{\delta^{\alpha \beta}}{\rho}-\frac{\rho_{\beta}}{\rho^{2}}\right) . \tag{A.62}
\end{align*}
$$

## Appendix B

## Additional Calculations required for Chapter 3

## B. 1 Conversion of Particle to Mass Concentration

The total Helmholtz free energy $\Phi$ of an equilibrium phase $\gamma$ follows by summation from Eq. (3.62):

$$
\begin{align*}
\Phi^{\gamma}= & \sum_{\alpha \in \gamma} E_{\alpha}-T S^{\gamma} \quad, \quad S^{\gamma}=-k_{\mathrm{B}} \sum_{\alpha \in \gamma}[y \ln y+(1-y) \ln (1-y)] \\
E_{\alpha} \stackrel{(3.62)}{=} & \frac{1}{2} g_{\mathrm{AA}}+y(1-y) g_{\phi}+y g_{\tilde{\phi}}+F_{\mathrm{A}}+y\left(F_{\mathrm{B}}-F_{\mathrm{A}}\right)+ \\
& +\frac{1}{2} G^{i j} G^{k l}\{\ldots\}^{i j k l}(y)+\left(\nabla_{m n}^{2} y\right)\{\ldots\}^{m n}(y), \tag{B.1}
\end{align*}
$$

where $\{\ldots\}^{i j k l}$ and $\{\ldots\}^{m n}$ represent the expressions within the curly brackets of the second and third block in Eq. (3.62). Furthermore $k_{\mathrm{B}}$ denotes Boltzmann's constant and $T S^{\gamma}$ the entropic part of $\Phi^{\gamma}$. Moreover, the sum is carried out with respect to all particles $\alpha$ of the phase $\gamma$, and $E_{\alpha}$ represents the energy of a particle due to its interactions with the neighbors $\beta$. The quantities $g_{\mathrm{AA}}, g_{\phi}, g_{\tilde{\phi}}, F_{\mathrm{A}}, F_{\mathrm{B}},\{\ldots\}^{i j k l}$, and $\{\ldots\}^{m n}$ are defined by means of the EAM potentials (cf., Eq. (3.62)) which, in turn, are determined by the distance $R_{\alpha \beta}^{2}$ between atom $\alpha$ and $\beta$. In order to obtain the stiffness coefficients and the HGCs as functions of $c$ the following procedure is performed:
(1) Relate the "macroscopic" Helmholtz free energy density $\mathbb{F}$ to the microscopic equation (B.1).
(2) Substitute the derivatives of the particle concentration $y$ for terms of the mass concentration $c$. Here one can use the relation:

$$
\begin{align*}
c_{\mathrm{B}} & =\left(1-c_{\mathrm{A}}\right) \equiv c=\frac{m_{\mathrm{B}}}{m_{\mathrm{B}}+m_{\mathrm{A}}}=\frac{y_{\mathrm{B}} M_{\mathrm{B}}}{y_{\mathrm{B}} M_{\mathrm{B}}+\left(1-y_{\mathrm{B}}\right) M_{\mathrm{A}}}  \tag{B.2}\\
\Rightarrow y_{\mathrm{B}} & =\left(1-y_{\mathrm{A}}\right) \equiv y=\tilde{y}(c)=\frac{c M_{\mathrm{A}}}{M_{\mathrm{B}}-c\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right)}, \tag{B.3}
\end{align*}
$$

where $M_{\mathrm{A} / \mathrm{B}}$ is the molecular weight of the components $\mathrm{A} / \mathrm{B}$, and $c_{\mathrm{B}}$ is the mass concentration of B.
(3) Compare the resulting equations with the macroscopic equations $(3.60,3.61)$ and identify the HGCs and stiffness coefficients.

We recall the following thermodynamics relations for one mol:

$$
\begin{align*}
\hat{\Phi} & =N_{\mathrm{A}}\left(E_{\alpha}-T s\right) \quad, \quad \mathbb{F}=\rho_{0} \frac{\hat{\Phi}}{m} \quad, \quad m=N_{\mathrm{A}} m_{H} M(c)  \tag{B.4}\\
\Rightarrow \mathbb{F} & =\delta(c)\left(E_{\alpha}-T s\right) \tag{B.5}
\end{align*}
$$

with $\delta(c)=\frac{1}{\Omega_{0}(c)}=\frac{\rho_{0}}{m_{H} M(c)} \quad$ and $\quad \frac{1}{\rho_{0}}=\frac{c_{0}}{\rho_{\mathrm{Cu}}}+\frac{1-c_{0}}{\rho_{\mathrm{Ag}}}$.
$\hat{\Phi}$ stands for the Helmholtz free energy per one mol, $N_{\mathrm{A}}=6.0237 \cdot 10^{23}$ is the number of particles in one mol (Avogadro's constant) and $s=-k_{\mathrm{B}}[y \ln y+(1-y) \ln (1-y)]$ represents the entropy with respect to one particle. Furthermore $m$ denotes the total mass, $\rho_{0}$ identifies the mass density of the alloy in the homogeneous reference state with the (homogeneous) concentration $c_{0}$ and $m_{H}=1.66 \cdot 10^{-27} \mathrm{~kg}$ stands for $\frac{1}{12}$ of the weight of a carbon 12 atom. The symbol $M(c)$ denotes an averaged molecular weight of the binary alloy A-B and can be obtained from the molecular weights of the pure components through the relation $M=\tilde{M}(c)=y(c) M_{\mathrm{B}}+[1-y(c)] M_{\mathrm{A}}$. The symbol $\delta$ identifies the reciprocal volume occupied by an atom and yields the following expression:

$$
\begin{align*}
\frac{\mathbb{F}}{\delta(c)} & =\frac{1}{2} g_{\mathrm{AA}}+y(1-y) g_{\phi}+y g_{\tilde{\phi}}+F_{\mathrm{A}}+y\left(F_{\mathrm{B}}-F_{\mathrm{A}}\right)+ \\
& +\frac{1}{2} G^{i j} G^{k l}\{\ldots\}^{i j k l}(y)+\left(\nabla_{m n}^{2} y\right)\{\ldots\}^{m n}(y)+k_{\mathrm{B}} T[y \ln y+(1-y) \ln (1-y)] \tag{B.7}
\end{align*}
$$

Considering the function $\tilde{y}(c)$ in Eq. (B.3) and applying the chain rule one can replace $\nabla_{m n}^{2} y$ with the following relation:

$$
\begin{align*}
\nabla_{m n}^{2} y & =\frac{\partial^{2} y}{\partial c^{2}} \frac{\partial c}{\partial X^{m}} \frac{\partial c}{\partial X^{n}}+\frac{\partial y}{\partial c} \frac{\partial^{2} c}{\partial X^{m} \partial X^{n}} \\
& =\frac{2 M_{\mathrm{A}} M_{\mathrm{B}}\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right)}{\left[M_{\mathrm{B}}-\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right) c\right]^{3}}\left(\nabla_{m} c\right)\left(\nabla_{n} c\right)+\frac{M_{\mathrm{A}} M_{\mathrm{B}}}{\left[M_{\mathrm{B}}-\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right) c\right]^{2}} \nabla_{m n}^{2} c  \tag{B.8}\\
& \equiv \mathbf{M}(c) \cdot \mathcal{D}_{m n}(c) \tag{B.9}
\end{align*}
$$

with the symbolic notation for the vector $\mathbf{M}(c)$ and for the vectorial differential operator $\mathcal{D}_{m n}(\diamond)$ as follows:

$$
\begin{align*}
\mathbf{M}(c) & =\binom{\mathrm{M}^{(1)}(c)}{\mathrm{M}^{(2)}(c)}=\binom{\frac{2 M_{\mathrm{A}} M_{\mathrm{B}}\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right)}{\left[M_{\mathrm{B}}-\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right) c\right]^{3}}}{\frac{M_{\mathrm{A}} M_{\mathrm{B}}}{\left[M_{\mathrm{B}}-\left(M_{\mathrm{B}}-M_{\mathrm{A}}\right)\right]^{2}}} \text { and } \\
\mathcal{D}_{m n}(\diamond) & =\binom{\mathcal{D}_{m n}^{(1)}}{\mathcal{D}_{m n}^{(2)}}=\binom{\nabla_{m}(\diamond) \nabla_{n}(\diamond)}{\nabla_{m n}^{2}(\diamond)} . \tag{B.10}
\end{align*}
$$

A combination of the relations (B.3,B.8) with Eq. (B.7) yields the following expressions:

$$
\begin{align*}
& \frac{\psi_{0}(c)}{\delta(c)}=\frac{1}{2} g_{\mathrm{AA}}+y(c)(1-y(c)) g_{\phi}+y(c) g_{\tilde{\phi}}+F_{\mathrm{A}}+y(c)\left(F_{\mathrm{B}}-F_{\mathrm{A}}\right)  \tag{B.11}\\
& \frac{\mathbb{F}_{0}^{\text {mech }}(c)}{\delta(c)}=E_{\alpha}^{\text {mech }}=\frac{\Omega_{0}^{\alpha}}{2} G^{i j} K^{i j k l}(c) G^{k l}  \tag{B.12}\\
& \frac{a^{m n}\left(c, G^{p q}\right)}{\delta(c)}=-\mathrm{M}^{(2)}(c) \mathbb{H}^{m n}\left(c, G^{p q}\right),  \tag{B.13}\\
& \frac{b^{m n}\left(c, G^{p q}\right)}{\delta(c)}=\mathrm{M}^{(1)}(c) \mathbb{H}^{m n}\left(c, G^{p q}\right)  \tag{B.14}\\
& K^{K^{i j k l}(c)=} \begin{aligned}
\Omega_{0}^{\alpha} & 1 \\
& +4\left(B_{\mathrm{A}}^{i j k l}+4 y(c)(1-y(c)) B_{\phi}^{i j k l}+y(c) W_{\Delta}^{i j k l}\right)\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right) \\
& \left.+4\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y(c) V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right]
\end{aligned}
\end{align*}
$$

$$
\begin{align*}
& \mathbb{H}^{m n}\left(c, G^{p q}\right)=\frac{1}{4}\left((1-2 y(c)) g_{\phi}^{m n}+g_{\dot{\phi}}^{m n}\right)+\frac{1}{2} \bar{\rho}_{\triangle}^{m n}\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right) \\
& + \\
& \frac{1}{2} G^{i j}\left[(1-2 y(c)) A_{\phi}^{i j m n}+A_{\tilde{\phi}}^{i j m n}+2 V_{\triangle}^{i j m n}\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right)\right. \\
& \left.\quad+2 \bar{\rho}_{\triangle}^{m n}\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)\right] \\
& + \\
& \frac{1}{2} G^{i j} G^{k l}\left[(1-2 y(c)) B_{\phi}^{i j k l m n}+B_{\tilde{\phi}}^{i j k l m n}\right. \\
& \quad+2 W_{\Delta}^{i j k l m n}\left(F_{\mathrm{A}}^{\prime}+y(c)\left(F_{\mathrm{B}}^{\prime}-F_{\mathrm{A}}^{\prime}\right)\right) \\
& \quad+2 \bar{\rho}_{\triangle}^{m n}\left(W_{\mathrm{A}}^{i j k l}+y(c) W_{\triangle}^{i j k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime \prime}\right)\right) \\
& \quad+2 V_{\triangle}^{k l m n}\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right)  \tag{B.16}\\
& \quad+2 V_{\triangle}^{i j m n}\left(V_{\mathrm{A}}^{k l}+y(c) V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime}-F_{\mathrm{A}}^{\prime \prime}\right)\right) \\
& \left.\quad+2 \bar{\rho}_{\triangle}^{m n}\left(V_{\mathrm{A}}^{i j}+y(c) V_{\triangle}^{i j}\right)\left(V_{\mathrm{A}}^{k l}+y(c) V_{\triangle}^{k l}\right)\left(F_{\mathrm{A}}^{\prime \prime \prime}+y(c)\left(F_{\mathrm{B}}^{\prime \prime \prime}-F_{\mathrm{A}}^{\prime \prime \prime}\right)\right)\right] .
\end{align*}
$$

The HGCs $A^{k l}$ can directly be calculated from (B.13) and (B.14) by means of the relation $A^{k l}=\frac{\partial a^{k l}}{\partial c}+b^{k l}$. Moreover it should be mentioned that Eqs. (B.11-B.14) hold for an equilibrium phase consisting of two components in which the composition is characterized by the mass concentration $c \equiv c_{\mathrm{B}}$.

## B. 2 Two Equations for $G$ and for $E_{\text {uvf }}$

We consider the Eqs. (3.79) and (3.28a) together with the definitions shown in Eqs. (3.80-3.83). In order to determine the coefficients $K^{1111}, K^{1122}$, and $K^{2323}$ we first calculate all the required derivatives:

$$
\begin{align*}
& \rho^{\prime}\left(R^{2}\right)=-\beta \frac{\rho_{\mathrm{e}}}{R^{2}} \quad, \quad \rho^{\prime \prime}\left(R^{2}\right)=\beta^{2} \frac{\rho_{\mathrm{e}}}{R^{4}} \quad, \quad \phi^{\prime}\left(R^{2}\right)=-\gamma \frac{\phi_{\mathrm{e}}}{R^{2}} \quad, \quad \phi^{\prime \prime}\left(R^{2}\right)=\gamma^{2} \frac{\phi_{\mathrm{e}}}{R^{4}},  \tag{B.17}\\
& F^{\prime}\left(\bar{\rho}_{\mathrm{e}}\right)=-6 \frac{\gamma \phi_{\mathrm{e}}}{\beta \bar{\rho}_{\mathrm{e}}} \quad, \quad F^{\prime \prime}\left(\bar{\rho}_{\mathrm{e}}\right)=\frac{E_{\text {sub }} \alpha^{2}+24 \gamma \phi_{\mathrm{e}}(\beta-\gamma)}{4 \beta^{2} \bar{\rho}_{\mathrm{e}}^{2}} . \tag{B.18}
\end{align*}
$$

Due to nearest neighbor interactions all neighbors of an atom $\alpha$ are separated by the same distance $R$. Thus the derivatives $\rho^{\prime}, \rho^{\prime \prime}$, and $\phi^{\prime \prime}$ do not depend on the sum and one can write for a pure substance:

$$
\begin{align*}
K^{i j k l}= & \frac{1}{\Omega_{0}}\left[2 \phi^{\prime \prime}\left(\sum_{\beta} R^{i} R^{j} R^{k} R^{l}\right)+4 F^{\prime} \rho^{\prime \prime}\left(\sum_{\beta} R^{i} R^{j} R^{k} R^{l}\right)\right. \\
& \left.+4 F^{\prime \prime} \rho^{\prime} \rho^{\prime}\left(\sum_{\beta} R^{i} R^{j}\right)\left(\sum_{\beta} R^{k} R^{l}\right)\right] \tag{B.19}
\end{align*}
$$

Note that for an FCC crystal the following relations hold: $\sum\left(R^{1}\right)^{4}=8(a / 2)^{4}$, $\sum\left(R^{1}\right)^{2}=\sum\left(R^{2}\right)^{2}=8(a / 2)^{2}, \sum\left(R^{2}\right)^{2}\left(R^{3}\right)^{2}=4(a / 2)^{2}(a / 2)^{2}$, and $\sum R^{2} R^{3}=0$, $c f$., Figure B.1. Therefore one finally finds for the elastic constants:


Figure B.1: The number of atoms with a contribution in $x^{1}, x^{2}$ and $x^{3}$ direction (the unshaded atoms do not contribute in the considered direction)

$$
\begin{equation*}
K^{1111}=\Xi_{a}+\Xi_{b} \quad, \quad K^{1122}=\frac{1}{2} \Xi_{a}+\Xi_{b} \quad, \quad K^{2323}=\frac{1}{2} \Xi_{a} \tag{B.20}
\end{equation*}
$$

with the definitions:

$$
\begin{equation*}
\Xi_{a}=\frac{a^{4}}{\Omega_{0}}\left[\phi^{\prime \prime}\left(R^{2}\right)+2 F^{\prime}\left(\bar{\rho}_{\mathrm{e}}\right) \rho^{\prime \prime}\left(R^{2}\right)\right] \quad, \quad \Xi_{b}=16 \frac{a^{4}}{\Omega_{0}} F^{\prime \prime}\left(\bar{\rho}_{\mathrm{e}}\right) \rho^{\prime}\left(R^{2}\right) \rho^{\prime}\left(R^{2}\right) . \tag{B.21}
\end{equation*}
$$

In the case of the average of the VoigT shear modulus it follows $\left(a^{4}=4 R^{4}\right)$ that:

$$
\begin{equation*}
G=\frac{2}{5} \Xi_{a}=\frac{2 a^{4}}{5 \Omega_{0}}\left[\phi^{\prime \prime}\left(R^{2}\right)+2 F^{\prime}\left(\bar{\rho}_{\mathrm{e}}\right) \rho^{\prime \prime}\left(R^{2}\right)\right]=\frac{8}{5} \frac{\phi_{e} \gamma(\gamma-\beta)}{\Omega_{0}} \tag{B.22}
\end{equation*}
$$

or:

$$
\begin{equation*}
G=\frac{24}{15} \frac{\Phi_{e} \gamma(\gamma-\beta)}{\Omega_{0}} \tag{B.23}
\end{equation*}
$$

In the same manner one can show for the bulk modulus: $\kappa=\frac{2}{3} \Xi_{a}+\Xi_{b}$.
We now consider the vacancy formation energy $E_{\text {uvf }}$. For this purpose we follow the strategy of R.A. Johnson in [67] and note that according to Eq. (3.78) the following
relation holds in equilibrium:

$$
\begin{align*}
E_{\mathrm{uvf}} \quad= & -6 \phi_{\mathrm{e}}-12 F\left(\bar{\rho}_{\mathrm{e}}\right)+12 F\left(\frac{11}{12} \bar{\rho}_{\mathrm{e}}\right)= \\
\stackrel{(3.75)}{=} & -\Phi_{\mathrm{e}}+12\left(E_{\text {sub }}+\Phi_{\mathrm{e}}\right)-12 E_{\text {sub }}\left[1+h\left(\frac{11}{12}\right)\right] \times \\
& \times \exp \left[-h\left(\frac{11}{12}\right)\right]-12 \Phi_{\mathrm{e}}\left(\frac{11}{12}\right)^{\frac{\gamma}{\beta}} \tag{B.24}
\end{align*}
$$

with $h(x)=\alpha\left(\sqrt{1-\frac{1}{\beta} \ln x}-1\right)$. We consider TAYLOR-expansions of the form:

$$
\begin{align*}
h(x) & =-\frac{1}{2} \frac{\alpha}{\beta}(x-1)+\frac{1}{4} \frac{\alpha}{\beta}\left(1-\frac{1}{2 \beta}\right)(x-1)^{2}+\ldots,  \tag{B.25}\\
\exp [-h(x)] & =1+\frac{1}{2} \frac{\alpha}{\beta}(x-1)-\frac{1}{4} \frac{\alpha}{\beta}\left(1-\frac{1}{2 \beta}-\frac{\alpha}{2 \beta}\right)(x-1)^{2}+\ldots  \tag{B.26}\\
x^{\frac{\gamma}{\beta}} & =1+\frac{\gamma}{\beta}(x-1)+\frac{1}{2} \frac{\gamma}{\beta}\left(\frac{\gamma}{\beta}-1\right)(x-1)^{2}+\ldots \tag{B.27}
\end{align*}
$$

and evaluate them at $x=\frac{11}{12}$ so that:

$$
\begin{equation*}
E_{\mathrm{uvf}}=\frac{E_{\mathrm{sub}}}{24}\left(\frac{\alpha}{\beta}\right)^{2}\left[\frac{337}{1152}+\frac{1}{2304} \beta^{2}\left(\frac{1}{2}+\frac{a}{2}\right)\right]+\Phi_{\mathrm{e}}\left(\frac{\gamma-\beta}{\beta}\right)\left(1-\frac{1}{24} \frac{\gamma}{\beta}\right) \tag{B.28}
\end{equation*}
$$

The various contributions in this equation can be also investigated by means of quantum mechanics. Following Johnson in [67] the leading term of Eq. (B.28) is $\Phi_{\mathrm{e}}\left(\frac{\gamma-\beta}{\beta}\right)$. Therefore it is reasonable to consider the approximation:

$$
\begin{equation*}
E_{\mathrm{uvf}} \cong \Phi_{\mathrm{e}}\left(\frac{\gamma-\beta}{\beta}\right) \tag{B.29}
\end{equation*}
$$

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Die vollkommene Kontinuierlichkeit einer Bewegung ist dem menschlichen Verstande unfasslich. Dem Menschen werden die Gesetze jeder Art von Bewegung nur dann fasslich, wenn er willkürlich aus ihrem Zusammenhang gerissene Teilstücke dieser Bewegung betrachtet. Indessen fliesst der grösste Teil der menschlichen Irrtümer gerade aus diesem willkürlichen Zerteilen der kontinuierlichen Bewegung. [...] Um genau das gleiche handelt es sich, wenn es gilt, die Bewegungsgesetze der Geschichte zu erforschen.

Lew N. Tolstoi (1828-1910) aus Krieg und Frieden


[^0]:    ${ }^{1}$ The minimal feature size defines $1 / 2$ of the distance between cells in a dynamic RAM (DRAM).

[^1]:    ${ }^{2}$ For example, Pb and Cd in optical and filter glasses, Pb in high melting temperature type solders (i.e. $\mathrm{Sn}-\mathrm{Pb}$ solders with more than $85 \% \mathrm{~Pb}$ ) and in solders, which internally complete a viable electrical connection to certain integrated circuit packages (Flip Chips) are further permitted (exemption until 2010).

[^2]:    ${ }^{3}$ Japan Electronics Industry Development Association.

[^3]:    ${ }^{4}$ In this manufacturing procedure the electronic components are directly - i.e., without the use of pins - soldered on the circuit board.
    ${ }^{5}$ Here the substrate/board is firstly completely assembled, and the joining connection is realized by a subsequent heat treatment of the whole electronic device, i.e., chip unit, substrate and (solid) solder.

[^4]:    ${ }^{6}$ The IMCs are often called in literature "Intermetallic Phases" or "ordered phases." This notation is quite misleading, since it leads to the confusion with phases known from thermodynamics, which are not formed from chemical reactions.

[^5]:    ${ }^{1}$ Some of the considerations of this Chapter already appeared in [10].

[^6]:    ${ }^{2}$ Here the work of Hillert appears before the work of Cahn and Hilliard, because Hillert already derived the formulae in 1956 in his PhD thesis.

[^7]:    ${ }^{3}$ Here the index notation of Cartesian vectors $\left(\mathbf{v} \equiv v^{i}\right)$ and tensors (e.g., $\left.\mathbf{T} \equiv T^{i j}\right)$ is used. Furthermore throughout this Chapter an upper index does not refer to contravariant coordinates. Rather it is used to avoid confusion with indices characterizing a particular constituent.

[^8]:    ${ }^{4}$ This paragraph is based on the preliminary considerations by Dreyer and Duderstadt, [35].

[^9]:    ${ }^{5}$ A popular counter-example are rubber balloons, cf., [90].
    ${ }^{6}$ Note that the definitions of $w^{\star}$ in Eq. $(2.103)_{2}$ is not equivalent to the ones in Eqs. $(2.100,2.96)_{2}$ due to the performed linearization. This is evident replacing in, e.g., Eq. $(2.96)_{2}$ the term $t^{i j} C^{i j}$ by the linearized form $\sigma^{i j}\left(2 \varepsilon^{i j}+\delta^{i j}\right)$.

[^10]:    ${ }^{7}$ Another notation frequently found is specific stored energy.

[^11]:    ${ }^{8}$ In the following we write by convenience $\mathbb{F}=\stackrel{\diamond}{\mathbb{F}}$.

[^12]:    ${ }^{9}$ The Cahn-Hilliard equation follows for constant HGCs $A^{k l}$ and $a^{k l}$. In this case only the first two summands within the parenthesis (...) of Eq. (2.145) remain.

[^13]:    ${ }^{1}$ The considerations of this Chapter already appeared in a modified form in [11].

[^14]:    ${ }^{2}$ Here the energy $E_{\alpha}$ of an particle (atom) $\alpha$ is given by $E_{\alpha}=\frac{1}{2} \sum_{\beta(\alpha \neq \beta)} \varphi_{\alpha \beta}\left(r_{\alpha \beta}\right)$, where $\varphi_{\alpha \beta}$ denotes the pairwise interaction potential between the atoms $\alpha$ and $\beta$ and depends only upon the radial distance $r_{\alpha \beta}$ between $\alpha$ and $\beta$.

[^15]:    ${ }^{3}$ Especially the form of the atomic electron density $\rho$ is borrowed from atoms with isotropic s-orbitals. This (for special cases) unrealistic assumption is later corrected by the fitting procedure.

[^16]:    ${ }^{4}$ Note that MTdata makes no difference between the Gibbs free energy and the Helmholtz free energy.

[^17]:    ${ }^{5}$ This assumption can be interpreted as an "effective" lattice, owing the same total cohesive energy as an lattice, where three different nearest neighbor distances occur, depending on the three different interactions.

[^18]:    ${ }^{1}$ Mixed derivatives of the form $\partial^{2} c / \partial X^{i} \partial x^{j}$ with $(i \neq j)$ are not considered since - as we will see below - they are not required during the simulations. However, the corresponding relations for the mixed derivatives can be found, e.g., in [91].

[^19]:    ${ }^{2}$ The same arguments hold for each component of the $N$ dimensional ODE, given in Eq. (4.18).

[^20]:    ${ }^{3}$ Another notation frequently found is backward EULER sheme/method.

[^21]:    ${ }^{4}$ This strain state denotes the one-dimensional equivalent to the two-dimensional case of plane strains.

[^22]:    ${ }^{5}$ Note that MTdata make no difference between the Helmholtz and the Gibbs free energy.

[^23]:    ${ }^{6}$ See also [14] for a detailed investigation of the impact of the different numerical parameters on the simulation.

[^24]:    ${ }^{7}$ The assistance of A. Brandmair during the numerical implementation is gratefully acknowledged. His diploma thesis developed in this context contains further interesting simulations, e.g., for different loading regimes, [14].
    ${ }^{8}$ The authors used a constant value of $\gamma_{\mathrm{CH}}=\kappa \lambda^{2}=1 \cdot 10^{-5} \mathrm{~N}$ (in their notation).
    ${ }^{9}$ Within this work the authors considered an Al-In system and chose a constant HGC of $\gamma=$ $2 \cdot 10^{-10} \mathrm{~N}$ (in their notation).

[^25]:    ${ }^{10}$ See also [14].

[^26]:    ${ }^{11}$ See footnote 7.

[^27]:    ${ }^{1}$ Note that the binary alloy Ag-Cu has a comparatively low eutectic temperature of $T_{\text {eut }} \cong 779{ }^{\circ} \mathrm{C}$ whereas the pure substances Ag and Cu have melting temperatures of $T_{\text {eut }} \cong 962^{\circ} \mathrm{C}(\mathrm{Ag})$ and $T_{\text {eut }} \cong 1085^{\circ} \mathrm{C}(\mathrm{Cu})$, i.e., considerably higher values. In order to mix both constituents within the liquid state, one needs an electric arc melting furnace, which can provide temperatures beyond $1100^{\circ} \mathrm{C}$.

[^28]:    ${ }^{2}$ The limit value, under which the software set $A_{\beta}^{i}=0 \mu \mathrm{~m}^{2}$ is an intern parameter of the image

[^29]:    analysis package.

