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

von Thomas Böhme

Von der Fakultät V, Verkehrs- und Maschinensysteme der Technischen Universität Berlin zur Verleihung des akademischen Grades - Doktor-Ingenieur (Dr.-Ing.) -

genehmigte Dissertation

PROMOTIONSAUSSCHUSS

Vorsitzender:	Prof. DrIng. H. Meyer
Erster Gutachter:	Prof. Dr. rer. nat. W.H. Müller
Zweiter Gutachter:	Priv. Doz. Dr. rer. nat. W. Dreyer

Tag der Einreichung der Dissertation:25.01.2008Tag der wissenschaftlichen Aussprache:07.03.2008

Berlin, 2008 D83 Institut für Mechanik, Sekr. MS-2, Lehrstuhl für Kontinuumsmechanik und Materialtheorie (LKM) Technische Universität Berlin

Einsteinufer 5 10587 Berlin, Germany



in cooperation with



PROMOTIONSAUSSCHUSS

Vorsitzender:	Prof. DrIng. H. Meyer, Institut für Konstruktion, Mikro- und Medizintechnik, TU Berlin
Erster Gutachter:	Prof. Dr. rer. nat. W.H. Müller, Institut für Mechanik, TU Berlin
Zweiter Gutachter:	Priv. Doz. Dr. rer. nat. W. Dreyer, Weierstraß Institut für angewandte Analysis und Stochastik, Mohrenstraße 39, 10117 Berlin
Tag der Einreichung: Tag der Aussprache:	25.01.2008 07.03.2008

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)



contact thomas.boehme@tu-berlin.de

Preface

The present thesis reflects my work during the last three years at the CHAIR OF CON-TINUUM 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.

First of all, I would like to especially thank my supervisors, Prof. Dr. rer. nat. W. H. Müller and Priv. Doz. Dr. rer. nat. W. Dreyer, for their scientific support of this work. In this context, I will not forget the uncountable, often controversial discussions on the one hand side, and the friendly and pleasant conversations beyond physics on the other. Their support and help enabled me to finish the Ph.D. thesis in the present form. Second, I am deeply grateful to Prof. Dr.-Ing. H. Meyer for taking the chair of the Ph.D. examination board. Furthermore I want to express my thanks to my family, in particular to my parents, my sister and to my grandparents. They continuously supported me during my study and Ph.D. time and gave me always a warm and familiar home. Special thanks are also due to my colleagues and friends, specially to G. Glass, B. Krahl, Dr. K. Weinberg, Dr. M. Apel (ACCESS e.V., Aachen), A. Brandmair, Dr. F. Duderstadt (WIAS), G. Harneit, Dr. A. Häse (Mannesmann Salzgitter Forschung GmbH, Duisburg), Dr. J. Hornig (Airbus Deutschland GmbH, Bremen), A. Juritza, Dr. S. Kaßbohm (Bundesanstalt für Materialforschung und prüfung, Berlin), Dr. O. Kastner (Ruhr-Universität Bochum), O. Rott (WIAS), S. Sperling (Bombardier Transportation, Hennigsdorf), J. Sterthaus, and Dr. R. Wille, who inspired me during "infinitely many" discussions, made suggestions, gave various advice or helped me with administration tasks. Moreover, I am notedly indebted to my girlfriend Tina. Her patience and love, in particular in times of "academic frustration," permanently motivated me and gave me the required power.

Finally the scholarship program itself as well as the financial support of the GERMAN FEDERAL ENVIRONMENTAL FOUNDATION (DBU) are grateful acknowledged.

Berlin, January 2008 Thomas Böhme

Zusammenfassung

In der vorliegenden Arbeit wird der Prozess der spinodalen Entmischung und der einhergehenden Vergröberung am Beispiel des bleifreien, binären Hartlotes Ag-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 Ag-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.

Contents

Pr	reface	9	\mathbf{V}
Ζu	ısamı	menfassung	vii
Co	onten	ts	ix
Li	st of	Figures	xiii
Li	st of	Tables	xviii
1	Intr	oduction	1
	1.1	Tendencies in Microelectronic Packaging	1
		1.1.1 Technological Trends	1
		1.1.2 Environmental Concerns	1
		a. Europe, in particular Germany	2
		b. Asia, in particular Japan and China	3
		c. USA	3
	1.2	Solder Materials	4
		1.2.1 Solders in Microelectronic Packaging	4
		1.2.2 Lead-free Materials $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	5
	1.3	Microstructures in Solders	6
		1.3.1 Phenomenology \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots	6
		1.3.2 Spinodal Decomposition and Coarsening	8
	1.4	Organisation of this Work	10
2	ΑH	ligher Gradient Theory of Mixtures	13
	2.1	Historical Remarks about Diffusion	13
	2.2	Symbols and Notation	15
	2.3	Elements of Nonequilibrium Thermodynamics	16
		2.3.1 Description of Motion and Deformation	16
		2.3.2 Balance Equations and Mass Diffusion Flux	18
		2.3.3 Particle Diffusion Flux	19
		2.3.4 Entropy Principle	19
		a. Simple Example: Thermoelasticity with Strain Gradients .	21
		b. Statement of the Entropy Principle	24

			c. The Role of the 2nd Law	25
	2.4	Invest	igations of a Single Phase	26
		2.4.1	Exploitation of the 2nd Law for non-reacting, thermo-elastic Solids	26
		242	Selected Results	20
		2.1.2	a Heat Flux and Diffusion Flux	20
			h. Mechanical Constitutive Equations	30
			c GIBBS-DUHEM Belation and GIBBS Equation	31
			d Splitting of the Free Energy	33
		2/3	Comparison with the Literature	30
	25	2.4.5 Multir	obaso Mixturos	
	2.0	2 5 1	Exploitation of the 2nd Law by Considering Higher Gradients	<u>41</u>
		2.5.1 2.5.2	Entropy, Heat and Diffusion Flux and Mechanical Constitutive	71
			Equations	45
		2.5.3	Isothermal Diffusion in Binary Mixtures	47
			a. Preliminary Calculations on the Chemical Potential	47
			b. Particle Diffusion Flux	48
			c. Mass Diffusion Flux	49
			d. Expansion of the Free Energy Density	50
			e. Extended Diffusion Equation	51
3	Cal	culatio	on of Higher Gradient and Stiffness Coefficients by using	6
	\mathbf{the}	\mathbf{EAM}		55
	3.1	Introd	uctional Remarks	55
	3.2	Introd	luction to EAM	57
		3.2.1	Basic Concepts	57
		3.2.2	Johnson's Analytic Nearest-Neighbor Model	59
	3.3	Evalua	ation of the EAM Energy Expression	61
		3.3.1	Lattice Deformation and Strain Measures	61
		3.3.2	Equilibrium Condition and Stiffness Coefficients	63
	3.4	EAM	for Binary Alloys	66
		3.4.1	Specification of the Energy-Expression: DPC Operator and	
			Higher Gradients	66
		3.4.2	Equilibrium Condition, Stiffness, Higher Gradient Coefficients	69
	3.5	Applic	cation to the Ag-Cu System	73
		3.5.1	The Fitting Procedure for Ag and Cu	75
			a. Determination of $\phi_{\rm e}$ and $\rho_{\rm e}$	76
			b. Determination of β and γ	77
		3.5.2	The Elastic Constants of Ag and Cu	78
		3.5.3	The Alloy Ag-Cu I: Evaluation of the Equilibrium Condition	80
		3.5.4	The Alloy Ag-Cu II: The Stiffness Coefficients	81
		3.5.5	The Alloy Ag-Cu III: The Higher Gradient Coefficients	82
	3.6	Const	ruction of the Phase Diagram	87
	3.7	Some	Concluding Remarks about this Chapter	91
	0.1			

4	Nui	merical Simulations	93
	4.1	Some Elements of Numerical Mathematics	93
		4.1.1 Discrete FOURIER Transforms and Spatial Discretization	93
		4.1.2 One-Step-Time-Integration Methods	97
		a. Explicit Methods	97
		b. (Semi-)Implicit Methods	101
		c. Time Adaptation	104
	4.2	Simulation of Phase Separation and Coarsening in Ag-Cu	105
		4.2.1 Restrictions and Assumptions	105
		4.2.2 Compilation of Materials Data	108
		a. Chemical Part of the Free Energy	108
		b. Mobility, Stiffness, and Thermal Expansion Coefficient	109
		c. Interpolation of the HGCs	110
		4.2.3 Remarks on the Numerical Realization	112
		4.2.4 One-Dimensional Simulations	114
		4.2.5 Two-Dimensional Simulations	119
		4.2.6 Quantification of the Coarsening Rate	120
5	Exp	perimental Investigations	131
	5.1	Methodology and Realization	131
		5.1.1 Purchase of the Material and Making of the Specimen	132
		5.1.2 Metallographic Preparation	133
		5.1.3 Optical Microscopy and Digital Image Analysis	134
		5.1.4 Heat Treatment	135
	5.2	On the Quantification of Coarsening	135
	5.3	Selected Results	137
		5.3.1 Micrographs	138
		5.3.2 Determination of the Mean Phase Radius	143
6	Ré	sumé	149
	6.1	Theory vs. Experiment	149
	6.2	Conclusion and Outlook	151
\mathbf{A}	Ado	litional Calculations required for Chapter 2	155
	A.1	Proof of Equation (2.45)	155
	A.2	LEGENDRE Transform between $\tilde{\mathcal{S}}$ and $\hat{\mathcal{S}}$	156
	A.3	LEGENDRE Transform between $\hat{\mathcal{F}}$ and $\bar{\mathcal{F}}$	157
	A.4	LEGENDRE Transform between $\bar{\mathcal{F}}$ and $\hat{\mathcal{F}}$	157
	A.5	LEGENDRE Transform between $\tilde{\mathbb{S}}$ and $\hat{\mathbb{S}}$	158
	A.6	LEGENDRE Transform between $\hat{\mathbb{F}}$ and $\overline{\mathbb{F}}$	159
	A.7	LEGENDRE Transform between $\overline{\mathbb{F}}$ and $\widehat{\mathbb{F}}$	162
	A.8	LEGENDRE Transform between $\widehat{\mathbb{F}}$ and $\overline{\overline{\mathbb{F}}}$	163

В	Add	litional Calculations required for Chapter 3	165
	B.1	Conversion of Particle to Mass Concentration	165
	B.2	Two Equations for G and for E_{uvf}	168
Bi	bliog	raphy	171
In	\mathbf{dex}		181

List of Figures

1.1	The development of the minimal feature size (partially expected) and the number of transistors in microelectronics, source: Intel, [62] and ITRS, [63]	2
1.2	Different types of Chip Scale Packages (CSPs)	4
1.3	Various mircrostructural effects observed in solder materials. 1st row (left): IMC scallops (Cu_6Sn_5) at the interface solder/substrate. 1st row (right): IMC needles (Ag_3Sn) in the solder bulk, source: [92]. 2nd row (left): Phase separation by spinodal decomposition in eutectic Ag-Cu after 40h heat treatment. 2nd row (right): KIRKENDALL void formation in the thin Cu_3Sn layer at the interface solder/substrate, source: [120].	6
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]	8
1.5	First row: Illustration of the eutectic solidification process and of the characteristic concentrations within the miscibility gap. Second row: Phase diagram of Ag-Cu, source [83].	10
2.1	Three states of a multi-component thermo-elastic solid. (a) The ref- erence state S_0 with the reference temperature T , the reference com- position y^0_{β} , and the reference (undeformed) strain state described by $F_0^{ij} = \delta^{ij}$. (b) The intermediate state S_* with $T_* = T$, $y^*_{\beta} = y_{\beta}$, and F_*^{ij} . (c) The current state S with T , y_{β} , and with F^{ij} for $S_0 \to S$ or with $F_{\rm el}^{ij}$ for $S_* \to S$.	35
3.1	The general principle of EAM as proposed by Daw & Baskes, [28, 29].	58
3.2	The nearest neighbors for an arbitrary atom α in a FCC-lattice	59
3.3	The different lattice vectors and their notation.	62
3.4	HELMHOLTZ free energy density $\mathbb{F}_0^{\text{chem}}(c)$ for Ag-Cu at 1000 Kelvin.	74
3.5	Various functions relevant in Eq. (3.72,3.75) and the resulting atomic energy E_{α} for Ag and Cu. Note that in the upper right picture $\phi_{AgCu} =$	
	ϕ_{CuAg}	79
3.6	Illustration of different results following from the exploitation of the equilibrium condition (3.63).	81

3.7	Calculated elastic constants for Ag-Cu as a function of the mass con- centration c. The continuous line represents the linear interpolation between the values of pure Ag and Cu	82
3.8	Higher gradient coefficients calculated for Ag-Cu as a function of the mass concentration c (strain free case).	84
3.9	Higher gradient coefficients calculated for Ag-Cu as a function of the mass concentration c and of the strains $\varepsilon^{ij} = \varepsilon \cdot \delta^{ij}$ (isotropic strains).	85
3.10	Higher gradient coefficients calculated for Ag-Cu as a function of the mass concentration c and of the strains $\varepsilon^{ij} = \varepsilon \cdot \delta^{i1} \delta^{j1} \delta^{ij}$ (line strains).	86
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 equi- librium points (dots). 2nd row: The nearest-neighbor-distance $R(y)$ for equilibrium and its deviation from linear interpolation (VEGARD's law, dashed line)	88
3.12	1st 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 Ag-Cu (filled and joined dots) vs. experimental data (unfilled dots). Right: The phase diagram generated by MTdata TM .	90
3.13	A comparison of the calculated functions $g^*(y, T = 1000 \text{K})$, $(\rho \psi)^*(c, T = 1000 \text{K})$, and $g^{\text{ex}}(y, T = 1000 \text{K})$ with the corresponding functions from MTdata TM (dashed line)	91
4.1	Left: Discretization of the representative volume element in the two- dimensional case $(N = 6)$. Right: Characterization of the microstruc- ture by periodic continuation of RVE's	94
4.2	Left: Illustration of the explicit EULER approximation. Right: Correction of the slope according to the V. HEUN procedure.	98
4.3	Illustration of the NEWTON iteration in order to find the root of the nonlinear function $g(\eta_{n+1})$.	103
4.4	Free energy density and its second derivative as functions of the mass concentration for Ag-Cu at $T = 1000$ Kelvin	108
4.5	Interpolated HGCs as bilinear functions of the mass concentration and the strains.	112
4.6	One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 Kelvin (strain-free case).	115
4.7	One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 Kelvin (tensile loading of $\sigma_0 = 5000$ MPa)	116
4.8	One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 Kelvin (pressure loading of $\sigma_0 = -5000$ MPa)	117

2	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 $A^{11} = A^{11}_{\text{EAM}}$, $A^{11} = 2 \cdot A^{11}_{\text{EAM}}$, and $A^{11} = 4 \cdot A^{11}_{\text{EAM}}$. Second Row: According zoomed interface	
		areas	118
2	4.10	The inhomogeneous strain field following from the phase evolution ex- emplarily calculated for a discretization of $N = 128$. First Row: tensile loading. Second Row: pressure loading	119
2	4.11	Initial concentration profiles used for the two-dimensional simulations.	120
2	4.12	Two dimensional simulation of spinodal decomposition and coarsening in Ag-Cu 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	121
2	4.13	Two dimensional simulation of spinodal decomposition and coarsening in Ag-Cu 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.	122
2	4.14	Two dimensional simulation of spinodal decomposition and coarsening in Ag-Cu 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	123
2	4.15	On the resolution of the interface width for the two dimensional case with $N = 128$ (the dashed square marks the interface)	124
2	4.16	Modification of the 1D concentration profiles exemplarily for two coars- ening 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.	125
4	4.17	The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at \approx 1000 Kelvin obtained from the strain-free 1D simulations.	126
2	4.18	The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin obtained from the 1D simulations. Left: tensile loading of 5000 MPa. Right: compressive loading of -5000 MPa	127
2	4.19	The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin obtained from the 2D simulations in Figure 4.12.	128
4	4.20	The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin obtained from the 2D simulations in	
		Figure 4.14. \ldots	129

5.1	Schematic procedures performed during the experimental investiga- tions of Ag-Cu	132
5.2	Illustration of making the rectangular specimen from the "buttton-like" sample.	133
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.	136
5.4	<i>Un-etched</i> photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after 10 h, 20 h, 40 h (scale factor 1:200).	138
5.5	Un-Etched photos of the temporal development of the micromorphol- ogy in Ag-Cu. From upper left to lower right: after 5 h, 10 h, 20 h, 40 h (scale factor 1:500).	139
5.6	<i>Etched</i> photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after solidification, 2 h, 5 h, 10 h, 20 h, 40 h (scale factor 1:500).	140
5.7	<i>Un-Etched</i> photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after 5 h, 10 h, 20 h, 40 h (scale factor 1:1000).	141
5.8	<i>Etched</i> photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after solidification, 2 h, 5 h, 10 h, 20 h, 40 h (scale factor 1:1000).	142
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.	143
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	144
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.	144
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.	146
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.	147

5.14	The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin observed in experiments. Dashed line: spherical phase shape. Continuous line: oblate spheroid-shaped	
	phase.	148
6.1	Comparison of the coarsening behavior predicted from the (strain-free) simulations and from the experiment.	150
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).	169

List of Tables

1.1	Various lead-free solder materials under discussion, source: $\left[83,112\right]$.	5
2.2	Specification of the three states required for the distinction between elastic and inelastic deformations in multi-component, thermo-elastic, diffusive solids.	34
$3.1 \\ 3.2$	Experimental data for Ag and Cu	78 78
3.3	Elastic constants for Ag and Cu in GPa. The values in parentheses stem from experiments, [71]	80
3.4	Elastic constants in GPa predicted for the α - and β -phases in an Ag-Cu system at 1000 K	81
3.5	Calculated higher gradient coefficients for the different α - and β -phases in eutectic Ag-Cu.	83
3.6	Calculated and experimental equilibrium concentrations for Ag-Cu at different temperatures. The experimental data for 700, 800, 900 Kelvin stem from [94] and for 1000 Kelvin from [119]	89
4.1	General form of the Butcher-diagram	100
4.1 4.2	General form of the Butcher-diagram	100 101
4.14.24.3	General form of the Butcher-diagram	100 101 108
4.14.24.34.4	General form of the Butcher-diagram	100 101 108 109
 4.1 4.2 4.3 4.4 4.5 	General form of the Butcher-diagram	 100 101 108 109 110
 4.1 4.2 4.3 4.4 4.5 4.6 	General form of the Butcher-diagram	 100 101 108 109 110 111
$ \begin{array}{c} 4.1 \\ 4.2 \\ 4.3 \\ 4.4 \\ 4.5 \\ 4.6 \\ 4.7 \\ \end{array} $	General form of the Butcher-diagram	100 101 108 109 110 111 113
$ \begin{array}{c} 4.1 \\ 4.2 \\ 4.3 \\ 4.4 \\ 4.5 \\ 4.6 \\ 4.7 \\ 4.8 \\ \end{array} $	General form of the Butcher-diagram	 100 101 108 109 110 111 113 126
$ \begin{array}{c} 4.1 \\ 4.2 \\ 4.3 \\ 4.4 \\ 4.5 \\ 4.6 \\ 4.7 \\ 4.8 \\ 4.9 \\ \end{array} $	General form of the Butcher-diagram Left: Butcher-diagram for the classical RUNGE-KUTTA method. Right: Butcher-diagram for the Simpson rule	 100 101 108 109 110 111 113 126 128
$\begin{array}{c} 4.1 \\ 4.2 \\ 4.3 \\ 4.4 \\ 4.5 \\ 4.6 \\ 4.7 \\ 4.8 \\ 4.9 \\ 4.10 \end{array}$	General form of the Butcher-diagram Left: Butcher-diagram for the classical RUNGE-KUTTA method. Right: Butcher-diagram for the Simpson rule	 100 101 108 109 110 111 113 126 128

5.1	Performed grinding and polishing steps for eutectic Ag-Cu	134
5.2	Values calculated by the image analysis software, exemplarily for the	
	illustrated Figures 5.9-5.13.	148
5.3	Mean phase radii for different coarsening stages and different types of phase shapes (assumed)	148
6.1	Comparison of the different coarsening rates following from the simulations and the experiment.	149

Das Fehlen von Wissenschaft, das heißt Unkenntnis von Ursachen, macht dazu geneigt, oder besser, zwingt dazu, sich auf den Rat und die Autorität anderer zu verlassen.

Thomas Hobbes, (1588 - 1679)

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 size¹ 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., Cd, Hg, 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]).

¹The minimal feature size defines 1/2 of the distance between cells in a dynamic RAM (DRAM).



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 Pb, 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 exemptions² were subsequently included, [56].

²For example, Pb and Cd in optical and filter glasses, Pb in high melting temperature type solders (*i.e.* Sn-Pb solders with more than 85% Pb) and in solders, which internally complete a viable electrical connection to certain integrated circuit packages (Flip Chips) are further permitted (exemption until 2010).

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 so-called *Environmental Protection Charters* to avoid waste and to save natural recourses. Based on the JEIDA³ 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

 $^{^3 {\}rm Japan}$ Electronics Industry Development Association.

(e.g. Pb, Hg, 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,

⁴In this manufacturing procedure the electronic components are directly -i.e., without the use of pins - soldered on the circuit board.

⁵Here 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.

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 Sn-Pb solder ($c_{\rm Sn} = 0.63$) represents a good compromise. On the one hand both components as well as the mixtures have sufficiently low melting temperatures, namely, [119, 1]:

$$T_{\rm Sn}^{\rm melt} = 232\,^{\circ}{\rm C}$$
 , $T_{\rm Pb}^{\rm melt} = 327\,^{\circ}{\rm C}$, $T_{\rm Sn-Pb}^{\rm eut} = 183\,^{\circ}{\rm C}$.

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, Ag-Cu, identifies a typical *brazing alloy* (*i.e.*, $T^{\text{melt}} > 450 \,^{\circ}\text{C}$). 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 Sn-Cu cannot be used for reflow soldering since the relatively high melting temperature (*cf.*, Table 1.1) does not allow sufficiently long soldering time. Here experts recommend to use Sn-Ag, whereas Sn-Cu is considered for *wave soldering* applications, [1].

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

Table 1.1: Various lead-free solder materials under discussion, source: [83],	[11	1	12	2	
---	-----	---	----	---	--

In contrast to soft solders, brazing materials, such as the binary solder Ag-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 (Cu_6Sn_5) at the interface solder/substrate. 1st row (right): IMC needles (Ag_3Sn) in the solder bulk, source: [92]. 2nd row (left): Phase separation by spinodal decomposition in eutectic Ag-Cu after 40h heat treatment. 2nd row (right): KIRKENDALL void formation in the thin Cu₃Sn layer at the interface solder/substrate, source: [120].

1.3 Microstructures in Solders

- (a) Formation and growth of scallop-shaped InterMetallic Compounds⁶ (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., Sn-Ag-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 Ag₃Sn precipitates observed in lead-free SAC solders (Sn-Ag-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 thermo-dynamical 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 Cu/Cu₃Sn into Cu₃Sn is much slower than the diffusion of Cu from Cu₃Sn into the Cu₆Sn₅ scallops, which also cannot be corrected by the invers diffusion of Sn through the Cu₆Sn₅/Cu₃ interface, [120]. As a consequence vacancies on the lattice sites remain within the Cu₃Sn 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.

⁶The 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.

Introduction



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 Sn-Pb ($c_{\text{Sn}} = 0.63$), [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 Ag-Cu** is chosen to be in the focus of this work, in which spinodal decomposition and OSTWALD ripening yields two equilibrium phases, the Ag-rich α -phase and the Cu-rich β -phase, *cf.*, Fig. 1.3 (*lower left*). It has qualitatively a similar miscibility gap (*i.e.*, phase equilibrium data) as the Sn-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_{crit} into two equilibrium phases α and β due to a *miscibility gap* resulting in a gain of the GIBBS free energy G(y, T), which is a function of particle concentration $y \equiv y_{\text{B}}$ (with $y_{\text{A}} + y_{\text{B}} = 1$) 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 $y_{1/2}^{sp}$:

$$\frac{\partial^2 G(y,T)}{\partial y^2} \bigg|_{y_{1/2}^{sp}} = 0 \quad \text{(spinodal concentrations)} . \tag{1.1}$$

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]:

$$\frac{\partial G(y,T)}{\partial y}\Big|_{y=y_{\alpha/\beta}} = \frac{G(y_{\beta},T) - G(y_{\alpha},T)}{y_{\beta} - y_{\alpha}} .$$
(1.2)

Figure 1.5 (upper right) illustrates the construction of the equilibrium concentrations $y_{\alpha/\beta}$ of the two solid phases α and β . 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 Ag-Cu, [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 Ag-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-Atom-Method (EAM) the HGCs are calculated for the binary alloy Ag-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.

Die Mathematik ist eine Art Spielzeug, welches die Natur uns zuwarf zum Troste und zur Unterhaltung in der Finsternis.

Jean-Baptist le Rond D'Alembert, (1717 - 1783)

Chapter 2

A Higher Gradient Theory of Mixtures¹

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

¹Some of the considerations of this Chapter already appeared in [10].

by Cahn and Hilliard², [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 LSWtheories, 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 nu*merical simulations initiated by the fast increasing computational capacities. The applied algorithms are mainly based on discrete FOURIER transforms, [117], or finite

 $^{^2{\}rm Here}$ the work of HILLERT appears before the work of CAHN and HILLIARD, because HILLERT already derived the formulae in 1956 in his PhD thesis.

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 Ag-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 $x^i y^i \doteq \sum_{i=1}^3 x^i y^i$ holds³.

quantities of motion

X^i	LAGRANGE position (cartesian)
$x^i = \chi^i(X^j, t)$	current position
$u^i = x^i - X^i$	displacements
$v^i = \mathrm{d}x^i/\mathrm{d}t = \dot{x}^i$	(barycentric) velocity
$F^{ij} = \partial \chi^i(X^k, t) / \partial X^j$	deformation gradient
$J = \det F^{ij} \ge 0$	JACOBIAN
$C^{ij} = F^{mi}F^{mj} \wedge \det C^{ij} = J^2$	right CAUCHY-GREEN tensor
$c^{ij} = J^{-2/3} C^{ij} \wedge \det c^{ij} = 1$	unimodular right CAUCHY-GREEN tensor
σ^{ij}	CAUCHY stress tensor
$t^{ij} = J(F^{im})^{-1} \sigma^{mn} (F^{jn})^{-1}$	2nd PIOLA-KIRCHHOFF tensor

³Here the index notation of Cartesian vectors ($\mathbf{v} \equiv v^i$) and tensors (*e.g.*, $\mathbf{T} \equiv T^{ij}$) 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.

thermodynamical quantities

number of components of the mixture ν $\alpha \in \{1,\ldots,\nu\}$ label for the constituents N_{α} number of particles of the component α $N = \sum_{\alpha=1}^{\nu} N_{\alpha}$ total number of particles of the mixture particle density of component α n_{α} $n = \sum_{\alpha=1}^{\nu} n_{\alpha}$ particle density of the mixture $y_{\alpha} = n_{\alpha}^{\alpha/n} = N_{\alpha}/N$ Mole fraction/particle concentration of α $m_H = 1.66 \cdot 10^{-27} \text{ kg}$ 1/12 of the carbon 12 isotope (reference mass) M_{α} molecular weight (dimensionless) $m_{\alpha} = m_H M_{\alpha}$ molecular mass (in kg) of component α $m = \sum_{\alpha=1}^{\nu} N_{\alpha} m_{\alpha}$ total mass (in kg) $\rho_{\alpha} = \overline{m_{\alpha}} n_{\alpha}$ $\rho = \sum_{\alpha=1}^{\nu} m_{\alpha} n_{\alpha}$ mass density of component α total mass density of the mixture $M = \tilde{M}(y_{\alpha}) = \sum_{\alpha=1}^{\nu} M_{\alpha} y_{\alpha}$ mean molecular weight of a mixture particle $c_{\alpha} = \rho_{\alpha}/\rho = n_{\alpha}m_{\alpha}/(nm)$ mass concentration of component α T, p, V(absolute) temperature, pressure, total volume internal energy, entropy per unit mass ϵ, η $\varphi = \epsilon - T\eta$ HELMHOLTZ free energy per unit mass $\psi = \varphi + p/\rho$ GIBBS free energy per unit mass chemical potential (in J/particle) of component α μ_{α} particle diffusion flux of component α j^i_{α} $\begin{array}{c}J^i_\alpha\\q^i\end{array}$ mass diffusion flux of component α 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 $(t = t_0)$ 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

$$x^{i} = \chi^{i}(t, X^{1}, X^{2}, X^{3}) \tag{2.1}$$

is called the *motion* of the body.

The function χ^i can be used to determine the barycentric velocity v_0^i as well as the
displacements of the material points, viz.:

$$v_0^i(t, X^j) = \frac{\partial \chi^i(t, X^j)}{\partial t}$$
 and $U^i = U^i(t, X^j) = \chi^i(t, X^j) - X^j$. (2.2)

Furthermore the displacement gradient H^{ij} and the *deformation* gradient F^{ij} is defined as:

$$H^{ij} = \frac{\partial U^i}{\partial X^j}$$
 and $F^{ij} = \frac{\partial \chi^i}{\partial X^j} = \delta^{ij} + H^{ij}$. (2.3)

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 $J = \det F^{ij} > 0$, so that we may invert $x^i = \chi^i(t, X^j)$. We write:

$$X^{i} = (\chi^{-1})^{i}(t, x^{j}) .$$
(2.4)

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

$$v^{i}(t,x^{j}) = v_{0}^{i}\left(t,(\chi^{-1})^{j}(t,x^{k})\right) , \qquad u^{i}(t,x^{j}) = U^{i}\left(t,(\chi^{-1})^{j}(t,x^{k})\right) ,$$

$$h^{ij} = H^{ij}\left(t,(\chi^{-1})^{j}(t,x^{k})\right) = \frac{\partial u^{i}}{\partial x^{j}} , \quad (F^{-1})^{ij} = \frac{\partial(\chi^{-1})^{i}}{\partial x^{j}} = \delta^{ij} - h^{ij} .$$
(2.5)

Beyond this, further "measures of strain" can be considered, *e.g.*, the right CAUCHY-GREEN tensor, C^{ij} , the GREEN strain tensor, G^{ij} or the linearized strains, ε^{ij} . It holds:

$$C^{ij} = F^{mi}F^{mj}$$
, $G^{ij} = \frac{1}{2}(C^{ij} - \delta^{ij})$ and $\varepsilon^{ij} = \frac{1}{2}(H^{ij} - H^{ji})$. (2.6)

Other than C^{ij} the unimodular right CAUCHY-GREEN tensor, c^{ij} , will prove very useful. It results from the decomposition of the deformation gradient into a pure volume-changing part, $J^{1/3}\delta^{mi}$, and into a unimodular part, $F_{\rm u}^{mj}$, as follows:

$$F^{ij} = (J^{1/3}\delta^{mi})F^{mj}_{u} \quad \Rightarrow \quad C^{ij} = J^{2/3}F^{mi}_{u}F^{mj}_{u} = J^{2/3}c^{ij} .$$
(2.7)

Thus C^{ij} is split into a pure volume-changing, $J^{2/3}$, and into a volume-preserving part, c^{ij} (with det $c^{ij} = 1$), 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 $\rho_{\alpha}(x^{j}, t)$ of the different constituents, the barycentric velocity $v^{i}(x^{j}, t)$ (in case of liquids) or the displacements $u^{i}(x^{j}, t)$ (in case of solids), and the internal energy density $\rho\epsilon(x^{j}, t)$ 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:

$$\frac{\partial \rho_{\alpha}}{\partial t} = -\frac{\partial (\rho_{\alpha} v_{\alpha}^{i})}{\partial x^{i}} + \tau_{\alpha}^{\rho} \qquad (\text{partial mass balance}) , \qquad (2.8)$$

$$\frac{\partial \rho v^{i}}{\partial t} = -\frac{\partial}{\partial x^{j}} \left(\rho v^{j} v^{i} - \sigma^{ij} \right) \qquad (\text{momentum balance}) , \qquad (2.9)$$

$$\frac{\partial \rho \epsilon}{\partial t} = -\frac{\partial}{\partial x^j} \left(\rho \epsilon v^j + q^j \right) + \sigma^{ij} \frac{\partial v^i}{\partial x^j} \qquad \text{(internal energy balance)} . \tag{2.10}$$

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, τ^{ρ}_{α} , on the right hand side of Eq. (2.8). Consequently the conservation of mass does not hold for the individual component α .

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:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial (\rho v^i)}{\partial x^i} \tag{2.11}$$

with
$$\sum_{\alpha=1}^{\nu} \rho_{\alpha} \stackrel{\text{(def)}}{=} \rho$$
 , $\sum_{\alpha=1}^{\nu} \rho_{\alpha} v_{\alpha}^{i} \stackrel{\text{(def)}}{=} \rho v^{i}$, $\sum_{\alpha=1}^{\nu} \tau_{\alpha}^{\rho} = 0$. (2.12)

An alternative form of Eq. (2.11) is given by $J = \rho_0/\rho$ where ρ_0 represents the mass density of the reference state, *cf.*, [86]. This relation follows by integrating Eq. (2.11) and by using the relation $dJ/dt = J \cdot \partial v^i/\partial x^i$, *cf.*, Eq. (A.2).

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

$$J_{\alpha}^{i} \stackrel{\text{(def)}}{=} \rho_{\alpha}(v_{\alpha}^{i} - v^{i}) \quad \text{which implies} \quad \sum_{\alpha=1}^{\nu} J_{\alpha}^{i} = 0 , \qquad (2.13)$$

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:

$$\frac{\partial \rho_{\alpha}}{\partial t} = -\frac{\partial (\rho_{\alpha} v^{i} + J^{i}_{\alpha})}{\partial x^{i}} + \tau^{\rho}_{\alpha} \qquad (\text{alternative partial mass balance}) . \tag{2.14}$$

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* $n_{\alpha}(x^{i}, t)$ instead of Eq. (2.8). By means of $\rho_{\alpha} = m_{\alpha}n_{\alpha}$ one finds:

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

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

$$j_{\alpha}^{i} \stackrel{\text{(def)}}{=} n_{\alpha}(v_{\alpha}^{i} - v^{i}) \text{ and } J_{\alpha}^{i} = m_{\alpha}j_{\alpha}^{i} , \quad \sum_{\alpha=1}^{\nu} m_{\alpha}j_{\alpha}^{i} = 0.$$
 (2.16)

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

$$\frac{\partial n_{\alpha}}{\partial t} = -\frac{\partial (n_{\alpha}v^{i} + j_{\alpha}^{i})}{\partial x^{i}} + \tau_{\alpha}^{n} \qquad \text{(alternative partial particle balance)} . \tag{2.17}$$

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. $\{\rho_{\alpha} \text{ or } n_{\alpha}, v^{i} \text{ or } u^{i}, \rho\epsilon\}$, as primary variables. Beyond these variables further quantities, so-called constitutive quantities, such as σ^{ij} , q^{i} , J^{i}_{α} , j^{i}_{α} and $\tau^{\rho/n}_{\alpha}$, 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^{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^{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^{nd} Law of Thermodynamics (2^{nd} law), and it reads without a contribution from radiation:

$$\frac{\mathrm{d}S}{\mathrm{d}t} \ge \frac{\dot{Q}}{T} \quad \text{or} \quad \frac{\mathrm{d}}{\mathrm{d}t} \int_{V} \rho \eta \,\mathrm{d}V \ge -\frac{1}{T} \oint_{\partial V} q^{i} n^{i} \,\mathrm{d}A \;. \tag{2.18}$$

The inequality concerns an arbitrary body with volume V, whose surface ∂V may exchange heat with the environment with rate \dot{Q} at a homogeneous temperature T. By means of this version of the 2nd 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 ϕ^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:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{V} \rho \eta \,\mathrm{d}V \ge -\oint_{\partial V} \frac{q^{i} n^{i}}{T} \,\mathrm{d}A \quad \Rightarrow \quad \frac{\partial \rho \eta}{\partial t} + \nabla_{i} \left(\rho \eta v^{i} + \frac{q^{i}}{T}\right) \ge 0 \;. \tag{2.19}$$

Consequently the entropy flux is $\phi^i = q^i/T$, as used in [27] or [57]. However, this form of ϕ^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 ϕ^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, cf., [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, ζ , 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 $\rho_0 = 1 \text{kg/m}^3$, 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

$$\ddot{u} - \frac{\partial \sigma}{\partial x} = 0, \quad \dot{e} + \frac{\partial q}{\partial x} = \sigma \dot{u}_x .$$
 (2.20)

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

In order to end up with a closed set of field equation we have to relate the two quantities stress, σ , 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

$$\sigma = \sigma_0(e, u_x) - a(e, u_x)u_{xxx} - b(e, u_x)u_{xx}^2, \qquad (2.21)$$

where σ_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.

$$s = h(e, u_x, u_{xx}, u_{xxx}). (2.22)$$

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:

$$\dot{s} = \frac{\partial h}{\partial e} \dot{e} + \frac{\partial h}{\partial u_x} \dot{u}_x + \frac{\partial h}{\partial u_{xx}} \dot{u}_{xx} + \frac{\partial h}{\partial u_{xxx}} \dot{u}_{xxx}, \qquad (2.23)$$

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:

$$\dot{s} = -\frac{\partial}{\partial x} \left(\frac{\partial h}{\partial e} q - \left(\frac{\partial h}{\partial u_{xx}} - \frac{\partial}{\partial x} \frac{\partial h}{\partial u_{xxx}} \right) \dot{u}_x + \frac{\partial h}{\partial u_{xxx}} \dot{u}_{xx} \right) + \\ + \left(\frac{\partial h}{\partial u_x} - \frac{\partial}{\partial x} \frac{\partial h}{\partial u_{xx}} + \frac{\partial^2}{\partial x^2} \frac{\partial h}{\partial u_{xxx}} + \frac{\partial h}{\partial e} \sigma \right) \dot{u}_x + q \frac{\partial}{\partial x} \frac{\partial h}{\partial e} .$$
(2.24)

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, ϕ , according to:

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

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

$$q\frac{\partial \frac{1}{T}}{\partial x} \ge 0, \tag{2.26}$$

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.*:

$$\frac{\sigma}{T} = -\frac{\partial h}{\partial u_x} + \frac{\partial}{\partial x}\frac{\partial h}{\partial u_{xx}} - \frac{\partial^2}{\partial x^2}\frac{\partial h}{\partial u_{xxx}} .$$
(2.27)

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

$$\dot{s} + \frac{\partial \phi}{\partial x} \ge 0 , \qquad (2.28)$$

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 × 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

$$s = h_0(e, u_x) - \frac{1}{2}\alpha(e, u_x)u_{xx}^2 + \gamma(e, u_x)u_{xxx} .$$
(2.29)

In order to describe two existing phases, the function $h_0(e, u_x)$ 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

$$\phi = (\alpha + \gamma')u_{xx}\dot{u}_x - \gamma u_{xx} , \qquad (2.30)$$

and the constitutive function for the stress

$$\frac{\sigma}{T} = -h'_0 - (\alpha + 2\gamma')u_{xxx} - \frac{1}{2}(\alpha' + 2\gamma'')u_{xx}^2 .$$
(2.31)

A comparison of this result with (2.21) implies that we have $\sigma_0 = -Th'_0$, $a = T(\alpha + 2\gamma')$ and $b = T\frac{1}{2}(\alpha' + 2\gamma'')$. We conclude that the entropy principle requires that the coefficient functions a and b are not independent of each other but must satisfy

$$b = \frac{1}{2}a'$$
 (2.32)

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

$$q = -\kappa \frac{\partial T}{\partial x}$$
 with $\kappa > 0$. (2.33)

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, ϕ^i . The constitutive relation of $\rho\eta$ has the form:

$$\rho\eta = \mathcal{S}(\text{variables}, (\text{functions of}) \text{ derivatives of the variables}), (2.34)$$

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.

 $\S2$) There exists a local entropy balance

$$\frac{\partial \rho \eta}{\partial t} + \frac{\partial (\rho \eta v^k + \phi^k)}{\partial x^k} = \zeta \quad \text{with} \quad \zeta \ge 0 \quad (\text{dissipation inequality}) . \quad (2.35)$$

The constraint of Eq. $(2.35)_2$, viz. the non-negative entropy-production ζ , represents the Second Law of Thermodynamics.

 $\S3$) We define the *absolute temperature* to be:

$$\frac{1}{T} \stackrel{\text{(def)}}{=} \frac{\partial \rho \eta}{\partial \rho \epsilon} , \qquad (2.36)$$

which corresponds to the concept of the integrating factor within classical thermodynamics.

§4) (a) Analogously to the concept of thermodynamical fluxes (F_z) and driving forces (D_z) known from the *Thermodynamics of Irreversible Processes*, [43], we postulate the following form for the entropy production:

$$\zeta = \sum_{z} F_{z} D_{z} \quad , \quad F_{z} \stackrel{e.g.}{=} \{ j_{\alpha}^{k} \text{ or } J_{\alpha}^{k}, \sigma_{\text{diss}}^{ij}, q^{k} \} \quad .$$

$$(2.37)$$

 $\sigma_{\rm diss}^{ij}$ (with $\sigma^{ij} = \sigma_{\rm el}^{ij} + \sigma_{\rm diss}^{ij}$) 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

$$D_z = \left\{ \nabla_i \left(\frac{\mu_\alpha - \mu_\nu}{T} \right), \nabla_{(i} v^{j)}, \nabla_i (1/T) \right\},$$
(2.38)

The newly introduced quantities μ_{α} 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.*, $F_z|_{eq} \doteq 0$, which, in turn, guarantees the absence of dissipation, *i.e.*, $\zeta|_{eq} = 0$, within equilibrium. Hence it follows that $\zeta|_{eq}$ is minimal. Relying on the assumption that the F_z depend on the D_z , we may conclude that $D_z|_{eq} = 0$ 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:

$$\left\{\underbrace{\rho_{\alpha}, \frac{\partial v^{i}}{\partial x^{i}}, v^{i}, \frac{\partial \rho_{\alpha}}{\partial x^{i}}, \frac{\partial J^{i}_{\alpha}}{\partial x^{i}}, \tau^{\rho}_{\alpha}}_{\partial x^{i}}, \underbrace{\rho, \rho v^{i}, \frac{\partial v^{\langle i}}{\partial x^{j \rangle}}, \frac{\partial \sigma^{ij}}{\partial x^{j}}}_{\partial x^{j}}, \underbrace{\rho \epsilon, \frac{\partial \rho \epsilon}{\partial x^{i}}, \frac{\partial q^{i}}{\partial x^{i}}, \sigma^{ij}}_{\partial x^{i}}}_{(2.39)}\right\}.$$

partial mass balance

momentum balance internal energy balance

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 ρ_{α} , J^{i}_{α} and τ^{ρ}_{α} in Eq. (2.39) must be replaced by n_{α} , j^{i}_{α} and τ^{n}_{α} .

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 ν non-reacting components, *i.e.*, $\sigma_{\text{diss}}^{ij} = 0 \Rightarrow \sigma^{ij} = \sigma_{\text{el}}^{ij}$ 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:

$$\rho\eta = \tilde{\mathcal{S}}(\rho\epsilon, n_1, \dots, n_{\nu}, c^{ij}) = \hat{\mathcal{S}}(T, n_1, \dots, n_{\nu}, c^{ij}) = \bar{\mathcal{S}}(T, y_1, \dots, y_{\nu-1}, \rho, c^{ij}) = \hat{\mathcal{S}}(T, y_1, \dots, y_{\nu-1}, C^{ij}).$$
(2.40)

 $\rho\epsilon$ identifies the thermal variable whereas the symbols n_{α} , $\alpha \in \{1, \ldots, \nu\}$, and c^{ij} characterizes the composition and the deformation of the solid. Note that c^{ij} only contains five independent elements due to the relation det $c^{ij} = (J^{-2/3})^3 J^2 = 1$ whereas C^{ij} in Eq. (2.40)₄ incorporates six independent elements. The set $\{\rho, c^{ij}\}$ can be used alternatively instead of C^{ij} , which is reasonable since ρ and C^{ij} are not independent due to the relation $\rho_0/\rho = J = \det F^{ij} = \det \sqrt{C^{ij}}$ (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{S} is extremely useful for the exploitation of the 2nd law whereas the sets of arguments in \bar{S} , \hat{S} and \hat{S} can be used for the definition of the chemical potential μ_{α} or for the calculation of the pressure p and the stresses t^{ij} .

In what follows we write for the entropy balance in Eq. $(2.35)_1$ by means of the product rule:

$$\underbrace{\frac{\partial \tilde{\mathcal{S}}}{\partial t}}_{A} + v^{i} \underbrace{\frac{\partial \tilde{\mathcal{S}}}{\partial x^{i}}}_{B} + \tilde{\mathcal{S}} \frac{\partial v^{i}}{\partial x^{i}} + \frac{\partial \phi^{i}}{\partial x^{i}} = \zeta .$$
(2.41)

The expressions A and B can be re-written using Eq. $(2.40)_1$ and the chain rule, viz.

$$\frac{\partial \tilde{S}}{\partial t} = \frac{\partial \tilde{S}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial t} + \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{S}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial t} + \frac{\partial \tilde{S}}{\partial c^{ij}} \frac{\partial c^{ij}}{\partial t} , \qquad (2.42)$$

$$\frac{\partial \tilde{S}}{\partial x^{i}} = \frac{\partial \tilde{S}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial x^{i}} + \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{S}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x^{i}} + \frac{\partial \tilde{S}}{\partial c^{kl}} \frac{\partial c^{kl}}{\partial x^{i}} .$$
(2.43)

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:

$$\zeta = \frac{1}{T} \left[-\frac{\partial}{\partial x^{j}} \left(\rho \epsilon v^{j} + q^{j} \right) + \sigma_{\text{el}}^{ij} \frac{\partial v^{i}}{\partial x^{j}} \right] + \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{S}}{\partial n_{\alpha}} \left[-\frac{\partial (n_{\alpha}v^{i} + j_{i}^{\alpha})}{\partial x^{i}} \right] + \frac{\partial \tilde{S}}{\partial c^{kl}} \underbrace{\left(\frac{\partial c^{kl}}{\partial t} + v^{i} \frac{\partial c^{kl}}{\partial x^{i}} \right)}_{=\mathrm{d}c^{kl}/\mathrm{d}t} + v^{i} \left(\frac{1}{T} \frac{\partial \rho \epsilon}{\partial x^{i}} + \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{S}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x^{i}} \right) + \tilde{S} \frac{\partial v^{i}}{\partial x^{i}} + \frac{\partial \phi^{i}}{\partial x^{i}} .$$

$$(2.44)$$

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

$$\dot{c}^{kl} = -\frac{2}{3}J^{-2/3}\frac{\partial v^i}{\partial x^i}C^{kl} + J^{-2/3}\frac{\partial v^i}{\partial x^j}\left(F^{jk}F^{il} + F^{jl}F^{ik}\right) .$$

$$(2.45)$$

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

$$\begin{aligned} \zeta &= \frac{\partial}{\partial x^{i}} \left(\phi^{i} - \frac{q^{i}}{T} - \sum_{\alpha=1}^{\nu} j^{i}_{\alpha} \frac{\partial \tilde{S}}{\partial n_{\alpha}} \right) + \underbrace{\sum_{\alpha=1}^{\nu} j^{i}_{\alpha} \frac{\partial}{\partial x^{i}} \left(\frac{\partial \tilde{S}}{\partial n_{\alpha}} \right) + q^{i} \frac{\partial 1/T}{\partial x^{i}}}_{\mathbf{Q}} + \\ &= \frac{\partial v^{i}}{\partial x^{j}} \left[\frac{\sigma_{\text{el}}^{ij}}{T} + J^{-2/3} \left(F^{jk} F^{il} + F^{jl} F^{ik} \right) \frac{\partial \tilde{S}}{\partial c^{kl}} + \\ &\delta^{ij} \left(\tilde{S} - \frac{\rho \epsilon}{T} - \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{S}}{\partial n_{\alpha}} - \frac{2}{3} J^{-2/3} C^{kl} \frac{\partial \tilde{S}}{\partial c^{kl}} \right) \right] \ge 0 , \end{aligned}$$

$$(2.46)$$

in which the symbol δ^{ij} 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 ζ according to Statement 4 of Section 2.3.4. In particular we arrange the expression \mathbb{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 ϕ^i as:

$$\phi^{i} \stackrel{\text{(def)}}{=} \frac{q^{i}}{T} + \sum_{\alpha=1}^{\nu} j^{i}_{\alpha} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} .$$
(2.47)

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

$$\mathsf{Px} + \mathsf{Q} \ge 0$$
, $\forall \mathsf{x} \in \mathbb{R} \implies \mathsf{P} = 0 \land \mathsf{Q} \ge 0$, (2.48)

with the abbreviations $\mathbf{x} = \partial v^i / \partial x^j$ for the velocity gradient and $\mathsf{P} = [\dots]$ 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 $\mathsf{P} = 0 \land \mathsf{Q} \ge 0$.

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 ϕ^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:

$$q^{i}\frac{\partial 1/T}{\partial x^{i}} + \sum_{\alpha=1}^{\nu} j^{i}_{\alpha}\frac{\partial}{\partial x^{i}} \left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}}\right) \ge 0.$$

$$(2.49)$$

A further evaluation of Eqs. (2.49) requires the substitution of the experimentally unmanageable expression $\partial \tilde{S} / \partial n_{\alpha}$ 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):

$$\rho \varphi = \tilde{\mathcal{F}}(\rho \epsilon, n_1, \dots, n_{\nu}, c^{ij}) = \hat{\mathcal{F}}(T, n_1, \dots, n_{\nu}, c^{ij})
= \bar{\mathcal{F}}(T, y_1, \dots, y_{\nu-1}, \rho, c^{ij}) = \hat{\mathcal{F}}(T, y_1, \dots, y_{\nu-1}, C^{ij}),$$
(2.50)

and define the *chemical potential* μ_{α} as:

$$\mu_{\alpha} \stackrel{\text{(def)}}{=} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} \,. \tag{2.51}$$

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

$$\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} = -\frac{1}{T} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} = -\frac{\mu_{\alpha}}{T} .$$
(2.52)

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:

$$q^{i}\frac{\partial 1/T}{\partial x^{i}} + \sum_{\alpha=1}^{\nu} j^{i}_{\alpha}\frac{\partial}{\partial x^{i}} \left(\frac{\partial\tilde{\mathcal{S}}}{\partial n_{\alpha}}\right) = q^{i}\frac{\partial 1/T}{\partial x^{i}} + \sum_{\beta=1}^{\nu-1} j^{i}_{\beta}\frac{\partial\left(\frac{m_{\beta}}{m_{\nu}}\mu_{\nu}-\mu_{\beta}\right)/T}{\partial x^{i}} = q^{i}\frac{\partial 1/T}{\partial x^{i}} + \sum_{\beta=1}^{\nu-1} m_{\beta}j^{i}_{\beta}\frac{\partial\left(\frac{\mu_{\nu}}{m_{\nu}}-\frac{\mu_{\beta}}{m_{\beta}}\right)/T}{\partial x^{i}} \geq 0.$$

$$(2.53)$$

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 , $\sigma_{\text{diss}}^{ij}$, j^i_{β} or $J^i_{\beta} = m_{\beta} j^i_{\beta}$ such that quadratic expressions in $\frac{\partial 1/T}{\partial x^i}$, $\frac{\partial (m_{\beta}\mu_{\nu}/m_{\nu}-\mu_{\beta})/T}{\partial x^i}$ or $\frac{\partial (\mu_{\nu}/m_{\nu}-\mu_{\beta}/m_{\beta})/T}{\partial x^i}$ with positive coefficients result. If thermodiffusion coupling (LUDWIG-SORET and DUFOUR effect, *cf.*, [31]) is neglected we put:

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

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

$$\mu_{\alpha}^{*} = \frac{\partial \widehat{\mathcal{F}}(T, \rho_{1}, \dots, \rho_{\nu}, c^{ij})}{\partial \rho_{\alpha}} = \frac{1}{m_{\alpha}} \frac{\partial \widehat{\mathcal{F}}}{\partial n_{\alpha}} \quad , \quad \alpha = \{1, \dots, \nu\} \; . \tag{2.55}$$

Note that the material-specific, positive definite diagonal matrices $M_{\beta\delta}^{ij}$, $B_{\beta\delta}^{ij}$ and κ^{ij} 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 $q^i = -\bar{\kappa}^{ij}(T)\frac{\partial T}{\partial x^j}$, with $\bar{\kappa}^{ij}(T) = \kappa^{ij}/T^2$. If $\bar{\kappa}^{ij} = \text{const}$ this equation is called FOURIER's law of heat conduction in which the symbol $\bar{\kappa}^{ij}$ 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 μ_{α} or μ^*_{α} . The matrices $M^{ij}_{\beta\delta}$ and $B^{ij}_{\beta\delta}$ are often called *mobilities*.

b. Mechanical Constitutive Equations

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

$$p = -\frac{1}{3}\sigma^{kk} = \frac{1}{3}J^{-2/3}T\left(F^{mk}F^{ml} + F^{ml}F^{mk}\right)\frac{\partial\tilde{S}}{\partial c^{kl}} + T\left(\rho\eta - \frac{\rho\epsilon}{T} - \sum_{\alpha=1}^{\nu}n_{\alpha}\frac{\partial\tilde{S}}{\partial n_{\alpha}} - \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial\tilde{S}}{\partial c^{kl}}\right). \quad (2.56)$$

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

$$p = -\rho\varphi - T\sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} \stackrel{(\text{App. A.2})}{=} -\rho\varphi + \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}}$$

$$\stackrel{(\text{App. A.3})}{=} -\rho\varphi + \sum_{\alpha=1}^{\nu} n_{\alpha} m_{\alpha} \frac{\partial \bar{\mathcal{F}}}{\partial \rho} + \underbrace{\sum_{\alpha=1}^{\nu} \sum_{\beta=1}^{\nu-1} y_{\alpha} \frac{\partial \bar{\mathcal{F}}}{\partial y_{\beta}} \left(\delta^{\alpha\beta} - \frac{n_{\beta}}{n}\right)}_{=0} \qquad (2.57)$$

$$= -\rho\varphi + \rho\frac{\partial\bar{\mathcal{F}}}{\partial\rho} = \rho^2\frac{\partial\bar{\varphi}}{\partial\rho}. \qquad (2.58)$$

The 2nd PIOLA-KIRCHHOFF stress tensor t^{ij} can be also expressed by a partial derivative of the HELMHOLTZ free energy. For this purpose we use the definition of t^{ij} in Section 2.2 and analyze the constraint P = 0 with respect to Eq. (2.46):

$$t^{ij} = J(F^{im})^{-1} \sigma^{mn}(F^{jn})^{-1}$$

$$= -J^{1/3}T \left[\delta^{jk} \delta^{il} + \delta^{jl} \delta^{ik} \right] \frac{\partial \tilde{S}}{\partial c^{kl}} - JT \underbrace{(F^{in})^{-1}(F^{jn})^{-1}}_{=(C^{ij})^{-1}} \left(\tilde{S} - \frac{\rho\epsilon}{T} - \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{S}}{\partial n_{\alpha}} - \frac{2}{3} J^{-2/3} C^{kl} \frac{\partial \tilde{S}}{\partial c^{kl}} \right)$$

$$= -2J^{1/3}T \frac{\partial \tilde{S}}{\partial c^{ij}} + J(C^{ij})^{-1} \left(\rho\varphi + T \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{S}}{\partial n_{\alpha}} + \frac{2}{3} J^{-2/3} T C^{kl} \frac{\partial \tilde{S}}{\partial c^{kl}} \right).$$

$$(2.59)$$

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

$$t^{ij} \stackrel{(\text{App. A.2, A.3)}}{=} 2J^{1/3} \frac{\partial \bar{\mathcal{F}}}{\partial c^{ij}} + J(C^{ij})^{-1} \left(\rho\varphi - \rho\frac{\bar{\mathcal{F}}}{\partial\rho} - \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial \bar{\mathcal{F}}}{\partial c^{kl}}\right)$$

$$\stackrel{(\text{App. A.4)}}{=} 2J^{1/3} \frac{\partial \acute{\mathcal{F}}}{\partial C^{kl}} \left(\frac{\rho_0}{\rho}\right)^{2/3} + J(C^{ij})^{-1} \times \\ \times \left(\rho\varphi + \frac{2}{3}J^{2/3}c^{kl}\frac{\partial \acute{\mathcal{F}}}{\partial C^{kl}} - \frac{2}{3}C^{kl}\frac{1}{2}(\delta^{mk}\delta^{nl} + \delta^{nk}\delta^{ml})\frac{\partial \acute{\mathcal{F}}}{\partial C^{mn}}\right)$$

$$= 2J\frac{\partial \acute{\mathcal{F}}}{\partial C^{ij}} + J(C^{ij})^{-1}(\rho\varphi)$$

$$= 2J\frac{\partial\rho}{\partial C^{ij}}\varphi + 2J\rho\frac{\partial \acute{\varphi}}{\partial C^{ij}} + J(C^{ij})^{-1}(\rho\varphi)$$

$$= 2J\rho\frac{\partial \acute{\varphi}}{\partial C^{ij}} = 2\rho_0\frac{\partial \acute{\varphi}}{\partial C^{ij}}. \qquad (2.60)$$

For the last step in Eq. (2.60) we used the relation $\partial \rho / \partial C^{ij} = \frac{\partial}{\partial C^{ij}} \left(\frac{\rho_0}{(\det \mathbf{C})^{1/2}} \right) = -\frac{\rho_0}{2} (\det \mathbf{C})^{-3/2} \frac{\partial}{\partial C^{ij}} (\det \mathbf{C}) = -\frac{\rho_0}{2} (\det \mathbf{C})^{-1/2} (C^{ij})^{-1} = -\frac{\rho}{2} (C^{ij})^{-1}.$

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. $(2.57)_2$:

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

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

$$d(\rho\varphi) = \frac{\partial\hat{\mathcal{F}}}{\partial T} dT + \sum_{\alpha=1}^{\nu} \frac{\partial\hat{\mathcal{F}}}{\partial n_{\alpha}} dn_{\alpha} + \frac{\partial\hat{\mathcal{F}}}{\partial c^{ij}} dc^{ij} .$$
(2.62)

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

$$\frac{\partial \hat{\mathcal{F}}}{\partial T} = \frac{\partial}{\partial T} \left(\hat{\mathcal{E}} - T \hat{S} \right) \stackrel{(\text{App. A.2})}{=} -\rho \eta \quad , \quad \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} = \mu_{\alpha} \quad , \tag{2.63}$$

$$\frac{\partial \hat{\mathcal{F}}}{\partial c^{ij}} \stackrel{(\text{App. A.3})}{=} \frac{\partial \bar{\mathcal{F}}}{\partial c^{ij}} = \rho \frac{\partial \varphi}{\partial c^{ij}} \stackrel{(\text{App. A.4})}{=} \rho J^{2/3} \frac{\partial \varphi}{\partial C^{ij}} \stackrel{(2.60)}{=} \frac{1}{2} J^{-1/3} t^{ij} .$$
(2.64)

In particular Eq. $(2.64)_2$ holds since ρ and c^{ij} are independent arguments within $\overline{\mathcal{F}}$. Thus we can finally write:

$$d(\rho\varphi) = -\rho\eta \,dT + \frac{1}{2}J^{-1/3}t^{ij}\,dc^{ij} + \sum_{\alpha=1}^{\nu}\mu_{\alpha}\,dn_{\alpha}\,,\quad (\text{GIBBS equation})\,.$$
(2.65)

Eq. (2.65) can be used for the direct identification of $\rho\eta$ and μ_{α} but *cannot* be used for the calculation of t^{ij} since the constraint det $c^{ij} = 1 \Leftrightarrow (c^{ij})^{-1} dc^{ij} = 0$ 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:

$$d\bar{\mathcal{F}} = \rho d\bar{\varphi} + \bar{\varphi} d\rho = \frac{\partial \bar{\mathcal{F}}}{\partial T} dT + \frac{\partial \bar{\mathcal{F}}}{\partial \rho} d\rho + \frac{\partial \bar{\mathcal{F}}}{\partial c^{ij}} dc^{ij} + \sum_{\beta}^{\nu-1} \frac{\partial \bar{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta}$$

$$\Leftrightarrow d\bar{\varphi} = -\eta dT + \frac{p}{\rho^{2}} d\rho + \frac{1}{\rho} \frac{\partial \bar{\mathcal{F}}}{\partial c^{ij}} dc^{ij} + \frac{1}{\rho} \sum_{\beta}^{\nu-1} \frac{\partial \bar{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta} , \qquad (2.66)$$

and

$$d\hat{\mathcal{F}} = \rho d\hat{\varphi} + \hat{\varphi} d\rho = \frac{\partial \hat{\mathcal{F}}}{\partial T} dT + \frac{\partial \hat{\mathcal{F}}}{\partial C^{ij}} dC^{ij} + \sum_{\beta}^{\nu-1} \frac{\partial \hat{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta}$$

$$\Leftrightarrow d\hat{\varphi} = -\eta dT + \frac{1}{2\rho_{0}} t^{ij} dC^{ij} + \frac{1}{\rho} \sum_{\beta}^{\nu-1} \frac{\partial \hat{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta} . \qquad (2.67)$$

Eqs. (2.66) and (2.67) allow for a direct identification of p and t^{ij} 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 μ_{α} . Furthermore Eqs. (2.65, 2.66) can be used for the *liquid* matter, where for purely volumetric deformations $c^{ij} = \delta^{ij} \Leftrightarrow dc^{ij} = 0$ holds. Consequently, one obtains from (2.65)

$$d(\rho\varphi) = -\rho\eta dT + \sum \mu_{\alpha} dn_{\alpha} \quad (\text{GIBBS equation for liquid mixtures}) \qquad (2.68)$$

and from (2.66):

$$d\varphi = -\eta dT + \frac{p}{\rho^2} d\rho \quad (\text{GIBBS equation for pure liquids}) , \qquad (2.69)$$

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

d. Splitting of the Free Energy into a Mechanical and a Chemical Part⁴

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 μ_{α} or μ_{α}^* according to Eqs. (2.51,2.55), which are necessary during calculation of the diffusion fluxes j_{α}^i or J_{α}^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 (T, y_{β}, F^{ij}) with $\beta = \{1, 2, \dots, \nu - 1\}$. These states are specified by the settings indicated in Table 2.2.

Furthermore the following conditions for the CAUCHY stresses, σ^{ij} , and for the deformation gradient, F^{ij} , are formulated for the transformations between the states, *cf.*, Figure 2.1:

$$\sigma^{ij} \begin{cases} = -\bar{p}\delta^{ij} \stackrel{!}{=} \text{const.}, & \text{for } \mathsf{S}_0 \to \mathsf{S}_* \\ \neq -\bar{p}\delta^{ij}, & \text{for } \mathsf{S}_* \to \mathsf{S} \end{cases}, \quad F^{ij} \begin{cases} = F_*^{ij}, & \text{for } \mathsf{S}_0 \to \mathsf{S}_* \\ = F_{\mathrm{el}}^{ij}, & \text{for } \mathsf{S}_* \to \mathsf{S} \end{cases}, \quad (2.70)$$

⁴This paragraph is based on the preliminary considerations by Dreyer and Duderstadt, [35].

	$\label{eq:state_state_state} \left \begin{array}{c} \mathrm{reference\ state\ } S_0 \end{array} \right $	$ \begin{array}{l} {\rm intermediate} \\ {\rm state} \ {\sf S}_* \end{array} $	${\rm current\ state\ } S$
temperature T	$\mid T_0$	$T_* = T$	T
composition y_{β}	y^0_{eta}	$y_{\beta}^* = y_{\beta}$	y_{eta}
deform. gradient F^{ij}	$F_0^{ij} = \delta^{ij}$	F_*^{ij}	F^{ij}

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

in which \bar{p} is the reference pressure.

In summary, the deformation gradient F_*^{ij} represents the inelastic part of the deformation at constant reference stress, whereas $F_{\rm el}^{ij}$ 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 $S_* \to S$, *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 S_0 , S_* , and S the mass densities ρ_0 , ρ_* and ρ , and the Jacobians J_* , J_{el} and J, in terms of concentrations and particle densities. For the mass densities we obtain (see also Section 2.2):

$$\rho_0 = m_H \cdot n_0 \cdot M(y^0_\alpha) \quad , \quad \rho_* = m_H \cdot n_* \cdot M(y_\alpha) \quad , \quad \rho = m_H \cdot n \cdot M(y_\alpha) \quad (2.71)$$

and the calculations of the Jacobians yields:

$$J_{*} \stackrel{\text{(def)}}{=} \det F_{*}^{ij} = \frac{\rho_{0}}{\rho_{*}} = \frac{M(y_{\alpha}^{0})}{M(y_{\alpha})} \frac{n_{0}}{n_{*}} , \quad J_{\text{el}} \stackrel{\text{(def)}}{=} \det F_{\text{el}}^{ij} = \frac{\rho_{*}}{\rho} = \frac{n_{*}}{n} ,$$

$$J \stackrel{\text{(def)}}{=} \det F^{ij} = \frac{\rho_{0}}{\rho} = \nu(y_{\beta})\frac{n_{0}}{n} . \qquad (2.72)$$

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

$$J = J_{\rm el} J_* . aga{2.73}$$



Figure 2.1: Three states of a multi-component thermo-elastic solid. (a) The reference state S_0 with the reference temperature T, the reference composition y^0_{β} , and the reference (undeformed) strain state described by $F_0^{ij} = \delta^{ij}$. (b) The intermediate state S_* with $T_* = T$, $y^*_{\beta} = y_{\beta}$, and F^{ij}_* . (c) The current state S with T, y_{β} , and with F^{ij} for $S_0 \to S$ or with F^{ij}_{el} for $S_* \to S$.

(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

$$F^{ij} = F^{ik}_{\rm el} F^{kj}_{*}.$$
 (2.74)

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

$$x^{i} = \chi^{i}(t, X^{j}) , \quad X^{i}_{*} = \chi^{i}_{*}(t, X^{j}) , \quad x^{i} = \chi^{i}_{el}(t, X^{j}_{*}) , \quad (2.75)$$

so that by virtue of the chain rule we may write

$$F^{ij} = \frac{\partial \chi^i}{\partial X^j} = \frac{\partial \chi^i_{\rm el}}{\partial X^k_*} \frac{\partial \chi^k_*}{\partial X^j} \qquad (2.76)$$

(IV) Example At this point we briefly consider an example to illustrate the deformation that might lead to the intermediate state, characterized by F_*^{ij} . 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

$$J_* = \nu(y_\beta) \prod_{i=1}^{n_0} \frac{n_0}{n_*} = \frac{n_0}{n_*} = \frac{V_*}{V_0} = [1 + \alpha(T - T_0)]^3 , \qquad (2.77)$$

where α 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

$$J_* = \nu(y_\beta) \frac{n_0}{n_*} = \nu(y_\beta) \frac{V_*}{V_0} = \det F_*^{ij} = \nu(y_\beta) \left[1 + \alpha(T - T_0)\right]^3 .$$
 (2.78)

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:

$$F_*^{ij} = \nu(y_\beta)^{1/3} \left[\delta^{ij} + \alpha^{ij} (T - T_0) \right] .$$
(2.79)

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

$$\sigma^{ij} = \frac{1}{J} F^{im} F^{jn} t^{mn} \quad , \quad \sigma^{ij} = \frac{1}{J_{\rm el}} F^{im}_{\rm el} F^{jn}_{\rm el} z^{mn} \; , \tag{2.80}$$

where t^{ij} refers to the reference state S_0 and z^{ij} to the intermediate state S_* . A combination of Eq. $(2.80)_{1,2}$ yields the relation:

$$t^{ij} = J_* (F_*^{-1})^{im} (F_*^{-1})^{jn} z^{mn} .$$
(2.81)

(VI) St. Venant-Kirchhoff law The ST. VENANT-KIRCHHOFF law relates a second PIOLA-KIRCHHOFF 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^{ij} . It reads:

$$z^{ij} = -\bar{p}J_{\rm el}(C_{\rm el}^{-1})^{ij} + \frac{1}{2}\bar{K}^{ijkl}(T, y_{\beta})\left(C_{\rm el}^{kl} - \delta^{kl}\right) \quad \text{with} \quad C_{\rm el}^{kl} = F_{\rm el}^{mk}F_{\rm el}^{ml} , \quad (2.82)$$

where the symbol $\bar{K}^{ijkl} = \bar{K}^{jikl} = \bar{K}^{ijlk} = \bar{K}^{klij}$ stands for the stiffness matrix, which is generally assumed to be a function of T and y_{β} .

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^{ij} . By inserting Eq. (2.82) into Eq. (2.81) we find after some rearrangements of the terms:

$$t^{ij} = -\bar{p}J(C^{-1})^{ij} + \frac{1}{2}K^{ijkl}(T, y_{\beta})\left(C^{kl} - C^{kl}_{*}(T, y_{\beta})\right)$$
(2.83)

with the relations:

$$C_{*}^{kl} = F_{*}^{mk} F_{*}^{ml} , \quad C^{kl} = F^{mk} F^{ml} \text{ and}$$

$$K^{ijkl} = J_{*} (F_{*}^{-1})^{im} (F_{*}^{-1})^{jn} (F_{*}^{-1})^{kp} (F_{*}^{-1})^{lq} \bar{K}^{mnpq} .$$
(2.84)

The Jacobian J_* as well as the deformation gradient F_*^{ij} depend on temperature Tand on the concentrations y_β , cf., Eqs. (2.79)₂ and (2.78). Thus $C_*^{ij} = C_*^{ij}(T, y_\beta)$ and $K^{ijkl} = K^{ijkl}(T, y_\beta)$ depend on the same variables. The newly introduced quantity C_*^{ij} 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:

$$\varphi = \varphi^{\text{mech}} + \varphi^{\text{chem}} \,, \tag{2.85}$$

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 φ^{chem} represents the HELMHOLTZ free energy of S_* , for which the stress state

 $\sigma^{ij} = -\bar{p}\delta^{ij}$ and the strain state $C^{ij} = C_*^{ij}$ holds. Therefore we define analogously to Eqs. (2.40, 2.50):

$$\varphi^{\text{chem}} \stackrel{\text{(def)}}{=} \varphi\left(T, y_1, \dots, y_{\nu-1}, C^{ij} = C^{ij}_*\right) ,$$

$$\varphi^{\text{mech}} \stackrel{\text{(def)}}{=} \varphi\left(T, y_1, \dots, y_{\nu-1}, C^{ij}\right) - \varphi^{\text{chem}} .$$
(2.86)

The chemical part, φ^{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, φ^{mech} , which is exclusively related to the elastic deformations during the transformation $S_* \to S$, is calculated from a given stressstrain relation, e.g., from Eq. (2.60). To this end recall that Eq. (2.83) only depends on $\{T, y_1, \ldots, y_{\nu-1}, C^{ij}\}$ using the relation $J = \hat{J}(C^{kl}) = \sqrt{\det C_{kl}}$. Therefore we can insert Eq. (2.83) into Eq. (2.60) and integrate the result w.r.t. C^{ij} . We obtain:

$$\dot{\varphi}(T, y_{\beta}, C^{ij}) = \frac{K^{ijkl}(T, y_{\beta})}{8\rho_0} \left(C^{ij} - C^{ij}_* \right) \left(C^{kl} - C^{kl}_* \right) - \frac{\bar{p}}{\rho_0} \left[J_*(T, y_{\beta}) - \hat{J} \right] \\
+ \mathcal{K}(T, y_{\beta}),$$
(2.87)

in which \mathcal{K} and $\bar{p}J_*/\rho_0$ denote integration "constants" because they depend exclusively on the variables $\{T, y_1, \ldots, y_{\nu-1}\}$. Furthermore we made use of the relation $(C^{-1})^{ij} = (\det C^{kl})^{-1} \partial_{C^{ij}} (\det C^{kl}).$

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

$$\hat{\mathcal{F}} = \frac{K^{ijkl}(T, y_{\beta})}{8\hat{J}} \left(C^{ij} - C^{ij}_{*} \right) \left(C^{kl} - C^{kl}_{*} \right) - \bar{p} \left(\frac{J_{*}(T, y_{\beta})}{\hat{J}} - 1 \right) + \hat{\rho} \mathcal{K}(T, y_{\beta}) , (2.88)$$

with $\rho = \rho(C^{ij}) = \rho_0 / \hat{J}(C^{ij})$. The mechanical part, $\rho \varphi^{\text{mech}}$, must vanish for the case $C^{ij} = C_*^{ij}$ and $J = J_*$. Thus we conclude:

$$\rho\varphi^{\text{mech}} = \acute{\mathcal{F}}^{\text{mech}} = \frac{K^{ijkl}(T, y_{\beta})}{8\acute{J}} \left(C^{ij} - C^{ij}_{*} \right) \left(C^{kl} - C^{kl}_{*} \right) - \bar{p} \left(\frac{J_{*}(T, y_{\beta})}{\acute{J}} - 1 \right) ,$$
(2.89)

$$\rho \varphi^{\text{chem}} = \acute{\mathcal{F}}^{\text{chem}} = \acute{\rho} \mathcal{K}(T, y_{\beta}).$$
(2.90)

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

$$\rho = \hat{\rho}(n_{\alpha}) = \sum_{\alpha} m_{\alpha} n_{\alpha} \qquad , \qquad J = \hat{J}(n_{\alpha}) = \frac{\rho_0}{\sum_{\alpha} m_{\alpha} n_{\alpha}} \quad , \tag{2.91}$$

$$C^{ij} = \hat{J}^{2/3} c^{ij} , \qquad y_{\beta} = \hat{y}_{\beta}(n_{\alpha}) = \frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}}$$
 (2.92)

we reformulate Eq. (2.88) as follows:

$$\hat{\mathcal{F}} = \hat{\mathcal{F}}^{\text{mech}} + \hat{\mathcal{F}}^{\text{chem}} =
= \frac{K^{ijkl}(T, \hat{y}_{\beta})}{8\hat{J}} \left(\hat{J}^{2/3} c^{ij} - C^{ij}_{*}(T, \hat{y}_{\beta}) \right) \left(\hat{J}^{2/3} c^{kl} - C^{kl}_{*}(T, \hat{y}_{\beta}) \right)
+ \hat{\rho} \mathcal{K}(T, \hat{y}_{\beta}) - \bar{p} \left(\frac{J_{*}(T, \hat{y}_{\beta})}{\hat{J}} - 1 \right) ,$$
(2.93)

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

$$\mu_{\alpha} \stackrel{\text{(def)}}{=} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} = \frac{(K^{ijkl})'}{8J} \frac{\partial \hat{y}_{\beta}}{n_{\alpha}} \left(C^{ij} - C^{ij}_{*} \right) \left(C^{kl} - C^{kl}_{*} \right) + \frac{K^{ijkl}m_{\alpha}}{8\rho_{0}} \left(C^{ij} - C^{ij}_{*} \right) \left(C^{kl} - C^{kl}_{*} \right) + \frac{K^{ijkl}}{8J} \left(-\frac{2}{3} \frac{m_{\alpha}}{\rho} C^{ij} - (C^{ij}_{*})' \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}} \right) \left(C^{kl} - C^{kl}_{*} \right) + \frac{K^{ijkl}}{8J} \left(-\frac{2}{3} \frac{m_{\alpha}}{\rho} C^{kl} - (C^{kl}_{*})' \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}} \right) \left(C^{ij} - C^{ij}_{*} \right) - \bar{p} \left(\frac{J'_{*}}{J} \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}} + J_{*} \frac{m_{\alpha}}{\rho_{0}} \right) + m_{\alpha} \mathcal{K} + \rho \mathcal{K}' \frac{\partial \hat{y}_{\beta}}{\partial n_{\alpha}} , \qquad (2.94)$$

where the symbol $(\Diamond)'$ stands for the partial derivative $\partial \Diamond / \partial y_{\beta}$. Furthermore holds: $\partial \hat{y}_{\beta} / \partial n_{\alpha} = \frac{1}{n} (\delta^{\alpha\beta} - y_{\beta})$, 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):

$$\mathrm{d}\varphi = -\eta \mathrm{d}T + \frac{1}{2\rho_0} t^{ij} \mathrm{d}C^{ij}$$
(2.95)

$$\Leftrightarrow \mathrm{d}w^{\star} = -\eta \mathrm{d}T - \frac{1}{2\rho_0} C^{ij} \mathrm{d}t^{ij} \quad \text{with} \quad w^{\star} \stackrel{\text{(def)}}{=} \varphi - \frac{1}{2\rho_0} t^{ij} C^{ij} , \qquad (2.96)$$

where $\varphi = \tilde{\varphi}(T, C^{ij})$ and $w^{\star} = \hat{w}^{\star}(T, t^{ij})$.

Note that Eq. (2.96) - in which we *temporarily* call the introduced quantity w^* the *strain potential* - holds solely, if the stress strain relation, *e.g.*, Eq. (2.83), is

invertible⁵. Furthermore Eq. (2.95) and (2.96) imply the following *hyper-elastic* relations for the stresses and strains:

$$2\rho_0 \frac{\partial \tilde{\varphi}}{\partial C^{ij}} = t^{ij} \quad , \quad 2\rho_0 \frac{\partial \hat{w}^*}{\partial t^{ij}} = -C^{ij} \; . \tag{2.97}$$

Another version of the GIBBS relations can be found by using the definition for the *first* PIOLA KIRCHHOFF *stress tensor*:

$$p^{ij} \stackrel{\text{(def)}}{=} J\sigma^{ik} (F^{-1})^{jk} \tag{2.98}$$

and the differentiation rule $dC^{ij} = (dF^{ki})F^{kj} + F^{ki}dF^{kj}$. Then one obtains from Eq. (2.95):

$$d\varphi = -\eta dT + \frac{1}{\rho_0} p^{ij} dF^{ij}$$
(2.99)

$$\Leftrightarrow \mathrm{d}w^{\star} = -\eta \mathrm{d}T - \frac{1}{\rho_0} F^{ij} \mathrm{d}p^{ij} \quad \text{with} \quad w^{\star} \stackrel{\text{(def)}}{=} \varphi - \frac{1}{\rho_0} p^{ij} F^{ij} , \qquad (2.100)$$

where $\varphi = \overline{\varphi}(T, F^{ij})$ and $w^* = \widehat{w}^*(T, p^{ij})$. Hence follows:

$$\rho_0 \frac{\partial \bar{\varphi}}{\partial F^{ij}} = p^{ij} \quad , \quad \rho_0 \frac{\partial \widehat{w}^{\star}}{\partial p^{ij}} = -F^{ij} \; . \tag{2.101}$$

It is worth mentioning that $\bar{\varphi}(T, F^{ij})$ cannot depend on all *nine independent* coefficients of F^{ij} due to the Principle of Objectivity, [27]. In particular φ only depend on six components following from symmetric combinations of F^{ij} , 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 $dC^{ij} \approx d(2\varepsilon^{ij} + \delta^{ij}) = 2d\varepsilon^{ij}$ and $t^{ij} = \sigma^{ij}$ in Eq. (2.95). Consequently they found (in our notation):

$$d\varphi = -\eta dT + \frac{1}{\rho_0} \sigma^{ij} d\varepsilon^{ij}$$
(2.102)

$$\Leftrightarrow \mathrm{d}w^{\star} = -\eta \mathrm{d}T - \frac{1}{\rho_0} \varepsilon^{ij} \mathrm{d}\sigma^{ij} \quad \text{with}^6 \quad w^{\star} \stackrel{(\mathrm{def})}{=} \varphi - \frac{1}{\rho_0} \sigma^{ij} \varepsilon^{ij} , \qquad (2.103)$$

where $\varphi = \breve{\varphi}(T, \varepsilon^{ij}), w^{\star} = \acute{w}^{\star}(T, \sigma^{ij})$ and furthermore

$$\rho_0 \frac{\partial \breve{\varphi}}{\partial \varepsilon^{ij}} = \sigma^{ij} \quad , \quad \rho_0 \frac{\partial \acute{w}^\star}{\partial \sigma^{ij}} = -\varepsilon^{ij} \; . \tag{2.104}$$

⁵A popular counter-example are rubber balloons, cf., [90].

⁶Note that the definitions of w^* 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 $t^{ij}C^{ij}$ by the linearized form $\sigma^{ij}(2\varepsilon^{ij} + \delta^{ij})$.

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 φ and w^* 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^* 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^* with the GIBBS free energy ψ . 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.:

$$\psi = \varphi + \frac{p}{\rho}$$
 with $p = -\frac{\sigma^{kk}}{3} = -\frac{1}{3J}t^{ij}C^{ij} = -\frac{1}{3J}p^{ij}F^{ij}$. (2.105)

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 α - or Cu-rich β -phases in eutectic Ag-Cu below the eutectic temperature, or in the lattice structures, e.g., ferrite (α -phase, BCT) and austenite (γ -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 $\sigma^{ij} = \sigma_{el}^{ij}$). Consequently the occurring phases differ in its composition, *i.e.*, in the partial particle densities n_{1}, \ldots, n_{ν} . Therefore we must incorporate phase boundaries containing considerable gradients $\nabla_{in} \alpha$, $\nabla_{ij} n_{\alpha}$, \ldots etc. ($\alpha = \{1, \ldots, \nu\}$), and we modify the

⁷Another notation frequently found is *specific stored energy*.

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

$$\rho\eta = \tilde{\mathbb{S}}(\rho\epsilon, n_{\alpha}, \nabla_{i}n_{\alpha}, \nabla_{ij}n_{\alpha}, c^{ij}) = \hat{\mathbb{S}}(T, n_{\alpha}, \nabla_{i}n_{\alpha}, \nabla_{ij}n_{\alpha}, c^{ij}) = \\
= \bar{\mathbb{S}}(T, y_{\beta}, \nabla_{i}y_{\beta}, \nabla_{ij}y_{\beta}, \nabla_{i}\rho, \nabla_{ij}\rho, \rho, c^{ij}) = \\
= \hat{\mathbb{S}}(T, y_{\beta}, \nabla_{i}y_{\beta}, \nabla_{ij}y_{\beta}, \nabla_{i}\rho, \nabla_{ij}\rho, C^{ij}).$$
(2.106)

The index $\alpha = \{1, ..., \nu\}$ and $\beta = \{1, ..., \nu - 1\}$ 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):

$$\frac{\partial \tilde{\mathbb{S}}}{\partial t} = \frac{\partial \tilde{\mathbb{S}}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial t} + \frac{\partial \tilde{\mathbb{S}}}{\partial c^{ij}} \frac{\partial c^{ij}}{\partial t} + \sum_{\alpha=1}^{\nu} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial t} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i} n_{\alpha}} \frac{\partial \nabla_{i} n_{\alpha}}{\partial t} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{ij} n_{\alpha}} \frac{\partial \nabla_{ij} n_{\alpha}}{\partial t} \right)$$
(2.107)

$$\frac{\partial \tilde{\mathbb{S}}}{\partial x^{i}} = \frac{\partial \tilde{\mathbb{S}}}{\partial \rho \epsilon} \frac{\partial \rho \epsilon}{\partial x^{i}} + \frac{\partial \tilde{\mathbb{S}}}{\partial c^{kl}} \frac{\partial c^{kl}}{\partial x^{i}} + \sum_{\alpha=1}^{\nu} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial x^{i}} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}} \frac{\partial \nabla_{k} n_{\alpha}}{\partial x^{i}} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_{\alpha}} \frac{\partial \nabla_{kl} n_{\alpha}}{\partial x^{i}} \right)$$
(2.108)

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 $\partial \nabla_{ij} n_{\alpha} / \partial t$ are replaced by the right hand side of the *differentiated* partial particle balance, Eq. (2.17), viz.:

$$\frac{\partial \nabla_k n_{\alpha}}{\partial t} = -\frac{\partial}{\partial x^k} \left[v^i \frac{\partial n_{\alpha}}{\partial x^i} + n_{\alpha} \frac{\partial v^i}{\partial x^i} + \frac{\partial j^i_{\alpha}}{\partial x^i} \right]
= -\frac{\partial v^i}{\partial x^k} \frac{\partial n_{\alpha}}{\partial x^i} - v^i \frac{\partial^2 n_{\alpha}}{\partial x^i \partial x^k} - \frac{\partial n_{\alpha}}{\partial x^k} \frac{\partial v^i}{\partial x^i} - n_{\alpha} \frac{\partial^2 v^i}{\partial x^i \partial x^k} - \frac{\partial^2 j^i_{\alpha}}{\partial x^i \partial x^k} , (2.109)
\frac{\partial \nabla_{kl} n_{\alpha}}{\partial t} = -\frac{\partial^2 v^i}{\partial x^k \partial x^l} \frac{\partial n_{\alpha}}{\partial x^i} - 2 \frac{\partial v^i}{\partial x^k} \frac{\partial^2 n_{\alpha}}{\partial x^i \partial x^l} - v^i \frac{\partial^3 n_{\alpha}}{\partial x^i \partial x^k \partial x^l} - \frac{\partial^2 n_{\alpha}}{\partial x^k \partial x^l} \frac{\partial v^i}{\partial x^i}
-2 \frac{\partial n_{\alpha}}{\partial x^k} \frac{\partial^2 v^i}{\partial x^i \partial x^l} - n_{\alpha} \frac{\partial^3 v^i}{\partial x^i \partial x^k \partial x^l} - \frac{\partial^3 j^i_{\alpha}}{\partial x^i \partial x^k \partial x^l} .$$
(2.110)

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 ζ according to Eq. (2.41):

$$\begin{aligned} \zeta &= \frac{\partial}{\partial x^{i}} \left[\phi^{i} - \frac{q^{i}}{T} - \sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} \right] + q^{i} \frac{\partial 1/T}{\partial x^{i}} + \sum_{\alpha=1}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} \right) \\ &+ \frac{\partial v^{i}}{\partial x^{j}} \left[\frac{\sigma_{\text{el}}^{ij}}{T} + J^{-2/3} (F^{jk} F^{il} + F^{ik} F^{jl}) \frac{\partial \tilde{\mathbb{S}}}{\partial c^{kl}} \right] \\ &- \delta^{ij} \left(\frac{\rho \epsilon}{T} - \tilde{\mathbb{S}} + \sum_{\alpha=1}^{\nu} n_{\alpha} \frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} + \frac{2}{3} J^{-2/3} C^{kl} \frac{\tilde{\mathbb{S}}}{\partial c^{kl}} \right) \right] \\ &- \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{k} n_{\alpha}} \left(\frac{\partial v^{i}}{\partial x^{k}} \frac{\partial n_{\alpha}}{\partial x^{i}} + \frac{\partial n_{\alpha}}{\partial x^{k}} \frac{\partial v^{i}}{\partial x^{i}} + n_{\alpha} \frac{\partial^{2} v^{i}}{\partial x^{i} \partial x^{k}} + \frac{\partial^{2} j_{\alpha}^{i}}{\partial x^{i} \partial x^{k}} \right) \\ &- \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_{\alpha}} \left(\frac{\partial^{2} v^{i}}{\partial x^{k} \partial x^{l}} \frac{\partial n_{\alpha}}{\partial x^{i}} + 2 \frac{\partial v^{i}}{\partial x^{k}} \frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{l}} + \frac{\partial^{2} n_{\alpha}}{\partial x^{k} \partial x^{l}} \frac{\partial v^{i}}{\partial x^{i}} \\ &= e \\ &+ 2 \frac{\partial n_{\alpha}}{\partial x^{k}} \frac{\partial^{2} v^{i}}{\partial x^{i} \partial x^{l}} + n_{\alpha} \frac{\partial^{3} v^{i}}{\partial x^{i} \partial x^{k} \partial x^{l}} + \frac{\partial^{3} j_{\alpha}^{i}}{\partial x^{i} \partial x^{k} \partial x^{l}} \right). \end{aligned}$$
(2.111)

The first four summands correspond to the result in Eq. (2.46). In what follows one has to include the HG-terms $\frac{\partial \tilde{S}}{\partial \nabla_k n_\alpha} (\mathbf{a} + \ldots + \mathbf{d})$ and $\frac{\partial \tilde{S}}{\partial \nabla_{kl} n_\alpha} (\mathbf{e} + \ldots + \mathbf{j})$ "suitably" into the first three rows of Eq. (2.111), which will later be used in order to define the entropy flux ϕ^i , the diffusion flux j^i_α , 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_{α}^{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:

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

$$(2.112)$$

$$-\frac{\partial \tilde{S}}{\partial \nabla_{kl} n_{\alpha}} (\mathsf{j}) = \frac{\partial}{\partial x^{i}} \left[-j_{\alpha}^{i} \frac{\partial^{2}}{\partial x^{k} \partial x^{l}} \left(\frac{\partial \tilde{S}}{\partial \nabla_{kl} n_{\alpha}} \right) + \frac{\partial j_{\alpha}^{l}}{\partial x^{l}} \frac{\partial}{\partial x^{k}} \left(\frac{\partial \tilde{S}}{\partial \nabla_{ki} n_{\alpha}} \right) \right]$$

$$-\frac{\partial}{\partial x^{k}} \left(\frac{\partial j_{\alpha}^{l}}{\partial x^{l}} \right) \frac{\partial \tilde{S}}{\partial \nabla_{ki} n_{\alpha}} \right] + j_{\alpha}^{i} \frac{\partial}{\partial x^{i}} \left[\frac{\partial^{2}}{\partial x^{k} \partial x^{l}} \left(\frac{\partial \tilde{S}}{\partial \nabla_{kl} n_{\alpha}} \right) \right] . \quad (2.113)$$

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

$$-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_{\alpha}} (\mathbf{a} + \mathbf{b} + \mathbf{c}) = n_{\alpha} \frac{\partial v^i}{\partial x^i} \frac{\partial}{\partial x^k} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_{\alpha}} \right) - \frac{\partial v^i}{\partial x^k} \frac{\partial n_{\alpha}}{\partial x^i} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_{\alpha}} - \frac{\partial}{\partial x^i} \left[n_{\alpha} \frac{\partial v^k}{\partial x^k} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_i n_{\alpha}} \right] , \qquad (2.114)$$

$$-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_{\alpha}} (\mathbf{e} + \mathbf{f}) = \frac{\partial v^{i}}{\partial x^{k}} \left[\frac{\partial n_{\alpha}}{\partial x^{i}} \frac{\partial}{\partial x^{l}} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_{\alpha}} \right) - \frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_{\alpha}} \right] - \frac{\partial}{\partial x^{i}} \left(\frac{\partial v^{k}}{\partial x^{l}} \frac{\partial n_{\alpha}}{\partial x^{k}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{li} n_{\alpha}} \right) , \qquad (2.115)$$

$$-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_{\alpha}} (\mathbf{g} + \mathbf{h} + \mathbf{i}) = \frac{\partial}{\partial x^{i}} \left[n_{\alpha} \frac{\partial v^{k}}{\partial x^{k}} \frac{\partial}{\partial x^{l}} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{il} n_{\alpha}} \right) - \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{ki} n_{\alpha}} \frac{\partial}{\partial x^{k}} \left(n_{\alpha} \frac{\partial v^{l}}{\partial x^{l}} \right) \right] - n_{\alpha} \frac{\partial v^{i}}{\partial x^{i}} \frac{\partial^{2}}{\partial x^{k} \partial x^{l}} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_{\alpha}} \right) .$$
(2.116)

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

$$\frac{\delta \Diamond}{\delta n_{\alpha}} \stackrel{\text{(def)}}{=} \frac{\partial \Diamond}{\partial n_{\alpha}} - \nabla_k \cdot \frac{\partial \Diamond}{\partial \nabla_k n_{\alpha}} + \nabla_{kl} \cdot \frac{\partial \Diamond}{\partial \nabla_{kl} n_{\alpha}} \tag{2.117}$$

and the partial particle balance in the form:

$$\dot{n}_{\alpha} \stackrel{\text{(def)}}{=} \frac{\partial n_{\alpha}}{\partial t} + v^{i} \frac{\partial n_{\alpha}}{\partial x^{i}} \stackrel{(2.17)}{=} -n_{\alpha} \frac{\partial v^{i}}{\partial x^{i}} - \frac{\partial j^{i}_{\alpha}}{\partial x^{i}} .$$
(2.118)

one can finally write for the **entropy production** ζ :

$$\begin{aligned} \zeta &= \frac{\partial}{\partial x^{i}} \Biggl\{ \phi^{i} - \frac{q^{i}}{T} - \sum_{\alpha}^{\nu} j_{\alpha}^{i} \frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}} + \sum_{\alpha}^{\nu} \dot{n}_{\alpha} \left[\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{i} n_{\alpha}} - \frac{\partial}{\partial x^{l}} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{li} n_{\alpha}} \right) \right] \\ &+ \sum_{\alpha}^{\nu} \frac{\partial \dot{n}_{\alpha}}{\partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{li} n_{\alpha}} - \sum_{\alpha}^{\nu} \frac{\partial v^{l}}{\partial x^{k}} \frac{\partial n_{\alpha}}{\partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{ki} n_{\alpha}} \Biggr\} \\ &+ q^{i} \frac{\partial 1/T}{\partial x^{i}} + \sum_{\alpha}^{\nu} j_{\alpha}^{i} \frac{\partial}{\partial x^{i}} \left(\frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}} \right) \\ &+ \frac{\partial v^{i}}{\partial x^{j}} \Biggl\{ \frac{\sigma_{\text{el}}^{ij}}{T} + J^{-2/3} (F^{jk} F^{il} + F^{ik} F^{jl}) \frac{\partial \tilde{\mathbb{S}}}{\partial c^{kl}} \\ &- \sum_{\alpha}^{\nu} \frac{\partial n_{\alpha}}{\partial x^{i}} \left[\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{j} n_{\alpha}} - \frac{\partial}{\partial x^{l}} \left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{jl} n_{\alpha}} \right) \right] - \sum_{\alpha}^{\nu} \frac{\partial^{2} n_{\alpha}}{\partial x^{i} \partial x^{l}} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{jl} n_{\alpha}} \\ &- \delta^{ij} \left[\frac{\rho \epsilon}{T} - \tilde{\mathbb{S}} + \sum_{\alpha}^{\nu} n_{\alpha} \frac{\delta \tilde{\mathbb{S}}}{\delta n_{\alpha}} + \frac{2}{3} J^{-2/3} C^{kl} \frac{\partial \tilde{\mathbb{S}}}{\partial c^{kl}} \right] \Biggr\} \ge 0 . \end{aligned}$$

$$(2.119)$$

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:

 \Diamond Entropy flux:

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

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

$$q^{i}\frac{\partial 1/T}{\partial x^{i}} + \sum_{\alpha}^{\nu} j_{\alpha}^{i}\frac{\partial}{\partial x^{i}}\left(\frac{\delta\tilde{\mathbb{S}}}{\delta n_{\alpha}}\right) \geq 0, \qquad (2.121)$$

$$-\frac{\sigma_{\text{el}}^{ij}}{T} = J^{-2/3}(F^{jk}F^{il} + F^{ik}F^{jl})\frac{\partial\tilde{\mathbb{S}}}{\partial c^{kl}} - \sum_{\alpha}^{\nu}\frac{\partial n_{\alpha}}{\partial x^{i}}\left[\frac{\partial\tilde{\mathbb{S}}}{\partial \nabla_{j}n_{\alpha}} - \frac{\partial}{\partial x^{l}}\left(\frac{\partial\tilde{\mathbb{S}}}{\partial \nabla_{jl}n_{\alpha}}\right)\right] - \sum_{\alpha}^{\nu}\frac{\partial^{2}n_{\alpha}}{\partial x^{i}\partial x^{l}}\frac{\partial\tilde{\mathbb{S}}}{\partial \nabla_{jl}n_{\alpha}} - \delta^{ij}\left[\frac{\rho\epsilon}{T} - \tilde{\mathbb{S}} + \sum_{\alpha}^{\nu}n_{\alpha}\frac{\delta\tilde{\mathbb{S}}}{\delta n_{\alpha}} + \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial\tilde{\mathbb{S}}}{\partial c^{kl}}\right]. \qquad (2.122)$$

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{S} must be substituted using the different functional representations of the HELMHOLTZ free energy ($\alpha = 1, ..., \nu$ and $\beta = 1, ..., \nu - 1$):

$$\rho \varphi = \tilde{\mathbb{F}}(\rho \epsilon, n_{\alpha}, \nabla_{i} n_{\alpha}, \nabla_{ij} n_{\alpha}, c^{ij}) = \hat{\mathbb{F}}(T, n_{\alpha}, \nabla_{i} n_{\alpha}, \nabla_{ij} n_{\alpha}, c^{ij})
= \bar{\mathbb{F}}(T, y_{\beta}, \nabla_{i} y_{\beta}, \nabla_{ij} y_{\beta}, \nabla_{i\rho}, \nabla_{ij} \rho, \rho, c^{ij})
= \acute{\mathbb{F}}(T, y_{\beta}, \nabla_{i} y_{\beta}, \nabla_{ij} y_{\beta}, \nabla_{i\rho}, \nabla_{ij} \rho, C^{ij})$$
(2.123)

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* μ_{α} in multi-phase mixtures according to Eq. (2.51) and (2.55) as:

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

with the alternative functional representation of the HELMHOLTZ free energy $\rho\varphi = \widehat{\mathbb{F}}(T, \rho_{\alpha}, \nabla_{i}\rho_{\alpha}, \nabla_{ij}\rho_{\alpha}, c^{ij})$ 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^i_{α} and q^i such that quadratic expressions result, *cf.*, Section 2.4.2. The LEGENDRE transform in Appendix A.5 yields $\delta \tilde{S} / \delta n_{\alpha} = -\delta(\hat{\mathbb{F}}/T) / \delta n_{\alpha}$. Therefore we find (without thermo-diffusion coupling):

\Diamond Diffusion flux:

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

 \diamond Heat flux:

$$q^{i} = \kappa^{ij} \frac{\partial 1/T}{\partial x^{j}}$$
 (FOURIER's law), (2.126)

where the symbols $M_{\beta\delta}^{ij}$, $B_{\beta\delta}^{ij}$ and κ^{ij} 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 PIOLA-KIRCHHOFF tensor t^{ij} 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 μ_{α} or μ_{α}^{*} in terms of $\delta \overline{\mathbb{F}}/\delta y_{\beta}$ or $\delta \overline{\overline{\mathbb{F}}}/\delta c_{\beta}$, 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):

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

Thus one obtains for the difference term in Eq. $(2.125)_1$:

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

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 μ_{α}^* in Eq. (2.124)₂ one needs the LEGENDRE transform between the following functional representations of $\rho\varphi$:

$$\rho\varphi = \widehat{\overline{\mathbb{F}}}(T, \rho_{\alpha}, \nabla_{i}\rho_{\alpha}, \nabla_{ij}\rho_{\alpha}, c^{ij}) = \overline{\overline{\mathbb{F}}}(T, c_{\beta}, \nabla_{i}c_{\beta}, \nabla_{ij}c_{\beta}, \nabla_{i}\rho, \nabla_{ij}\rho, \rho, c^{ij}) , \quad (2.129)$$

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

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

and for the difference term in Eq. $(2.125)_2$:

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

$$(2.131)$$

Note that the variational derivatives $\delta \overline{\mathbb{F}}/\delta \rho$ and $\delta \overline{\overline{\mathbb{F}}}/\delta \rho$ 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:

$$n = n_{\rm A} + n_{\rm B}$$
, $y_{\rm B} = 1 - y_{\rm A}$. (2.132)

For the case of isothermal diffusion as defined before, Eq. $(2.125)_1$ reduces to:

$$j_{\rm A}^{i} = \frac{M_{\rm AA}^{ij}}{T} \frac{\partial \left(\frac{m_{\rm A}}{m_{\rm B}}\mu_{\rm B} - \mu_{\rm A}\right)}{\partial x^{j}} \quad \text{and} \quad j_{\rm B}^{i} = -\frac{m_{\rm A}}{m_{\rm B}} j_{\rm A}^{i} .$$

$$(2.133)$$

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

$$\frac{m_{\rm A}}{m_{\rm B}}\mu_{\rm B} - \mu_{\rm A} = \frac{m_{\rm A}}{m_{\rm B}}\frac{\delta\hat{\mathbb{F}}}{\delta n_{\rm B}} - \frac{\delta\hat{\mathbb{F}}}{\delta n_{\rm A}}$$

$$\stackrel{(2.128)}{=} \frac{m_{\rm A}}{m_{\rm B}}\frac{\delta\bar{\mathbb{F}}}{\delta y_{\rm A}}\left(\frac{\delta_{\rm BA}}{n} - \frac{n_{\rm A}}{n^2}\right) - \frac{\delta\bar{\mathbb{F}}}{\delta y_{\rm A}}\left(\frac{\delta_{\rm AA}}{n} - \frac{n_{\rm A}}{n^2}\right)$$

$$= -\frac{1}{n}\frac{\delta\bar{\mathbb{F}}}{\delta y_{\rm A}}\left(\frac{m_{\rm A}}{m_{\rm B}}y_{\rm A} + y_{\rm B}\right).$$
(2.134)

Thus a combination of Eq. (2.134) and $(2.133)_1$ yields for the *particle diffusion flux* of component **A**:

$$j_{A}^{i} = -\frac{M_{AA}^{ij}}{T} \nabla^{j} \left[\frac{1}{n} \frac{\delta \bar{\mathbb{F}}}{\delta y_{A}} \left(\frac{m_{A}}{m_{B}} y_{A} + y_{B} \right) \right]$$
$$\stackrel{(App. A.7)}{=} -\frac{M_{AA}^{ij}}{T} \nabla^{j} \left[\frac{1}{n} \frac{\delta \hat{\mathbb{F}}}{\delta y_{A}} \left(\frac{m_{A}}{m_{B}} y_{A} + y_{B} \right) \right] , \qquad (2.135)$$

in which the diffusion flux of component **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 **A**:

$$\rho = \rho_{\rm A} + \rho_{\rm B} \quad , \quad c_{\rm A} = 1 - c_{\rm B}$$
(2.136)

and with Eq. $(2.125)_2$

$$J_{\rm A}^{i} = \frac{B_{\rm AA}^{ij}}{T} \frac{\partial \left(\mu_{\rm B}^{*} - \mu_{\rm A}^{*}\right)}{\partial x^{j}} \quad \text{with} \quad J_{\rm B}^{i} = -J_{\rm A}^{i} .$$

$$(2.137)$$

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

$$\mu_{\rm B}^* - \mu_{\rm A}^* = \frac{\delta \widehat{\overline{\mathbb{F}}}}{\delta \rho_{\rm B}} - \frac{\delta \widehat{\overline{\mathbb{F}}}}{\delta \rho_{\rm A}}$$

$$\stackrel{(2.131)}{=} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\rm A}} \left(\underbrace{\frac{\delta_{\rm BA}}{\rho}}_{=0} - \frac{\rho_{\rm A}}{\rho^2} \right) - \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\rm A}} \left(\underbrace{\frac{\delta_{\rm AA}}{\rho}}_{\rho} - \frac{\rho_{\rm A}}{\rho^2} \right) = -\frac{1}{\rho} \frac{\delta \overline{\overline{\mathbb{F}}}}{\delta c_{\rm A}} . \quad (2.138)$$

Hence we finally obtain from Eq. (2.137) and (2.138) and the LEGENDRE transforms in Appendix A.7 and A.8:

$$J_{\rm A}^{i} = -\frac{B_{\rm AA}^{ij}}{T} \nabla^{j} \left(\frac{1}{\rho} \frac{\delta \stackrel{\circ}{\mathbb{F}}}{\delta c_{\rm A}} \right) \quad \text{and} \quad J_{\rm B}^{i} = -\frac{B_{\rm AA}^{ij}}{T} \nabla^{j} \left(\frac{1}{\rho} \frac{\delta \stackrel{\circ}{\mathbb{F}}}{\delta c_{\rm B}} \right) , \qquad (2.139)$$

in which the functional representation: $\rho \varphi = \overset{\diamond}{\mathbb{F}} (T, c_{\beta}, \nabla_i c_{\beta}, \nabla_i c_{\beta}, \nabla_i \rho, \nabla_{ij} \rho, C^{ij})$ was used.

Eq. (2.139) implies that, in contrast to the 'multiphase-field approach' of Eiken *et al.* in [44], the relation $\rho(\mu_{\rm B}^* - \mu_{\rm A}^*) = \delta \mathring{\mathbb{F}} / \delta c_{\rm B} = -\delta \mathring{\mathbb{F}} / \delta c_{\rm A}$ holds *exclusively*, if the mass concentration c_{β} 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 $\overset{\diamond}{\mathbb{F}}$ depends on the higher gradients, *e.g.*, $\nabla_i c_{\rm B}$, $\nabla_i p_{\rm i}$, and $\nabla_{ij} \rho$. 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) state⁸:

$$\mathbb{F} = \mathbb{F}_{0}(T, c_{\mathrm{B}}, C^{ij}) + \underbrace{\frac{\partial \mathbb{F}_{0}}{\partial \nabla_{k} c_{\mathrm{B}}}}_{(\overset{\mathrm{(def)}}{=}l^{k}} \cdot \nabla_{k} c_{\mathrm{B}} + \underbrace{\frac{\partial \mathbb{F}_{0}}{\partial \nabla_{kl} c_{\mathrm{B}}}}_{(\overset{\mathrm{(def)}}{=}-a^{kl}} \cdot \nabla_{kl} c_{\mathrm{B}} + \frac{1}{2} \underbrace{\frac{\partial^{2} \mathbb{F}_{0}}{\partial \nabla_{k} c_{\mathrm{B}} \partial \nabla_{l} c_{\mathrm{B}}}}_{(\overset{\mathrm{(def)}}{=}2b^{kl}} \cdot \nabla_{k} c_{\mathrm{B}} \cdot \nabla_{l} c_{\mathrm{B}} + \dots, \qquad (2.140)$$

where the introduced so-called *Higher Gradient Coefficients* (HGCs) depend on the temperature T, the (homogeneous) composition $c_{\rm B}$, and the strain tensor C^{ij} , *i.e.*, $l^k = l^k(T, c_{\rm B}, C^{ij})$, $a^{kl} = a^{kl}(T, c_{\rm B}, C^{ij})$, and $b^{kl} = b^{kl}(T, c_{\rm B}, C^{ij})$. Furthermore we neglect in Eq. (2.140) the higher gradients $\nabla_i \rho$ and $\nabla_{ij} \rho$, 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

⁸In the following we write by convenience $\mathbb{F} = \stackrel{\circ}{\mathbb{F}}$.

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 $a^{kl} = a \cdot \delta^{kl}$ and $b^{kl} = b \cdot \delta^{kl}$.

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 $c_{\rm B} = c(x^i, t)$ within a non-reacting elastic solid mixture we rewrite Eq. (2.14) by means of the relation $\rho_{\alpha} = c_{\alpha}\rho$ as follows:

$$\rho \frac{\mathrm{d}c}{\mathrm{d}t} + \frac{\partial J^i}{\partial x^i} = 0 \qquad \text{(partial mass balance)},$$
(2.141)

where we put $J_{\rm B}^i = J^i$ and used the total temporal derivative $d_t c = \partial_t c + v^i (\nabla_i c)$. 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 $l^k = 0$:

$$\frac{\partial \mathbb{F}}{\partial c} = \frac{\partial \mathbb{F}_0}{\partial c} - \frac{\partial a^{kl}}{\partial c} \frac{\partial^2 c}{\partial x^k \partial x^l} + \frac{\partial b^{kl}}{\partial c} \frac{\partial c}{\partial x^k} \frac{\partial c}{\partial x^l} ,
\frac{\partial \mathbb{F}}{\partial (\partial c/\partial x^m)} = 2b^{ml} \frac{\partial c}{\partial x^l} , \quad \frac{\partial \mathbb{F}}{\partial (\partial^2 c/\partial x^m \partial x^n)} = -a^{kl} .$$
(2.142)

Thus it follows by virtue of the chain rule:

$$\frac{\partial}{\partial x^m} \left(\frac{\partial \mathbb{F}}{\partial (\partial c/\partial x^m)} \right) = 2 \frac{\partial b^{ml}}{\partial c} \frac{\partial c}{\partial x^m} \frac{\partial c}{\partial x^l} + 2 \frac{\partial b^{ml}}{\partial C^{rs}} \frac{\partial C^{rs}}{\partial x^m} \frac{\partial c}{\partial x^l} + 2 b^{ml} \frac{\partial^2 c}{\partial x^m \partial x^l} , \quad (2.143)$$

$$\frac{\partial^2}{\partial x^m \partial x^n} \left(\frac{\partial \mathbb{F}}{\partial (\partial^2 c / \partial x^m \partial x^n)} \right) = -\frac{\partial^2 a^{mn}}{\partial c^2} \frac{\partial c}{\partial x^m} \frac{\partial c}{\partial x^n} - \frac{\partial a^{mn}}{\partial c} \frac{\partial^2 c}{\partial x^m \partial x^n} - 2\frac{\partial^2 a^{mn}}{\partial c \partial C^{rs}} \frac{\partial C}{\partial x^m} \frac{\partial c}{\partial x^n} - \frac{\partial^2 a^{mn}}{\partial C^{op} C^{rs}} \frac{\partial C^{op}}{\partial x^m} \frac{\partial C^{rs}}{\partial x^n} - \frac{\partial a^{mn}}{\partial C^{rs}} \frac{\partial^2 C^{rs}}{\partial x^m \partial x^n} \right)$$
(2.144)

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

$$A^{ij} = \frac{\partial a^{ij}}{\partial c} + b^{ij}:$$

$$J^{i} = -\frac{B^{ij}_{AA}}{T} \nabla^{j} \left[\frac{1}{\rho} \left(\frac{\partial \mathbb{F}_{0}}{\partial c} - 2A^{kl} \frac{\partial^{2}c}{\partial x^{k} \partial x^{l}} - \frac{\partial A^{kl}}{\partial c} \frac{\partial c}{\partial x^{k}} \frac{\partial c}{\partial x^{l}} - 2\frac{\partial A^{kl}}{\partial C^{mn}} \frac{\partial C^{mn}}{\partial x^{k}} \frac{\partial C^{mn}}{\partial x^{l}} - \frac{\partial^{2}a^{kl}}{\partial C^{op}C^{mn}} \frac{\partial C^{op}}{\partial x^{k}} \frac{\partial C^{mn}}{\partial x^{l}} - \frac{\partial a^{kl}}{\partial C^{mn}} \frac{\partial^{2}C^{mn}}{\partial x^{k} \partial x^{l}} \right]. (2.145)$$

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 $c(x^i, t)$ and can be interpreted as the *generalization* of the CAHN-HILLIARD equation⁹.

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^{ij} . 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 ε^{ij} instead of the right CAUCHY-GREEN strain tensor, *i.e.*, $\mathbb{F}_0 = \mathbb{F}_0(T, c, \varepsilon^{ij})$, $a^{kl} = a^{kl}(T, c, \varepsilon^{ij}), b^{kl} = b^{kl}(T, c, \varepsilon^{ij})$, and $A^{kl} = A^{kl}(T, c, \varepsilon^{ij})$. 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 $c(X^j, t)$, namely:

$$\rho_0 \frac{\mathrm{d}c}{\mathrm{d}t} + \frac{\partial J^i}{\partial X^i} = 0 \quad \text{(partial mass balance)} \tag{2.146}$$

and

$$J^{i} = -\rho_{0}\mathcal{M}^{ij}(T)\nabla^{j}\left[\frac{\partial\mathbb{F}_{0}}{\partial c} - 2A^{kl}\frac{\partial^{2}c}{\partial X^{k}\partial X^{l}} - \frac{\partial A^{kl}}{\partial c}\frac{\partial c}{\partial X^{k}}\frac{\partial c}{\partial X^{l}}\right] - 2\frac{\partial A^{kl}}{\partial\varepsilon^{mn}}\frac{\partial c}{\partial X^{k}}\frac{\partial \varepsilon^{mn}}{\partial X^{l}} - \frac{\partial^{2}a^{kl}}{\partial\varepsilon^{op}\varepsilon^{mn}}\frac{\partial \varepsilon^{op}}{\partial X^{k}}\frac{\partial \varepsilon^{mn}}{\partial X^{l}} - \frac{\partial a^{kl}}{\partial\varepsilon^{mn}}\frac{\partial^{2}\varepsilon^{mn}}{\partial X^{k}\partial X^{l}}\right]. \quad (2.147)$$

Here the reference configuration is typically chosen to be the one of the melt, characterized by the homogeneous mass density $\rho_0 = \text{const.}, \forall X^i$. Consequently, the different mobilities, B^{ij} in Eq. (2.145) and $\mathcal{M}^{ij}(T)$ in Eq. (4.53), are connected by the relation $\rho_0^2 \mathcal{M}^{ij}(T) = B_{AA}^{ij}/T$ with the unit $[\mathcal{M}^{ij}] = \mathrm{m}^5/(\mathrm{Js})$.

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

$$\frac{\partial p^{ij}}{\partial X^j} = 0$$
 (static momentum balance). (2.148)

⁹The CAHN-HILLIARD equation follows for constant HGCs A^{kl} and a^{kl} . In this case only the first two summands within the parenthesis (...) of Eq. (2.145) remain.
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^{ij} and t^{ij} , respectively, are approximated by the CAUCHY stresses σ^{ij} . Thus one can write by means of Eq. (2.104)₁ with $\rho_0 = \text{const.}$:

$$p^{ij} \approx \sigma^{ij} \approx \frac{\partial \mathbb{F}}{\partial \varepsilon^{ij}} \stackrel{(2.140)}{=} \underbrace{\frac{\partial \mathbb{F}_0}{\partial \varepsilon^{ij}}}_{=\sigma^{ij}_{\text{local}}} - \frac{\partial a^{kl}}{\partial \varepsilon^{ij}} \frac{\partial^2 c}{\partial X^k \partial X^l} + \frac{\partial b^{kl}}{\partial \varepsilon^{ij}} \frac{\partial c}{\partial X^k} \frac{\partial c}{\partial X^l} .$$
(2.149)

Here the local stresses $\sigma_{\text{local}}^{ij}$ can be calculated, *e.g.*, by HOOKE's law, *viz.* $\sigma_{\text{local}}^{ij} = K^{ijkl}(T,c) \left(\varepsilon^{kl} - \alpha^{kl}\Delta T\right)$, where $a^{kl} = \alpha \cdot \delta^{kl}$ 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*.

Jules Verne, (1828 - 1905)

Chapter 3

Calculation of Higher Gradient and Stiffness Coefficients by using the Embedded Atom Method¹

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 $c(X^i, t)$, cf. 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^{kl} , a^{kl} , b^{kl} and K^{ijkl} must be specified. Note that, for a prescribed external load, the stiffness constants, K^{ijkl} , are, in the simplest case, combined with the linearized strains, ε^{kl} , 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, $c_{\rm A}$ or $c_{\rm B} = (1 - c_{\rm A})$, respectively. For instance in pure solid mixtures below the eutectic temperature two different phases can be observed, the α -phase (A-rich) and the β -phase (B-rich) with equilibrium concentrations, c_{α} and c_{β} , respectively (*cf.*, 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 α - and β -phases, which is typical for so-called phase field theories. Consequently, it is reasonable to concentrate on

¹The considerations of this Chapter already appeared in a modified form in [11].

the material data of, first, the α -phase, second, the β -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^{ijkl} and the higher gradient coefficients a^{kl} , b^{kl} and A^{kl} 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

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

between the material data $\Xi_{\alpha/\beta} = \{K_{\alpha/\beta}^{ijkl}, A_{\alpha/\beta}^{kl}, a_{\alpha/\beta}^{kl}, b_{\alpha/\beta}^{kl}\}$ 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_{Ag}^{ijkl} and K_{Cu}^{ijkl} , respectively. Due to the use of pair potentials (LENNARD-JONES potentials) the CAUCHY paradox ($K^{1122} = K^{2323}$) 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 Embedded-Atom 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 Ag-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-potentials² the mathematical key to EAM consists of introducing a nonlinear function $F_{\alpha} = \tilde{F}_{\alpha}(\bar{\rho}_{\alpha})$ in the energy expression for atom α , in addition to the pairwise-interaction term:

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

 F_{α} is known as the embedding function and $\bar{\rho}_{\alpha}$ is the (constant) electron density at the position r_{α}^{i} of atom α due to all neighbors β . 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 β , ρ_{β} , is a function of the scalar distance $r_{\alpha\beta}$ between atom α and the nucleus of β . 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 α due to the presence of its neighbors β .

The embedding function, $F_{\alpha}(\bar{\rho}_{\alpha})$, can be interpreted as the energy required to incorporate an atom α in a homogeneous electron gas with the constant electron density $\bar{\rho}_{\alpha}$. Note that the functional form of F_{α} depends only on the type of the (embedded) atom α and the argument of F_{α} refers to the electron density of the medium in which atom α is embedded.

 $\phi_{\alpha\beta} = \phi_{\alpha\beta}(r_{\alpha\beta})$ characterizes the (purely repulsive) interactions between the nuclei of atom α and β . It depends on the scalar distance $r_{\alpha\beta}$ between α and β and is, according to [67], a positive, monotonically decreasing function.

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

²Here the energy E_{α} of an particle (atom) α is given by $E_{\alpha} = \frac{1}{2} \sum_{\beta(\alpha \neq \beta)} \varphi_{\alpha\beta}(r_{\alpha\beta})$, where $\varphi_{\alpha\beta}$ denotes the pairwise interaction potential between the atoms α and β and depends only upon the radial distance $r_{\alpha\beta}$ between α and β .



Figure 3.1: The general principle of EAM as proposed by Daw and Baskes, [28], [29].

 ϕ_{AA} , ϕ_{BB} , and ϕ_{AB} . With the exception of ϕ_{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 ϕ_{AB} a model will be used that relates this quantity to the interactions ϕ_{AA} and ϕ_{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 α 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, $R = a_e/\sqrt{2}$), where a denotes the lattice parameter.



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

In order to obtain E_{α} in Eq. (3.2) it is necessary to specify $\phi_{\alpha\beta}$, F_{α} and $\rho_{\beta} (\Rightarrow \bar{\rho}_{\alpha})$. More specifically we have to choose a suitable functional form. In particular for a binary alloy A-B the functions $F_{\rm A}$, $F_{\rm B}$, $\rho_{\rm A}$, $\rho_{\rm B}$, $\phi_{\rm AA}$, $\phi_{\rm BB}$, and $\phi_{\rm AB}$ must be specified. For that reason Johnson proposed in [67] to use the following form³ for $\rho_{\rm A/B}$ and $\phi_{\rm AA/BB}$ (where the indices A and B of the two atom species have been omitted for simplicity):

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

³Especially the form of the atomic electron density ρ is borrowed from atoms with isotropic s-orbitals. This (for special cases) unrealistic assumption is later corrected by the fitting procedure.

The four parameters $\rho_{\rm e}$, $\phi_{\rm e}$, β , and γ 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 $a_{\rm e}$ as indicated before.

For the interaction ϕ_{AB} between nuclei of different atom types Johnson used the following form:

$$\phi_{\rm AB}(r) = \frac{1}{2} \left[\frac{\rho_{\rm B}(r)}{\rho_{\rm A}(r)} \phi_{\rm AA}(r) + \frac{\rho_{\rm A}(r)}{\rho_{\rm B}(r)} \phi_{\rm BB}(r) \right].$$
(3.4)

This relation can easily be quantified using data for the pure substances A and B.

Finally it remains to specify $F_{\rm A}$ and $F_{\rm B}$. 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:

$$E(a) = -E_{\rm sub} \left[1 + a^*(a) \right] e^{-a^*(a)} \quad , \quad a^*(a) = \left(\frac{a}{a_{\rm e}} - 1 \right) \left(\frac{E_{\rm sub}}{9\kappa\Omega_0} \right)^{-\frac{1}{2}}, \tag{3.5}$$

where $E_{\rm sub}$ denotes the sublimation energy per atom of the material, κ is the incompressibility (bulk modulus) and Ω_0 is the volume occupied by an atom in the lattice at equilibrium. Hence Ω_0 is a function of $a_{\rm e}$ and, for an FCC-lattice, can be obtained from

$$\Omega_0 = \frac{a_{\rm e}^3}{4} , \qquad (3.6)$$

since there are four atoms in the unit cell $(8 \times \frac{1}{8} \text{ atoms in the corner}; 6 \times \frac{1}{2} \text{ atoms on the faces})$. 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 $a_{\rm e} = R\sqrt{2}$ by the inverse relation resulting from Eq. (3.3), namely:

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

the following form is obtained for F:

$$F(\bar{\rho}) = -E_{\rm sub} \left[1 - \frac{\alpha}{\beta} \ln \left(\frac{\bar{\rho}}{\bar{\rho}_{\rm e}} \right) \right] \left(\frac{\bar{\rho}}{\bar{\rho}_{\rm e}} \right)^{\frac{\alpha}{\beta}} - 6\phi_{\rm e} \left(\frac{\bar{\rho}}{\bar{\rho}_{\rm e}} \right)^{\frac{\gamma}{\beta}} \text{ with } \alpha = 3 \left(\frac{\kappa \Omega_0}{E_{\rm sub}} \right)^{\frac{1}{2}} (3.8)$$

For this result the relations:

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

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 α , β , γ , $\phi_{\rm e}$, and $\bar{\rho}_{\rm e} = 12\rho_{\rm e}$ 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 α is given by its reference position vector X^i_{α} . Analogously the atom of the deformed lattice configuration outside of equilibrium is characterized by the current position vector $x^i_{\alpha} = X^i_{\alpha} + \xi^i_{\alpha}$, where ξ^i_{α} denotes the displacement of atom α 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 $(X^i_{\alpha}, X^i_{\beta}, X^i_{\gamma}, \ldots)$ and current positions $(x^i_{\alpha}, x^i_{\beta}, x^i_{\gamma}, \ldots)$ contains the whole information on the undeformed and deformed lattice, respectively. Moreover, the distance between two arbitrary atoms α and β is written as $R^i_{\alpha\beta} \equiv X^i_{\beta} - X^i_{\alpha}$ or $r^i_{\alpha\beta} \equiv x^i_{\beta} - x^i_{\alpha}$ (also note Figure 3.3 for an illustration of the situation). Consequently the following relations can easily be obtained:

$$x^i_{\alpha} = X^i_{\alpha} + \xi^i_{\alpha} \quad , \quad x^i_{\beta} = X^i_{\beta} + \xi^i_{\beta}, \tag{3.10}$$

$$r_{\alpha\beta}^{i} = x_{\beta}^{i} - x_{\alpha}^{i} = X_{\beta}^{i} - X_{\alpha}^{i} + \xi_{\beta}^{i} - \xi_{\alpha}^{i} = R_{\alpha\beta}^{i} + \xi_{\beta}^{i} - \xi_{\alpha}^{i}.$$
 (3.11)

By performing the so-called *mean field limit*, *i.e.*, by introducing a continuous displacement function $U^i = \tilde{U}^i(X^j_{\alpha})$ instead of the discrete displacements ξ^i_{α} , a TAYLOR



Figure 3.3: The different lattice vectors and their notation.

expansion, [36], yields:

$$\xi^i_{\alpha} = U^i(X^j_{\alpha}) \equiv U^i(X^j), \qquad (3.12)$$

$$\xi^{i}_{\beta} = U^{i}(X^{j}_{\beta}) = U^{i}(X^{j}_{\alpha} + R^{j}_{\alpha\beta}) = U^{i}(X^{j}) + \frac{\partial U^{i}}{\partial X^{j}}R^{j}_{\alpha\beta} + \dots, \qquad (3.13)$$

$$\Rightarrow r^{i}_{\alpha\beta} = R^{i}_{\alpha\beta} + \frac{\partial U^{i}}{\partial X^{j}} R^{j}_{\alpha\beta} = \left(\delta^{ij} + H^{ij}\right) R^{j}_{\alpha\beta} \equiv F^{ij} R^{j}_{\alpha\beta}.$$
(3.14)

Here $F^{ij} = \delta^{ij} + H^{ij}$ denotes the coefficients of the deformation gradient and $H^{ij} = \frac{\partial U^i}{\partial X^j}$ 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, $\Phi(r_1^i, \ldots, r_N^i)$, as a function of the current distance vector between the atoms and expand the energy in a TAYLOR series as follows, [65]:

$$\Phi(r_1^i, \dots, r_N^i) = \Phi(R_1^i + H^{ij}R_1^j, \dots, R_N^i + H^{ij}R_N^j) =$$

= $\Phi(R_1^i, \dots, R_N^i) + \sum_b \frac{\partial \Phi}{\partial r_b^j} \bigg|_{R_b^j} \vartheta_b^j + \frac{1}{2} \sum_b \frac{\partial^2 \Phi}{\partial r_b^k \partial r_b^l} \bigg|_{R_b^k, R_b^l} \vartheta_b^k \vartheta_b^l + \dots$ (3.15)

In this equation the index b identifies the bond between the different atoms α and β and the symbol ϑ_b^i denotes the coefficients of the difference vector between the displacements of α and β , 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:

$$\Phi(r_1^i, \dots, r_N^i) = \Phi(R_1^i, \dots, R_N^i) + + H^{ij} \sum_b \frac{\partial \Phi}{\partial r_{\alpha\beta}^i} \bigg|_{R_{\alpha\beta}^i} R_{\alpha\beta}^j + \frac{1}{2} H^{ij} H^{kl} \sum_b \frac{\partial^2 \Phi}{\partial r_{\alpha\beta}^j \partial r_{\alpha\beta}^l} \bigg|_{R_{\alpha\beta}^j, R_{\alpha\beta}^l} R_{\alpha\beta}^i R_{\alpha\beta}^k.$$
(3.16)

The first derivatives of Φ 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^{ij} by its symmetric part (*i.e.*, the coefficients of the strain tensor ε^{ij}) this term can be linked to the stiffness coefficients K^{ijkl} , [66].

Unfortunately I could not find a completely convincing argument to justify the substitution $H^{ij} \rightarrow \varepsilon^{ij}$ 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):

$$r_{\alpha\beta}^{2} = r_{\alpha\beta}^{i}r_{\alpha\beta}^{i} = F^{ij}F^{ik}R_{\alpha\beta}^{j}R_{\alpha\beta}^{k} = C^{jk}R_{\alpha\beta}^{j}R_{\alpha\beta}^{k} = R_{\alpha\beta}^{2} + (C^{jk} - \delta^{jk})R_{\alpha\beta}^{j}R_{\alpha\beta}^{k}$$
$$= R_{\alpha\beta}^{2} + 2G^{jk}R_{\alpha\beta}^{j}R_{\alpha\beta}^{k} \quad , \qquad (3.17)$$

where $C^{jk} = F^{ij}F^{ik} \equiv \mathbf{F}^T \cdot \mathbf{F}$ stands for the right CAUCHY-GREEN tensor and $G^{jk} = \frac{1}{2}(C^{jk} - \delta^{jk}) \equiv \frac{1}{2}(\mathbf{C} - \mathbf{I})$ for GREEN's strain tensor. By means of G^{jk} we can write for the energy of a lattice:

$$\Phi(r_{\alpha\beta}^{2}) = \Phi(R_{\alpha\beta}^{2} + 2G^{jk}R_{\alpha\beta}^{j}R_{\alpha\beta}^{k}) = \Phi(R_{\alpha\beta}^{2}) + 2G^{ij}\sum_{b} \frac{\partial\Phi}{\partial r_{\alpha\beta}^{2}} \bigg|_{R_{\alpha\beta}^{2}} R_{\alpha\beta}^{i}R_{\alpha\beta}^{j} + \frac{4}{2}G^{ij}G^{kl}\sum_{b} \frac{\partial^{2}\Phi}{\partial r_{\alpha\beta}^{2}\partial r_{\alpha\beta}^{2}} \bigg|_{R_{\alpha\beta}^{2}} R_{\alpha\beta}^{i}R_{\alpha\beta}^{j}R_{\alpha\beta}^{k}R_{\alpha\beta}^{l} + \dots$$
(3.18)

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_{α} is given by Eq. (3.2). Since $\phi_{\alpha\beta}$, ρ_{β} and $\bar{\rho}_{\alpha}$ depend only on the scalar distance $r_{\alpha\beta}$ between α and β it is also possible to use $r_{\alpha\beta}^2$ in the argument. The corresponding functions are $\hat{\phi} = \tilde{\phi}(r_{\alpha\beta}^2)$ and $\hat{\rho}_{\beta} = \tilde{\rho}_{\beta}(r_{\alpha\beta}^2)$ and one can write:

$$E_{\text{tot}} = \sum_{\alpha} E_{\alpha} = \frac{1}{2} \sum_{\substack{\alpha,\beta\\(\beta\neq\alpha)}} \hat{\phi}_{\alpha\beta}(r_{\alpha\beta}^2) + \sum_{\alpha} \hat{F}_{\alpha}(\hat{\rho}_{\alpha}) \quad \text{and} \quad \hat{\rho}_{\alpha} = \sum_{\substack{\beta\\(\beta\neq\alpha)}} \hat{\rho}_{\beta}(r_{\alpha\beta}^2). \quad (3.2a)$$

For convenience we will omit the circumflexes $\hat{\rho}_{\alpha\beta}$ in the following sections. $\phi_{\alpha\beta}$, ρ_{β} 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:

$$\phi_{\alpha\beta}(r_{\alpha\beta}^2) = \phi_{\alpha\beta}(R_{\alpha\beta}^2 + 2G^{ij}R_{\alpha\beta}^i R_{\alpha\beta}^j) =
= \phi_{\alpha\beta}(R_{\alpha\beta}^2) + 2\phi_{\alpha\beta}'(R_{\alpha\beta}^2)G^{ij}R_{\alpha\beta}^i R_{\alpha\beta}^j + 2\phi_{\alpha\beta}''(R_{\alpha\beta}^2)G^{ij}G^{kl}R_{\alpha\beta}^i R_{\alpha\beta}^j R_{\alpha\beta}^k R_{\alpha\beta}^l. (3.19)$$

In an analogous manner one obtains:

$$\rho_{\beta}(r^{\alpha\beta^{2}}) = \rho_{\beta}(R^{\alpha\beta^{2}}) + 2\rho_{\beta}'(R^{\alpha\beta^{2}})G_{ij}R_{j}^{\alpha\beta}R_{j}^{\alpha\beta} + 2\rho_{\beta}''(R^{\alpha\beta^{2}})G_{ij}G_{kl}R_{i}^{\alpha\beta}R_{j}^{\alpha\beta}R_{k}^{\alpha\beta}R_{l}^{\alpha\beta}.$$
(3.20)

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

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

$$(3.21)$$

By introducing

$$A^{ij}_{\alpha} = \sum_{\beta} \phi'_{\alpha\beta}(R^2_{\alpha\beta}) R^i_{\alpha\beta} R^j_{\alpha\beta} \quad , \quad B^{ijkl}_{\alpha} = \sum_{\beta} \phi''_{\alpha\beta}(R^2_{\alpha\beta}) R^i_{\alpha\beta} R^j_{\alpha\beta} R^k_{\alpha\beta} R^l_{\alpha\beta} \quad , \qquad (3.22)$$

$$V_{\alpha}^{ij} = \sum_{\beta} \rho_{\beta}'(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j \quad , \quad W_{\alpha}^{ijkl} = \sum_{\beta} \rho_{\beta}''(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j R_{\alpha\beta}^k R_{\alpha\beta}^l \tag{3.23}$$

one can find the following important relation for the energy of an arbitrary atom α :

$$E_{\alpha} = \frac{1}{2} \sum_{\beta} \phi_{\alpha\beta}(R_{\alpha\beta}^{2}) + F_{\alpha}(\bar{\rho}_{\alpha}^{0}) + G^{ij} \left[A_{\alpha}^{ij} + 2F_{\alpha}'(\bar{\rho}_{\alpha}^{0})V_{\alpha}^{ij} \right] + G^{ij}G^{kl} \left[B_{\alpha}^{ijkl} + 2F_{\alpha}'(\bar{\rho}_{\alpha}^{0})W_{\alpha}^{ijkl} + 2F_{\alpha}''(\bar{\rho}_{\alpha}^{0})V_{\alpha}^{ij}V_{\alpha}^{kl} \right], \qquad (3.24)$$

where $F'_{\alpha}(\bar{\rho}^0_{\alpha})$ and $F''_{\alpha}(\bar{\rho}^0_{\alpha})$ refer the derivatives with respect to the argument at $\bar{\rho}^0_{\alpha} = \sum_{\beta} \mathcal{A}_{\beta} = \sum_{\beta} \rho_{\beta}(R^2_{\alpha\beta})$. Note that in order to derive Eq. (3.24) the chain rule was

applied as follows:

$$\frac{\partial F_{\alpha}}{\partial \mathcal{X}_{\alpha\beta}}\Big|_{\mathcal{X}_{\alpha\beta}=0} = F_{\alpha}'\left(\sum_{\beta} \mathcal{A}_{\beta}\right) \cdot \sum_{\beta} \mathcal{B}_{\beta} , \qquad (3.25)$$

$$\frac{\partial^2 F_{\alpha}}{\partial \mathcal{X}_{\alpha\beta} \partial \mathcal{X}_{\alpha\gamma}} \bigg|_{\mathcal{X}_{\alpha\beta} = \mathcal{X}_{\alpha\gamma} = 0} = F_{\alpha}^{\prime\prime} \bigg(\sum_{\beta} \mathcal{A}_{\beta} \bigg) \cdot \sum_{\beta,\gamma} \mathcal{B}_{\beta} \mathcal{B}_{\gamma} + F_{\alpha}^{\prime} \bigg(\sum_{\beta} \mathcal{A}_{\beta} \bigg) \cdot \sum_{\beta} \mathcal{C}_{\beta} . \quad (3.26)$$

Eq. (3.24) represents an important relation for the energy of atom α . 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 α and of its neighbors β in more detail.

Moreover, if thermal expansion is neglected, it is reasonable to postulate that E_{α} 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*:

$$A_{\alpha}^{ij} + 2F_{\alpha}'(\bar{\rho}_{\alpha}^{0})V_{\alpha}^{ij} = 0.$$
(3.27)

Furthermore it holds that $E_{\text{elast}}/V = \frac{1}{2}G^{ij}K^{ijkl}G^{kl}$ (law of ST.-VENANT-KIRCHHOFF), [40]. Defining Ω_0^{α} as the volume occupied by an atom α we obtain for the *stiffness* coefficients from Eq. (3.24):

$$K_{\alpha}^{ijkl} = \frac{1}{\Omega_{0}^{\alpha}} \left[2B_{\alpha}^{ijkl} + 4F_{\alpha}'(\bar{\rho}_{\alpha}^{0})W_{\alpha}^{ijkl} + 4F_{\alpha}''(\bar{\rho}_{\alpha}^{0})V_{\alpha}^{ij}V_{\alpha}^{kl} \right].$$
(3.28)

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 $\hat{\phi}'_{\alpha\beta}(R_{\alpha\beta}^2) = \frac{\phi'_{\alpha\beta}(R_{\alpha\beta})}{2R_{\alpha\beta}}, \hat{\rho}'_{\beta}(R_{\alpha\beta}^2) = \frac{\rho'_{\beta}(R_{\alpha\beta})}{2R_{\alpha\beta}}, \hat{\phi}''_{\alpha\beta}(R_{\alpha\beta}^2) = \frac{1}{4}(\frac{\phi''_{\alpha\beta}(R_{\alpha\beta})}{R_{\alpha\beta}^2} - \frac{\phi'_{\alpha\beta}(R_{\alpha\beta})}{R_{\alpha\beta}^3}),$ and $\hat{\rho}''_{\beta}(R_{\alpha\beta}^2) = \frac{1}{4}(\frac{\rho''_{\beta}(R_{\alpha\beta})}{R_{\alpha\beta}^2} - \frac{\rho'_{\beta}(R_{\alpha\beta})}{R_{\alpha\beta}^3}),$ 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].

$$\hat{y}_{\gamma} = \begin{cases} 0 , & \gamma = \mathbf{A} \\ 1 , & \gamma = \mathbf{B} \end{cases}$$

$$(3.29)$$

We now have to specify the following expressions of Eq. (3.24): $\phi_{\alpha\beta}$, $\bar{\rho}^0_{\alpha}$, F_{α} , A^{ij}_{α} , B^{ijkl}_{α} , $F'_{\alpha}V^{ij}_{\alpha}$, $F''_{\alpha}V^{ij}_{\alpha}V^{kl}_{\alpha}$ and $F'_{\alpha}W^{ijkl}_{\alpha}$. For this purpose we begin the analysis with the decomposition of $\phi_{\alpha\beta}$ and $\bar{\rho}^0_{\alpha}$ in the following manner:

$$\phi_{\alpha\beta} = (1 - \hat{y}_{\alpha}) (1 - \hat{y}_{\beta}) \phi_{AA} + \hat{y}_{\alpha} \hat{y}_{\beta} \phi_{BB} + [(1 - \hat{y}_{\alpha}) \hat{y}_{\beta} + (1 - \hat{y}_{\beta}) \hat{y}_{\alpha}] \phi_{AB}$$

= $\phi_{AA} + [\hat{y}_{\alpha} + (1 - 2\hat{y}_{\alpha}) \hat{y}_{\beta}] \phi + (\hat{y}_{\alpha} + \hat{y}_{\beta}) \tilde{\phi},$ (3.30)

$$\bar{\rho}_{\alpha}^{0} = \sum_{\beta} \left[\left(1 - \hat{y}_{\beta} \right) \rho_{A} + \hat{y}_{\beta} \rho_{B} \right] = \sum_{\beta} \left[\hat{y}_{\beta} \left(\rho_{B} - \rho_{A} \right) + \rho_{A} \right]$$
(3.31)

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

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

$$\hat{y}_{\alpha} = y(X_i^{\alpha}) \equiv y(X_i), \qquad (3.32)$$

$$\hat{y}_{\beta} = y(X_{i}^{\beta}) = y(X_{i} + R_{i}^{\alpha\beta}) =
= y(X_{i}) + \underbrace{\frac{\partial y}{\partial X_{i}}}_{=\nabla_{i}y} R_{i}^{\alpha\beta} + \frac{1}{2} \underbrace{\frac{\partial^{2} y}{\partial X_{i} \partial X_{j}}}_{=\nabla_{i}^{2}y} R_{i}^{\alpha\beta} R_{j}^{\alpha\beta} + \dots$$
(3.33)

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

$$\phi_{\alpha\beta} = \phi_{AA} + 2y(1-y)\phi + 2y\tilde{\phi} + \nabla_i y \left[(1-2y)\phi + \tilde{\phi} \right] R^i_{\alpha\beta} + \frac{1}{2} \nabla^2_{ij} y \left[(1-2y)\phi + \tilde{\phi} \right] R^i_{\alpha\beta} R^j_{\alpha\beta}, \qquad (3.34)$$

$$\bar{\rho}^{0}_{\alpha} = \sum_{\beta} \rho_{A} + y \sum_{\beta} (\rho_{B} - \rho_{A}) + \nabla_{i} y \sum_{\beta} (\rho_{B} - \rho_{A}) R^{i}_{\alpha\beta} + \frac{1}{2} \nabla^{2}_{ij} y \sum_{\beta} (\rho_{B} - \rho_{A}) R^{i}_{\alpha\beta} R^{j}_{\alpha\beta}$$

$$(3.35)$$

$$= \bar{\rho}_{\mathcal{A}} + y\bar{\rho}_{\bigtriangleup} + (\nabla_{i}y)\bar{\rho}_{\bigtriangleup}^{i} + \frac{1}{2}(\nabla_{ij}^{2}y)\bar{\rho}_{\bigtriangleup}^{ij}$$

$$(3.36)$$

with the definitions $\bar{\rho}_{\rm A} = \sum_{\beta} \rho_{\rm A}$; $\bar{\rho}_{\Delta} = \sum_{\beta} (\rho_{\rm B} - \rho_{\rm A})$; $\bar{\rho}^i_{\Delta} = \sum_{\beta} (\rho_{\rm B} - \rho_{\rm A}) R^i_{\alpha\beta}$ and $\bar{\rho}^{ij}_{\Delta} = \sum_{\beta} (\rho_{\rm B} - \rho_{\rm A}) R^i_{\alpha\beta} R^j_{\alpha\beta}$. At this point it is important to mention that for any scalar function $f(R_{\alpha\beta})$ depending only on the *radial* distance $R_{\alpha\beta}$ between atom α and β the following sum vanishes:

$$\sum_{\beta} f(R_{\alpha\beta}^2) R_{\alpha\beta}^{i_1} \dots R_{\alpha\beta}^{i_N} = 0 \quad , \quad (\forall N = \text{odd number}).$$
(3.37)

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

$$\phi_{\alpha\beta} = \phi_{AA} + 2y(1-y)\phi + 2y\tilde{\phi} + \frac{1}{2}\nabla_{ij}^2 y \big[(1-2y)\phi + \tilde{\phi} \big] R^i_{\alpha\beta} R^j_{\alpha\beta}, \qquad (3.38)$$

$$\bar{\rho}^0_{\alpha} = \bar{\rho}_{\mathcal{A}} + y\bar{\rho}_{\triangle} + \frac{1}{2}(\nabla^2_{ij}y)\bar{\rho}^{ij}_{\triangle} .$$
(3.39)

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

$$F_{\alpha}(\bar{\rho}_{\alpha}^{0}) = F_{\alpha}\left(\underbrace{\bar{\rho}_{A} + y\bar{\rho}_{\triangle}}_{=\bar{\rho}_{av}} + \frac{1}{2}(\nabla_{ij}^{2}y)\bar{\rho}_{\triangle}^{ij}\right) = F_{\alpha}\left(\bar{\rho}_{av}\right) + \frac{1}{2}F_{\alpha}'\left(\bar{\rho}_{av}\right) \bar{\rho}_{\triangle}^{ij}(\nabla_{ij}^{2}y) + \dots$$

$$(3.40)$$

Note that gradient terms of higher than second order were assumed not to contribute to the energy of the system. Moreover F_{α} itself is also decomposed analogously to Eq. (3.31) and we write:

$$F_{\alpha}(\bar{\rho}_{\alpha}^{0}) = (1-y)F_{A} + yF_{B} , \qquad (3.41)$$

$$F_{\rm A} = F_{\rm A} \left(\bar{\rho}_{av}\right) + \frac{1}{2} F_{\rm A}' \left(\bar{\rho}_{av}\right) \bar{\rho}_{ij}^{\triangle} (\nabla_{ij}^2 y) \dots ,$$

$$F_{\rm B} = F_{\rm B} \left(\bar{\rho}_{av}\right) + \frac{1}{2} F_{\rm B}' \left(\bar{\rho}_{av}\right) \bar{\rho}_{ij}^{\triangle} (\nabla_{ij}^2 y) \dots .$$
(3.42)

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^{ij}_{α} , B^{ijkl}_{α} , $F'_{\alpha}V^{ij}_{\alpha}$, $F''_{\alpha}V^{ij}_{\alpha}V^{kl}_{\alpha}$ and $F'_{\alpha}W^{ijkl}_{\alpha}$ of Eq. (3.24). Here it is worth mentioning that the products of the last three expressions $F'_{\alpha}V^{ij}_{\alpha}$, $F''_{\alpha}V^{ij}_{\alpha}V^{kl}_{\alpha}$ and $F'_{\alpha}W^{ijkl}_{\alpha}$ cannot be separated and evaluated separately since they are coupled by the same index α . Hence the decomposition by means of the DCP-operator must be applied to the complete product.

The first two abbreviations, A_{α}^{ij} and B_{α}^{ijkl} , can be written in the same manner as in Eq. (3.34):

$$A_{\alpha}^{ij} = A_{A}^{ij} + 2y(1-y)A_{\phi}^{ij} + 2yA_{\tilde{\phi}}^{ij} + \frac{1}{2}\nabla_{kl}^{2}y\Big[(1-2y)A_{\phi}^{ijkl} + A_{\tilde{\phi}}^{ijkl}\Big], \qquad (3.43)$$

$$B_{\alpha}^{ijkl} = B_{A}^{ijkl} + 2y(1-y)B_{\phi}^{ijkl} + 2yB_{\tilde{\phi}}^{ijkl} + \frac{1}{2}\nabla_{mn}^{2}y\Big[(1-2y)B_{\phi}^{ijklmn} + B_{\tilde{\phi}}^{ijklmn}\Big]$$
(3.44)

with the definitions:

$$A_{\rm A}^{ij} = \sum_{\beta} \phi_{\rm AA}'(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j , \quad A_{\phi}^{ijkl} = \sum_{\beta} \phi'(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j R_{\alpha\beta}^k R_{\alpha\beta}^l , \quad (3.45)$$
$$A_{\tilde{\phi}}^{ijkl} = \sum_{\beta} \tilde{\phi}'(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j R_{\alpha\beta}^k R_{\alpha\beta}^l , \quad B_{\rm A}^{ijkl} = \sum_{\beta} \phi_{\rm AA}'(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j R_{\alpha\beta}^k R_{\alpha\beta}^l , \quad (3.45)$$

$$B^{ijklmn}_{\phi} = \sum_{\beta} \phi''(R^2_{\alpha\beta}) R^i_{\alpha\beta} \dots R^n_{\alpha\beta} , \quad B^{ijklmn}_{\tilde{\phi}} = \sum_{\beta} \tilde{\phi}''(R^2_{\alpha\beta}) R^i_{\alpha\beta} \dots R^n_{\alpha\beta} .$$
(3.47)

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

$$F'_{\alpha}(\bar{\rho}^{0}_{\alpha})V^{ij}_{\alpha} = (1-y)F'_{A} V^{ij}_{\alpha}\Big|_{\alpha=A} + yF'_{B} V^{ij}_{\alpha}\Big|_{\alpha=B},$$
(3.48)

$$F'_{\alpha}(\bar{\rho}^{0}_{\alpha})W^{ijkl}_{\alpha} = (1-y)F'_{A} W^{ijkl}_{\alpha}\Big|_{\alpha=A} + yF'_{B} W^{ijkl}_{\alpha}\Big|_{\alpha=B},$$
(3.49)

$$F_{\alpha}^{\prime\prime}(\bar{\rho}_{\alpha}^{0})V_{\alpha}^{ij}V_{\alpha}^{kl} = (1-y)F_{A}^{\prime\prime}V_{\alpha}^{ij}V_{\alpha}^{kl}\Big|_{\alpha=A} + yF_{B}^{\prime\prime}V_{\alpha}^{ij}V_{\alpha}^{kl}\Big|_{\alpha=B}.$$
(3.50)

The derivatives F'_{α} and F''_{α} can be calculated analogously to Eqs. (3.42). We increase the order of derivatives in these equations consistently:

$$F'_{A/B} = F'_{A/B}(\bar{\rho}_{av}) + \frac{1}{2}F''_{A/B}(\bar{\rho}_{av})\bar{\rho}^{ij}_{\triangle}(\nabla^2_{ij}y), \qquad (3.51)$$

$$F_{A/B}'' = F_{A/B}''(\bar{\rho}_{av}) + \frac{1}{2} F_{A/B}'''(\bar{\rho}_{av}) \bar{\rho}_{\Delta}^{ij}(\nabla_{ij}^2 y) .$$
(3.52)

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

$$V_{\alpha}^{ij} = V_{A}^{ij} + yV_{\Delta}^{ij} + \frac{1}{2}(\nabla_{kl}^{2}y)V_{\Delta}^{ijkl} , \qquad (3.53)$$

$$W^{ijkl}_{\alpha} = W^{ijkl}_{A} + yW^{ijkl}_{\Delta} + \frac{1}{2}(\nabla^2_{mn}y)W^{ijklmn}_{\Delta}$$
(3.54)

with the abbreviations:

$$V_{\rm A}^{ij} = \sum_{\beta} \rho_{\rm A}'(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j , \quad V_{\Delta}^{i_1,\dots,i_n} = \sum_{\beta} \left[\rho_{\rm B}'(R_{\alpha\beta}^2) - \rho_{\rm A}'(R_{\alpha\beta}^2) \right] R_{\alpha\beta}^{i_1} \dots R_{\alpha\beta}^{i_n} , \qquad (3.55)$$

$$W_{\mathcal{A}}^{ijkl} = \sum_{\beta} \rho_{\mathcal{A}}^{\prime\prime}(R_{\alpha\beta}^2) R_{\alpha\beta}^i \dots R_{\alpha\beta}^l , \quad W_{\Delta}^{i_1,\dots,i_n} = \sum_{\beta} \left[\rho_{\mathcal{B}}^{\prime\prime}(R_{\alpha\beta}^2) - \rho_{\mathcal{A}}^{\prime\prime}(R_{\alpha\beta}^2) \right] R_{\alpha\beta}^{i_1} \dots R_{\alpha\beta}^{i_n}$$
(3.56)

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:

$$g_{AA} = \sum_{\beta} \phi_{AA} \quad , \quad g_{\phi} = \sum_{\beta} \phi \quad , \quad g_{\tilde{\phi}} = \sum_{\beta} \tilde{\phi} \quad , \quad (3.57)$$

$$g^{ij}_{\phi} = \sum_{\beta} \phi R^{i}_{\alpha\beta} R^{j}_{\alpha\beta} \quad , \quad g^{ij}_{\tilde{\phi}} = \sum_{\beta} \tilde{\phi} R^{i}_{\alpha\beta} R^{j}_{\alpha\beta} \; . \tag{3.58}$$

we obtain for the energy of atom α :

$$\begin{split} E_{\alpha} &= \frac{1}{2} g_{AA} + y(1-y) g_{\phi} + y g_{\tilde{\phi}} + \frac{1}{4} (\nabla_{ij}^{2} y) \left[(1-2y) g_{\phi}^{ij} + g_{\phi}^{ij} \right] \\ &+ F_{A} + y \left(F_{B} - F_{A} \right) + \frac{1}{2} (\nabla_{ij}^{2} y) \bar{\rho}_{\Delta}^{ij} \left[F_{A}^{\prime} + y \left(F_{B}^{\prime} - F_{A}^{\prime} \right) \right] \\ &+ G^{ij} \left\{ A_{A}^{ij} + 2y(1-y) A_{\phi}^{ij} + 2y A_{\phi}^{ij} + \frac{1}{2} (\nabla_{kl}^{2} y) \left[(1-2y) A_{\phi}^{ijkl} + A_{\phi}^{ijkl} \right] \\ &+ 2 \left(V_{A}^{ij} + y V_{\Delta}^{ij} \right) \left(F_{A}^{\prime} + y (F_{B}^{\prime} - F_{A}^{\prime}) \right) \\ &+ (\nabla_{kl}^{2} y) \left[V_{\Delta}^{ijkl} \left(F_{A}^{\prime} + y (F_{B}^{\prime} - F_{A}^{\prime}) \right) + \bar{\rho}_{\Delta}^{kl} \left(V_{A}^{ij} + y V_{\Delta}^{ij} \right) \left(F_{A}^{\prime\prime} + y (F_{B}^{\prime\prime} - F_{A}^{\prime\prime}) \right) \right] \right\} \\ &+ \frac{1}{2} G^{ij} G^{kl} \left\{ 2 B_{A}^{ijkl} + 4y(1-y) B_{\phi}^{ijkl} + 4y B_{\phi}^{ijkl} + (\nabla_{mn}^{2} y) \left[(1-2y) B_{\phi}^{ijklmn} + B_{\phi}^{ijklmn} \right] \\ &+ 4 \left(W_{A}^{ijkl} + y W_{\Delta}^{ijkl} \right) \left(F_{A}^{\prime} + y (F_{B}^{\prime} - F_{A}^{\prime}) \right) \\ &+ 2 (\nabla_{mn}^{2} y) \left[W_{\Delta}^{ijklmn} \left(F_{A}^{\prime} + y (F_{B}^{\prime} - F_{A}^{\prime}) \right) + \bar{\rho}_{\Delta}^{mn} \left(W_{A}^{ijkl} + y W_{\Delta}^{ijkl} \right) \times \\ &\times \left(F_{A}^{\prime\prime} + y (F_{B}^{\prime\prime} - F_{A}^{\prime\prime}) \right) \right] + 4 \left(V_{A}^{ij} + y V_{\Delta}^{ij} \right) \left(V_{A}^{kl} + y V_{\Delta}^{kl} \right) \left(F_{A}^{\prime\prime} + y (F_{B}^{\prime\prime} - F_{A}^{\prime\prime\prime}) \right) \\ &+ 2 (\nabla_{mn}^{2} y) \left[V_{\Delta}^{kimn} \left(V_{A}^{ij} + y V_{\Delta}^{ij} \right) \left(F_{A}^{\prime\prime} + y (F_{B}^{\prime\prime} - F_{A}^{\prime\prime\prime}) \right) + V_{\Delta}^{ijkl} - V_{A}^{ijkl} + y V_{\Delta}^{ijkl} \right) \times \\ &\times \left(F_{A}^{\prime\prime} + y (F_{B}^{\prime\prime} - F_{A}^{\prime\prime\prime}) \right) + \bar{\rho}_{\Delta}^{mn} \left(V_{A}^{ij} + y V_{\Delta}^{ij} \right) \left(V_{A}^{kl} + y V_{\Delta}^{kl} \right) \left(F_{A}^{\prime\prime\prime} + y (F_{B}^{\prime\prime\prime} - F_{A}^{\prime\prime\prime\prime}) \right) \right] \right\} \\ & (3.59)$$

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

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 $c(x^i, t)$ can be characterized by the equation (without eigenstrains and thermal expansion):

$$\mathbb{F} = \mathbb{F}_0(c, G^{ij}) - a^{kl}(c, G^{ij}) \nabla_{kl}^2 c + b^{kl}(c, G^{ij}) (\nabla_k c) (\nabla_l c) .$$
(3.60)

The first term, $\mathbb{F}_0(c, G^{ij})$, 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^{kl} . Therefore one can split \mathbb{F}_0 into two parts (here for pure elastic deformations):

$$\mathbb{F}_0(c, G^{ij}) = \mathbb{F}_0^{\text{chem}}(c) + \underbrace{\frac{1}{2} G^{ij} \ K^{ijkl}(c) \ G^{kl}}_{=\mathbb{F}_0^{\text{mech}}}, \qquad (3.61)$$

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:

$$\begin{split} E_{\alpha} &= \frac{1}{2} g_{AA} + y(1-y) g_{\phi} + y g_{\tilde{\phi}} + F_{A} + y \left(F_{B} - F_{A}\right) \\ &+ \frac{1}{2} G^{ij} G^{kl} \left\{ 2B_{A}^{ijkl} + 4y(1-y) B_{\phi}^{ijkl} + 4y B_{\tilde{\phi}}^{ijkl} + 4 \left(W_{A}^{ijkl} + y W_{\Delta}^{ijkl}\right) \times \right. \\ &\times \left(F_{A}' + y(F_{B}' - F_{A}')\right) + 4 \left(V_{A}^{ij} + y V_{\Delta}^{ij}\right) \left(V_{A}^{kl} + y V_{\Delta}^{kl}\right) \left(F_{A}'' + y(F_{B}'' - F_{A}'')\right) \right\} \\ &+ \left. \left(\nabla_{mn}^{2} y\right) \left\{ \frac{1}{4} \left((1 - 2y) g_{\phi}^{mn} + g_{\phi}^{mn} \right) + \frac{1}{2} \bar{\rho}_{\Delta}^{mn} \left(F_{A}' + y(F_{B}' - F_{A}')\right) \right. \\ &+ \left. \frac{1}{2} G^{ij} \left[(1 - 2y) A_{\phi}^{ijmn} + A_{\phi}^{ijmn} + 2V_{\Delta}^{ijmn} \left(F_{A}' + y(F_{B}' - F_{A}')\right) \right. \\ &+ \left. 2 \bar{\rho}_{\Delta}^{mn} \left(V_{A}^{ij} + y V_{\Delta}^{ij}\right) \left(F_{A}'' + y(F_{B}'' - F_{A}'')\right) \right] \\ &+ \left. \frac{1}{2} G^{ij} G^{kl} \left[(1 - 2y) B_{\phi}^{ijklmn} + B_{\phi}^{ijklmn} \right. \\ &+ \left. 2 W_{\Delta}^{ijklmn} \left(F_{A}' + y(F_{B}' - F_{A}')\right) + 2 \bar{\rho}_{\Delta}^{mn} \left(W_{A}^{ijkl} + y W_{\Delta}^{ijkl}\right) \left(F_{A}'' + y(F_{B}'' - F_{A}'')\right) \\ &+ \left. 2 V_{\Delta}^{klmn} \left(V_{A}^{ij} + y V_{\Delta}^{ij}\right) \left(F_{A}'' + y(F_{B}'' - F_{A}'')\right) + 2 V_{\Delta}^{ijmn} \left(V_{A}^{kl} + y V_{\Delta}^{kl}\right) \times \\ &\times \left(F_{A}'' + y(F_{B}'' - F_{A}'')\right) + 2 \bar{\rho}_{\Delta}^{mn} \left(V_{A}^{ij} + y V_{\Delta}^{ij}\right) \left(V_{A}^{kl} + y V_{\Delta}^{kl}\right) \left(F_{A}''' + y(F_{B}'' - F_{A}''')\right) \right] \right\} \\ \\ &+ \left. G^{ij} \left\{ A_{A}^{ij} + 2y(1 - y) A_{\phi}^{ij} + 2y A_{\phi}^{ij} + 2 \left(V_{A}^{ij} + y V_{\Delta}^{ij}\right) \left(F_{A}' + y(F_{B}' - F_{A}'')\right) \right\}. \quad (3.62)$$

Equation (3.62) consists of four parts (1st row; 2nd and 3rd row; 4th-10th row; last row).

• The first part represents the energy of an atom α 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 $\nabla_{kl}^2 y$ occur. A substitution to $\nabla_{kl}^2 c$ will later allow the identification of a^{kl} and b^{kl} of Eq. (3.60).
- The last part stands for the equilibrium condition of a binary mixture A-B (minimum of energy), namely $\partial E_{\alpha}/\partial G^{ij}|_{G^{ij}=0,y=y^{eq}} = 0 \Rightarrow A^{ij}_{A} + 2y(1-y)A^{ij}_{\phi} + 2yA^{ij}_{\tilde{\phi}} + 2(V^{ij}_{A} + yV^{ij}_{\Delta})(F'_{A} + y(F'_{B} F'_{A})) = 0$. By knowing the equilibrium concentration y^{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:

$$A_{\rm A}^{ij} + 2y(c)(1 - y(c))A_{\phi}^{ij} + 2y(c)A_{\tilde{\phi}}^{ij} + 2\left(V_{\rm A}^{ij} + y(c)V_{\Delta}^{ij}\right)\left(F_{\rm A}' + y(c)(F_{\rm B}' - F_{\rm A}')\right) = 0$$
(3.63)

 \diamond Stiffness coefficients:

$$K^{ijkl}(c) = \frac{1}{\Omega_0^{\alpha}} \left[2B_{\rm A}^{ijkl} + 4y(c)(1 - y(c))B_{\phi}^{ijkl} + 4y(c)B_{\phi}^{ijkl} + 4\left(W_{\rm A}^{ijkl} + y(c)W_{\Delta}^{ijkl}\right) \left(F_{\rm A}' + y(c)(F_{\rm B}' - F_{\rm A}')\right) + 4\left(V_{\rm A}^{ij} + y(c)V_{\Delta}^{ij}\right) \left(V_{\rm A}^{kl} + y(c)V_{\Delta}^{kl}\right) \left(F_{\rm A}'' + y(c)(F_{\rm B}'' - F_{\rm A}'')\right) \right] (3.64)$$

 \diamond Higher gradient coefficients:

$$a^{mn}(c, G^{pq}) = -\delta(c) \operatorname{M}^{(2)}(c) \operatorname{\mathbb{H}}^{mn}(c, G^{pq}),$$
 (3.65)

$$b^{mn}(c, G^{pq}) = \delta(c) \operatorname{M}^{(1)}(c) \operatorname{\mathbb{H}}^{mn}(c, G^{pq}),$$
 (3.66)

$$A^{mn}(c, G^{pq}) = \frac{\partial a^{mn}(c, G^{pq})}{\partial c} + b^{mn}(c, G^{pq})$$
(3.67)

with

$$\begin{split} \delta(c) &= \frac{\rho_0}{m_H M(c)} \quad , \\ \mathbf{M}^{(1)}(c) &= \frac{2M_{\mathbf{A}} \ M_{\mathbf{B}}(M_{\mathbf{B}} - M_{\mathbf{A}})}{[M_{\mathbf{B}} - (M_{\mathbf{B}} - M_{\mathbf{A}})c]^3} \quad , \quad \mathbf{M}^{(2)}(c) &= \frac{M_{\mathbf{A}} M_{\mathbf{B}}}{[M_{\mathbf{B}} - (M_{\mathbf{B}} - M_{\mathbf{A}})c]^2} \quad , \quad (3.68) \\ \mathbb{H}^{mn}(c, G^{pq}) &= \frac{1}{4} \Big((1 - 2y(c))g_{\phi}^{mn} + g_{\phi}^{mn} \Big) + \frac{1}{2} \bar{\rho}_{\Delta}^{mn} \Big(F'_{\mathbf{A}} + y(c)(F'_{\mathbf{B}} - F'_{\mathbf{A}}) \Big) \\ &+ \frac{1}{2} G^{ij} \Big[(1 - 2y(c))A_{\phi}^{ijmn} + A_{\phi}^{ijmn} + 2V_{\Delta}^{ijmn} \Big(F'_{\mathbf{A}} + y(c)(F'_{\mathbf{B}} - F'_{\mathbf{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathbf{A}}^{ij} + y(c)V_{\Delta}^{ij} \Big) \Big(F''_{\mathbf{A}} + y(c)(F''_{\mathbf{B}} - F''_{\mathbf{A}}) \Big) \Big] \\ &+ \frac{1}{2} G^{ij} G^{kl} \Big[(1 - 2y(c))B_{\phi}^{ijklmn} + B_{\phi}^{ijklmn} \\ &+ 2W_{\Delta}^{ijklmn} \Big(F'_{\mathbf{A}} + y(c)(F'_{\mathbf{B}} - F'_{\mathbf{A}}) \Big) + 2\bar{\rho}_{\Delta}^{mn} \Big(W_{\mathbf{A}}^{ijkl} + y(c)W_{\Delta}^{ijkl} \Big) \times \\ &\times \Big(F''_{\mathbf{A}} + y(c)(F''_{\mathbf{B}} - F''_{\mathbf{A}}) \Big) + 2V_{\Delta}^{klmn} \Big(V_{\mathbf{A}}^{ij} + y(c)V_{\Delta}^{ij} \Big) \Big(F''_{\mathbf{A}} + y(c)(F''_{\mathbf{B}} - F''_{\mathbf{A}}) \Big) \\ &+ 2V_{\Delta}^{ijmn} \Big(V_{\mathbf{A}}^{kl} + y(c)V_{\Delta}^{kl} \Big) \Big(F''_{\mathbf{A}} + y(c)(F''_{\mathbf{B}} - F''_{\mathbf{A}}) \Big) \\ &+ 2\bar{\rho}_{\Delta}^{mn} \Big(V_{\mathbf{A}}^{ij} + y(c)V_{\Delta}^{ij} \Big) \Big(V_{\mathbf{A}}^{kl} + y(c)V_{\Delta}^{kl} \Big) \Big(F'''_{\mathbf{A}} + y(c)(F'''_{\mathbf{B}} - F'''_{\mathbf{A}}) \Big] \,. \tag{3.69}$$

Recall that all atomistic quantities refer to arguments $R^2_{\alpha\beta}$ and $\bar{\rho}_{av}$, respectively. In the following section we consider the specific binary alloy Ag-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 $y \equiv y_{\text{Cu}}$ ($c \equiv c_{\text{Cu}}$) 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 α - and the β -phase, with the equilibrium concentrations c_{α} and c_{β} , respectively (*cf.*, Fig. 1.3 (lower left)). Fig. 3.4 shows the HELMHOLTZ free energy density curve⁴, ($\rho\varphi$)(*c*), at 1000 Kelvin. It was obtained from a commercial database, [83]. By means of the common tangent rule construction the following

⁴Note that MTdata makes no difference between the GIBBS free energy and the HELMHOLTZ free energy.

equilibrium concentrations $c_{\alpha/\beta}$ were determined:

$$c_{\alpha} = 0.063 \quad \Leftrightarrow \quad y_{\alpha} = 0.102 , \qquad (3.70)$$

$$c_{\beta} = 0.945 \quad \Leftrightarrow \quad y_{\beta} = 0.967 . \tag{3.71}$$

Moreover both species Ag and Cu as well as the random alloy Ag-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_{α} stands for the energy of an atom α 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 lattice⁵. 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_{AA/φ/φ̃}, B^{ijkl}_{A/φ/φ̃}, F_{A/B}, F'_{A/B}, F''_{A/B}, F'''_{A/B}, V^{ij}_{A/Δ}, W^{ijkl}_{A/Δ}, 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), ∇²_{mn}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^{eq} . In this context we can revert to the equilibrium condition given by Eq. (3.63), provided that c^{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 Ag and Cu are fitted in terms of $R^2_{\alpha\beta}$. (2)



Figure 3.4: HELMHOLTZ free energy density $\mathbb{F}_0^{\text{chem}}(c)$ for Ag-Cu at 1000 Kelvin.

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

 $^{^{5}}$ 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.

the α - and β -phase in Ag-Cu at 1000 K. (4) The stiffness coefficients of the different phases $K_{\alpha/\beta}^{ijkl}$ are determined and the pure-substance-limit (*i.e.*, for Ag: $\lim c^{\alpha/\beta} = 0$ and for Cu: $\lim c^{\alpha/\beta} = 1$) is performed. (5) The HGCs in the α - and β -phases and as functions of the concentration are calculated. (6) The phase-diagram of Ag-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:

$$\rho(r^2) = \rho_{\rm e} \, \exp\left[-\beta\left(\frac{r^2}{R^2} - 1\right)\right] \quad , \quad \phi(r^2) = \phi_{\rm e} \, \exp\left[-\gamma\left(\frac{r^2}{R^2} - 1\right)\right] . \quad (3.72)$$

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 $a_e/\sqrt{2}$ (*cf.*, Fig. 3.2). Moreover the following relations hold:

$$\bar{\rho}(r^2) = 12\rho(r^2)$$
, $\bar{\rho}_{\rm e} = 12\rho_{\rm e}$, $\frac{1}{2}\sum_{\beta}\phi(r^2) = 6\phi(r^2)$, $6\phi_{\rm e} \equiv \Phi_{\rm e}$. (3.73)

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:

$$\frac{r}{R} = \sqrt{1 - \frac{1}{\beta} \ln \frac{\bar{\rho}}{\bar{\rho}_{e}}} \qquad , \qquad \frac{\phi}{\phi_{e}} = \left(\frac{\bar{\rho}}{\bar{\rho}_{e}}\right)^{\frac{\gamma}{\beta}}.$$
(3.74)

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

$$F(\bar{\rho}) = -E_{\rm sub} \left[1 + \alpha \left(\sqrt{1 - \frac{1}{\beta} \ln \frac{\bar{\rho}}{\bar{\rho}_{\rm e}}} - 1 \right) \right] \times \\ \times \exp \left[-\alpha \left(\sqrt{1 - \frac{1}{\beta} \ln \frac{\bar{\rho}}{\bar{\rho}_{\rm e}}} - 1 \right) \right] - \Phi_{\rm e} \left(\frac{\bar{\rho}}{\bar{\rho}_{\rm e}} \right)^{\frac{\gamma}{\beta}}, \qquad (3.75)$$

with $\alpha = 3\sqrt{\frac{\kappa\Omega_0}{E_{\rm sub}}}$.

In what follows we focus on the pure substances Ag and Cu as well as on the binary alloy Ag-Cu (silver-copper). In the case of the pure materials the following functions must be determined: ϕ_{AgAg} , ϕ_{CuCu} , ρ_{Ag} (= $1/12\bar{\rho}_{Ag}$), ρ_{Cu} (= $1/12\bar{\rho}_{Cu}$), $F_{Ag}(\bar{\rho}_{Ag})$, and $F_{Cu}(\bar{\rho}_{Cu})$. Thus for *both* pure components five parameters must be adjusted, namely α , β , γ , ϕ_e , ρ_e . Consequently ten parameters are unknown. Note that the interaction between an Ag and a Cu nucleus, *i.e.*, ϕ_{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 κ
- 3. sublimation energy $E_{\rm sub}$ (with respect to one particle)
- 4. (unrelaxed) vacancy formation energy $E_{\rm uvf}$
- 5. (equilibrium) lattice parameter $a_{\rm e}$

 α is already given by Eq. (3.8)₂, *i.e.*, it only remains to determine β , γ , $\phi_{\rm e}$, and $\rho_{\rm e}$.

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

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: $E_{\rm sub} = \frac{1}{2} \cdot 12 \cdot \phi(r^2)$. Hence it follows for equilibrium:

$$\phi_{\rm e} = \frac{E_{\rm sub}}{6} \ . \tag{3.76}$$

From the physical point of view it is plausible to establish that $\rho_{\rm e} \propto 1/\Omega_0$ and $\rho_{\rm e} \propto E_{\rm sub}$ and, consequently, we simply write:

$$\rho_{\rm e} = \frac{E_{\rm sub}}{\Omega_0} \,. \tag{3.77}$$

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

b. Determination of β and γ

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

$$E_{\rm uvf} = -\frac{1}{2} \sum_{\beta=1}^{12} \phi(r^2) - \sum_{\beta=1}^{12} F\left[12\rho(r^2)\right] + \sum_{\beta=1}^{12} F\left[11\rho(r^2)\right], \qquad (3.78)$$

$$G = \frac{1}{5}(3K^{2323} + 2K^*) \quad , \quad K^* = \frac{1}{2}(K^{1111} - K^{1122}) \tag{3.79}$$

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^{ijkl} of a pure substance A (*cf.*, Eq. (3.28)) we have:

$$K_{\rm A}^{ijkl} = \frac{1}{\Omega_0^{\rm A}} \Big[2B_{\rm AA}^{ijkl} + 4F_{\rm A}'(\bar{\rho}_{\rm A}^0) W_{\rm A}^{ijkl} + 4F_{\rm A}''(\bar{\rho}_{\rm A}^0) V_{\rm A}^{ij} V_{\rm A}^{kl} \Big]$$
(3.28a)

with the definitions:

$$\bar{\rho}_{\rm A}^0 = \sum_{\beta} \rho_{\rm A} \left(R_{\alpha\beta}^2 \right) \quad , \quad B_{\rm AA}^{ijkl} = \sum_{\beta} \phi_{\rm AA}''(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j R_{\alpha\beta}^k R_{\alpha\beta}^l \, , \tag{3.80}$$

$$V_{\rm A}^{ij} = \sum_{\beta} \rho_{\rm A}'(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j \quad , \quad W_{\rm A}^{ijkl} = \sum_{\beta} \rho_{\rm A}''(R_{\alpha\beta}^2) R_{\alpha\beta}^i R_{\alpha\beta}^j R_{\alpha\beta}^k R_{\alpha\beta}^l \quad , \qquad (3.81)$$

$$F'_{A} = \frac{\partial F_{A}}{\partial \bar{\rho}_{A}}\Big|_{\bar{\rho}_{A} = \bar{\rho}_{A}^{0}} \quad , \quad F''_{A} = \frac{\partial^{2} F_{A}}{\partial \bar{\rho}_{A}^{2}}\Big|_{\bar{\rho}_{A} = \bar{\rho}_{A}^{0}} \quad , \quad \phi''_{AA} = \frac{\partial^{2} \phi_{AA}}{\partial (r_{\alpha\beta}^{2})^{2}}\Big|_{r_{\alpha\beta}^{2} = R_{\alpha\beta}^{2}}, \tag{3.82}$$

$$\rho_{\rm A}' = \frac{\partial \rho_{\rm A}}{\partial r_{\alpha\beta}^2} \Big|_{r_{\alpha\beta}^2 = R_{\alpha\beta}^2} \quad , \quad \rho_{\rm A}'' = \frac{\partial^2 \rho_{\rm A}}{\partial (r_{\alpha\beta}^2)^2} \Big|_{r_{\alpha\beta}^2 = R_{\alpha\beta}^2} \,, \tag{3.83}$$

where $r_{\alpha\beta}^2$ or $R_{\alpha\beta}^2$ represent the distance between the atoms α and β 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):

$$G = \frac{8}{5} \frac{\phi_{\rm e} \gamma(\gamma - \beta)}{\Omega_0} \,. \tag{3.84}$$

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

$$E_{\rm uvf} \approx \frac{15}{4} \frac{G\Omega_0}{\gamma\beta} = 6\phi_{\rm e} \; \frac{\gamma - \beta}{\beta} \;. \tag{3.85}$$

The last two relations represent two equations for β and γ . 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]:

type of			Input		
atom	Ω_0 in \AA^3	$E_{\rm sub}$ in eV	$E_{\rm uvf}$ in eV	$\Omega_0 \kappa$ in eV	$\Omega_0 G$ in eV
Ag Cu	17.10 11.81	$2.85 \\ 3.54$	1.10 1.30	11.10 10.17	$3.61 \\ 4.05$

 Table 3.1: Experimental data for Ag and Cu.

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

$$a_{\rm Ag} = 4.09 \text{ Å} , \quad R_{\rm Ag} = 2.89 \text{ Å} , \quad R_{\rm Ag}^2 = 8.36 \text{ Å}^2$$
 (3.86)

$$a_{\rm Cu} = 3.61 \,\text{\AA} , \quad R_{\rm Cu} = 2.56 \,\text{\AA} , \quad R_{\rm Cu}^2 = 6.53 \,\text{\AA}^2$$
 (3.87)

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	α	β	γ	$\phi_{\rm e}$ in eV	$ ho_{\rm e} \mbox{ in eV/\AA}^3$	$\bar{\rho}_{\rm e} \mbox{ in eV/\AA}^3$
Ag Cu	$5.9205 \\ 5.0849$	2.9799 2.9232	$4.1300 \\ 3.9966$	$0.4750 \\ 0.5900$	$0.1672 \\ 0.2998$	$2.0064 \\ 3.5971$

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% (K_{Ag}^{1122}) and 9.4% (K_{Cu}^{1111}). Moreover the CAUCHY-Paradox ($K^{1122} = K^{2323}$) no longer exists which is a considerable improvement.



copper atom



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



copper atom

$\begin{array}{c c} K_{\mathrm{Ag}}^{ijkl} & kl \\ ij \end{array}$	11	22	33	23	31	12	$\begin{array}{c} K_{\rm Cu}^{ijkl} \ kl \\ ij \end{array}$	11	22	33	23	31	12
11	132.6 (124)	90.2 (94)	90.2 (94)	0	0	0	11	183.7 (168)	115.1 (121)	115.1 (121)	0	0	0
22	90.2 (94)	132.6 (124)	90.2 (94)	0	0	0	22	$115.1 \\ (121)$	183.7 (168)	115.1 (121)	0	0	0
33	90.2 (94)	90.2 (94)	132.6 (124)	0	0	0	33	$115.1 \\ (121)$	115.1 (121)	183.7 (168)	0	0	0
23	0	0	0	42.4 (46)	0	0	23	0	0	0		0	0
31	0	0	0	0	42.4 (46)	0	31	0	0	0	0	68.7 (75)	0
12	0	0	0	0	0	42.4 (46)	12	0	0	0	0	0	

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

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 A=Ag and B=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 $f: \sum f(R^2)R^iR^j = 0$, $(i \neq j)$ and $\sum f(R^2)R^iR^i = \text{const}$, $(\forall i, j = \{1, 2, 3\})$. 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 α or β 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 $R = (1 - c)R_{Ag} + cR_{Cu}$ which is represented by the continuous line in Figure 3.6 (Right). Especially for the α - and β -phase we can conclude:

$$R_{\alpha} = \sqrt{8.202} \text{ \AA} = 2.864 \text{ \AA} , \quad \Omega_0^{\alpha} = 16.61 \text{ \AA}^3 , \quad (3.88)$$

$$R_{\beta} = \sqrt{6.631} \text{ \AA} = 2.575 \text{ \AA} , \quad \Omega_0^{\beta} = 12.07 \text{ \AA}^3 .$$
 (3.89)



 β -phase (i = j)

Equilibrium nearest neighbor distances for different concentrations c.

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 Ω_0^{α} occupied by an atom α as well as all quantities in (3.64) can be calculated. In order to investigate the stiffness of the different phases in Ag-Cu we consider the equilibrium concentrations c_{α} and c_{β} and analyze Eq. (3.64) at the distances R_{α} and R_{β} presented in the previous section. The results are compiled in Table 3.4.

at 1000 K	•												
$\begin{array}{c} K^{ijkl}_{\alpha} \ kl \\ ij \end{array}$	11	22	33	23	31	12	$\begin{array}{c} K_{\beta}^{ijkl} \ kl \\ ij \end{array}$	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

Table 3.4: Elastic constants in GPa predicted for the α - and β -phases in an Ag-Cu system at 1000 K.

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 Ag-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_{Ag}^{ijkl} and K_{Cu}^{ijkl} 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):

$$\mathbb{H}^{mn}(c, G^{ij} = 0) = \frac{1}{4} \bigg[\bigg(1 - 2y(c) \bigg) g_{\phi}^{mn} + g_{\tilde{\phi}}^{mn} \bigg] + \frac{1}{2} \bar{\rho}_{\Delta}^{mn} \bigg[F_{\mathrm{A}}' + y(c) \bigg(F_{\mathrm{B}}' - F_{\mathrm{A}}' \bigg) \bigg].$$
(3.90)

Furthermore the following data can be compiled for eutectic Ag-Cu:

$$\rho_{\rm Ag} = 10490 \,\frac{\rm kg}{\rm m^3} \,, \quad \rho_{\rm Cu} = 8920 \,\frac{\rm kg}{\rm m^3} \,, \quad \rho_0 = 9980.57 \,\frac{\rm kg}{\rm m^3} \,, \quad \delta(c) = \frac{\rho_0}{m_H M(c)}.$$
(3.91)

By applying $c_{\alpha/\beta}$ and $R_{\alpha/\beta}$ in Eqs. (3.65,3.66,3.90,3.91₄) one can determine the higher gradient coefficients a^{ij} and b^{ij} for the α - and β -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 $a^{ij}(c)$ and $b^{ij}(c)$ (*cf.*, Figure 3.8). Note that for an (undeformed) FCC crystal we have $a^{ij} = b^{ij} = 0$ 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 α - and β -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
$egin{array}{c} lpha \ eta \end{array}$	$4.59 \cdot 10^{-11} 1.23 \cdot 10^{-10}$	$\begin{array}{c} 6.14 \cdot 10^{-11} \\ 1.03 \cdot 10^{-10} \end{array}$	$\begin{array}{c} 1.55 \cdot 10^{-10} \\ 1.88 \cdot 10^{-10} \end{array}$	$7.34 \cdot 10^{-11} 2.86 \cdot 10^{-11}$

For the determination of $A_{\alpha/\beta}^{ij}$ or (more generally) $A^{ij}(c)$ and the corresponding derivative one has to find a closed form expression for the equilibrium distances $R_{\alpha/\beta} = R(c_{\alpha/\beta})$ or R = R(c) first. Note that the derivatives $\partial a^{ij}/\partial c$, $\partial^2 a^{ij}/\partial c^2$ and $\partial b^{ij}/\partial c$ 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.*,

$$R(c) \approx (1-c)R_{\rm Ag} + cR_{\rm Cu}$$
 (3.92)

Now we can evaluate $A_{\alpha/\beta}^{ij}$ (cf., Table 3.5) as well as $A^{ij}(c)$ and the corresponding derivatives with respect to c (cf., Figure 3.8). Analogously we have for FCC crystals $A^{ij} = 0$ 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 $G^{ij} = G^{ji}$. However, for a graphical illustration of these dependencies we consider the following two strain states:

i) isotropic strains, *i.e.*:

$$G^{ij} \simeq \varepsilon^{ij} = \varepsilon \cdot \delta^{ij}$$
 (3.93)

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

$$\Xi^{ij} = \begin{pmatrix} \Xi^{11} & 0 & 0\\ 0 & \Xi^{11} & 0\\ 0 & 0 & \Xi^{11} \end{pmatrix} \quad \text{with} \quad \Xi = \{a, b, A\} \;. \tag{3.94}$$



Figure 3.8: Higher gradient coefficients calculated for Ag-Cu as a function of the mass concentration c (strain free case).

ii) so-called "line" strains, *i.e.*:

$$G^{ij} \simeq \varepsilon^{ij} = \varepsilon \cdot \delta^{i1} \delta^{j1} \delta^{ij} = \begin{pmatrix} \varepsilon & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} .$$
(3.95)

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 $\varepsilon(X^i, t)$ within the multiphase material.

In contrast to item (i) the calculated HGCs are of the following non-isotropic form:

$$\Xi^{ij} = \begin{pmatrix} \Xi^{11} & 0 & 0\\ 0 & \Xi^{22} & 0\\ 0 & 0 & \Xi^{22} \end{pmatrix} \quad \text{with} \quad \Xi = \{a, b, A\} .$$
(3.96)

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 Ag-Cu as a function of the mass concentration c and of the strains $\varepsilon^{ij} = \varepsilon \cdot \delta^{ij}$ (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 Ag-Cu as a function of the mass concentration c and of the strains $\varepsilon^{ij} = \varepsilon \cdot \delta^{i1} \delta^{j1} \delta^{ij}$ (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 α - and β -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 $\mu_{Ag/Cu}$. Consequently, the subsequent formalism relies on the following jump conditions: $[[\mu_{Ag/Cu}]] = 0$ and $[[\mu_{Cu} - \mu_{Ag}]] = 0$ 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:

$$g(y,T) \equiv E_{\alpha} - Ts = \frac{1}{2}g_{AA} + y(1-y)g_{\phi} + yg_{\tilde{\phi}} + F_{A} + y(F_{B} - F_{A}) - Ts$$

= $(1-y)\Big(6\phi_{AA}(R^{2}) + F_{A}(\bar{\rho}_{av}(R^{2}))\Big) + y\Big(6\phi_{BB}(R^{2}) + F_{B}(\bar{\rho}_{av}(R^{2}))\Big)$
+ $12y(1-y)g_{\phi}(R^{2}) + k_{B}T\Big(y\ln y + (1-y)\ln(1-y)\Big).$ (3.97)

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

$$\frac{\partial g(y,T)}{\partial y}\Big|_{y=y_{\alpha}} = \frac{\partial g(y,T)}{\partial y}\Big|_{y=y_{\beta}} = \frac{g(y_{\beta},T) - g(y_{\alpha},T)}{y_{\beta} - y_{\alpha}}.$$
(3.98)

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

$$c_{\rm Cu} \equiv c = \frac{m_{\rm Cu}}{m_{\rm Cu} + m_{\rm Ag}} = \frac{y M_{\rm Cu}}{y M_{\rm Cu} + (1 - y) M_{\rm Ag}}.$$
 (3.99)

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 (1st row) as well as the relation R(y) (2nd 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 (1st 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 (2nd row, left). The full diagram on the right hand side is the one obtained from MTdataTM, [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 α -phase (left part of the phase diagram) are in good agreement but, nevertheless, the values of the β -phase are poorly reproduced.

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

Temp.		predicted	by EA	M		experimental data				
in K	y_{lpha}	y_eta	c_{α}	c_{eta}	y_{α}	y_{eta}	c_{α}	c_{eta}		
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 $g^*(y,T)$ (cf., Figure 3.12, 1st 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 $g^*(y,T =$ 1000K) as well as $(\rho\psi)^*(c,T = 1000\text{K})$ following from the atomistic calculations and from MTdataTM. Moreover it is also possible to calculate the so-called excess enthalpy g^{ex} , the non-ideal heat of mixing, which can be obtained from the following relation:

$$g(y,T) = yg(y=0,T) + (1-y)g(y=1,T) + k_{\rm B}T \Big(y\ln y + (1-y)\ln(1-y) \Big) + g^{\rm ex}(y,T).$$
(3.100)

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^{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^{mix} . Thus values of g^{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: 1st 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 Ag-Cu (filled and joined dots) vs. experimental data (unfilled dots). Right: The phase diagram generated by MTdataTM.

is observable in our theoretical calculations where the calculated g^{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^{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 $g^*(y, T = 1000\text{K})$, $(\rho\psi)^*(c, T = 1000\text{K})$, and $g^{\text{ex}}(y, T = 1000\text{K})$ with the corresponding functions from MTdataTM (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 α , 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 Ag-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 Ag-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^{ij} is close to those found in literature (*e.g.*, [72], $A^{ij} = 2 \cdot 10^{-10} \delta^{ij}$ 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. Gute Sitten haben für die Gesellschaft mehr Wert als alle Berechnungen Newtons.

Friedrich II., preußischer König (1712 - 1786)

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 $c(X^i, t)$, which generally reads, [15]:

$$F\left(c(X^{i},t),\frac{\partial c(X^{i},t)}{\partial t},\frac{\partial^{m}c(X^{i},t)}{(\partial X^{j})^{m}}\right) = 0 \quad , \quad m = \{1,2,3,4\} \; .$$

$$(4.1)$$

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.*

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

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:

$$X^{i} = \frac{2\pi L}{N} \alpha^{i} \quad \text{with} \quad \alpha^{i} \stackrel{(3D)}{=} \begin{pmatrix} \alpha^{1} \\ \alpha^{2} \\ \alpha^{3} \end{pmatrix} \wedge \quad \alpha^{1/2/3} \in \{0, 1, 2, \dots, N-1\} , \quad (4.3)$$

where the grid point vector α^i identifies the position of an arbitrary grid point within the discrete grid-point-array, [91].

For a *scalar* function :

$$c: \{0, 1, 2, \dots, N-1\}^3 \to \mathbb{R}$$

$$\alpha^i \mapsto c(\alpha^i)$$
(4.4)

with the following *periodicity* property:

$$c(\alpha^{i}) = c(\alpha^{i} + Nr^{i}) \text{ and } r^{i} \stackrel{(3D)}{=} \begin{pmatrix} r^{1} \\ r^{2} \\ r^{3} \end{pmatrix} \wedge r^{1/2/3} \in \mathbb{Z}$$
 (4.5)

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

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

$$\mathfrak{F}^{-1}[\hat{c}(k^{j})] \stackrel{\text{(def)}}{=} \frac{1}{N^{d/2}} \sum_{\alpha^{1}=0}^{N-1} \dots \sum_{\alpha^{d}=0}^{N-1} \hat{c}(k^{j}) \exp\left[-\mathrm{i}\frac{2\pi L}{N} k^{l} \alpha^{l}\right] , \qquad (4.7)$$

where $j \in \{1, ..., d\}$ 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 α^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:

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

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

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

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

and for the one-dimensional case:

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

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 $c(X^i, t)$ occurring in the EDE we replace the spatial derivatives by *finite differences* defined on an arbitrary discrete grid-point $(\alpha^1, \alpha^2, \alpha^3) = (k, l, m)$:

$$\frac{\partial c(X^{i})}{\partial X^{1}} \simeq \frac{\Delta c(\alpha^{i})}{\Delta \alpha^{1}} \stackrel{\text{(def)}}{=} \frac{c(k+1,l,m) - c(k-1,l,m)}{2h},$$

$$\frac{\partial c(X^{i})}{\partial X^{2}} \simeq \frac{\Delta c(\alpha^{i})}{\Delta \alpha^{2}} \stackrel{\text{(def)}}{=} \frac{c(k,l+1,m) - c(k,l-1,m)}{2h},$$

$$\frac{\partial c(X^{i})}{\partial X^{3}} \simeq \frac{\Delta c(\alpha^{i})}{\Delta \alpha^{3}} \stackrel{\text{(def)}}{=} \frac{c(k,l,m+1) - c(k,l,m-1)}{2h},$$
(4.12)

with $h = 2\pi L/N$. For the second derivatives the following finite differences approximation is used¹ [17, 91]:

$$\frac{\partial^2 c(X^i)}{\partial (X^1)^2} \simeq \frac{\Delta^2 c(\alpha^i)}{\Delta (\alpha^1)^2} \stackrel{\text{(def)}}{=} \frac{c(k+1,l,m) + c(k-1,l,m) - 2c(k,l,m)}{h^2}, \\
\frac{\partial^2 c(X^i)}{\partial (X^2)^2} \simeq \frac{\Delta^2 c(\alpha^i)}{\Delta (\alpha^2)^2} \stackrel{\text{(def)}}{=} \frac{c(k,l+1,m) + c(k,l-1,m) - 2c(k,l,m)}{h^2}, \\
\frac{\partial^2 c(X^i)}{\partial (X^3)^2} \simeq \frac{\Delta^2 c(\alpha^i)}{\Delta (\alpha^3)^2} \stackrel{\text{(def)}}{=} \frac{c(k,l,m+1) + c(k,l,m-1) - 2c(k,l,m)}{h^2}.$$
(4.13)

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:

$$\mathfrak{F}\left[\frac{\Delta c(\alpha^i)}{\Delta \alpha^j}\right] = \mathfrak{F}[c(\alpha^i)] \cdot \xi_j^{(1)} , \quad \xi_j^{(1)} = -\frac{\mathrm{i}}{h} \sin\left(\frac{2\pi L}{N}k^j\right) , \qquad (4.14)$$

$$\mathfrak{F}\left[\frac{\Delta^2 c(\alpha^i)}{\Delta(\alpha^j)^2}\right] = \mathfrak{F}[c(\alpha^i)] \cdot \xi_j^{(2)} , \quad \xi_j^{(2)} = \frac{2}{h^2} \left[\cos\left(\frac{2\pi L}{N}k^j\right) - 1\right] . \tag{4.15}$$

The corresponding relations in **one dimension** read:

$$\mathfrak{F}\left[\frac{\Delta c(\alpha)}{\Delta \alpha}\right] = \mathfrak{F}[c(\alpha)] \cdot \xi^{(1)} \quad , \quad \xi^{(1)} = -\frac{\mathrm{i}}{h} \sin\left(\frac{2\pi L}{N}k\right) \; , \tag{4.16}$$

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

¹Mixed 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].

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 $\exp[i\alpha] = \cos \alpha + i \sin \alpha$, [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 $c(X^i, t)$ 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:

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

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 $c(X^i, t)$ 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 form² [18]:

$$\frac{\mathrm{d}\hat{c}}{\mathrm{d}t} = f(\hat{c}) , \qquad (4.19)$$

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 $\hat{c}(t_i + \Delta t)$ by starting from a *known* initial value $\hat{c}_i = \hat{c}(t_i)$ and applying the discrete time step Δt . 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 $\hat{c}(t = t_0) = \hat{c}_0$ and discretize the time t by $t_k = t_0 + k \cdot \Delta t$ (k =

²The same arguments hold for each component of the N dimensional ODE, given in Eq. (4.18).



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 Δt . The ODE is now approximated by finite differences as follows:

$$f(\hat{c}) = \frac{\hat{c}(t + \Delta t) - \hat{c}(t)}{\Delta t} \quad \text{or} \quad \hat{c}(t + \Delta t) = \hat{c}(t) + \Delta t \cdot f(\hat{c}) , \quad (4.20)$$

Furthermore the approximation of the solution $\hat{c}_i = \hat{c}(t_i)$ is defined by η_i with $\eta_0 \stackrel{\text{(def)}}{=} \hat{c}_0$. Then the explicit EULER method is given by the formulae, [106]:

$$\eta_{i+1} = \eta_i + \Delta t \cdot f(\eta_i)$$
 and $t_{i+1} = t_i + \Delta t$ (4.21)

or in a more general way:

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

EULER: $\Gamma(\hat{c}_i, \Delta t) = f(\hat{c}_i) = d\hat{c}(t_i)/dt$, (4.22)

i.e., in case of the EULER method the function Γ is independent from Δt . 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* τ . For this reason we define the *difference quotient* of the *exact* solution by:

$$\boldsymbol{\Delta}(\hat{c}, \Delta t) = \begin{cases} \frac{\hat{c}(t+\Delta t)-\hat{c}(t)}{\Delta t} & \text{if } \Delta t \neq 0\\ f(\hat{c}) & \text{if } \Delta t = 0 \end{cases}$$
(4.23)

From Eq. $(4.22)_1$ one finds the the corresponding difference quotient of the approximated solution, namely:

$$\Gamma(\hat{c}_i, \Delta t) = \frac{\eta_{i+1} - \eta_i}{\Delta t} .$$
(4.24)

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

$$\lim_{\Delta t \to 0} \tau = 0 \tag{4.25}$$

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 τ converges to 0 for $\Delta t \to 0$, we assume f to be sufficiently smooth (differentiable). The TAYLOR series of \hat{c} reads:

$$\hat{c}(t + \Delta t) = \hat{c}(t) + \Delta t \cdot f(\hat{c}) + \frac{(\Delta t)^2}{2} \cdot f'(\hat{c}) + \dots + \frac{(\Delta t)^p}{p!} \cdot f^{(p-1)}(\hat{c})$$
(4.26)

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

$$\tau(\hat{c},\Delta t) = \frac{\Delta t}{2} \cdot f'(\hat{c}) + \dots = \mathcal{O}(\Delta t) .$$
(4.27)

In general a method is called to be of *convergence-order* p, if $\tau = \mathcal{O}[(\Delta t)^p]$. 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 $\Gamma(\hat{c}_i, \Delta t)$ in Eq. $(4.22)_{1,2}$ such, that after the TAYLOR expansion in Eq. (4.26) and after the calculation of τ in Eq. (4.27) higher order terms of Δt remain.

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

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

v. HEUN: $\Gamma(\hat{c}_i, \Delta t) = \frac{1}{2} \left[f(\hat{c}_i) + f(\hat{c}_i + \Delta t \cdot f(\hat{c}_i)) \right],$ (4.28)

which can be understood as the average between the slope of \hat{c}_i and \hat{c}_{i+1} , cf., Figure 4.2 (Right). This method is called the v. HEUN approximation and its convergence-order is 2, [106].

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

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

n-th-order R.-K. : $\Gamma(\hat{c}_i, \Delta t) = \gamma_1 k_1 + \gamma_2 k_2 + \gamma_3 k_3 + \ldots + \gamma_n k_n$. (4.29)

The different k_i 's (i = 1, 2, 3, ..., n) can be calculated by the following relations, [82]:

$$k_{1} = f(\hat{c}_{i}),$$

$$k_{2} = f(\hat{c}_{i} + \Delta t \cdot \beta_{21} \cdot k_{1}),$$

$$k_{3} = f(\hat{c}_{i} + \Delta t \cdot [\beta_{31} \cdot k_{1} + \beta_{32} \cdot k_{2}]),$$

$$\vdots$$

$$k_{n} = f(\hat{c}_{i} + \Delta t \cdot [\beta_{n1} \cdot k_{1} + \beta_{n2} \cdot k_{2} + \dots + \beta_{n(n-1)} \cdot k_{n-1}]).$$
(4.30)

The coefficients β_{kl} and γ_k (k = 1, 2, 3, ..., n and l = 1, 2, 3, ..., (n-1)) are constant and can be found from the so-called *Butcher-diagram*, [82], which has the form:

$$\begin{array}{c|ccccc} 0 & & \\ \alpha_2 & \beta_{21} & \\ \alpha_3 & \beta_{31} & \ddots & \\ \vdots & \vdots & \\ \alpha_n & \beta_{n1} & \dots & \beta_{n(n-1)} \\ \hline & & \gamma_1 & \dots & \gamma_{n-1} & \gamma_n \end{array}$$

 Table 4.1: General form of the Butcher-diagram.

Note that the coefficients α_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: Butcher-diagram for the Simpson rule.

 \diamond classical RUNGE-KUTTA method (4th order):

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

$$\Gamma(\hat{c}_i, \Delta t) = \frac{1}{6} [k_1 + 2 \cdot k_2 + 2 \cdot k_3 + k_4] \quad \text{and}$$
(4.31)

$$k_1 = f(\hat{c}_i) , \qquad (4.32)$$

$$k_2 = f\left(\hat{c}_i + \frac{1}{2} \cdot \Delta t \cdot k_1\right) , \qquad (4.33)$$

$$k_3 = f\left(\hat{c}_i + \frac{1}{2} \cdot \Delta t \cdot k_2\right) , \qquad (4.34)$$

$$k_4 = f\left(\hat{c}_i + \Delta t \cdot k_3\right) \tag{4.35}$$

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

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

$$\Gamma(\hat{c}_i, \Delta t) = \frac{1}{6} [k_1 + 4 \cdot k_2 + k_3] \quad \text{and}$$
(4.36)

$$k_1 = f(\hat{c}_i) , \qquad (4.37)$$

$$k_2 = f\left(\hat{c}_i + \frac{1}{2} \cdot \Delta t \cdot k_1\right) , \qquad (4.38)$$

$$k_3 = f(\hat{c}_i + \Delta t \cdot [-k_1 + 2 \cdot k_2]) .$$
(4.39)

b. (Semi-)Implicit Methods

For various problems (for example for ODE's with exponentially decreasing solutions, e.g., $d_t c(t) = \lambda \cdot c(t)$, c(0) = 1 and $\lambda < 0$, cf, [19]) 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 $f^i: \mathbb{R}^N \to \mathbb{R}$:

$$\frac{\mathrm{d}\hat{c}^{i}}{\mathrm{d}t} = f^{i}(\hat{c}^{j}) \qquad , \qquad \hat{c}^{i}(t_{0}) = \hat{c}^{i}_{0} \qquad , \qquad (i, j = 1, 2, 3, \dots, N) .$$

$$(4.40)$$

We denote the approximation of the exact solution, $\hat{c}_n = \hat{c}(t_n) \wedge t_{n+1} = t_n + \Delta t$, according to the previous paragraph, by η_n . Then the *implicit* EULER scheme³ is defined by the recursive equation, [19]:

$$\eta_{n+1}^i = \eta_n^i + \Delta t \cdot f^i(\eta_{n+1}^j) \qquad , \qquad \eta_0^i \stackrel{\text{(def)}}{=} \hat{c}_0^i \qquad \text{(impl. EULER sheme)} \ . \ (4.41)$$

For known variables η_n^i in Eq. (4.41) generally represents a (most cumbersome) nonlinear, *algebraic system of equations* of the form:

$$g^i(\eta^j_{n+1}) = 0 (4.42)$$

for the unknown variables η_{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 $\bar{\eta}_{n+1}^{j}$:

$$0 = g^{i}(\bar{\eta}_{n+1}^{j}) = g^{i}(\eta_{n+1,(0)}^{j}) + \frac{\partial g^{i}}{\partial \eta_{n+1}^{j}} \Big|_{\eta_{n+1,(0)}^{j}} \cdot (\bar{\eta}_{n+1}^{j} - \eta_{n+1,(0)}^{j}) + \dots$$
(4.43)

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

$$\eta_{n+1,(k+1)}^{j} = \eta_{n+1,(k)}^{j} - \frac{g^{i}(\eta_{n+1,(k)}^{j})}{[\mathcal{D}g]^{ij}(\eta_{n+1,(k)}^{j})} \qquad (\text{NEWTON iteration}) , \qquad (4.44)$$

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

³Another notation frequently found is *backward* EULER *sheme/method*.



Figure 4.3: Illustration of the NEWTON iteration in order to find the root of the nonlinear function $g(\eta_{n+1})$.

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 $g(\eta_{n+1}) = 0$.

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:

$$\eta_{n+1}^{i} = \eta_{n}^{i} + \Delta t \cdot \left[f^{i}(\eta_{n}^{j}) + \frac{\partial f^{i}(\eta_{n}^{j})}{\partial \eta_{n}^{j}} \cdot (\eta_{n+1}^{j} - \eta_{n}^{j}) + \dots \right]$$
(4.45)

and by rearrangement:

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

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 $[\mathbf{1} - \Delta t \cdot \mathbf{Df}]$ containing the JACOBI matrix $\mathbf{Df} \in \mathbb{R}^{N \times N}$.

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 $q > p \land p, q \in \mathbb{N}_{\setminus \{0\}}$, and to adjust the time step such that the derivation between the different solutions goes below a critical (user specific) tolerance value ε .

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 $\stackrel{(p)_i}{\eta}_{n+1}$ and $\stackrel{(q)_i}{\eta}_{n+1}$, for instance:

$$z = \max_{i} \left| \begin{array}{c} \eta_{n+1}^{(q)_{i}} - \begin{array}{c} \eta_{n+1}^{(p)_{i}} \\ \eta_{n+1}^{(q)_{i}} - \begin{array}{c} \eta_{n+1}^{(p)_{i}} \\ \eta_{n+1}^{(q)_{i}} - \begin{array}{c} \eta_{n+1}^{(p)_{i}} \\ \eta_{n+1}^{(q)_{i}} \end{array} \right|^{2}.$$
(4.48)

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

IF THE RELATION

$$\frac{\varepsilon}{10} \le z < \varepsilon \quad , \quad (\varepsilon > 0) \tag{4.49}$$

HOLDS, THEN KEEP Δt and go to the next time iteration, else repeat the iteration with

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

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 ε and increases the time step for values $z > \varepsilon$. Furthermore p and α 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 "5th-order solution," a fact, that saves much computational time, [21].

4.2 Simulation of Phase Separation and Coarsening in Ag-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* $c(X^j, t)$ and the *displacements* $U^i(X^j, t)$, which are determined by the following balances:

$$\rho_0 \frac{\mathrm{d}c}{\mathrm{d}t} + \frac{\partial J^i}{\partial X^i} = 0 \quad \text{(partial mass balance)}, \qquad (4.51)$$

$$\frac{\partial p^{ij}}{\partial X^j} = 0 \quad \text{(static momentum balance)} . \tag{4.52}$$

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

$$J^{i} = -\rho_{0}\mathcal{M}^{ij}(T)\nabla^{j}\left[\frac{\partial(\mathbb{F}_{0}^{\text{chem}} + \mathbb{F}_{0}^{\text{mech}})}{\partial c} - 2A^{kl}\frac{\partial^{2}c}{\partial X^{k}\partial X^{l}} - \frac{\partial A^{kl}}{\partial c}\frac{\partial c}{\partial X^{k}}\frac{\partial c}{\partial X^{l}}\right] - 2\frac{\partial A^{kl}}{\partial \varepsilon^{mn}}\frac{\partial c}{\partial X^{k}}\frac{\partial \varepsilon^{mn}}{\partial X^{l}} - \frac{\partial^{2}a^{kl}}{\partial \varepsilon^{op}\varepsilon^{mn}}\frac{\partial \varepsilon^{op}}{\partial X^{k}}\frac{\partial \varepsilon^{mn}}{\partial X^{l}} - \frac{\partial a^{kl}}{\partial \varepsilon^{mn}}\frac{\partial^{2}\varepsilon^{mn}}{\partial X^{k}\partial X^{l}}\right], \quad (4.53)$$

$$p^{ij} \approx \sigma^{ij} \approx \frac{\partial \mathbb{F}}{\partial \varepsilon^{ij}} = \sigma^{ij}_{\text{local}} - \frac{\partial a^{kl}}{\partial \varepsilon^{ij}} \frac{\partial^2 c}{\partial X^k \partial X^l} + \frac{\partial b^{kl}}{\partial \varepsilon^{ij}} \frac{\partial c}{\partial X^k} \frac{\partial c}{\partial X^l} ,$$
 (4.54)

in which the following dependencies exist: $\rho_0 = \text{const.}$, $\mathbb{F}_0 = \mathbb{F}_0(T, c, \varepsilon^{ij})$, $a^{kl} = a^{kl}(T, c, \varepsilon^{ij})$, $b^{kl} = b^{kl}(T, c, \varepsilon^{ij})$, and $A^{kl} = A^{kl}(T, c, \varepsilon^{ij})$. By considering Eq. (4.54) we assume that $\sigma_{\text{local}}^{ij}$ 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, $\sigma_{\text{local}}^{ij}$, can be calculated from HOOKE's law, *i.e.*,

$$\sigma_{\text{local}}^{ij} = K^{ijkl}(T,c) \left(\varepsilon^{kl} - \alpha^{kl} \Delta T \right) \quad , \quad \mathbb{F}_0^{\text{mech}} = \frac{1}{2} \sigma^{ij} \left(\varepsilon^{ij} - \alpha^{ij} \Delta T \right) \quad , \quad (4.55)$$

$$\varepsilon^{ij} = \frac{1}{2} \left(\frac{\partial U^i}{\partial X^j} + \frac{\partial U^j}{\partial X^i} \right) , \quad \alpha^{ij} = \alpha \delta^{ij} \quad \text{(therm. expan. coeff.)}. \quad (4.56)$$

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.*, $\varepsilon_{\text{elast}}^{kl} = \varepsilon^{kl} \alpha^{kl} \Delta T = 0, \forall \{k, l\}.$
- (b) 1D simulations under the presence of one-dimensional local thermo-mechanical strains⁴ ("line strains"), *i.e.*, $\varepsilon_{\text{elast}}^{11} = \varepsilon_{\text{elast}} \neq 0 \land \varepsilon_{\text{elast}}^{kl} = 0, \forall \{k, l\} = \{k, l | k \cdot l > 0\}.$
- (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^{ijkl} and for the thermal expansion coefficient α^{kl} within the smoothly changing phase boundary between the two equilibrium phase α and β , *viz*.:

$$\Xi(c) = \Theta(c) \Xi_{\alpha} + (1 - \Theta(c)) \Xi_{\beta} , \quad \Xi_{\alpha/\beta} = \{K_{\alpha/\beta}^{ijkl}, \alpha_{\alpha/\beta}^{kl}\} ,$$

$$\Theta(c) = \frac{c_{\beta} - c(X, t)}{c_{\beta} - c_{\alpha}} \quad \text{(shape function)}. \tag{4.57}$$

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

 $^{^4{\}rm This}$ strain state denotes the one-dimensional equivalent to the two-dimensional case of *plane strains*.

 $K^{55} = K^{66}$ (VOIGT notation), *cf.*, Table 3.3. By assuming in Eq. (4.54) $\sigma_{\text{local}}^{ij}$ to be the leading term one obtains from HOOKE's law:

$$\sigma^{11} = \left[K_{\beta}^{11} - \Theta(c) (K_{\beta}^{11} - K_{\alpha}^{11}) \right] (\varepsilon^{11} - \alpha^{11} \Delta T) , \qquad (4.58)$$

$$\sigma^{22} = \left[K_{\beta}^{12} - \Theta(c) (K_{\beta}^{12} - K_{\alpha}^{12}) \right] (\varepsilon^{11} - \alpha^{11} \Delta T) , \qquad (4.59)$$

$$\sigma^{33} = \left[K_{\beta}^{13} - \Theta(c) (K_{\beta}^{13} - K_{\alpha}^{13}) \right] (\varepsilon^{11} - \alpha^{11} \Delta T) , \qquad (4.60)$$

$$\sigma^{12} = \sigma^{13} = \sigma^{23} = 0. (4.61)$$

From the static balance of momentum in the form $\partial \sigma^{ij} / \partial X^j = 0$ 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:

$$\frac{\mathrm{d}\sigma^{11}}{\mathrm{d}X} = 0 \quad \Rightarrow \quad \sigma^{11} = \sigma_0 = \mathrm{const.}$$
(4.62)

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

$$\varepsilon_{\text{elast}}^{11} = \frac{\sigma_0}{K_{\beta}^{11} - \frac{c_{\beta} - c(X,t)}{c_{\beta} - c_{\alpha}} (K_{\beta}^{11} - K_{\alpha}^{11})} \quad , \tag{4.63}$$

$$\mathbb{F}_{0}^{\text{mech}} = \frac{1}{2} \frac{\sigma_{0}^{2}}{K_{\beta}^{11} - \frac{c^{\beta} - c(X,t)}{c_{\beta} - c_{\alpha}} (K_{\beta}^{11} - K_{\alpha}^{11})} \quad .$$
(4.64)

Eqs. (4.63, 4.64) can be directly used in order to substitute the $\mathbb{F}_0^{\text{mech}}$ -term as well as the ε^{ij} -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 HELMHOLTZ free energy $\mathbb{F}_0^{\text{chem}}$,
- (ii) the stiffness matrix $K^{11}_{\alpha/\beta}$ and the thermal expansion coefficients α^{11} ,
- (iii) the mobility \mathcal{M}^{ij} , and
- (iv) the HGCs a^{kl} , b^{kl} , and A^{kl} .

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

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 MTdataTM database⁵ [83], which provides a field of discrete values $\mathbb{F}_0^{\text{chem}}(c_i)$, $c_i = \{0, 0.01, 0.02, \ldots, 0.99, 1\}$ 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

$$\mathbb{F}_{0}^{\text{chem}}(c) = (1-c)g_{a} + cg_{b} + g_{c}RT [c \ln c + (1-c)\ln(1-c)] + c(1-c) [\chi_{I}c + \chi_{II}(1-c)] ,$$
(4.65)

where R = 8.314 [J/(mol K)] stands for the universal gas constant. The introduced fit parameters g_a , g_b , g_c , χ_I , and χ_{II} 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, $c_{1/2}^{\rm sp}$, resulting from the roots of $\partial^2 \mathbb{F}_0^{\rm chem} / \partial c^2$. The corresponding curves are displayed in Figure 4.4.

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

$g_{\rm a} \left[\frac{{\rm GJ}}{{ m m}^3} \right]$	$g_{\rm b} \left[\frac{{\rm GJ}}{{ m m}^3} ight]$	$g_{\rm c} \left[\frac{{ m mole}}{{ m m}^3} ight]$	$\chi_{\rm I} \left[\frac{{\rm GJ}}{{ m m}^3} \right]$	$\chi_{\rm II} \left[\frac{{\rm GJ}}{{ m m}^3} \right]$	$ c_{\rm eut} $	c_{α}	c_{β}	c_1^{sp}	c_2^{sp}
-5.20	-7.27	$1.11\cdot 10^5$	2.97	3.01	0.29	0.063	0.945	0.19	0.79
$\mathbb{F}_{0}^{\rm chem}$ in GJ/m ³ 				$egin{array}{l} egin{array}{ll} \partial^2 \mathbb{F}_0^{ m chem}/\partial c^2 \ { m in} \ { m GJ}/{ m m}^3 \ { m CJ} \ { m chem} \$					
0	0.2	0.4 0.6	U.8 I		0 (J.2 U	.4 0.6	0.8	1

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

⁵Note that MT data make no difference between the HELMHOLTZ and the GIBBS free energy.

b. Mobility, Stiffness, and Thermal Expansion Coefficient

By comparison of the first and second FICK's law, *i.e.*, $d_t c = -\partial J^i / \partial X^i$ with $J^i = -D^{ij}(\partial c / \partial X^j)$ 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^{ij} and the mobility \mathcal{M}^{ij} :

$$D^{ij} = \mathcal{M}^{ij} \frac{\partial^2 \mathbb{F}_0^{\text{chem}}}{\partial c^2} \quad \Rightarrow \quad \mathcal{M}^{ij}_{\alpha/\beta} = \frac{D^{ij}_{\alpha/\beta}}{\frac{\partial^2 \mathbb{F}_0^{\text{chem}}}{\partial c^2}} \bigg|_{c=c_{\alpha/\beta}}.$$
(4.66)

The diffusion coefficients for the pure substances $D_{Ag/Cu}^{ij} = D_{Ag/Cu} \delta^{ij}$ 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 $c_1^{\text{sp}} < c < c_2^{\text{sp}}$. 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 α - and β -phases are extremely Ag- or Cu-containing. Therefore it is reasonable to approximate for the equilibrium phases:

$$\Xi_{\alpha} \approx \Xi_{Ag}$$
 and $\Xi_{\beta} \approx \Xi_{Cu}$ with $\Xi = \{K^{11}, \alpha^{11}, \mathcal{M}^{ij}\}.$ (4.67)

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.

$\left. K_{ij}^{kl} \right _{\mathrm{Ag}}$	11	22	33	23	31	12	$\left \begin{array}{c} K_{ij}^{kl} \end{array} \right _{\mathrm{Cu}}$	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 4.4: Stiffness matrix of pure silver and copper in GPa and in VOIGT notation, Source: [71].

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

$D_{\alpha} [\mathrm{m}^2/\mathrm{s}]$	$D_{\beta} [\mathrm{m}^2/\mathrm{s}]$	$M_{\alpha} [\mathrm{m}^5/\mathrm{Js}]$	$M_{\beta} [\mathrm{m}^5/\mathrm{Js}]$	$\alpha_{\alpha}^{11} \; [10^6/\mathrm{K}]$	$\alpha_\beta^{11} \ [10^6/\mathrm{K}]$
1.01×10^{-14}	4.09×10^{-15}	7.25×10^{-25}	3.65×10^{-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 cand of the strains ε^{kl} , cf., Section 3.4.2 and 3.5.5. According to Eqs. (3.65–3.69) the following compact form holds for the HGCs:

$$a^{kl}(c,\varepsilon^{ij}) = -\delta(c)\frac{\partial\tilde{y}(c)}{\partial c} \cdot \mathbb{H}^{kl}(c,\varepsilon^{ij}) , \quad b^{kl}(c,\varepsilon^{ij}) = \delta(c)\frac{\partial^2\tilde{y}(c)}{\partial c^2} \cdot \mathbb{H}^{kl}(c,\varepsilon^{ij}) , \quad (4.68)$$

$$A^{kl} \stackrel{\text{(def)}}{=} \frac{\partial a^{kl}}{\partial c} + b^{kl} , \quad \tilde{y}(c) = \frac{cM_{\rm A}}{M_{\rm B} - c(M_{\rm B} - M_{\rm A})} , \quad \text{and}$$
(4.69)

$$\mathbb{H}^{kl}(c,\varepsilon^{ij}) = \mathbb{H}^{kl}_0(c) + \varepsilon^{mn} \mathbb{H}^{mnkl}_1(c) + \varepsilon^{mn} \varepsilon^{pq} \mathbb{H}^{mnpqkl}_2(c) .$$
(4.70)

The functions \mathbb{H}_{0}^{kl} (cf., first row of Eq. (3.69)), \mathbb{H}_{1}^{mnkl} (cf., second and third row of Eq. (3.69)), and \mathbb{H}_{2}^{mnpqkl} (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}^{kl} contains a linear term w.r.t. ε^{ij} , 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 $(\mathbf{a}-\mathbf{c})$ 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 $\Xi^{kl} = \Xi^{11}\delta^{kl}$ 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 Δt 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:

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

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_{ε}^{Ξ} , $k_{c\varepsilon}^{\Xi}$, $k_{c\varepsilon}^{\Xi}$, and k_{0}^{Ξ} . For this reason the HGC values following from the curves in Figure 3.10 (first column) with the *ad hoc* chosen arguments

$$(c,\varepsilon) = \left\{ (c_{\alpha},0), (c_{\beta},0), (c_{\alpha},\pm0.2), (c_{\beta},\pm0.2) \right\}$$
(4.72)

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

Ξ	k_{ε}^{Ξ} in N	k_c^{Ξ} in N	$k_{c\varepsilon}^{\Xi}$ in N	k_0^{Ξ} in N
$\varepsilon > 0$ (tensile loading)				
$ \begin{array}{c} a^{11} \\ b^{11} \\ A^{11} \end{array} $	$\begin{array}{r} -3.79 \cdot 10^{-10} \\ -5.22 \cdot 10^{-10} \\ -5.74 \cdot 10^{-10} \end{array}$	$\begin{array}{c} 8.74 \cdot 10^{-11} \\ 4.72 \cdot 10^{-11} \\ 3.74 \cdot 10^{-11} \end{array}$	$-6.40 \cdot 10^{-11} \\ 1.64 \cdot 10^{-10} \\ 1.50 \cdot 10^{-10}$	$\begin{array}{c} 4.04 \cdot 10^{-11} \\ 5.84 \cdot 10^{-11} \\ 1.53 \cdot 10^{-10} \end{array}$
$\varepsilon < 0$ (compres. loading)				
$ \begin{array}{c} a^{11} \\ b^{11} \\ A^{11} \end{array} $	$\begin{array}{r} -1.11\cdot 10^{-9} \\ -1.52\cdot 10^{-9} \\ -1.10\cdot 10^{-9} \end{array}$	$\begin{array}{c} 8.74 \cdot 10^{-11} \\ 4.72 \cdot 10^{-11} \\ 3.74 \cdot 10^{-11} \end{array}$	$\begin{array}{c} 1.91 \cdot 10^{-10} \\ 7.77 \cdot 10^{-10} \\ 3.80 \cdot 10^{-10} \end{array}$	$\begin{array}{c} 4.04 \cdot 10^{-11} \\ 5.84 \cdot 10^{-11} \\ 1.53 \cdot 10^{-10} \end{array}$

Table 4.6: Interpolated coefficients for the HGCs as bilinear functions of c and ε .

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]:

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

in which the factors L, Ψ_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 $\Delta \tilde{t}$

 $^{^6\}mathrm{See}$ also [14] for a detailed investigation of the impact of the different numerical parameters on the simulation.

1		0			
Simulations	Ψ_0 in $\frac{GJ}{m^3}$	$2\pi L$ in μm	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	128×128	$0.1\cdot 10^{-5}$
2D (Euler, 16 fluc.)	0.1	0.05	1.462	128×128	$0.1\cdot 10^{-5}$
2D (RADAU)	0.1	0.05	1.462	128×128	

Table 4.7: Numerical parameters used during the simulations.

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:

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

with the definition for the symbol Υ :

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

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

$$\mathfrak{F}\left[\frac{\Delta c(\alpha)}{\Delta \alpha}\right] = \mathfrak{F}[c(\alpha)] \cdot \tilde{\xi}^{(1)} \quad , \quad \tilde{\xi}^{(1)}(s) = -\frac{\mathrm{i}}{\tilde{h}} \sin\left(\frac{2\pi s}{N}\right) \; , \tag{4.76}$$

$$\mathfrak{F}\left[\frac{\Delta^2 c(\alpha)}{\Delta \alpha^2}\right] = \mathfrak{F}[c(\alpha)] \cdot \tilde{\xi}^{(2)} \quad , \quad \tilde{\xi}^{(2)}(s) = \frac{2}{\tilde{h}^2} \left[\cos\left(\frac{2\pi s}{N}\right) - 1\right] \quad . \tag{4.77}$$

hold, in which the symbol $s = L \cdot k = 0, 0, 2, ..., N - 1$ 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 {...} of Eq. (4.74), reads:

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

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 Ag-Cu.

4.2.4 One-Dimensional Simulations⁷

First, we investigate the one dimensional case according to Eq. (4.74). Figures 4.6– 4.8 display the spinodal decomposition and coarsening process along a "line" in Ag-Cu at 1000 Kelvin. Here we started with an *eutectic* homogeneous concentration profile ($c_{eut} = 0.29$), 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 α - and β -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

⁷The 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].

⁸The authors used a constant value of $\gamma_{\rm CH} = \kappa \lambda^2 = 1 \cdot 10^{-5}$ N (in their notation).

⁹Within this work the authors considered an Al-In system and chose a constant HGC of $\gamma = 2 \cdot 10^{-10}$ N (in their notation).



Figure 4.6: One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 Kelvin (strain-free case).



Figure 4.7: One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 Kelvin (tensile loading of $\sigma_0 = 5000$ MPa).



Figure 4.8: One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 Kelvin (pressure loading of $\sigma_0 = -5000$ 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 cf., 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:

$$256 \text{ grid points} = 0.06 \,\mu\text{m} \quad \Leftrightarrow \quad 9 \text{ grid points} = 2.1 \,\text{nm} = 21 \,\text{\AA} \,, \quad (4.79)$$

which corresponds to approximately *seven* atomic distances $(r_{Ag} = 2.88 \text{ Å})$ 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 $A^{11} = A^{11}_{\text{EAM}}$, $A^{11} = 2 \cdot A^{11}_{\text{EAM}}$, and $A^{11} = 4 \cdot A^{11}_{\text{EAM}}$. Second Row: According zoomed interface areas.

 10 See also [14].

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 $\sigma_0 = \pm 5000$ 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 Simulations¹¹

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 β -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

 $^{^{11}\}mathrm{See}$ footnote 7.



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, cf, 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 β 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 Ag-Cu 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 Ag-Cu 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 Ag-Cu 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:

$$c = \begin{cases} c_{\alpha} & \text{if } c \le c^{\text{crit}} \\ c_{\beta} & \text{if } c \ge c^{\text{crit}} \end{cases} \quad \text{with} \quad c^{\text{crit}} = \frac{c_{\alpha} + c_{\beta}}{2} . \tag{4.80}$$

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 s (10 000 000 loops) and t = 151.6 s (180 000 000 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 MathematicaTM in order to determine the total intercept length, l^{β} , as well as the total number, N, of the β -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 135ff. Analogously to the Eqs. (5.4,5.5) one can use the following relations to calculate a 3D-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):

$$\bar{r}^{\beta} = \frac{3}{4} \cdot \bar{l}^{\beta} \quad \text{(spherical phases)}, \qquad (4.81)$$
$$\bar{a}^{\beta} = \frac{1}{1.278} \cdot \bar{l}^{\beta} \quad \text{(oblate spheroids with } b/a = 0.5, cf., Figure 5.3), \qquad (4.82)$$

where we assumed the phases to be spherical with the mean phase radius \bar{r}^{β} or oblatespheroid with \bar{a}^{β} , 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:

$$\bar{r}^{\beta} = 0.00082 \cdot t^{1/3}$$
 and $\bar{a}^{\beta} = 0.00086 \cdot t^{1/3}$ (1D, strain-free case). (4.83)

Finally, we consider the coarsening behavior under tensile and pressure loading (±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).

8			
\tilde{t} in sec	\bar{l}^{β} in μm	$ar{r}^{eta}$ in $\mu { m m}$	\bar{a}^{β} in μm
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

Table 4.8: Coarsening values obtained from the analysis of the simulated 1D-micrographs in Figure 4.6–4.8.



Figure 4.17: The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin obtained from the strain-free 1D simulations.



Figure 4.18: The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 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 DHS[©], which yields the total number, N, as well as the total intercept area, A^{β} , of the β -phases. Following the considerations in Section 5.2 on page 135ff. we calculate the mean radii \bar{r}^{β} (for spherical shapes) and \bar{a}^{β} (for oblate-spheroid shapes) of the β -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:

$$\bar{r}^{\beta} = 0.0071 \cdot t^{1/3}$$
, $\bar{a}^{\beta} = 0.0092 \cdot t^{1/3}$ (2D, strain-free, EULER), (4.84)

and for the RADAU solver:

$$\bar{r}^{\beta} = 0.0098 \cdot t^{1/3}$$
, $\bar{a}^{\beta} = 0.013 \cdot t^{1/3}$ (2D, strain-free, RADAU). (4.85)

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 ≈ 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.

$\tilde{t} \cdot t_0$ in sec	$\mid N$	$ar{A}^{eta}$ in $\mu \mathrm{m}^2$	\bar{r}^{β} in μm	\bar{a}^{β} in μm
$0.015 \cdot 1.462$	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 4.9: Different values obtained from the digital image analysis of the simulated 2D micrographs in Figure 4.12.

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	$\mid N$	\bar{A}^{β} in μm^2	\bar{r}^{β} in μm	\bar{a}^{β} in μm
$0.0088 \cdot 1.462$	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}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin obtained from the 2D simulations in Figure 4.12.



Figure 4.20: The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin obtained from the 2D simulations in Figure 4.14.

Konstantin Simonow (1915 - 1979)

Chapter 5

Experimental Investigations

In this section the eutectic, binary brazing alloy Ag-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 Ag-Cu (*i.e.*, 71 wt% Ag and 29 wt% 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 Ag-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 Cu¹) a "splodge- or button-like" sample of eutectic Ag-Cu was produced (diameter: ≈ 40

¹Note that the binary alloy Ag-Cu has a comparatively low eutectic temperature of $T_{\text{eut}} \cong 779 \,^{\circ}\text{C}$ whereas the pure substances Ag and Cu have melting temperatures of $T_{\text{eut}} \cong 962 \,^{\circ}\text{C}$ (Ag) and $T_{\text{eut}} \cong 1085 \,^{\circ}\text{C}$ (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 $^{\circ}\text{C}$.

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 (*cf.*, 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 H₂O: five drops,

GRINDING				
step	graining (grain diameter in μ m)	press capacity	time	
01.	220 (66)	10 N	15 s	
02.	500 (30)	20 N	60 s	
03.	1000 (18)	20 N	60 s	
04.	1000	10 N	60 s	
05.	4000 (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	

Table 5.1: Performed grinding and polishing steps for eutectic Ag-Cu.

- diluted ammoniac, (25%): five drops,
- diluted hydrogen peroxide $(30\%, H_2O_2)$: 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 Ag-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 (α) 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 micro-morphological 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 Ag-Cu the following working temperature is chosen in these experiments:

$$T = 700 \,^{\circ}\text{C} = 973.15 \,\text{K} \qquad \Rightarrow \qquad T_{\text{hom}} = \frac{T}{T_{\text{eut}}} = 0.899 \;.$$
 (5.1)

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 h, 5 h, 10 h, 20 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 $t \geq 5$ h.

5.2 On the Quantification of Coarsening

In order to determine the coarsening rate of the precipitated Cu-rich (β) 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 β -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 β -phases for a fixed *intercept area*. Consequently the observed amount of β -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^{β} : surface area of a single β -phase,
- A^{β} : averaged surface area of a β -phase of an individual photo (*i.e.*, for a fixed intercept area),
- \bar{A}^{β} : averaged surface area of a β -phase of the coarsening stage (results from all photos of a fixed stage),
- N: number of β -phases of one photo/intercept area,
- \bar{r}^{β} : mean phase radius using the assumption of spherical phase shapes,
- \bar{a}^{β} : mean phase radius using the assumption of oblate spheroids.

Thus the following relations can be formulated:

$$A^{\beta} = \frac{1}{N} \sum_{i=1}^{N} A_{i}^{\beta} \quad \text{(for the individual photos)}, \qquad (5.2)$$

$$\bar{A}^{\beta} = \frac{1}{6} \sum_{\text{photos}} A^{\beta}$$
 (for the individual stages). (5.3)

Additionally one can also calculate the *mean phase radius* \bar{r} and \bar{a} . Here it holds with [114]:

$$\bar{r}^{\beta} = \sqrt{\frac{3\bar{A}^{\beta}}{2\pi}} \quad \text{(spherical phases)}, \qquad (5.4)$$

$$\bar{a}^{\beta} = \sqrt{\frac{A^{\beta}}{1.235}}$$
 (oblate spheroids with $b/a = 0.5$). (5.5)

Note that the volume of the oblate spheroid is given by $V = \frac{4}{3}\pi a^2 b$ for a = b (*cf.*, 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 Ag-Cu at ≈ 1000 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 α -matrix ($c^{\alpha} = 0.063$), whereas the dark areas denote the Cu-rich β -phase ($c^{\beta} = 0.945$).



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 β -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 h, 10 h, 20 h, 40 h (scale factor 1:500).



Figure 5.6: *Etched* photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after solidification, 2 h, 5 h, 10 h, 20 h, 40 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 h, 10 h, 20 h, 40 h (scale factor 1:1000).



Figure 5.8: *Etched* photos of the temporal development of the micromorphology in Ag-Cu. From upper left to lower right: after solidification, 2 h, 5 h, 10 h, 20 h, 40 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 β -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 2h 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 h, 5 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_{β} and N illustrated, exemplarily for the displayed photos, in Table 5.2. The software ignored all regions with a value of $A^i_{\beta} = 0 \,\mu \text{m}^2$ (e.g. small dark points), which are assumed to be imperfections² (e.g., due to uncleanliness).

²The limit value, under which the software set $A^i_\beta = 0 \,\mu \mathrm{m}^2$ is an intern parameter of the image



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}_{β} 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

analysis package.



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:

$$\bar{r}^{\beta} = 0.024 \cdot t^{1/3}$$
 and $\bar{a}^{\beta} = 0.032 \cdot t^{1/3}$. (5.6)

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 OSTWALD-ripening, [96] - by means of the GIBBS-THOMSON effect.

Time	Scaling factor	$A_{\beta} \text{ in } \mu \text{m}^2$	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 5.2: Values calculated by the image analysis software, exemplarily for the illustrated Figures 5.9-5.13.

Table 5.3: Mean phase radii for different coarsening stages and different types of phase shapes (assumed).

time	spherical shaped	oblate spheroid shaped
	$ar{r}^{eta}$ in $\mu { m m}$	$ar{a}^{eta}$ in $\mu { m m}$
2 h	0.76 ± 0.28	0.99 ± 0.37
5 h	0.61 ± 0.18	0.79 ± 0.23
10 h	0.82 ± 0.33	1.07 ± 0.43
20 h	1.04 ± 0.48	1.36 ± 0.63
40 h	1.24 ± 0.30	1.62 ± 0.39



Figure 5.14: The temporal development of the mean phase radius \bar{r}^{β} and \bar{a}^{β} in eutectic Ag-Cu at ≈ 1000 Kelvin observed in experiments. Dashed line: spherical phase shape. Continuous line: oblate spheroid-shaped phase.

Wir alle lassen uns vom Streben nach Anerkennung mitreißen. Gerade die besten lassen sich durch den Gedanken an Ruhm leiten. Denn selbst jene Philosophen, die über die Geringschätzung des Ruhmes schreiben, setzten ihre Namen auf die Bücher.

Cicero, (106 - 43 v. Chr.)

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 (sphere, $\bar{r}^{\beta} = k_s \cdot t^{1/3}$)	k_o (oblate-spheroids, $\bar{a}^{\beta} = k_o \cdot t^{1/3}$)
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}^{β} or \bar{a}^{β} 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 2D.

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, *cf.*, 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 Ag-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 Ag-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 Ag-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 Ag-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 Ag-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 Ag-Cu in 1D and 2D 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 $(\tau_{\alpha}^{\rho/n} \neq 0)$ 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 $(\sigma_{diss}^{ij} \neq 0)$ are conceivable for future studies. Nevertheless, questions regarding (3) the microstructural evolution in ternary systems, such as Sn-Ag-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, cf., 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 Sn-Ag or Sn-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.

Isaac Newton, (1643 - 1727)

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 CAUCHY-GREEN tensor c^{kl} and the CAUCHY-GREEN tensor C^{kl} according to Section 2.2:

$$\dot{c}^{kl} = \frac{\mathrm{d}}{\mathrm{d}t} \left(J^{-2/3} C^{kl} \right) = -\frac{2}{3} J^{-5/3} \dot{J} C^{kl} + J^{-2/3} \dot{C}^{kl} .$$
(A.1)

Moreover we have the identity:

$$\dot{J} = \frac{\mathrm{d}}{\mathrm{d}t} \left(\det F^{ij} \right) = \left[\frac{\partial}{\partial F^{kl}} \left(\det F^{ij} \right) \right] \dot{F}^{kl} = \left[(\det F^{ij}) (F^{-1})^{lk} \right] \frac{\partial v^k}{\partial X^l} = J \frac{\partial v^k}{\partial x^k}$$
(A.2)

and

$$\dot{C}^{kl} = \frac{\mathrm{d}}{\mathrm{d}t} \left(F^{mk} F^{ml} \right) = \dot{F}^{mk} F^{ml} + F^{mk} \dot{F}^{ml} = \frac{\partial v^m}{\partial X^k} F^{ml} + \frac{\partial v^m}{\partial X^l} F^{mk} \\ = \frac{\partial v^m}{\partial x^s} \frac{\partial x^s}{\partial X^k} F^{ml} + \frac{\partial v^m}{\partial x^s} \frac{\partial x^s}{\partial X^l} F^{mk} = \frac{\partial v^i}{\partial x^j} \left(F^{jk} F^{il} + F^{jl} F^{ik} \right) .$$
(A.3)

The result of Eqs. (A.3) and (A.2) can be inserted into Eq. (A.1). We finally find:

$$\dot{c}^{kl} = -\frac{2}{3}J^{-2/3}\frac{\partial v^i}{\partial x^i}C^{kl} + J^{-2/3}\frac{\partial v^i}{\partial x^j}\left(F^{jk}F^{il} + F^{jl}F^{ik}\right) .$$
(A.4)

A.2 Legendre Transform between \tilde{S} and \hat{S}

We start with the functional representation \tilde{S} of the entropy density $\rho\eta$ and write for the total differential:

$$d(\rho\eta) = d\tilde{\mathcal{S}} = \frac{\partial\tilde{\mathcal{S}}}{\partial\rho\epsilon} d(\rho\epsilon) + \sum_{\alpha=1}^{\nu} \frac{\partial\tilde{\mathcal{S}}}{\partial n_{\alpha}} dn_{\alpha} + \frac{\partial\tilde{\mathcal{S}}}{\partial c^{ij}} dc^{ij}$$
(A.5)

$$= d\hat{\mathcal{S}} = \frac{\partial\hat{\mathcal{S}}}{\partial T} dT + \sum_{\alpha=1}^{\nu} \frac{\partial\hat{\mathcal{S}}}{\partial n_{\alpha}} dn_{\alpha} + \frac{\partial\hat{\mathcal{S}}}{\partial c^{ij}} dc^{ij} , \qquad (A.6)$$

with $\frac{\partial \tilde{\mathcal{S}}}{\partial \rho \epsilon} = 1/T$. Furthermore it holds with $\rho \epsilon = \hat{\mathcal{E}}(T, n_1, \dots, n_{\nu}, c^{ij})$:

$$d(\rho\epsilon) = d\hat{\mathcal{E}} = \frac{\partial\hat{\mathcal{E}}}{\partial T} dT + \sum_{\alpha=1}^{\nu} \frac{\partial\hat{\mathcal{E}}}{\partial n_{\alpha}} dn_{\alpha} + \frac{\partial\hat{\mathcal{E}}}{\partial c^{ij}} dc^{ij} .$$
(A.7)

The term $d(\rho\epsilon)$ 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:

$$d(\rho\eta) = \underbrace{\frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial T}}_{=\frac{\partial \hat{\mathcal{S}}}{\partial T}} dT + \sum_{\alpha=1}^{\nu} \underbrace{\left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} + \frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial n_{\alpha}}\right)}_{=\frac{\partial \hat{\mathcal{S}}}{\partial n_{\alpha}}} dn_{\alpha} + \underbrace{\left(\frac{\partial \tilde{\mathcal{S}}}{\partial c^{ij}} + \frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial c^{ij}}\right)}_{=\frac{\partial \hat{\mathcal{S}}}{\partial c^{ij}}} dc^{ij} \qquad (A.8)$$

and we identify with $d(\rho\eta) = d\hat{S}$:

$$\frac{\partial \hat{\mathcal{S}}}{\partial T} = \frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial T} \quad , \quad \frac{\partial \hat{\mathcal{S}}}{\partial n_{\alpha}} = \frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} + \frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial n_{\alpha}} \quad , \quad \frac{\partial \hat{\mathcal{S}}}{\partial c^{ij}} = \frac{\partial \tilde{\mathcal{S}}}{\partial c^{ij}} + \frac{1}{T} \frac{\partial \hat{\mathcal{E}}}{\partial c^{ij}} \,. \tag{A.9}$$

Since the variables T and n_{α} are independent within the domain of $\hat{\mathcal{S}}$ one can, in particular, find from Eq. (A.9)₂ the relation ($\beta \neq \alpha$):

$$\frac{\partial \tilde{\mathcal{S}}}{\partial n_{\alpha}} = -\frac{1}{T} \left(\frac{\partial \hat{\mathcal{E}}}{\partial n_{\alpha}} - T \frac{\partial \hat{\mathcal{S}}}{\partial n_{\alpha}} \right) = -\frac{1}{T} \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} = -\frac{1}{T} \frac{\partial (\rho \varphi)}{\partial n_{\alpha}} \bigg|_{T, n_{\beta}, c^{ij}} .$$
(A.10)

A.3 Legendre Transform between $\hat{\mathcal{F}}$ and $\bar{\mathcal{F}}$

Recall the functional representations shown in Eq. $(2.50)_{2,3}$. Consequently we can write:

$$d(\rho\varphi) = d\hat{\mathcal{F}} = \frac{\partial\hat{\mathcal{F}}}{\partial T} dT + \sum_{\alpha=1}^{\nu} \frac{\partial\hat{\mathcal{F}}}{\partial n_{\alpha}} dn_{\alpha} + \frac{\partial\hat{\mathcal{F}}}{\partial c^{ij}} dc^{ij} , \qquad (A.11)$$

$$= d\bar{\mathcal{F}} = \frac{\partial\bar{\mathcal{F}}}{\partial T} dT + \sum_{\beta=1}^{\nu-1} \frac{\partial\bar{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta} + \frac{\partial\bar{\mathcal{F}}}{\partial\rho} d\rho + \frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}} dc^{ij} .$$
(A.12)

Obviously the transfer from $\bar{\mathcal{F}}$ to $\hat{\mathcal{F}}$ requires the substitution of dy_{β} and $d\rho$ by dn_{α} . For this reason we calculate:

$$\rho(n_1, \dots, n_\nu) = \sum_{\alpha=1}^{\nu} m_\alpha n_\alpha \quad \Rightarrow \quad \mathrm{d}\rho = \sum_{\alpha=1}^{\nu} \frac{\partial\rho}{\partial n_\alpha} \mathrm{d}n_\alpha = \sum_{\alpha=1}^{\nu} m_\alpha \mathrm{d}n_\alpha \tag{A.13}$$

$$y_{\beta}(n_1, \dots, n_{\nu}) = \frac{n_{\beta}}{\sum_{\alpha=1}^{\nu} n_{\alpha}} \quad \Rightarrow \quad \mathrm{d}y_{\beta} = \sum_{\alpha=1}^{\nu} \frac{\partial y_{\beta}}{\partial n_{\alpha}} \mathrm{d}n_{\alpha} = \sum_{\alpha=1}^{\nu} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^2}\right) \mathrm{d}n_{\alpha} \; .$$
(A.14)

Eqs. (A.13) and (A.14) can be inserted into Eq. (A.12). We obtain:

$$d(\rho\varphi) = \frac{\partial\bar{\mathcal{F}}}{\partial T} dT + \sum_{\alpha=1}^{\nu} \left[m_{\alpha} \frac{\partial\bar{\mathcal{F}}}{\partial\rho} + \sum_{\beta=1}^{\nu-1} \frac{\partial\bar{\mathcal{F}}}{\partial y_{\beta}} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^2} \right) \right] dn_{\alpha} + \frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}} dc^{ij} . (A.15)$$

By comparing the coefficients between Eqs. (A.11) and (A.15) results:

$$\frac{\partial \hat{\mathcal{F}}}{\partial T} = \frac{\partial \bar{\mathcal{F}}}{\partial T} \quad , \quad \frac{\partial \hat{\mathcal{F}}}{\partial n_{\alpha}} = m_{\alpha} \frac{\partial \bar{\mathcal{F}}}{\partial \rho} + \sum_{\beta=1}^{\nu-1} \frac{\partial \bar{\mathcal{F}}}{\partial y_{\beta}} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^2} \right) \quad , \quad \frac{\partial \hat{\mathcal{F}}}{\partial c^{ij}} = \frac{\partial \bar{\mathcal{F}}}{\partial c^{ij}} \quad (A.16)$$

A.4 Legendre Transform between $\bar{\mathcal{F}}$ and $\hat{\mathcal{F}}$

According to Eq. $(2.50)_{3,4}$ we write:

$$d(\rho\varphi) = d\bar{\mathcal{F}} = \frac{\partial\bar{\mathcal{F}}}{\partial T} dT + \sum_{\beta=1}^{\nu-1} \frac{\partial\bar{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta} + \frac{\partial\bar{\mathcal{F}}}{\partial\rho} d\rho + \frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}} dc^{ij}$$
(A.12)

$$= d\hat{\mathcal{F}} = \frac{\partial\hat{\mathcal{F}}}{\partial T} dT + \sum_{\beta=1}^{\nu-1} \frac{\partial\hat{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta} + \frac{\partial\hat{\mathcal{F}}}{\partial C^{ij}} dC^{ij} .$$
(A.17)

Hence we have to substitute $d\rho$ and dc^{ij} by means of dC^{ij} . For this reason we find:

$$C^{ij}(c^{ij},\rho) = J^{2/3}c^{ij} = c^{ij} \left(\frac{\rho_0}{\rho}\right)^{2/3} \Rightarrow dC^{ij} = \frac{\partial C^{ij}}{\partial c^{kl}} dc^{kl} + \frac{\partial C^{ij}}{\partial \rho} d\rho , \quad (A.18)$$

with
$$\frac{\partial C^{ij}}{\partial c^{kl}} \stackrel{(C^{ij}=C^{ji})}{=} \frac{1}{2} \frac{\partial}{\partial c^{kl}} (C^{ij}+C^{ji}) = \frac{1}{2} \left(\frac{\rho_0}{\rho}\right)^{2/3} (\delta^{ik} \delta^{jl} + \delta^{jk} \delta^{il})$$
(A.19)

and
$$\frac{\partial C^{ij}}{\partial \rho} = -\frac{2}{3} \frac{c^{ij}}{\rho} \left(\frac{\rho_0}{\rho}\right)^{2/3}$$
. (A.20)

Insertion of Eqs. $(A.18)_2$, (A.19) and (A.20) into Eq. (A.17) results in:

$$d(\rho\varphi) = \frac{\partial \acute{\mathcal{F}}}{\partial T} dT + \sum_{\beta=1}^{\nu-1} \frac{\partial \acute{\mathcal{F}}}{\partial y_{\beta}} dy_{\beta} + \frac{\partial \acute{\mathcal{F}}}{\partial C^{ij}} \left[\frac{1}{2} \left(\frac{\rho_0}{\rho} \right)^{2/3} (\delta^{ik} \delta^{jl} + \delta^{jk} \delta^{il}) dc^{kl} - \frac{2}{3} \frac{c^{ij}}{\rho} \left(\frac{\rho_0}{\rho} \right)^{2/3} d\rho \right]. \quad (A.21)$$

Comparison of Eqs. (A.12) and (A.21) yields for the coefficients:

$$\frac{\partial \bar{\mathcal{F}}}{\partial T} = \frac{\partial \acute{\mathcal{F}}}{\partial T} , \quad \frac{\partial \bar{\mathcal{F}}}{\partial y_{\beta}} = \frac{\partial \acute{\mathcal{F}}}{\partial y_{\beta}} , \quad \frac{\partial \bar{\mathcal{F}}}{\partial \rho} = -\frac{2}{3} \frac{c^{ij}}{\rho} \left(\frac{\rho_{0}}{\rho}\right)^{2/3} \frac{\partial \acute{\mathcal{F}}}{\partial C^{ij}} ,$$

$$\frac{\partial \bar{\mathcal{F}}}{\partial c^{kl}} = \frac{1}{2} \frac{\partial \acute{\mathcal{F}}}{\partial C^{ij}} \left(\frac{\rho_{0}}{\rho}\right)^{2/3} \left(\delta^{ik} \delta^{jl} + \delta^{jk} \delta^{il}\right) .$$
(A.22)

A.5 Legendre Transform between $\tilde{\mathbb{S}}$ and $\hat{\mathbb{S}}$

According to the functional representations in Eq. $(2.106)_{1,2}$ the following total differentials are formulated $(\alpha = 1, ..., \nu)$:

$$d(\rho\eta) = d\tilde{\mathbb{S}} = \frac{\partial\tilde{\mathbb{S}}}{\partial\rho\epsilon} d(\rho\epsilon) + \frac{\partial\tilde{\mathbb{S}}}{\partial n_{\alpha}} dn_{\alpha} + \frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^{i}n_{\alpha}} d(\nabla^{i}n_{\alpha}) + \frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^{ij}n_{\alpha}} d(\nabla^{ij}n_{\alpha}) + \frac{\partial\tilde{\mathbb{S}}}{\partial\epsilon^{ij}} dc^{ij}$$
(A.23)
$$= d\hat{\mathbb{S}} = \frac{\partial\hat{\mathbb{S}}}{\partial T} dT + \frac{\partial\hat{\mathbb{S}}}{\partial n_{\alpha}} dn_{\alpha} + \frac{\partial\hat{\mathbb{S}}}{\partial\nabla^{i}n_{\alpha}} d(\nabla^{i}n_{\alpha}) + \frac{\partial\hat{\mathbb{S}}}{\partial\nabla^{ij}n_{\alpha}} d(\nabla^{ij}n_{\alpha}) + \frac{\partial\hat{\mathbb{S}}}{\partial\epsilon^{ij}} dc^{ij} ,$$
(A.24)

with the definition of the absolute temperature $\frac{\partial \tilde{S}}{\partial \rho \epsilon} = 1/T$. The total differential of the internal energy density $\rho \epsilon = \hat{\mathbb{E}}(T, n_{\alpha}, \nabla^{i} n_{\alpha}, \nabla^{ij} n_{\alpha}, c^{ij})$ in Eq. (A.23) can be

replaced by means of:

$$d(\rho\epsilon) = d\hat{\mathbb{E}} = \frac{\partial\hat{\mathbb{E}}}{\partial T}dT + \frac{\partial\hat{\mathbb{E}}}{\partial n_{\alpha}}dn_{\alpha} + \frac{\partial\hat{\mathbb{E}}}{\partial\nabla^{i}n_{\alpha}}d(\nabla^{i}n_{\alpha}) + \frac{\partial\hat{\mathbb{E}}}{\partial\nabla^{ij}n_{\alpha}}d(\nabla^{ij}n_{\alpha}) + \frac{\partial\hat{\mathbb{E}}}{\partial c^{ij}}dc^{ij}.$$
(A.25)

Hence it follows from Eq. (A.23):

$$d\tilde{S} = \frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial T} dT + \left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial n_{\alpha}} + \frac{\partial \tilde{S}}{\partial n_{\alpha}}\right) dn_{\alpha} + \left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial \nabla^{i} n_{\alpha}} + \frac{\partial \tilde{S}}{\partial \nabla^{i} n_{\alpha}}\right) d(\nabla^{i} n_{\alpha}) + \left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial \nabla^{ij} n_{\alpha}} + \frac{\partial \tilde{S}}{\partial \nabla^{ij} n_{\alpha}}\right) d(\nabla^{ij} n_{\alpha}) + \left(\frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial c^{ij}} + \frac{\partial \tilde{S}}{\partial c^{ij}}\right) dc^{ij} .$$
(A.26)

Since T and n_{α} are independent arguments within the functional representations $\hat{\mathbb{E}}$ and $\hat{\mathbb{S}}$ we identify:

$$\frac{\partial \hat{\mathbb{S}}}{\partial T} = \frac{1}{T} \frac{\partial \hat{\mathbb{E}}}{\partial T} , \quad -T \frac{\partial \tilde{\mathbb{S}}}{\partial n_{\alpha}} = \frac{\partial \hat{\mathbb{F}}}{\partial n_{\alpha}} , \quad -T \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{i} n_{\alpha}} = \frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{i} n_{\alpha}}$$
$$-T \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla^{ij} n_{\alpha}} = \frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{ij} n_{\alpha}} , \quad -T \frac{\partial \tilde{\mathbb{S}}}{\partial c^{ij}} = \frac{\partial \hat{\mathbb{F}}}{\partial c^{ij}} , \qquad (A.27)$$

where $\hat{\mathbb{F}}(T, n_{\alpha}, \nabla^{i} n_{\alpha}, \nabla^{ij} n_{\alpha}, c^{ij})$ is the functional representation of the HELMHOLTZ free energy density $\rho\varphi$.

A.6 Legendre Transform between $\hat{\mathbb{F}}$ and $\bar{\mathbb{F}}$

Using the representations in Eq. (2.123) we find the following total differentials $(\alpha = 1, ..., \nu \text{ and } \beta = 1, ..., \nu - 1)$:

$$d(\rho\varphi) = d\hat{\mathbb{F}} = \frac{\partial\hat{\mathbb{F}}}{\partial T}dT + \frac{\partial\hat{\mathbb{F}}}{\partial n_{\alpha}}dn_{\alpha} + \frac{\partial\hat{\mathbb{F}}}{\partial\nabla^{i}n_{\alpha}}d(\nabla^{i}n_{\alpha}) + \frac{\partial\hat{\mathbb{F}}}{\partial\nabla^{ij}n_{\alpha}}d(\nabla^{ij}n_{\alpha}) + \frac{\partial\hat{\mathbb{F}}}{\partialc^{ij}}dc^{ij}$$
(A.28)
$$= d\bar{\mathbb{F}} = \frac{\partial\bar{\mathbb{F}}}{\partial T}dT + \frac{\partial\bar{\mathbb{F}}}{\partial y_{\beta}}dy_{\beta} + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{i}y_{\beta}}d(\nabla^{i}y_{\beta}) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}y_{\beta}}d(\nabla^{ij}y_{\beta}) + \frac{\partial\bar{\mathbb{F}}}{\partial\rho}d\rho + \frac{\partial\bar{\mathbb{F}}}{\partial\rho}d\rho + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho}d(\nabla^{ij}\rho) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho}dc^{ij}.$$
(A.29)

Now the terms with brackets must be "suitably" replaced by expressions of dn_{α} , $d(\nabla^i n_{\alpha})$ and $d(\nabla^{ij} n_{\alpha})$. For this reason we write as follows:

$$\rho = \sum_{\alpha} m_{\alpha} n_{\alpha} \quad \Rightarrow \quad \mathrm{d}\rho = \sum_{\alpha} m_{\alpha} \mathrm{d}n_{\alpha} , \qquad (A.30)$$

$$\nabla^{i}\rho = \sum_{\alpha} m_{\alpha} \nabla^{i} n_{\alpha} \quad \Rightarrow \quad \mathrm{d}(\nabla^{i}\rho) = \sum_{\alpha} m_{\alpha} \mathrm{d}(\nabla^{i} n_{\alpha}) , \qquad (A.31)$$

$$\nabla^{ij}\rho = \sum_{\alpha} m_{\alpha} \nabla^{ij} n_{\alpha} \quad \Rightarrow \quad \mathbf{d}(\nabla^{ij}\rho) = \sum_{\alpha} m_{\alpha} \mathbf{d}(\nabla^{ij} n_{\alpha}) . \tag{A.32}$$

Furthermore holds:

$$y_{\beta} = \frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}} \Rightarrow y_{\beta} = \hat{\mathbb{Y}}_{\beta}(n_{\alpha}) , \qquad (A.33)$$

$$\nabla^{i} y_{\beta} = \nabla^{i} \left(\frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}} \right) \quad \Rightarrow \quad \nabla^{i} y_{\beta} = \hat{\mathbb{Y}}^{i}_{\beta}(n_{\alpha}, \nabla^{i} n_{\alpha}) , \qquad (A.34)$$

$$\nabla^{ij} y_{\beta} = \nabla^{ij} \left(\frac{n_{\beta}}{\sum_{\alpha} n_{\alpha}} \right) \quad \Rightarrow \quad \nabla^{ij} y_{\beta} = \hat{\mathbb{Y}}^{ij}_{\beta} (n_{\alpha}, \nabla^{i} n_{\alpha}, \nabla^{ij} n_{\alpha}) \tag{A.35}$$

and after a straightforward calculation:

$$dy_{\beta} = \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}}{\partial n_{\alpha}} dn_{\alpha} = \sum_{\alpha} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) dn_{\alpha}$$
(A.36)

$$d(\nabla^{i}y_{\beta}) = \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{i}}{\partial n_{\alpha}} dn_{\alpha} + \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{i}}{\partial \nabla^{i}n_{\alpha}} d(\nabla^{i}n_{\alpha})$$

$$= \sum_{\alpha} \nabla^{i} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) dn_{\alpha} + \sum_{\alpha} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) d(\nabla^{i}n_{\alpha})$$
(A.37)

$$d(\nabla^{ij}y_{\beta}) = \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{ij}}{\partial n_{\alpha}} dn_{\alpha} + \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{ij}}{\partial \nabla^{k}n_{\alpha}} d(\nabla^{k}n_{\alpha}) + \sum_{\alpha} \frac{\partial \hat{\mathbb{Y}}_{\beta}^{ij}}{\partial \nabla^{kl}n_{\alpha}} d(\nabla^{kl}n_{\alpha})$$

$$= \sum_{\alpha} \nabla^{ij} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) dn_{\alpha} + 2 \sum_{\alpha} \nabla^{j} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) d(\nabla^{i}n_{\alpha})$$

$$+ \sum_{\alpha} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) d(\nabla^{ij}n_{\alpha}) .$$
(A.38)
Substituting the underbracket terms in Eq. (A.29) by the results in Eqs. (A.30-A.32) and (A.36-A.38) yields:

$$d\bar{\mathbb{F}} = \frac{\partial\bar{\mathbb{F}}}{\partial T}dT + \frac{\partial\bar{\mathbb{F}}}{\partial c^{ij}}dc^{ij} + \sum_{\alpha} \left\{ m_{\alpha}\frac{\partial\bar{\mathbb{F}}}{\partial\rho} + \sum_{\beta} \left[\frac{\partial\bar{\mathbb{F}}}{\partial y_{\beta}} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{i}y_{\beta}} \nabla^{ij} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) \right] \right\} dn_{\alpha} + \sum_{\alpha} \left\{ m_{\alpha}\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{i}\rho} + \sum_{\beta} \left[\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{i}y_{\beta}} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) + 2\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}y_{\beta}} \nabla^{j} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) \right] \right\} d(\nabla^{i}n_{\alpha}) + \sum_{\alpha} \left\{ m_{\alpha}\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho} + \sum_{\beta} \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}y_{\beta}} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) \right\} d(\nabla^{ij}n_{\alpha}) .$$
(A.39)

and we identify with $d\bar{\mathbb{F}} = d\hat{\mathbb{F}}$:

$$\frac{\partial \hat{\mathbb{F}}}{\partial T} = \frac{\partial \bar{\mathbb{F}}}{\partial T} , \quad \frac{\partial \hat{\mathbb{F}}}{\partial c^{ij}} = \frac{\partial \bar{\mathbb{F}}}{\partial c^{ij}} , \qquad (A.40)$$

$$\frac{\partial \hat{\mathbb{F}}}{\partial n_{\alpha}} = m_{\alpha} \frac{\partial \bar{\mathbb{F}}}{\partial \rho} + \sum_{\beta} \left[\frac{\partial \bar{\mathbb{F}}}{\partial y_{\beta}} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) + \frac{\partial \bar{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}} \nabla^{i} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) + \frac{\partial \bar{\mathbb{F}}}{\partial \nabla^{ij} y_{\beta}} \nabla^{ij} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) \right], \qquad (A.41)$$

$$\frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{i} n_{\alpha}} = m_{\alpha} \frac{\partial \bar{\mathbb{F}}}{\partial \nabla^{i} \rho} + \sum_{\beta} \left[\frac{\partial \bar{\mathbb{F}}}{\partial \nabla^{i} y_{\beta}} \left(\frac{\delta^{\alpha \beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) + 2 \frac{\partial \bar{\mathbb{F}}}{\partial \nabla^{ij} y_{\beta}} \nabla^{j} \left(\frac{\delta^{\alpha \beta}}{n} - \frac{n_{\beta}}{n^{2}} \right) \right],$$
(A.42)

$$\frac{\partial \hat{\mathbb{F}}}{\partial \nabla^{ij} n_{\alpha}} = m_{\alpha} \frac{\partial \bar{\mathbb{F}}}{\partial \nabla^{ij} \rho} + \sum_{\beta} \frac{\partial \bar{\mathbb{F}}}{\partial \nabla^{ij} y_{\beta}} \left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_{\beta}}{n^2} \right) .$$
(A.43)

A.7 Legendre Transform between $\overline{\mathbb{F}}$ and $\underline{\mathbb{F}}$

This calculation is similar to that one of Appendix A.4. We start with the total differentials for $\overline{\mathbb{F}}$ and $\underline{\mathbb{F}}$, *viz*:

$$d(\rho\varphi) = d\bar{\mathbb{F}} = d\hat{\mathbb{F}} = d\hat{\mathbb{F}} = d\hat{\mathbb{F}} = \frac{\partial\bar{\mathbb{F}}}{\partial T}dT + \frac{\partial\bar{\mathbb{F}}}{\partial y_{\beta}}dy_{\beta} + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{i}y_{\beta}}d(\nabla^{i}y_{\beta}) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}y_{\beta}}d(\nabla^{ij}y_{\beta}) + \frac{\partial\bar{\mathbb{F}}}{\partial\rho}d\rho + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{i}\rho}d(\nabla^{i}\rho) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho}d(\nabla^{ij}\rho) + \frac{\partial\bar{\mathbb{F}}}{\partialc^{ij}}dc^{ij}$$
(A.44)
$$= \frac{\partial\bar{\mathbb{F}}}{\partial T}dT + \frac{\partial\bar{\mathbb{F}}}{\partial y_{\beta}}dy_{\beta} + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{i}y_{\beta}}d(\nabla^{i}y_{\beta}) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}y_{\beta}}d(\nabla^{ij}y_{\beta}) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}y_{\beta}}d(\nabla^{ij}\rho) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho}d(\nabla^{ij}\rho) + \frac{$$

The term with the bracket, *i.e.*, dC^{ij} , can be substituted by the relation

$$dC^{ij} = \frac{1}{2} \left(\frac{\rho_0}{\rho}\right)^{2/3} \left(\delta^{ik} \delta^{jl} + \delta^{jk} \delta^{il}\right) dc^{kl} - \frac{2}{3} \frac{c^{ij}}{\rho} \left(\frac{\rho_0}{\rho}\right)^{2/3} d\rho$$
(A.46)

following the calculations shown in Eqs. (A.18-A.20). The resulting total differential for $d\bar{\mathbb{F}}$ can be used to identify the coefficients $\partial \bar{\mathbb{F}}/\partial T, \ldots, \partial \bar{\mathbb{F}}/\partial c^{ij}$. In particular it follows that:

$$\frac{\partial \bar{\mathbb{F}}}{\partial \Xi} = \frac{\partial \hat{\mathbb{F}}}{\partial \Xi} \quad , \quad \Xi = \{T, y_{\beta}, \nabla^{i} y_{\beta}, \nabla^{ij} y_{\beta}, \nabla^{i} \rho, \nabla^{ij} \rho\}$$
(A.47)

and

$$\frac{\partial \bar{\mathbb{F}}}{\partial \rho} = -\frac{2}{3} \frac{C^{ij}}{\rho} \frac{\partial \acute{\mathbb{F}}}{\partial C^{ij}} \quad , \quad \frac{\partial \bar{\mathbb{F}}}{\partial c^{kl}} = \frac{1}{2} \left(\frac{\rho_0}{\rho}\right)^{\frac{2}{3}} (\delta^{ik} \delta^{jl} + \delta^{il} \delta^{kj}) \frac{\partial \acute{\mathbb{F}}}{\partial C^{ij}} . \tag{A.48}$$

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 $\rho \varphi$ ($\alpha = 1, ..., \nu$ and $\beta = 1, ..., \nu - 1$):

$$d(\rho\varphi) = d\widehat{\widehat{\mathbb{F}}} = \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial T} dT + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial\rho_{\alpha}} d\rho_{\alpha} + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial\nabla^{i}\rho_{\alpha}} d(\nabla^{i}\rho_{\alpha}) + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial\nabla^{ij}\rho_{\alpha}} d(\nabla^{ij}\rho_{\alpha}) + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial c^{ij}} dc^{ij}$$
(A.49)

$$= d\overline{\overline{\mathbb{F}}} = \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial T} dT + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial c_{\beta}} dc_{\beta} + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^{i}c_{\beta}} d(\nabla^{i}c_{\beta}) + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^{ij}c_{\beta}} d(\nabla^{ij}c_{\beta}) + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^{ij}\rho} d(\nabla^{ij}\rho) + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^{ij}\rho} d\rho + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\rho} d\rho + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\sigma^{ij}} dc^{ij}.$$
(A.50)

The highlighted terms must be substituted by the expressions $d\rho_{\alpha}$, $d(\nabla^i \rho_{\alpha})$ and $d(\nabla^{ij} \rho_{\alpha})$. Analogously to the Eqs. (A.30-A.32) and (A.33-A.35) one finds:

$$\rho = \sum_{\alpha} \rho_{\alpha} \quad \Rightarrow \quad \mathrm{d}\rho = \sum_{\alpha} \mathrm{d}\rho_{\alpha} , \qquad (A.51)$$

$$\nabla^{i}\rho = \sum_{\alpha} \nabla^{i}\rho_{\alpha} \Rightarrow d(\nabla^{i}\rho) = \sum_{\alpha} d(\nabla^{i}\rho_{\alpha}), \qquad (A.52)$$

$$\nabla^{ij}\rho = \sum_{\alpha} m_{\alpha} \nabla^{ij} n_{\alpha} \quad \Rightarrow \quad \mathbf{d}(\nabla^{i}\rho) = \sum_{\alpha} \mathbf{d}(\nabla^{ij}\rho_{\alpha}) , \qquad (A.53)$$

and

$$c_{\beta} = \frac{\rho_{\beta}}{\sum_{\alpha} \rho_{\alpha}} \Rightarrow c_{\beta} = \widehat{\widehat{\mathbb{C}}}_{\beta}(\rho_{\alpha}), \qquad (A.54)$$

$$\nabla^{i} c_{\beta} = \nabla^{i} \left(\frac{\rho_{\beta}}{\sum_{\alpha} \rho_{\alpha}} \right) \quad \Rightarrow \quad \nabla^{i} c_{\beta} = \widehat{\widehat{\mathbb{C}}}^{i}_{\beta} (\rho_{\alpha}, \nabla^{i} \rho_{\alpha}) , \qquad (A.55)$$

$$\nabla^{ij}c_{\beta} = \nabla^{ij}\left(\frac{\rho_{\beta}}{\sum_{\alpha}\rho_{\alpha}}\right) \quad \Rightarrow \quad \nabla^{ij}c_{\beta} = \widehat{\widehat{\mathbb{C}}}^{ij}_{\beta}(\rho_{\alpha}, \nabla^{i}\rho_{\alpha}, \nabla^{ij}\rho_{\alpha}) . \tag{A.56}$$

Thus we derive in the same manner as in the Eqs. (A.36-A.38):

$$dc_{\beta} = \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}}{\partial \rho_{\alpha}} d\rho_{\alpha} = \sum_{\alpha} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^2} \right) d\rho_{\alpha} , \qquad (A.57)$$

$$d(\nabla^{i}c_{\beta}) = \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{i}}{\partial \rho_{\alpha}} d\rho_{\alpha} + \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{i}}{\partial \nabla^{i} \rho_{\alpha}} d(\nabla^{i} \rho_{\alpha})$$

$$= \sum_{\alpha} \nabla^{i} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) d\rho_{\alpha} + \sum_{\alpha} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) d(\nabla^{i} \rho_{\alpha}) , \quad (A.58)$$

$$d(\nabla^{ij}c_{\beta}) = \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{ij}}{\partial \rho_{\alpha}} d\rho_{\alpha} + \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{ij}}{\partial \nabla^{k} \rho_{\alpha}} d(\nabla^{k} \rho_{\alpha}) + \sum_{\alpha} \frac{\partial \widehat{\widehat{\mathbb{C}}}_{\beta}^{ij}}{\partial \nabla^{kl} \rho_{\alpha}} d(\nabla^{kl} \rho_{\alpha})$$

$$= \sum_{\alpha} \nabla^{ij} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) d\rho_{\alpha} + 2 \sum_{\alpha} \nabla^{j} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) d(\nabla^{i} \rho_{\alpha}) + \sum_{\alpha} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) d(\nabla^{ij} \rho_{\alpha}) . \quad (A.59)$$

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:

$$\frac{\partial \widehat{\overline{\mathbb{F}}}}{\partial T} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial T}, \quad \frac{\partial \widehat{\overline{\mathbb{F}}}}{\partial c^{ij}} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c^{ij}}, \quad (A.60)$$

$$\frac{\partial \widehat{\overline{\mathbb{F}}}}{\partial \rho_{\alpha}} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \rho} + \sum_{\beta} \left[\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c_{\beta}} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) + \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{i} c_{\beta}} \nabla^{i} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) + \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{ij} c_{\beta}} \nabla^{ij} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) \right], \quad (A.61)$$

$$\partial \widehat{\overline{\mathbb{F}}} = \partial \overline{\overline{\mathbb{F}}} + \sum_{\beta} \left[-\partial \overline{\overline{\mathbb{F}}} \left(\delta^{\alpha\beta} - \rho_{\beta} \right) + 2 -\partial \overline{\overline{\mathbb{F}}} - \nabla_{i} \left(\delta^{\alpha\beta} - \rho_{\beta} \right) \right]$$

$$\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} \rho_{\alpha}} = \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} \rho} + \sum_{\beta} \left[\frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{i} c_{\beta}} \left(\frac{\delta^{\alpha \beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) + 2 \frac{\partial \overline{\mathbb{F}}}{\partial \nabla^{ij} c_{\beta}} \nabla^{j} \left(\frac{\delta^{\alpha \beta}}{\rho} - \frac{\rho_{\beta}}{\rho^{2}} \right) \right],$$
(A.62)

$$\frac{\partial \widehat{\overline{\mathbb{F}}}}{\partial \nabla^{ij} \rho_{\alpha}} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{ij} \rho} + \sum_{\beta} \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{ij} c_{\beta}} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_{\beta}}{\rho^2} \right) .$$
(A.63)

Wer von Anfang an schon sicher weiß, wohin sein Weg führen wird, wird es nicht sehr weit bringen.

Napoleon, (1769 - 1821)

Appendix B

Additional Calculations required for Chapter 3

B.1 Conversion of Particle to Mass Concentration

The total HELMHOLTZ free energy Φ of an equilibrium phase γ follows by summation from Eq. (3.62):

$$\Phi^{\gamma} = \sum_{\alpha \in \gamma} E_{\alpha} - TS^{\gamma} , \quad S^{\gamma} = -k_{\rm B} \sum_{\alpha \in \gamma} [y \ln y + (1-y) \ln(1-y)] ,$$

$$E_{\alpha} \stackrel{(3.62)}{=} \frac{1}{2} g_{\rm AA} + y(1-y) g_{\phi} + y g_{\tilde{\phi}} + F_{\rm A} + y(F_{\rm B} - F_{\rm A}) + \frac{1}{2} G^{ij} G^{kl} \{\dots\}^{ijkl} (y) + (\nabla^{2}_{mn} y) \{\dots\}^{mn} (y) , \qquad (B.1)$$

where $\{\ldots\}^{ijkl}$ and $\{\ldots\}^{mn}$ represent the expressions within the curly brackets of the second and third block in Eq. (3.62). Furthermore $k_{\rm B}$ denotes Boltzmann's constant and TS^{γ} the entropic part of Φ^{γ} . Moreover, the sum is carried out with respect to all particles α of the phase γ , and E_{α} represents the energy of a particle due to its interactions with the neighbors β . The quantities $g_{\rm AA}$, g_{ϕ} , $g_{\tilde{\phi}}$, $F_{\rm A}$, $F_{\rm B}$, $\{\ldots\}^{ijkl}$, and $\{\ldots\}^{mn}$ are defined by means of the EAM potentials (*cf.*, Eq. (3.62)) which, in turn, are determined by the distance $R^2_{\alpha\beta}$ between atom α and β . 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:

$$c_{\rm B} = (1 - c_{\rm A}) \equiv c = \frac{m_{\rm B}}{m_{\rm B} + m_{\rm A}} = \frac{y_{\rm B}M_{\rm B}}{y_{\rm B}M_{\rm B} + (1 - y_{\rm B})M_{\rm A}}$$
 (B.2)

$$\Rightarrow y_{\rm B} = (1 - y_{\rm A}) \equiv y = \tilde{y}(c) = \frac{cM_{\rm A}}{M_{\rm B} - c(M_{\rm B} - M_{\rm A})} , \qquad (B.3)$$

where $M_{A/B}$ is the molecular weight of the components A/B, and c_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**:

$$\hat{\Phi} = N_{\rm A} \left(E_{\alpha} - Ts \right) \quad , \quad \mathbb{F} = \rho_0 \frac{\hat{\Phi}}{m} \quad , \quad m = N_{\rm A} \ m_H M(c) \tag{B.4}$$

$$\Rightarrow \mathbb{F} = \delta(c)(E_{\alpha} - Ts) \tag{B.5}$$

with
$$\delta(c) = \frac{1}{\Omega_0(c)} = \frac{\rho_0}{m_H M(c)}$$
 and $\frac{1}{\rho_0} = \frac{c_0}{\rho_{\rm Cu}} + \frac{1-c_0}{\rho_{\rm Ag}}$. (B.6)

 $\hat{\Phi}$ stands for the HELMHOLTZ free energy per one mol, $N_{\rm A} = 6.0237 \cdot 10^{23}$ is the number of particles in one mol (AVOGADRO's constant) and $s = -k_{\rm B} [y \ln y + (1-y) \ln(1-y)]$ represents the entropy with respect to one particle. Furthermore m denotes the total mass, ρ_0 identifies the mass density of the alloy in the homogeneous reference state with the (homogeneous) concentration c_0 and $m_H = 1.66 \cdot 10^{-27}$ 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 $M = \tilde{M}(c) = y(c)M_{\rm B} + [1 - y(c)]M_{\rm A}$. The symbol δ identifies the reciprocal volume occupied by an atom and yields the following expression:

$$\frac{\mathbb{F}}{\delta(c)} = \frac{1}{2}g_{AA} + y(1-y)g_{\phi} + yg_{\tilde{\phi}} + F_{A} + y(F_{B} - F_{A}) + \frac{1}{2}G^{ij}G^{kl}\{\dots\}^{ijkl}(y) + (\nabla_{mn}^{2}y)\{\dots\}^{mn}(y) + k_{B}T[y\ln y + (1-y)\ln(1-y)].$$
(B.7)

Considering the function $\tilde{y}(c)$ in Eq. (B.3) and applying the chain rule one can replace $\nabla_{mn}^2 y$ with the following relation:

$$\nabla_{mn}^{2} y = \frac{\partial^{2} y}{\partial c^{2}} \frac{\partial c}{\partial X^{m}} \frac{\partial c}{\partial X^{n}} + \frac{\partial y}{\partial c} \frac{\partial^{2} c}{\partial X^{m} \partial X^{n}}$$

$$= \frac{2M_{A}}{[M_{B} - (M_{B} - M_{A})c]^{3}} (\nabla_{m}c)(\nabla_{n}c) + \frac{M_{A}M_{B}}{[M_{B} - (M_{B} - M_{A})c]^{2}} \nabla_{mn}^{2}c \quad (B.8)$$

$$\equiv \mathbf{M}(c) \cdot \mathcal{D}_{mn}(c) , \qquad (B.9)$$

with the symbolic notation for the vector $\mathbf{M}(c)$ and for the vectorial differential operator $\mathcal{D}_{mn}(\diamond)$ as follows:

$$\mathbf{M}(c) = \begin{pmatrix} \mathbf{M}^{(1)}(c) \\ \mathbf{M}^{(2)}(c) \end{pmatrix} = \begin{pmatrix} \frac{2M_{\mathrm{A}}}{[M_{\mathrm{B}}-(M_{\mathrm{B}}-M_{\mathrm{A}})c]^{3}} \\ \frac{M_{\mathrm{A}}M_{\mathrm{B}}}{[M_{\mathrm{B}}-(M_{\mathrm{B}}-M_{\mathrm{A}})c]^{2}} \end{pmatrix} \text{ and}$$
$$\mathcal{D}_{mn}(\diamond) = \begin{pmatrix} \mathcal{D}_{mn}^{(1)} \\ \mathcal{D}_{mn}^{(2)} \end{pmatrix} = \begin{pmatrix} \nabla_{m}(\diamond)\nabla_{n}(\diamond) \\ \nabla_{mn}^{2}(\diamond) \end{pmatrix}.$$
(B.10)

A combination of the relations (B.3,B.8) with Eq. (B.7) yields the following expressions:

$$\frac{\psi_0(c)}{\delta(c)} = \frac{1}{2}g_{AA} + y(c)(1 - y(c))g_\phi + y(c)g_{\tilde{\phi}} + F_A + y(c)(F_B - F_A) , \quad (B.11)$$

$$\frac{\mathbb{F}_0^{\text{mech}}(c)}{\delta(c)} = E_\alpha^{\text{mech}} = \frac{\Omega_0^\alpha}{2} G^{ij} K^{ijkl}(c) G^{kl} , \qquad (B.12)$$

$$\frac{a^{mn}(c, G^{pq})}{\delta(c)} = -\mathcal{M}^{(2)}(c) \ \mathbb{H}^{mn}(c, G^{pq}) , \qquad (B.13)$$

$$\frac{b^{mn}(c, G^{pq})}{\delta(c)} = \mathcal{M}^{(1)}(c) \,\mathbb{H}^{mn}(c, G^{pq}) \,, \tag{B.14}$$

$$K^{ijkl}(c) = \frac{1}{\Omega_0^{\alpha}} \left[2B_A^{ijkl} + 4y(c)(1 - y(c))B_{\phi}^{ijkl} + 4y(c)B_{\tilde{\phi}}^{ijkl} + 4\left(W_A^{ijkl} + y(c)W_{\Delta}^{ijkl}\right) \left(F_A' + y(c)(F_B' - F_A')\right) + 4\left(V_A^{ij} + y(c)V_{\Delta}^{ij}\right) \left(V_A^{kl} + y(c)V_{\Delta}^{kl}\right) \left(F_A'' + y(c)(F_B'' - F_A'')\right) \right], \quad (B.15)$$

$$\begin{split} \mathbb{H}^{mn}(c, G^{pq}) &= \frac{1}{4} \Big((1 - 2y(c)) g_{\phi}^{mn} + g_{\phi}^{mn} \Big) + \frac{1}{2} \bar{\rho}_{\Delta}^{mn} \Big(F'_{\mathrm{A}} + y(c) (F'_{\mathrm{B}} - F'_{\mathrm{A}}) \Big) \\ &+ \frac{1}{2} G^{ij} \Big[(1 - 2y(c)) A_{\phi}^{ijmn} + A_{\phi}^{ijmn} + 2V_{\Delta}^{ijmn} \Big(F'_{\mathrm{A}} + y(c) (F'_{\mathrm{B}} - F'_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(F''_{\mathrm{A}} + y(c) (F''_{\mathrm{B}} - F''_{\mathrm{A}}) \Big) \Big] \\ &+ \frac{1}{2} G^{ij} G^{kl} \Big[(1 - 2y(c)) B_{\phi}^{ijklmn} + B_{\phi}^{ijklmn} \\ &+ 2W_{\Delta}^{ijklmn} \Big(F'_{\mathrm{A}} + y(c) (F'_{\mathrm{B}} - F'_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(W_{\mathrm{A}}^{ijkl} + y(c) W_{\Delta}^{ijkl} \Big) \Big(F''_{\mathrm{A}} + y(c) (F''_{\mathrm{B}} - F''_{\mathrm{A}}) \Big) \\ &+ 2V_{\Delta}^{klmn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(F''_{\mathrm{A}} + y(c) (F''_{\mathrm{B}} - F''_{\mathrm{A}}) \Big) \\ &+ 2V_{\Delta}^{ijmn} \Big(V_{\mathrm{A}}^{kl} + y(c) V_{\Delta}^{ij} \Big) \Big(F''_{\mathrm{A}} + y(c) (F''_{\mathrm{B}} - F''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(F''_{\mathrm{A}} + y(c) (F''_{\mathrm{B}} - F''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(F''_{\mathrm{A}} + y(c) (F''_{\mathrm{B}} - F''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(V_{\mathrm{A}}^{kl} + y(c) V_{\Delta}^{kl} \Big) \Big(F'''_{\mathrm{A}} + y(c) (F'''_{\mathrm{B}} - F''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(V_{\mathrm{A}}^{kl} + y(c) V_{\Delta}^{kl} \Big) \Big(F'''_{\mathrm{A}} + y(c) (F'''_{\mathrm{B}} - F'''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(V_{\mathrm{A}}^{kl} + y(c) V_{\Delta}^{kl} \Big) \Big(F'''_{\mathrm{A}} + y(c) (F'''_{\mathrm{B}} - F'''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(V_{\mathrm{A}}^{kl} + y(c) V_{\Delta}^{kl} \Big) \Big(F'''_{\mathrm{A}} + y(c) (F'''_{\mathrm{B}} - F'''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(V_{\mathrm{A}}^{kl} + y(c) V_{\Delta}^{kl} \Big) \Big(F''''_{\mathrm{A}} + y(c) (F''''_{\mathrm{B}} - F'''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(V_{\mathrm{A}}^{kl} + y(c) V_{\Delta}^{kl} \Big) \Big(F''''_{\mathrm{A}} + y(c) (F''''_{\mathrm{B}} - F'''_{\mathrm{A}}) \Big) \\ &+ 2 \bar{\rho}_{\Delta}^{mn} \Big(V_{\mathrm{A}}^{ij} + y(c) V_{\Delta}^{ij} \Big) \Big(V_{\mathrm{A}$$

The HGCs A^{kl} can directly be calculated from (B.13) and (B.14) by means of the relation $A^{kl} = \frac{\partial a^{kl}}{\partial c} + b^{kl}$. 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 $c \equiv c_{\rm B}$.

B.2 Two Equations for G and for E_{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:

$$\rho'(R^2) = -\beta \frac{\rho_{\rm e}}{R^2} \quad , \quad \rho''(R^2) = \beta^2 \frac{\rho_{\rm e}}{R^4} \quad , \quad \phi'(R^2) = -\gamma \frac{\phi_{\rm e}}{R^2} \quad , \quad \phi''(R^2) = \gamma^2 \frac{\phi_{\rm e}}{R^4} \quad , \tag{B.17}$$

$$F'(\bar{\rho}_{\rm e}) = -6\frac{\gamma\phi_{\rm e}}{\beta\bar{\rho}_{\rm e}} \quad , \quad F''(\bar{\rho}_{\rm e}) = \frac{E_{\rm sub} \ \alpha^2 + 24\gamma\phi_{\rm e}(\beta - \gamma)}{4\beta^2\bar{\rho}_{\rm e}^2} \ . \tag{B.18}$$

Due to nearest neighbor interactions all neighbors of an atom α are separated by the same distance R. Thus the derivatives ρ' , ρ'' , and ϕ'' do not depend on the sum and one can write for a pure substance:

$$K^{ijkl} = \frac{1}{\Omega_0} \Big[2\phi'' \Big(\sum_{\beta} R^i R^j R^k R^l \Big) + 4F' \rho'' \Big(\sum_{\beta} R^i R^j R^k R^l \Big) + 4F'' \rho' \rho' \Big(\sum_{\beta} R^i R^j \Big) \Big(\sum_{\beta} R^k R^l \Big) \Big]$$
(B.19)

Note that for an FCC crystal the following relations hold: $\sum (R^1)^4 = 8(a/2)^4$, $\sum (R^1)^2 = \sum (R^2)^2 = 8(a/2)^2$, $\sum (R^2)^2 (R^3)^2 = 4(a/2)^2(a/2)^2$, and $\sum R^2 R^3 = 0$, *cf.*, 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)

$$K^{1111} = \Xi_a + \Xi_b$$
 , $K^{1122} = \frac{1}{2}\Xi_a + \Xi_b$, $K^{2323} = \frac{1}{2}\Xi_a$ (B.20)

with the definitions:

$$\Xi_a = \frac{a^4}{\Omega_0} \left[\phi''(R^2) + 2F'(\bar{\rho}_e) \rho''(R^2) \right] \quad , \quad \Xi_b = 16 \frac{a^4}{\Omega_0} F''(\bar{\rho}_e) \rho'(R^2) \rho'(R^2) \quad (B.21)$$

In the case of the average of the VOIGT shear modulus it follows $(a^4 = 4R^4)$ that:

$$G = \frac{2}{5}\Xi_a = \frac{2a^4}{5\Omega_0} \left[\phi''(R^2) + 2F'(\bar{\rho}_e)\rho''(R^2) \right] = \frac{8}{5} \frac{\phi_e \gamma(\gamma - \beta)}{\Omega_0}$$
(B.22)

or:

$$G = \frac{24}{15} \frac{\Phi_e \gamma(\gamma - \beta)}{\Omega_0} \,. \tag{B.23}$$

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_{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:

$$E_{\rm uvf} = -6\phi_{\rm e} - 12F(\bar{\rho}_{\rm e}) + 12F(\frac{11}{12}\bar{\rho}_{\rm e}) = \stackrel{(3.75)}{=} -\Phi_{\rm e} + 12(E_{\rm sub} + \Phi_{\rm e}) - 12E_{\rm sub} \left[1 + h\left(\frac{11}{12}\right)\right] \times \times \exp\left[-h\left(\frac{11}{12}\right)\right] - 12\Phi_{\rm e} \left(\frac{11}{12}\right)^{\frac{\gamma}{\beta}}$$
(B.24)

with $h(x) = \alpha \left(\sqrt{1 - \frac{1}{\beta} \ln x} - 1 \right)$. We consider TAYLOR-expansions of the form:

$$h(x) = -\frac{1}{2}\frac{\alpha}{\beta}(x-1) + \frac{1}{4}\frac{\alpha}{\beta}\left(1 - \frac{1}{2\beta}\right)(x-1)^2 + \dots , \qquad (B.25)$$

$$\exp[-h(x)] = 1 + \frac{1}{2}\frac{\alpha}{\beta}(x-1) - \frac{1}{4}\frac{\alpha}{\beta}\left(1 - \frac{1}{2\beta} - \frac{\alpha}{2\beta}\right)(x-1)^2 + \dots , \quad (B.26)$$

$$x^{\frac{\gamma}{\beta}} = 1 + \frac{\gamma}{\beta}(x-1) + \frac{1}{2}\frac{\gamma}{\beta}\left(\frac{\gamma}{\beta} - 1\right)(x-1)^2 + \dots$$
 (B.27)

and evaluate them at $x = \frac{11}{12}$ so that:

$$E_{\rm uvf} = \frac{E_{\rm sub}}{24} \left(\frac{\alpha}{\beta}\right)^2 \left[\frac{337}{1152} + \frac{1}{2304}\beta^2 \left(\frac{1}{2} + \frac{a}{2}\right)\right] + \Phi_{\rm e} \left(\frac{\gamma - \beta}{\beta}\right) \left(1 - \frac{1}{24}\frac{\gamma}{\beta}\right). \tag{B.28}$$

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 $\Phi_{\rm e} \left(\frac{\gamma - \beta}{\beta}\right)$. Therefore it is reasonable to consider the approximation:

$$E_{\rm uvf} \cong \Phi_{\rm e} \left(\frac{\gamma - \beta}{\beta}\right).$$
 (B.29)

Bibliography

- M. Abtew and G. Selvaduray. Lead-free Solders in Microelectronics. *Materials Science and Engineering*, 27:95–141, 2000.
- [2] S.M. Allen and J.W. Cahn. A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening. Acta Metallurgica et Materialia, 27:1085–1095, 1979.
- [3] H.W. Alt and I. Pawlow. On the entropy principle of phase transition models with a conserved order parameter. Advances in Mathematical Science and Applications, 6(1):291–376, 1996.
- [4] A.J. Ardell and R.B. Nicholson. The coarsening of γ' in Ni-Al alloys. Journal of Physics and Chemistry of Solids, 27:1793–1804, 1966.
- [5] M.I. Baskes. Modified embedded-atom potentials for cubic materials and impurities. *Physical Review B*, 46:2727–2742, 1992.
- [6] E. Becker and W. Bürger. Kontinuumsmechanik. Chapter 4.6 and 4.7 (pp. 87, 95).
 B.G. Teubner, Stuttgart, 1975.
- [7] R. Becker. Über den Aufbau binärer Legierungen. Zeitschrift für Metallkunde, 29(8):245–249, 1937.
- [8] R. Becker and W. Döring. Kinetische Behandlung der Keimbildung in übersättigten Dämpfen. Annalen der Physik (Leipzig), 24:719–752, 1935.
- [9] W.J. Boettinger, J.A. Warren, C. Beckermann, and A. Karma. Phase-field simulation of solidification. *Annual Review of Materials Research*, 32:163–194, 2002.
- [10] T. Böhme, W. Dreyer, F. Duderstadt, and W.H. Müller. A higher gradient theory of mixtures for multi-component materials with numerical examples for binary alloys. preprint No. 1286, ISSN 0946-8633. Weierstraß Institut für Angewandte Analysis und Stochastik, Berlin, 2007.
- [11] T. Böhme, W. Dreyer, and W.H. Müller. Determination of stiffness and higher gradient coefficients by means of the embedded-atom method - an approach for binary alloys. *Continuum Mechanics and Thermodynamics*, 18:411–441, 2007.

- [12] T. Böhme and W.H. Müller. Theoretical and experimental investigations of micromorphological changes in lead-free solders. *Computational Materials Science*, DOI: 10.1016/j.commatsci.2007.07.034, 2007 (in press).
- [13] E.A. Brandes and G.B. Brook, editors. Smithells Metals Reference Book. 7th edition, Chapter Mechanism of Diffusion (pp. 13-15, 13-18). Reed Educational and Professional Publishing Ltd., Oxford, 1992.
- [14] A. Brandmair. Anwendung höherer Gradiententheorien zur Simulation des Entmischungs- und Vergröberungsprozesses in bleifreien Lotwerkstoffen. Master's thesis, Institut für Mechanik, Technische Universität Berlin, 2007.
- [15] I.N. Bronstein, K.A. Semendjajew, G. Musiol, and H. Mühlig. Taschenbuch der Mathematik. 4., überarbeitete und erweiterte Auflage, Chapter 9.2 (pp. 513– 549). Verlag Harri Deutsch, 1999.
- [16] I.N. Bronstein, K.A. Semendjajew, G. Musiol, and H. Mühlig. Taschenbuch der Mathematik. 4., überarbeitete und erweiterte Auflage, Chapter 7.4 (pp. 415 ff.) and Chapter 19.6 (pp. 923). Verlag Harri Deutsch, 1999.
- [17] I.N. Bronstein, K.A. Semendjajew, G. Musiol, and H. Mühlig. Taschenbuch der Mathematik. 4., überarbeitete und erweiterte Auflage, Chapter 19.4 (pp. 898 ff.). Verlag Harri Deutsch, 1999.
- [18] I.N. Bronstein, K.A. Semendjajew, G. Musiol, and H. Mühlig. Taschenbuch der Mathematik. 4., überarbeitete und erweiterte Auflage, Chapter 17.1 (pp. 791–810). Verlag Harri Deutsch, 1999.
- [19] A. Bunse-Gerstner, P. Benner, and H. Faßbender. Numerik für Ingenieure und Naturwissenschaftler. Vorlesungsskript, Section 4.3 (pp. 111 ff.). Zentrum für Technomathematik, Universität Bremen, 2000.
- [20] A. Bunse-Gerstner, P. Benner, and H. Faßbender. Numerik für Ingenieure und Naturwissenschaftler. Vorlesungsskript, Section 3.3 (pp. 64 ff.). Zentrum für Technomathematik, Universität Bremen, 2000.
- [21] A. Bunse-Gerstner, P. Benner, and H. Faßbender. Numerik für Ingenieure und Naturwissenschaftler. Vorlesungsskript, Section 4.5 (pp. 123 ff.). Zentrum für Technomathematik, Universität Bremen, 2000.
- [22] J.W. Cahn. On spinodal decomposition. Acta Metallurgica et Materialia, 9:795– 801, 1962.
- [23] J.W. Cahn. Spinodal decomposition. Transaction of the Methallurgical Society of AIME, 242:166–180, 1968.
- [24] J.W. Cahn and J.E. Hilliard. Free energy of a Nonuniform System. I. Interfacial Free Energy. *The Journal of Chemical Physics*, 28(2):258–267, 1958.

- [25] J.W. Cahn and J.E. Hilliard. Spinodal decomposition: A reprise. Acta Metallurgica, 19:151–161, 1971.
- [26] P.P. Castañeda and P. Suquet. Nonlinear Composites. Advances in Applied Mechanics, 34:171–302, 1998.
- [27] B.D. Coleman and W. Noll. The thermodynamics of elastic materials with heat conduction and viscosity. Archive for Rational Mechanics and Analysis, 13:167–178, 1963.
- [28] M.S. Daw and M.I. Baskes. Semiempirical, quantum mechanical calculation of hydrogen embrittlement in metals. *Physical Review Letters*, 50:1285–1288, 1983.
- [29] M.S. Daw and M.I. Baskes. Embedded-atom method: derivation and application to impurities, surfaces and other defects in metals. *Physical Review B*, 29:6443–6453, 1984.
- [30] D. de Fontain. Clustering effects in solid solutions. Treatise on Solid State Chemistry, Vol. 5 Changes of State (edited by N.B. Hannay), pp. 129–178. Plenum, New York, 1975.
- [31] S.R. de Groot. Thermodynamik Irreversibler Prozesse. Chapter VII, (pp. 103-111). Bibliographisches Institut AG, Mannheim, 1960.
- [32] Directive 2002/95/EC of the European Parliament and of the Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS). Official Journal of the European Union, L 37/19, 2003.
- [33] Directive 2002/96/EC of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE). Official Journal of the European Union, L 37/24, 2003.
- [34] W. Dreyer. On Jump Conditions at Phase Boundaries for Ordered and Disordered Phases. preprint No. 869, ISSN 0946-8633. Weierstraß Institut für Angewandte Analysis und Stochastik, Berlin, 2003.
- [35] W. Dreyer and F. Duderstadt. On the modelling of semi-insulating GaAs including surface tension and bulk stresses. preprint No. 995, ISSN 0946-8633.
 Weierstraß Institut für Angewandte Analysis und Stochastik, Berlin, 2004.
- [36] W. Dreyer and W.H. Müller. Toward quantitative modeling of morphology changes in solids with phase field theories: Atomistic arguments for the determination of higher gradient coefficients. *Key Engineering Materials*, 240-242:113–126, 2003.
- [37] W. Dreyer and W.H. Müller. A study of coarsening in tin/lead solders. International Journal of Solids and Structures, 37:3841–3871, 2000.

- [38] W. Dreyer, W.H. Müller, and W. Weiss. Tales of thermodynamics and oscure applications of the second law. *Continuum Mechanics and Thermodynamics*, 12:151–184, 2000.
- [39] W. Dreyer and B. Wagner. Sharp-interface model for eutectic alloys part I: Concentration dependend surface tension. *Interfaces and Free Boundaries*, 7:199– 227, 2005.
- [40] F. Duderstadt. Anwendung der von Kármán'schen Plattentheorie und der Hertz'schen Pressung für die Spannungsanalyse zur Biegung von GaAs-Wafern im modifzierten Doppelringtest. PhD thesis, Fakultät V (Verkehrs- und Maschinensysteme), Technische Universität Berlin, 2004.
- [41] J.E. Dunn and J. Serrin. On the thermomechanics of interstitial working. Archive for Rational Mechanics and Analysis, 88:95–133, 1985.
- [42] G. Dziuk. Numerik I. Vorlesungsskript, Teil 18 (Available online at: http://www.mathematik.uni-freiburg.de/IAM/homepages/). Abteilung für Angewandte Mathematik, Universität Freiburg, 2005/2006.
- [43] C. Eckard. The thermodynamics of irreversible processes II. fluid mixtures. *Physical Review B*, 58:269–275, 1940.
- [44] J. Eiken, B. Böttger, and I. Steinbach. Multiphase-field approach for multicomponent alloys with extrapolation scheme for numerical application. *Physical Review E*, 73:066122–1–066122–9, 2006.
- [45] K.R. Elder, M. Grant, N. Provatas, and J.M. Kosterlitz. Sharp interface limits of phase-field models. *Physical Review E*, 64:021604–1–021604–18, 2001.
- [46] A. Fick. Uber Diffusion. Annalen der Physik (Leipzig), 94:59–86, 1855.
- [47] W.C.M. Filho, M. Brizoux, H. Frémont, and Y. Danto. Improved physical understanding of intermittent failure in continuous monitoring method. *Microelectronics Reliability*, 46:1886–1891, 2006.
- [48] B.K. Fishbein. Waste in the Wireless World: The Challenge of Cell Phones. New York: Inform Inc., 2002. URL: www.informinc.org.
- [49] Fraunhofer Institute for Reliability and Microintegration IZM. Infopool - Stand der Gesetzgebung zu umweltgerechten Elektronik-Produkten. URL: http://ak-bleifrei.izm.fraunhofer.de/servlet/is/224/. last online check: Oktober 8th, 2007.
- [50] Y. Fukuda, M.G. Pecht, K. Fukuda, and S. Fukuda. Lead-free Soldering in the Japanese Electronics Industry. *IEEE Transactions on Components and Packaging Technologies*, 26(3):616–624, 2003.

- [51] C. Făciu and A. Molinari. Evolution of layered structures in a gradientdependent viscoplastic material. *Journal de Physique IV*, 6:C1–45–C1–54, 1996.
- [52] H. Garcke, M. Rumpf, and U. Weikard. The Cahn-Hilliard equation with elasticity: Finite element approximation and qualitative studies. *Interfaces and Free Boundaries*, 3:101–118, 2001.
- [53] Gesetz über das Inverkehrbringen, die Rücknahme und die umweltverträgliche Entsorgung von Elektro- und Elektronikgeräten (Elektro- und Elektronikgerätegesetz - ElektroG). Bundesgesetzblatt, Teil I, Nr. 17, 2005.
- [54] G. Giacomin and J.L. Lebowitz. Phase segragation dynamics in particle systems with long range interactions. I. macroscopic limits. *Journal of Statistical Physics*, 87(1/2):37–61, 1997.
- [55] J.W. Gibbs. Thermodynamische Studien. Chapter: Theorie der Capillarität (pp. 258–387). Verlag von Wilhelm Engelmann (editor: W. Ostwald), Leipzig, 1892.
- [56] P. Goodman, P. Strudwick, and R. Skipper. Technical adaptation under Directive 2002/95/EC (RoHS) - Investigation of exemptions. ERA Report 2004-0603. ERA Technology Ltd., 2004.
- [57] A.E. Green and P.M. Naghdi. On basic equations for mixtures. Quaterly Journal of Mechanics and Applied Mathematics, 22(4):427–438, 1969.
- [58] M.E. Gurtin. Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance. *Physica D*, 92:178–192, 1996.
- [59] M.E. Gurtin and M.T. Lusk. Sharp-interface and phase-field theories of recrystallization in the plane. *Physica D*, 130:133–154, 1999.
- [60] E. Hairer and G. Wanner. Universite de Geneve, Dept. de Mathematiques, CH-1211 Geneve, Switzerland, 2002. Available online at: http://www.unige.ch/ hairer/prog/stiff/radau.f. last online check: November 29th, 2007.
- [61] M. Hillert. A solid-solution model for inhomogeneous systems. Acta Metallurgica et Materialia, 9:525–535, 1961.
- [62] Intel Corporation. Innovation from the Start. Microprocessor Poster, URL: http://download.intel.com/museum/Moores_Law/Printed_Materials, last online check: Oktober 7th, 2007.
- [63] ITRS Reports 2001 (Edition). URL: http://www.itrs.net/reports.html, last online check: Oktober 7th, 2007.

- [64] J.D. James, J.A. Spittle, S.G.R. Brown, and R.W. Evans. A review of measurement techniques for the thermal expansion coefficient of metals and alloys at elevated temperatures. *Measurement Science and Technology*, 12(3):R1–R15, 2001.
- [65] R.A. Johnson. Relationship between two-body interatomic potentials in a lattice model and elastic constants. *Physical Review B*, 6:2094–2100, 1972.
- [66] R.A. Johnson. Relationship between two-body interatomic potentials in a lattice model and elastic constants. II. *Physical Review B*, 9:1304–1308, 1974.
- [67] R.A. Johnson. Analytic nearest-neighbor model for FCC metals. *Physical Review B*, 37:3924–3931, 1988.
- [68] R.A. Johnson. Alloy model with the embedded-atom-method. *Physical Review B*, 39:12554–12559, 1989.
- [69] R.L. Keusseyan and J.L. Dilday. Development of brazing interconnection to low thermal expansion glass-ceramics for high performance multichip packaging. In *Proceedings of the 43rd Electronic Components and Technology Conference*, pages 896–903, Orlando, FL., USA, June 1st-6th 1993. IEEE.
- [70] H.K. Kim and K.N. Tu. Kinetic analysis of the soldering reaction between eutectic SnPb alloy and Cu accompanied by ripening. *Physical Review B*, 53:16027– 16034, 1996.
- [71] C. Kittel. Introduction to Solid State Physics. Chapter 4: Elastic Constants for Crystals (pp. 93). John Wiley & Sons, Inc., New York, 2nd edition, 1962.
- [72] T. Küpper and N. Masbaum. Simulation of particle growth and Ostwald ripening via the Cahn-Hilliard equation. Acta Metallurgica et Materialia, 42:1847– 1858, 1994.
- [73] L.D. Landau and E.M. Lifschitz. Lehrbuch der Theoretischen Physik, Band VII Elastizitätstheorie. Chapter Grundgleichungen (pp. 10). Akademie-Verlag, Berlin, 2nd edition, 1966.
- [74] J.S. Langer. Theory of spinodal decomposition in alloys. Annals of Physics, 65:53–86, 1971.
- [75] F.C. Larché and J.W. Cahn. The effect of self-stress on diffusion in solids. Acta Metallurgica et Materialia, 30:1835–1845, 1982.
- [76] J. Lau, D. Shangguan, T. Castello, R. Horsley, J. Smetana, N. Hoo, W. Dauksher, D. Love, I. Menis, and B. Sullivan. Failure analysis of lead-free solder joints for high-density packages. *Soldering & Surface Mount Technology*, 16(2):69–76, 2004. DOI: 10.1108/09540910410537345.

- [77] B.-J. Lee, M.I. Baskes, H. Kim, and Y.K. Cho. Second nearest-neighbor modified embedded atom method potentials for bcc transition metals. *Physical Review B*, 64:184102–1–184102–10, 2001.
- [78] L. Li and W.H. Müller. Computer modeling of the coarsening process in tin-lead solders. Computational Materials Science, 21:159–184, 2001.
- [79] I.M. Lifshitz and V.V. Slyozov. The kinetics of precipitation from supersaturated solid solutions. The Journal of Physics and Chemistry of Solids, 19(1/2):35–50, 1961.
- [80] I.-S. Liu. Method of Lagrange multipliers for exploitation of the entropy principle. Archive for Rational Mechanics and Analysis, 46:131–148, 1972.
- [81] V. Mehrmann. *Praktische Mathematik I.* Vorlesungsskript, Chapter 2 (pp. 13 ff.). Fakultät II, Institut für Mathematik, Technische Universität Berlin, 2001.
- [82] V. Mehrmann. Praktische Mathematik I. Vorlesungsskript, Chapter 6 (pp. 85 ff.). Fakultät II, Institut für Mathematik, Technische Universität Berlin, 2001.
- [83] MTdata NPL databank for materials thermochemistry. National Physical Laboratory, Queens Road, Teddington, Middlesex, TW11 0LW, 1998.
- [84] I. Müller. A thermodynamic theory of mixtures of fluids. Archive for Rational Mechanics and Analysis, 28:1–39, 1968.
- [85] I. Müller. Die Kältefunktion, eine universelle Funktion in der Thermodynamik viskoser wärmeleitender Flüssigkeiten. Archive for Rational Mechanics and Analysis, 40:1–36, 1971.
- [86] I. Müller. Thermodynamics. Chapter: Equations of Balance (pp. 62). Pitman Advanced Publishing Program, Boston, London, Melbourne, 1985.
- [87] I. Müller. Thermodynamics. Chapter: Thermodynamics of Mixtures of Nonviscos Fluids (pp. 186). Pitman Advanced Publishing Program, Boston, London, Melbourne, 1985.
- [88] I. Müller. Thermodynamics. Chapter: Nature and Scope of Thermodynamics (pp. 19) and Chapter: Thermodynamics of Mixtures of Non-viscos Fluids (pp. 186). Pitman Advanced Publishing Program, Boston, London, Melbourne, 1985.
- [89] I. Müller. Grundzüge der Thermodynamik. 2. Auflage. Berlin, Heidelberg, New York: Springer-Verlag, 1999.
- [90] I. Müller and P. Strehlow. Rubber and Rubber Balloons Paradigms of Thermodynamics. Chapter 5 (pp. 51). Springer Verlag, Berlin, Heidelberg, New York, 2004.

- [91] W.H. Müller. Zur Simulation des Mikroverhaltens thermo-mechanisch fehlangepaβter Verbundwerkstoffe. Fortschritt-Berichte VDI, Reihe 18 (Mechanik/Bruchmechanik), Nr. 234, Chapter 2.3 (pp. 36 ff.). VDI Verlag GmbH, Düsseldorf, 1998.
- [92] W.H. Müller. Morphology changes in solder joints experimental evidence and physical understanding. *Microelectronics Reliability*, 44:1901–1914, 2004.
- [93] W.H. Müller and T. Böhme. Quantitative Description of Micro-Structural Changes in lead-free Solder Alloys. In *Proceedings of the 8th Electronics Packaging Technology Conference*, pages 390–397, Singapore, December 6th-8th 2006. IEEE.
- [94] R. Najafabadi, D.J. Srolovitz, E. Ma, and M. Atzmon. Thermodynamic properties of metastable Ag-Cu alloys. *Journal of Applied Physics*, 74(5):3144–3149, 1993.
- [95] Nordic Innovation Centre. NoNE lead-free soldering guideline. Volume 2. SIN-TEF Report: STF90 A04620, 2004.
- [96] W. Ostwald. Über die vermeintliche Isomerie des roten und gelben Quecksilberoxids und die Oberflächenspannung fester Körper. Zeitschrift für Physikalische Chemie, 34:495–503, 1900.
- [97] J.-W. Park and T.W. Eagar. Application of the transient liquid phase bonding to microelectronics and MEMS packaging. In *Proceedings of the 8th Symposium* on Advanced Packaging Materials, pages 30–38, Stone Mountain, GA., USA, March 3rd-6th 2002. IEEE.
- [98] R. Pasianot and E.J. Savino. Embedded-atom-method interatomic potentials for HCP metals. *Physical Review B*, 45:12704–12710, 1992.
- [99] PC Welt. Umweltschutz: Intel setzt auf bleifrei (Hans-Christian Dirscherl). http://http://www.pcwelt.de/start/computer/prozessor/, May 22th, 2007. last online check: October 9th, 2007.
- [100] G. Petzow. Metallographisches Ätzen. 5., völlig neu bearbeitete Auflage. Berlin, Stuttgart: Borntraeger, 1976.
- [101] F. Pignatiello, M. De Rosa, P. Ferraro, S. Grilli, P. De Natale, A. Arie, and S. De Nicola. Measurement of the thermal expansion coefficients of ferroelectric crystals by a moiré interferometer. *Optics Communications*, 277:14–18, 2007.
- [102] W.H. Press, S.A. Teukolsky, W.T. Vertterling, and B.P. Flannery. Numerical Recipes in Fortran 77, The Art of Scientific Computing. 2nd edition, Chapter 16 (pp. 701 ff.). Cambridge University Press, 1992.
- [103] J.H. Rose, J.R. Smith, F. Guinea, and J. Ferrante. Universal features of the equation of state of metals. *Physical Review B*, 29:2963–2969, 1984.

- [104] P. Schwarztrauber and R. Valent. University Corporation for Atmoshperic Research, 2004. Available online at: www.cisl.ucar.edu/css/software/. last online check: November 27th, 2007.
- [105] F. Sontag. Ein Beitrag zur Bestimmung mechanischer Materialparameter für BCT-Gitter mit Hilfe atomarer Potentiale. student research thesis, 2007.
- [106] J. Stoer and R. Bulirsch. Einführung in die Numerische Mathematik II. Chapter 7.2 (pp. 101 ff.). Springer-Verlag, Berlin, Heidelberg, New York, 1973.
- [107] M. Tanaka. Recent trends in recycling activities and waste management in Japan. Journal of Material Cycles and Waste Management, 1(1):10–16, 1999.
- [108] C. Truesdell and W. Noll. The Non-linear Field Theories of Mechanics. In: Encyclopedia of Physics, Volume III/3 (edited by S. Flügge), pp. 309, 348. Springer-Verlag, Berlin, Heidelberg, New York, 1965.
- [109] C. Truesdell and W. Noll. The Non-linear Field Theories of Mechanics. In: Encyclopedia of Physics, Volume III/3 (edited by S. Flügge), pp. 302, 309, 327. Springer-Verlag, Berlin, Heidelberg, New York, 1965.
- [110] C. Truesdell and R. Toupin. The Classical Field Theories. In: Encyclopedia of Physics, Volume III/1 Principles of Classical Mechanics and Field Theories (edited by S. Flügge), pp. 226–793. Springer-Verlag, Berlin, Göttingen, Heidelberg, 1960.
- [111] C. Truesdell and R. Toupin. The Classical Field Theories. In: Encyclopedia of Physics, Volume III/1 Principles of Classical Mechanics and Field Theories (edited by S. Flügge), Eq. (251.1) on pp. 627 and the explanations on pp. 621. Springer-Verlag, Berlin, Göttingen, Heidelberg, 1960.
- [112] L.J. Turbini, G.C. Munie, D. Bernier, J. Gamalski, and D.W. Bergman. Examining the Environmental Impact of Lead-Free Soldering Alternatives. *IEEE Transactions on Electronics Packaging Manufacturing*, 24(1):4–9, 2001.
- [113] R.L.J.M. Ubachs, P.J.G. Schreurs, and M.G.D. Geers. A nonlocal diffuse interface model for microstructure evolution of tin-lead solder. *Journal of the Mechanics and Physics of Solids*, 52:1763–1792, 2004.
- [114] E. E. Underwood. Quantitative Stereology. Menlo Park (California), London, Don Mills (Ontario): Addison-Wesley Publishing, pp. 91-92, 1970.
- [115] P.W. Voorhees. The Theory of Ostwald Ripening. Journal of Statistical Physics, 38(1/2):231–252, 1985.
- [116] C. Wagner. Theorie der Alterung von Niederschlägen durch Umlösen (Ostwald Reifung). Zeitschrift für Elektrochemie, 65(7/8):581–591, 1961.

- [117] Y. Wang and A.G. Khachaturyan. Shape instability during precipitate growth in coherent solids. *Acta Metallurgica et Materialia*, 43(5):1837–1857, 1995.
- [118] Welt online. Entsorger fordern schnelle Regelung für Elektronikschrott. http://www.welt.de/print-welt/, February 18th, 2000. last online check: October 7th, 2007.
- [119] M. Winter. WebelementsTM. The University of Sheffield and WebElements Ltd., UK, Available online at: http://www.webelements.com/, 1993. last online check: October 16th, 2007.
- [120] L. Xu and J.H.L. Pang. Interfacial IMC and Kirkendall void on SAC Solder Joints subject to Thermal Cycling. In *Proceedings of the 7th Electronics Packag*ing Technology Conference, pages 863–867, Singapore, December 7th-9th 2005. IEEE.

Index

A

Ag-Cu, 41, 56, 73 f., 80 ff., 84 ff., 89 f., 105, 107 f., 114 – 117, 121 ff., 126 – 129, 131, 138 - 142eutectic, 41, 73, 82 f., 131 f., 134, 148 allov binary, 55 f., 66 brazing, 5, 73, 131 ammoniac, 134 arbitrary terms, 25 area intercept, 136 spinodal, 9 surface, 135, 137, 145 averaged, 137 array grid point, 94

В

B-W picture, 143 – 147 Bürger, W., 41 balance, 25 alternative partial mass, 19 alternative total mass, 18 internal energy, 18 local entropy, 24, 26 momentum, 18 partial mass, 18, 105 partial particle, 19, 44 static momentum, 52, 105, 107 total mass, 18 Baskes, M. I., 56 f., 65 Becker, E., 41 Becker, R., 13 body, 20 thermo-elastic, 21 f.

Brandmair, A., 114 Butcher diagram, 100

\mathbf{C}

Cahn, J. W., 14, 50, 70 Carnot, N. L. S., 20 Castigliano 1st and 2nd theorem, 41 Cauchy paradox, 56, 78 change micro-structural, 6 micromorphological, 11 Clausius, R., 19 f., 22 coarsening, 7 f., 10, 41, 105, 114 - 117, 121 ff., 125 f., 131, 135 rate, 118 ff., 124, 143, 146 stage, 145 coefficient diffusion, 109 f. linear thermal expansion, 36, 53, 106 f., 110 Coleman, B. D., 27 f. common tangent rule, 9, 73, 87 concentration equilibrium, 9, 74, 80, 87 ff., 108 f., 114 field, 52, 105, 114 initial, 120 mass, 16, 51, 70, 80 ff., 88, 112 particle, 8, 16 spinodal, 9, 108, 114 conductivity, 47 thermal, 30 conservation mass, 18consistent, 99

constituents, 16 convergence order, 99 copper (Cu), 74 f., 78 ff., 82, 109 crack initiation, 8 propagation, 8 curve concave, 9

D

Döring, W., 13 Daw, M. S., 56 f., 65 deformation, 33 elastic, 33 ff., 37, 71 inelastic, 33 lattice, 61 volumetric, 33 density, 24 atomic electron, 57, 59, 79 average electron, 67 background electron, 57 electron, 57 entropy, 21 ff., 26 free energy, 50, 108Gibbs free energy, 88 Helmholtz free energy, 28, 32, 70, 74 homogeneous mass, 52 internal energy, 18, 21 mass, 16, 34 partial mass, 18 particle, 16, 19, 34 reference mass, 21 total mass, 49 derivative Euler-Lagrange, 44, 46, 48, 51 spatial, 96 total temporal, 27, 51 variational, 51 description Euler, 17, 52 Lagrange, 17, 21, 52 material, 17 spatial, 17 deviation

average quadratic, 105 difference quotient, 98 diffusion, 33, 35 ff. downhill, 13 isothermal, 47 uphill, 13, 109 vacancy, 7 digital image analysis, 128, 131 f., 134, 143 -147 discrete Fourier Transforms, 11, 93, 95, 112, 114 discretization, 94, 118 local error of, 98 displacements, 15, 17 f., 21, 61, 105 discrete, 61 dissipation, 25 distance atomic, 118 equilibrium nearest neighbor, 74, 80 f., 83, 87 f., 90 radial, 67 Dreyer, W., 56, 70 driving force, 25

\mathbf{E}

effect dimension, 127 Dufour, 29 Gibbs-Thomson, 10, 14, 147 Ludwig-Soret, 29 effective lattice, 74 elastic constants, 78, 80 ff. electron gas homogeneous, 57 f. electron shells, 58 ElektroG, 2 Embedded-Atom-Method, 11, 50, 56 f. energy expression, 63 energy cohesive, 74, 76 complementary specific strain, 41 elastic, 72 free, 33, 108 Gibbs free, 8, 16, 41, 87, 90

Helmholtz free, 16, 30, 37, 46, 50 f., FFTPACK5, 112 107interfacial, 10, 14 internal, 16 of an atom, 64, 70 f., 74, 79 particle-specific, 60 specific stored, 41 specific strain, 41 sublimation, 60, 76 total elastic lattice, 63 total lattice, 62 vacancy formation, 76 ff. enthalpy excess, 89, 91 entropy, 16, 19 f., 24 entropy production, 24 f., 28, 43, 45 equation balance, 18 Cahn-Hilliard, 14, 52 constitutive, 19, 26 extended diffusion, 11, 51 ff. dimensionless, 112 field, 19, 25 Gibbs, 31 f., 39 f. Gibbs (alternative forms), 32 Gibbs (liquid mixture), 33 Gibbs (pure liquid), 33 Gibbs-Duhem, 31 mechanical constitutive, 30 ordinary differential, 93, 97 autonomous, 97 dimensionless, 113 non-autonomous, 100 stiff, 101 partial differential, 19, 52, 93 equations system of algebraic, 25 equilibrium, 20, 23, 25, 64 condition, 63, 65, 69, 72, 74, 80 f. etching, 131 f., 134 f., 138 experimental investigations, 131

F

failure, 7

Fick, A., 13 finite differences, 93, 96, 112 Flip Chips, 2 fluctuation, 9 flux diffusion, 28, 33, 46 f., 105 entropy, 20 - 24, 28, 45heat, 16, 21, 23, 28, 46 f. mass diffusion, 16, 18, 49 particle diffusion, 16, 19, 48 f. thermodynamical, 25 fraction mole, 16 function bilinear, 111 f. constitutive, 20 displacement, 61 embedding, 57, 75, 79 shape, 106 furnace electric arc melting, 132

G

Gibbs, J. W., 13 gradient deformation, 15, 17, 33, 35 f., 62 displacement, 17, 62 strain, 21 temperature, 23 velocity, 23, 28 graining, 134 Green, A. E., 28 grid point, 94, 96 grinding, 131 - 134

Η

 H_2O distilled, 133 H_2O_2 , 134 heat, 20heat engine, 20 heat of mixing, 89 heat treatment, 131 f., 135 higher derivative, 21 higher gradient, 11, 41, 50, 67 coefficients, 11, 50, 52 f., 55 f., 69, 72, 82 - 86, 92, 107, 110 ff., 114, 118 term, 43 Hillert, M., 13 Hilliard, J. E., 14, 50, 70

Ι

ideal gas, 20 incompressibility, 60 inequality Clausius-Duhem, 20, 24 dissipation, 42 entropy, 23 initial value problem, 102 interactions, 74 atom-electron, 57 atomic, 57 nearest neighbor, 61 repulsive (nuclei-nuclei), 57, 76, 79 intermetallic compound, 5, 7 interpolation bilinear, 111 iron, 41 ITRS, 2

J

Jacobi matrix, 103 Jacobian, 15, 17, 34 Johnson, R. A., 56, 59, 76, 92 jump condition, 87

Κ

Kirkendall effect, 7 void, 6

\mathbf{L}

Landau, L. D., 40 f. lattice (un)deformed, 61 cubic, 106

relaxation, 91 vibration, 92 lattice parameter, 60, 76, 110 law 2nd, 15, 20 f., 24 ff. Fick's, 13, 109 Fourier's, 13, 24, 30, 47 Hooke's, 53, 106 St. Venant Kirchhoff, 37, 65 Vegard's, 88 layer $Cu_3Sn, 6$ lead-free, 2-5length intercept, 124 Lifshitz, I. M., 14, 40 f. Liu method of, 21, 42 Liu, I.-S., 21 loading linear elastic, 105 pressure, 110 f., 117, 119, 125 tensile, 110 f., 116, 119, 125

\mathbf{M}

Müller, I., 21 Müller, W. H., 56, 70 Margules ansatz, 108 mass molecular, 16 reference, 16 total, 16 material data, 108 multi-phase, 41 maximum norm, 105 Maxwell tangent construction, see common tangent rule Maxwell's tangent, 88 f. mean field limit, 61, 66 melt, 52method (semi-)implicit, 101 f. (semi-)implicit Euler, 102 f.

explicit Euler, 97 f., 112, 119, 127 explicit Kutta, 100 f. explicit Runge-Kutta, 100 classical, 100 f. general, 100 explicit Runge-Kutta-Fehlberg, 105 explicit v. Heun, 98 f. implicit Euler, 102 implicit Runge-Kutta, 119 time integration, 11 one-step, 93, 97, 114 micro-graph, 135, 138 – 147 micromorphological evolution, 111 micromorphology, 11, 138 – 142 microscope, 133 microscopy optical, 133 f. microstructure, 6, 8 miniaturization, 1 miscibility gap, 8, 10 misfit, 33, 37 mixture, 18 binary, 47 f. eutectic, 9 multi-component, 11 multi-phase, 11, 41 thermo-elastic, solid, 33 mobility, 30, 47, 52, 107, 109 f. model nearest neighbor, 59 phase field, 14, 21 sharp interface, 14 Modified Embedded-Atom-Method, 92 modulus bulk, 60, 76 Voigt shear, 76 ff. momentum, 21 motion, 16, 35 multiplicative decomposition, 34

Ν

Naghdi, P. M., 28 nearest neighbor, 59 distance, 60, 72 needles $Ag_3Sn, 6$ Newton iteration, 102 f. Noll, W., 27 f. non-equilibrium, 20, 23 nucleation, 41 nucleus, 58

0

operator particle concentration, 66 Ostwald ripening, 7, 10, 110, 131, 138, 147

Ρ

packaging Chip Scale, 4 microelectronic, 4 f. parameter experimental, 76, 78 fit, 76, 78 particle shape, 136 perimeter phase, 135 periodic boundary conditions, 97 periodic continuation, 94, 97, 124 periodicity, 95 phase, 7, 133 Ag-rich(α), 8, 41, 81, 83, 89, 109, 114, 134, 138 boundary, 8, 41, 109, 118, 120, 124 $Cu-rich(\beta)$, 8, 41, 81, 83, 89, 109, 114, 135, 138 equilibrium, 8 f., 55, 109 intermetallic, 7 oblate-spheroid, 125 - 129, 137 ordered, 7 separation, 7 f., 105, 131 single, 26 spherical, 125 - 129, 137 phase diagram, 9 f., 87 - 90phase equilibria measurements, 34, 38 phase transformation, 41 polishing, 131 - 134

potential chemical, 16, 25 f., 29, 38 f., 46 ff. chemical (alternative), 29 strain, 39 potentials EAM, 74, 90 f. interatomic, 50, 56, 110 Lennard-Jones, 50, 56 precipitate, 136 $Ag_3Sn, 7$ preparation metallographic, 131, 133 pressure, 16, 26, 30, 34, 38 principle energy-minimization, 91, 147 entropy, 15, 19, 24 of equipresence, 24 of objectivity, 27, 40 printed circuit board, 4 pure-substance-limit, 82

Q

quantitiy constitutive, 19

R

RADAU, 113, 120, 123, 127 radius average phase, 134 equivalent phase, 134 mean phase, 124 – 129, 137, 143, 145 f., 1483D-equivalent, 124 relation algebraic, 96 Euler's, 97 hyper-elastic, 40 stress-strain, 24 representation functional, 26, 28, 42, 46, 48, 50, 75 representative volume element (RVE), 93 f., 97 Reynold's transport theorem, 20 RoHS, 2

\mathbf{S}

scallops, 7 $Cu_6Sn_5, 6$ shape oblate-spheroid, 136, 148 spherical, 136, 148 sharp interface boundary, 118 shift theorem, 95, 97 silver (Ag), 74 f., 78 ff., 82, 109 Simpson rule, 100 f. simulation 1D, 115ff., 124 2D, 119 - 123, 127 Slyozov, V. V., 14 solder, 5 Ag-Cu, 5, 8, 10 brazing, 5 f. joints, 5 lead, 1 SAC, 7 Sn-Ag, 5 Sn-Ag-Cu, 5, 7 Sn-Bi, 5 Sn-Cu, 5 Sn-Pb, 5, 8, 56 Sn-Zn, 5 soft, 5 soldering reflow, 4 f. wave, 5 solid multicomponent, 15, 35 multiphase, 15 non-reacting, multi-component, 41 non-reacting, thermo-elastic, 26 solidification eutectic, 10 space Fourier, 95 f., 112 real, 95 specimen, 133, 135 spinodal decomposition, 7, 9, 41, 109, 114 – 117, 121 ff.

stability, 103 criteria, 20 state, 33 current, 34 f. equilibrium, 61 homogeneous, 50 f. intermediate, 34 f. liquid, 9 reference, 16, 34 f. solid, 9 strain, 83 universal function of, 60, 75 statistical mechanics, 22 stiffness, 81, 106 coefficients, 55 f., 63, 65, 69, 72, 81 f. matrix, 14, 37, 77, 106 f., 109 strains, 111 f., 119 eigen, 37 elastic, 107 isotropic, 83 ff. line, 84, 86, 106 thermo-mechanical, 106 stresses, 21, 23, 26, 105 thermo-elastic, 11 structure BCC, 92 BCT, 56 FCC, 56, 59 f., 74, 83 HCP. 92 sum convention, 15 surface mount technology, 4 symbol Kronecker, 27

\mathbf{T}

temperature, 16, 18, 20 f., 23, 135 absolute, 22, 25 critical, 8 eutectic, 9, 41, 55 homogeneous, 20 homologeous, 135 tensor 1st Piola-Kirchhoff, 40, 106 2nd Piola-Kirchhoff, 15, 30, 36 f.

Cauchy stress, 15, 33, 36, 53, 106 Green strain, 17, 63, 83 linearized strain, 17, 52 right Cauchy-Green, 15, 17, 26, 52, 63 stress, 30 unimodular right Cauchy-Green, 15, 17, 26 theory higher gradient, 13 LSW, 14, 125, 146 phase field, 55, 67 thermal expansion, 33, 35 ff. thermodynamics second law of, 15 Thermodynamics of Irreversible Processes, 25thermoelasticity, 21 time adaptation, 104 Toupin, R., 41 transform Legendre, 29, 31 f., 41, 46, 48, 50 Truesdell, C., 41

U

unit cell, 60 universal gas constant, 108 unstable solution, 101

V

vacancy, 7, 19 variable, 19, 25 primary, 19, 105 vector Cartesian, 15 current position, 15, 61 grid point, 94 Lagrange position, 15 reference position, 61 wave, 95 velocity, 15 barycentric, 16, 18 void macroscopic, 7 Voigt notation, 107, 109 volume, 16 atomic, 60, 65 volume fraction, 143

\mathbf{W}

Wagner, C., 14 WEEE, 2 weight mean molecular, 16 molecular, 16 width interface, 120, 124 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