Weierstraß-Institut
für Angewandte Analysis und Stochastik

im Forschungsverbund Berlin e.V.

Preprint ISSN 0946 – 8633

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submitted: 20 Dez 2007

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No. 1286
Berlin 2007

2000 *Mathematics Subject Classification.* 74A15 74A50 74N15 74N25 80A17 80A20 82D35.

Key words and phrases. Thermodynamics, structured surfaces and interfaces, coexistent phases, Analysis of microstructure, Transformations involving diffusion.

Edited by
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WIAS preprint · No. 1286 (2007) · 1–48

A higher gradient theory of mixtures for multi-component materials with numerical examples for binary alloys

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(Dezember 2007)

A theory of mixture for multi-component materials is presented based on a novel, straightforward method for the exploitation of the Second Law of thermodynamics. In particular the constitutive equations for entropy, heat and diffusion flux as well as the stress tensor are formulated as a consequence of the non-negative entropy production. Furthermore we derive the established Gibbs equation as well as the Gibbs Duhem relation which also follow from the formalism. Moreover, it is illustrated, how local mechanical strains due to eigenstrains or external loadings, modify the free energy and, consequently, change the chemical potentials of the components. All consecutive steps are illustrated, first, for simple mixtures and, second, for a system containing two different phases. So-called higher gradients of the concentrations are considered, which take the nonuniform composition into account. It will also become apparent that more/other variables of modified/different physical problems beyond the illustrated ones can be easily treated within the presented framework. This work ends with the specification to binary alloys and with the presentation of various numerical simulations.

1 Introduction

The quantitative description of diffusion processes in solid mixtures represent an ongoing and important aspect in modern materials science. The reason for this is evident, since there is a continuously increasing demand in strength and lifetime of today's engineering materials (*e.g.*, lead-free solders or nickel-base alloys) which are permanently subjected to aging processes. One aspect of aging is given by diffusion in the bulk resulting in formation and growth of precipitated (dis)ordered phases. Accompanying phenomena are phase separation by spinodal decomposition and nucleation as well as coarsening by Ostwald-ripening both of which considerably change the internal microstructure of the materials and, consequently, their global behavior.

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. 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 nucleation and spinodal decomposition during which concentrations gradients are amplified. Although the latter processes are well-known from the experimental point of view, *cf.*, Ostwald (1900), 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 uphill diffusion. Already Gibbs (1892) was concerned about the conditions for the stability and formation of "discontinuities" in liquids and solids. 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. Becker (1937) also published a *molecular model* in order to describe the formation of superstructures and precipitations within binary solids. 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

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Weierstraß-Institut für Angewandte Analysis und Stochastik Berlin
preprint No. 1286 · ISSN 0946-8633 · 2007
http://www.wias-berlin.de/main/publications/wias-publ

solids» (sic!). This approach was generalized by Cahn & Hilliard (1958)[1]. 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.*, Cahn (1961, 1968), 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.* Langer (1971), and one finds a multitude of modifications, *cf.*, Giacomin & Lebowitz (1996), extentions, *e.g.* Allen & Cahn (1979), and generalizations, Gurtin (1996).

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*, Gurtin & Lusk (1999), Dreyer & Wagner (2005). However, note that it is also possible to treat a nonzero interface width within the SIM framework, Elder *et al.* (2001). A "subgroup" within SIM are so-called *LSW theories*, named after the seminal works of Lifshitz & Slyozov (1961) and Wagner (1961). 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.*, Ardell & Nicholson (1966). 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.*, Voorhees (1985).

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 (1961, 1968) incorporated *ad hoc* a separate elastic energy term for isotropic solids. 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 & Cahn (1982). They modified the elastic energy expression by a *concentration dependent stiffness matrix* but questions about the influence of strains to the interfacial energy remain.

Regardless of the open questions the focus has recently changed to *quantitative numerical simulations* initiated by the fast increasing computational capacities. The applied algorithms are mainly based on discrete FOURIER transforms, Wang & Khachaturyan (1995), or finite elements, Garcke *et al.* (2001), in order to solve the governing PDEs. In particular PFMs have been applied to simulations of the microstructure in solders, *cf.*, Dreyer & Müller (2000), Ubachs *et al.* (2004) as well as to solidification problems, Boettinger *et al.* (2002).

In the present work we want to turn the attention *back* to the theoretical aspects of diffusion. Our 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 we propose five statements of an entropy principle, which reflect the "*undisputed elements*" within the already existing principles (*cf.*, Section 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

[1]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.

end with the application of the theory in order to predict the phase evolution within the binary case study alloy Ag-Cu.

2 Symbols and Notation

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

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
$J = \det F^{ij} \geq 0$	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

thermodynamical quantities

ν	number of components of the mixture
$\alpha \in \{1, \ldots, \nu\}$	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
n_α	particle density of component α
$n = \sum_{\alpha=1}^{\nu} n_\alpha$	particle density of the mixture
$y_\alpha = n_\alpha/n = N_\alpha/N$	Mole fraction/particle concentration of α
$m_H = 1.66 \cdot 10^{-27}$ 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)
$\rho_\alpha = m_\alpha n_\alpha$	mass density of component α
$\rho = \sum_{\alpha=1}^{\nu} m_\alpha n_\alpha$	total mass density of the mixture
$M = M(y_\alpha) = \sum_{\alpha=1}^{\nu} M_\alpha y_\alpha$	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
ϵ, η	energy, entropy per unit mass
$\varphi = \epsilon - T\eta$	HELMHOLTZ free energy per unit mass
$\psi = \varphi + p/\rho$	GIBBS free energy per unit mass
μ_α	chemical potential (in J/particle) of component α
j_α^i	particle diffusion flux of component α
J_α^i	mass diffusion flux of component α
q^i	heat flux

[1]We use the index notation of Cartesian vectors ($\mathbf{v} \equiv v^i$) and tensors (*e.g.*, $\mathbf{T} \equiv T^{ij}$). Furthermore throughout this paper an upper index does *not* refer to contravariant coordinates. Rather it is used to avoid confusion with indices characterizing a particular constituent.

3 Some Elements of Nonequilibrium Thermodynamics

3.1 *Description of Motion and Deformation*

In order to measure the motion and deformation of a body a reference state is required, in which the position of the material points is referred to the coordinates 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

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

is called the motion.

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

$$v_0^i(t, X^j) = \frac{\partial \chi^i(t, X^j)}{\partial t} \quad \text{and} \quad U^i(t, X^j) = \chi^i(t, X^j) - X^j \ . \tag{2}$$

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

$$H^{ij} = \frac{\partial U^i}{\partial X^j} \quad \text{and} \quad F^{ij} = \frac{\partial \chi^i}{\partial X^j} = \delta^{ij} + H^{ij} \ . \tag{3}$$

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

$$X^i = (\chi^{-1})^i(t, x^j) \tag{4}$$

and eliminate the Lagrange coordinates in the equations (2) and (3). We define

$$\begin{aligned} v^i(t, x^j) &= v_0^i\Big(t, (\chi^{-1})^j(t, x^k)\Big) \quad , \qquad u^i(t, x^j) = U^i\Big(t, (\chi^{-1})^j(t, x^k)\Big) \ , \\ h^{ij} &= H^{ij}\Big(t, (\chi^{-1})^j(t, x^k)\Big) = \frac{\partial u^i}{\partial x^j} \quad , \quad (F^{-1})^{ij} = \frac{\partial (\chi^{-1})^i}{\partial x^j} = \delta^{ij} - h^{ij} \ . \end{aligned} \tag{5}$$

and call the newly introduced quantities the EULER or spatial description.

Next we introduce as measures of strain the right CAUCHY-GREEN tensor, C^{ij}, and the GREEN strain tensor, G^{ij}:

$$C^{ij} = F^{mi} F^{mj} \quad \text{and} \quad G^{ij} = \frac{1}{2}(C^{ij} - \delta^{ij}) \ . \tag{6}$$

Furthermore we introduce the *unimodular* right CAUCHY-GREEN tensor, c^{ij}, because it is useful to split C^{ij} into a pure volume-changing, $J^{2/3}$, and into a volume-preserving part, c^{ij}, which describes pure changes of the shape of the body:

$$C^{ij} = J^{2/3} c^{ij} \quad \text{with} \quad \det(c^{ij}) = 1 \ . \tag{7}$$

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:

$$\frac{\partial \rho_\alpha}{\partial t} = -\frac{\partial(\rho_\alpha v_\alpha^i)}{\partial x^i} + \tau_\alpha^\rho \qquad \text{(partial mass balance)}\,, \tag{8}$$

$$\frac{\partial \rho v^i}{\partial t} = -\frac{\partial}{\partial x^j}\left(\rho v^j v^i - \sigma^{ij}\right) \qquad \text{(momentum balance)}\,, \tag{9}$$

$$\frac{\partial \rho\epsilon}{\partial t} = -\frac{\partial}{\partial x^j}\left(\rho\epsilon v^j + q^j\right) + \sigma^{ij}\frac{\partial v^i}{\partial x^j} \qquad \text{(internal energy balance)}\,. \tag{10}$$

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. (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_α^ρ, on the right hand side of Eq. (8). Consequently the conservation of mass does not hold for the individual component α.

By summation of Eq. (8) w.r.t. all constituents $\alpha \in \{1,\dots,\nu\}$ the *conservation law of mass* for the whole mixture results. We write:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial(\rho v^i)}{\partial x^i} \tag{11}$$

$$\text{with} \quad \sum_{\alpha=1}^{\nu}\rho_\alpha \overset{\text{(def)}}{=} \rho \;,\; \sum_{\alpha=1}^{\nu}\rho_\alpha v_\alpha^i \overset{\text{(def)}}{=} \rho v^i \;,\; \sum_{\alpha=1}^{\nu}\tau_\alpha^\rho = 0\,. \tag{12}$$

An alternative form of Eq. (11) is given by $J = \rho_0/\rho$ where ρ_0 represents the mass density of the reference state, *cf.*, Müller (1985*a*). This relation follows by integrating Eq. (11) and by using the relation $\mathrm{d}J/\mathrm{d}t = J\cdot\partial v^i/\partial x^i$, *cf.*, Eq. (A2).

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:

$$J_\alpha^i \overset{\text{(def)}}{=} \rho_\alpha(v_\alpha^i - v^i) \qquad \text{which implies} \qquad \sum_{\alpha=1}^{\nu} J_\alpha^i = 0\,, \tag{13}$$

by means of Eq. $(12)_2$. The definition of the mass diffusion flux, *viz.* Eq. $(13)_1$, can be used in order to rewrite Eq. (8) in the following form:

$$\frac{\partial \rho_\alpha}{\partial t} = -\frac{\partial(\rho_\alpha v^i + J_\alpha^i)}{\partial x^i} + \tau_\alpha^\rho \qquad \text{(alternative partial mass balance)}\,. \tag{14}$$

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. (8). By means of $\rho_\alpha = m_\alpha n_\alpha$ we find:

$$\frac{\partial n_\alpha}{\partial t} = -\frac{\partial(n_\alpha v_\alpha^i)}{\partial x^i} + \tau_\alpha^n \quad \text{with} \quad \tau_\alpha^\rho = m_\alpha\tau_\alpha^n \quad , \quad \sum_{\alpha=1}^{\nu} m_\alpha\tau_\alpha^n = 0\,. \tag{15}$$

The *particle diffusion flux* is defined analogously to Eq. (13), *viz.*:

$$j_\alpha^i \overset{(\text{def})}{=} n_\alpha(v_\alpha^i - v^i) \quad \text{and} \quad J_\alpha^i = m_\alpha j_\alpha^i \quad , \quad \sum_{\alpha=1}^{\nu} m_\alpha j_\alpha^i = 0 \, . \tag{16}$$

Hence Eq. (15) can be written correspondingly to Eq. (14):

$$\frac{\partial n_\alpha}{\partial t} = -\frac{\partial (n_\alpha v^i + j_\alpha^i)}{\partial x^i} + \tau_\alpha^n \qquad \text{(alternative partial particle balance)} \, . \tag{17}$$

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.* $\{\rho_\alpha$ or n_α, v^i or $u^i, \rho\epsilon\}$, as *primary variables*. Beyond these variables further quantities, so-called *constitutive quantities*, such as σ^{ij}, q^i, J_α^i, j_α^i and $\tau_\alpha^{\rho/n}$, occur. They must be specified by means of *constitutive equations* which relate them to the variables and their derivatives in a material-dependent manner. The resulting so-called *field equations* represent a system of Partial Differential Equations (PDE) for the variables, which, in turn, can be solved with initial/boundary conditions.

3.4 *Entropy Principle*

Clausius introduced the concept of *entropy* in the 19th century (*cf.*, Dreyer *et al.* (2000) 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 *1st 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 *2nd 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 *2nd Law of Thermodynamics* (2^{nd} law), and it reads without a contribution from radiation:

$$\frac{\mathrm{d}S}{\mathrm{d}t} \geq \frac{\dot{Q}}{T} \quad \text{or} \quad \frac{\mathrm{d}}{\mathrm{d}t} \int_V \rho\eta \, \mathrm{d}V \geq -\frac{1}{T} \oint_{\partial V} q^i n^i \, \mathrm{d}A \, . \tag{18}$$

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 2^{nd} Law Clausius introduced a new additive quantity, which he called the *entropy* of the body. The equality sign holds in *equilibrium* and in *non-equilibrium* the variation of the entropy is larger than $\dot{Q}/T$.

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

In this paper we focus on the materials science point-of-view, and here the Eq. (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. $(18)_2$ 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. $(35)_1$ 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:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\eta \,\mathrm{d}V \geq -\oint_{\partial V} \frac{q^i n^i}{T}\,\mathrm{d}A \quad \Rightarrow \quad \frac{\partial \rho\eta}{\partial t} + \nabla_i\left(\rho\eta v^i + \frac{q^i}{T}\right) \geq 0\,. \tag{19}$$

Consequently the entropy flux is $\phi^i = q^i/T$, *cf.*, Colemann & Noll (1963), or Green & Naghdi (1969). However, this form of ϕ^i already fails in case of ideal gases, *cf.*, Dreyer *et al.* (2000), or binary fluid mixtures, *cf.*, Müller (1968). 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). 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.*, Făciu & Molinari (1996). 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 five, 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.

3.4.1 ***Simple One-dimensional Example: Thermoelasticity with Strain Gradients*** . In this section we give a simple illustration how an a priori assumption on the entropy flux can be avoided in order to base the entropy principle on firm grounds.

To this end we consider a one-dimensional thermo-elastic body with reference mass density $\rho_0 = 1\mathrm{kg/m}^3$, 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

$$\ddot{u} - \frac{\partial \sigma}{\partial x} = 0, \quad \dot{e} + \frac{\partial q}{\partial x} = \sigma \dot{u}_x\,. \tag{20}$$

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

$$\sigma = \sigma_0(e, u_x) - a(e, u_x)u_{xxx} - b(e, u_x)u_{xx}^2, \tag{21}$$

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 (20) with (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.*

$$s = h(e, u_x, u_{xx}, u_{xxx}). \tag{22}$$

We do not discuss here how to obtain that function. For example, it could be calculated within the frame-

work of statistical mechanics, as it is in fact usually done, *cf.*, Böhme *et al.* (2007).

We now form the time derivative of s:

$$\dot{s} = \frac{\partial h}{\partial e}\dot{e} + \frac{\partial h}{\partial u_x}\dot{u}_x + \frac{\partial h}{\partial u_{xx}}\dot{u}_{xx} + \frac{\partial h}{\partial u_{xxx}}\dot{u}_{xxx}, \tag{23}$$

and proceed with the elimination of $\dot{e}$ by means of the balance equation $(20)_2$. Next the product rule is used to rearrange terms. The result is:

$$\begin{aligned}\dot{s} = &- \frac{\partial}{\partial x}\left(\frac{\partial h}{\partial e}q - \left(\frac{\partial h}{\partial u_{xx}} - \frac{\partial}{\partial x}\frac{\partial h}{\partial u_{xxx}}\right)\dot{u}_x + \frac{\partial h}{\partial u_{xxx}}\dot{u}_{xx}\right) + \\ &+ \left(\frac{\partial h}{\partial u_x} - \frac{\partial}{\partial x}\frac{\partial h}{\partial u_{xx}} + \frac{\partial^2}{\partial x^2}\frac{\partial h}{\partial u_{xxx}} + \frac{\partial h}{\partial e}\sigma\right)\dot{u}_x + q\frac{\partial}{\partial x}\frac{\partial h}{\partial e}\ .\end{aligned} \tag{24}$$

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:

$$\frac{1}{T} = \frac{\partial h}{\partial e}, \quad \text{and} \quad \phi = \frac{q}{T} - \left(\frac{\partial h}{\partial u_{xx}} - \frac{\partial}{\partial x}\frac{\partial h}{\partial u_{xxx}}\right)\dot{u}_x + \frac{\partial h}{\partial u_{xxx}}\dot{u}_{xx}\ . \tag{25}$$

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

$$q\frac{\partial \frac{1}{T}}{\partial x} \geq 0, \tag{26}$$

i.e., the heat flux must be antiparallel to the temperature gradient.

3. The identity (24) is linear in the velocity gradient $\dot{u}_x$, however, it can arbitrarily chosen to construct an arbitrary solution of the system (20) and (21). In particular, it can be chosen so that the last line of (24) becomes negative. This can only be avoided by the requirement that the factor of $\dot{u}_x$ in (24) must vanish, *i.e.*:

$$\frac{\sigma}{T} = -\frac{\partial h}{\partial u_x} + \frac{\partial}{\partial x}\frac{\partial h}{\partial u_{xx}} - \frac{\partial^2}{\partial x^2}\frac{\partial h}{\partial u_{xxx}}\ . \tag{27}$$

Thus the identity (24) has turned into the entropy inequality:

$$\dot{s} + \frac{\partial \phi}{\partial x} \geq 0\ , \tag{28}$$

which results here as a consequence of the field equations and some additional assumptions: (**i**) The definition $(25)_1$ 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 (27), and (26), respectively, so that the field equations imply a further equation of balance, *viz.* (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 (22) is given by the

representation

$$s = h_0(e, u_x) - \frac{1}{2}\alpha(e, u_x)u_{xx}^2 + \gamma(e, u_x)u_{xxx} \ . \tag{29}$$

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 $(25)_2$ and (27) then yields the entropy flux

$$\phi = (\alpha + \gamma')u_{xx}\dot{u}_x - \gamma u_{xx} \ , \tag{30}$$

and the constitutive function for the stress

$$\frac{\sigma}{T} = -h_0' - (\alpha + 2\gamma')u_{xxx} - \frac{1}{2}(\alpha' + 2\gamma'')u_{xx}^2 \ . \tag{31}$$

A comparison of this result with (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

$$b = \frac{1}{2}a'. \tag{32}$$

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 (26), which is the classical FOURIER law

$$q = -\kappa\frac{\partial T}{\partial x} \quad \text{with} \quad \kappa > 0 \ . \tag{33}$$

Note that Dunn & Serrin (1985) 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 4.2.1.

3.4.2 ***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:

$$\rho\eta = \mathcal{S}\big(\text{variables, (functions of) derivatives of the variables}\big) \ , \tag{34}$$

   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* (Truesdell & Toupin 1960*a*), the arguments can differ.
2. There exists a local entropy balance

$$\frac{\partial\rho\eta}{\partial t} + \frac{\partial(\rho\eta v^k + \phi^k)}{\partial x^k} = \zeta \quad \text{with} \quad \zeta \geq 0 \quad (\text{dissipation inequality}) \ . \tag{35}$$

   The constraint of Eq. $(35)_2$, *viz.* the *non-negative entropy-production* ζ, represents the *Second Law of Thermodynamics*.

3. We define the *absolute temperature* to be:

$$\frac{1}{T} \overset{(\mathrm{def})}{=} \frac{\partial \rho\eta}{\partial \rho\epsilon} \,, \tag{36}$$

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*, Eckard (1940), we postulate the following form for the entropy production:

$$\zeta = \sum_z F_z D_z \quad , \quad F_z \overset{e.g.}{=} \{ j^k_\alpha \text{ or } J^k_\alpha, \sigma^{ij}_{\mathrm{diss}}, q^k \} \quad . \tag{37}$$

$\sigma^{ij}_{\mathrm{diss}}$ (with $\sigma^{ij} = \sigma^{ij}_{\mathrm{el}} + \sigma^{ij}_{\mathrm{diss}}$) 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, Eckard (1940), that the driving forces corresponding to the fluxes in (37) are

$$D_z = \Big\{ \nabla_i \Big(\frac{\mu_\alpha - \mu_\nu}{T} \Big), \nabla_{(i} v^{j)}, \nabla_i (1/T) \Big\} \,, \tag{38}$$

The newly introduced quantities μ_α are the chemical potentials, see Section 4 for their definition in the current study.

(b) For *equilibrium* the fluxes F_z vanish, *i.e.*, $F_z|_{\mathrm{eq}} \doteq 0$, which, in turn, guarantees the absence of dissipation, *i.e.*, $\zeta|_{\mathrm{eq}} = 0$, within equilibrium. Hence it follows that $\zeta|_{\mathrm{eq}}$ is minimal. Relying on the assumption that the F_z depend on the D_z, we may conclude that $D_z|_{\mathrm{eq}} = 0$ holds additionally.

3.4.3 ***The Role of the 2nd Law.*** The field equations (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 (9, 10,14) 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 Alt & Pawlow (1996). Due to the product rule the *arbitrary terms* on the right hand sides are:

$$\Big\{ \underbrace{\rho_\alpha, \frac{\partial v^i}{\partial x^i}, v^i, \frac{\partial \rho_\alpha}{\partial x^i}, \frac{\partial J^i_\alpha}{\partial x^i}, \tau^\rho_\alpha}_{\text{partial mass balance}}, \underbrace{\rho, \rho v^i, \frac{\partial v^{\langle i}}{\partial x^{j\rangle}}, \frac{\partial \sigma^{ij}}{\partial x^j}}_{\text{momentum balance}}, \underbrace{\rho\epsilon, \frac{\partial \rho\epsilon}{\partial x^i}, \frac{\partial q^i}{\partial x^i}, \sigma^{ij}}_{\text{internal energy balance}} \Big\} \,. \tag{39}$$

Alternatively, in order to investigate particle diffusion (*cf.*, Section 3.3), one must consider the balances (9, 10,17). Hence the quantities ρ_α, J^i_α and τ^ρ_α in Eq. (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. (39) representing an arbitrary solution of the balances.

4 Investigations of a Single Phase

4.1 *Exploitation of the 2nd Law for non-reacting, thermo-elastic Solids*

In what follows we consider a thermo-*elastic* solid mixture consisting of ν *non-reacting* components, *i.e.*, $\sigma^{ij}_{\mathrm{diss}} = 0 \Rightarrow \sigma^{ij} = \sigma^{ij}_{\mathrm{el}}$ and $\tau^n_\alpha = 0$. In particular we assume for the constitutive function of the entropy density $\rho\eta$ in Eq. (34) a quite simple form, for which we need, as we shall see, four alternative representations:

$$\rho\eta = \tilde{\mathcal{S}}(\rho\epsilon, n_1, \ldots, n_\nu, c^{ij}) = \hat{\mathcal{S}}(T, n_1, \ldots, n_\nu, c^{ij}) = \bar{\mathcal{S}}(T, y_1, \ldots, y_{\nu-1}, \rho, c^{ij}) = \acute{\mathcal{S}}(T, y_1, \ldots, y_{\nu-1}, C^{ij}) \,. \tag{40}$$

$\rho\epsilon$ identifies the thermal variable whereas the symbols n_α, $\alpha \in \{1,\dots,\nu\}$, 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. $(40)_4$ 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 3.2).

The alternative representations of the Eqs. $(40)_{1-4}$ give $\rho\eta$ by $\nu+6$ arguments and will be needed for different purposes. For instance we will see that the function $\tilde{\mathcal{S}}$ is extremely useful for the exploitation of the 2nd law whereas the sets of arguments in $\bar{\mathcal{S}}$, $\hat{\mathcal{S}}$ and $\acute{\mathcal{S}}$ 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. $(35)_1$ by means of the product rule:

$$\underbrace{\frac{\partial\tilde{\mathcal{S}}}{\partial t}}_{\mathsf{A}} + v^i \underbrace{\frac{\partial\tilde{\mathcal{S}}}{\partial x^i}}_{\mathsf{B}} + \tilde{\mathcal{S}}\frac{\partial v^i}{\partial x^i} + \frac{\partial\phi^i}{\partial x^i} = \zeta \,. \tag{41}$$

The expressions A and B can be re-written using Eq. $(40)_1$ and the chain rule, *viz.*

$$\frac{\partial\tilde{\mathcal{S}}}{\partial t} = \frac{\partial\tilde{\mathcal{S}}}{\partial\rho\epsilon}\frac{\partial\rho\epsilon}{\partial t} + \sum_{\alpha=1}^{\nu}\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial t} + \frac{\partial\tilde{\mathcal{S}}}{\partial c^{ij}}\frac{\partial c^{ij}}{\partial t} \quad , \quad \frac{\partial\tilde{\mathcal{S}}}{\partial x^i} = \frac{\partial\tilde{\mathcal{S}}}{\partial\rho\epsilon}\frac{\partial\rho\epsilon}{\partial x^i} + \sum_{\alpha=1}^{\nu}\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial x^i} + \frac{\partial\tilde{\mathcal{S}}}{\partial c^{kl}}\frac{\partial c^{kl}}{\partial x^i} \,. \tag{42}$$

The terms $\partial\rho\epsilon/\partial t$ and $\partial n_\alpha/\partial t$ in Eq. $(42)_1$ can be substituted by the right hand sides of the according balances, Eqs. (10) and (17). The resulting equation as well as the Eqs. $(42)_2$ and (36) can be inserted into Eq. (41). It follows:

$$\begin{aligned}\zeta = {}& \frac{1}{T}\left[-\frac{\partial}{\partial x^j}\left(\rho\epsilon v^j + q^j\right) + \sigma^{ij}_{\mathrm{el}}\frac{\partial v^i}{\partial x^j}\right] + \sum_{\alpha=1}^{\nu}\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha}\left[-\frac{\partial(n_\alpha v^i + j^\alpha_i)}{\partial x^i}\right] \\ & + \frac{\partial\tilde{\mathcal{S}}}{\partial c^{kl}}\underbrace{\left(\frac{\partial c^{kl}}{\partial t} + v^i\frac{\partial c^{kl}}{\partial x^i}\right)}_{=\mathrm{d}c^{kl}/\mathrm{d}t} + v^i\left(\frac{1}{T}\frac{\partial\rho\epsilon}{\partial x^i} + \sum_{\alpha=1}^{\nu}\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial x^i}\right) + \tilde{\mathcal{S}}\frac{\partial v^i}{\partial x^i} + \frac{\partial\phi^i}{\partial x^i} \,.\end{aligned} \tag{43}$$

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

$$\dot{c}^{kl} = -\frac{2}{3}J^{-2/3}\frac{\partial v^i}{\partial x^i}C^{kl} + J^{-2/3}\frac{\partial v^i}{\partial x^j}\left(F^{jk}F^{il} + F^{jl}F^{ik}\right) \,. \tag{44}$$

Rearrangement and reduction of the terms in Eq. (43) yield:

$$\begin{aligned}\zeta = {}& \frac{\partial}{\partial x^i}\left(\phi^i - \frac{q^i}{T} - \sum_{\alpha=1}^{\nu} j^i_\alpha\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha}\right) + \underbrace{\sum_{\alpha=1}^{\nu} j^i_\alpha\frac{\partial}{\partial x^i}\left(\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha}\right) + q^i\frac{\partial 1/T}{\partial x^i}}_{\mathsf{Q}} + \\ & \frac{\partial v^i}{\partial x^j}\left[\frac{\sigma^{ij}_{\mathrm{el}}}{T} + J^{-2/3}\left(F^{jk}F^{il} + F^{jl}F^{ik}\right)\frac{\partial\tilde{\mathcal{S}}}{\partial c^{kl}} + \delta^{ij}\left(\tilde{\mathcal{S}} - \frac{\rho\epsilon}{T} - \sum_{\alpha=1}^{\nu} n_\alpha\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha} - \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial\tilde{\mathcal{S}}}{\partial c^{kl}}\right)\right] \geq 0 \,,\end{aligned} \tag{45}$$

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. (45) is in agreement with the *Principle of Objectivity* formulated by Colemann & Noll (1963).

The arrangement of Eq.(45) presumes a priori knowledge on the entropy production ζ according to Statement 4 of Section 3.4. In particular we arrange the expression Q to be of the form $\sum F_z D_z$ and extract the terms linear in $\partial v^i/\partial x^j$ due to the arbitrary list elements in Eq. (39). Now we define the entropy flux ϕ^i as:

$$\phi^i \overset{(\mathrm{def})}{=} \frac{q^i}{T} + \sum_{\alpha=1}^{\nu} j_\alpha^i \frac{\partial \tilde{\mathcal{S}}}{\partial n_\alpha} \,. \tag{46}$$

Thus the parenthesis of the first summand in Eq. (45) vanishes and we obtain the form:

$$\mathsf{P}\mathsf{x} + \mathsf{Q} \geq 0 \quad , \quad \forall \mathsf{x} \in \mathbb{R} \qquad \Rightarrow \qquad \mathsf{P} = 0 \quad \wedge \quad \mathsf{Q} \geq 0 \,, \tag{47}$$

with the abbreviations $\mathsf{x} = \partial v^i/\partial x^j$ for the velocity gradient and $\mathsf{P} = [\ldots]$ for the bracket of the fourth term. The conclusion in Eq. (47) results since Eq. $(47)_1$ is linear in x, which can be *arbitrarily* chosen. Therefore we can violate the inequality except for the case $\mathsf{P} = 0 \wedge \mathsf{Q} \geq 0$.

Finally the definition of the entropy flux in Eq. (46) remedied the aforementioned flaw within the works of Coleman & Noll (1963) and Green & Naghdi (1969), in which the entropy flux is assumed to be $\phi^i = q^i/T$. The flux ϕ^i in Eq. (46) additionally incorporates diffusional contributions, which corresponds to the results of Müller (1985*b*).

4.2 *Selected Results*

4.2.1 *Heat Flux and Diffusion Flux.*

As a consequence of Eq. (45) and (47) we conclude:

$$q^i \frac{\partial 1/T}{\partial x^i} + \sum_{\alpha=1}^{\nu} j_\alpha^i \frac{\partial}{\partial x^i}\left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_\alpha}\right) \geq 0 \,. \tag{48}$$

A further evaluation of Eqs. (48) requires the substitution of the experimentally unmanageable expression $\partial\tilde{\mathcal{S}}/\partial n_\alpha$ by a measurable physical value. For this reason we introduce the following functional representations for the HELMHOLTZ free energy density $\rho\varphi$ according to Eq. (40):

$$\rho\varphi = \tilde{\mathcal{F}}(\rho\epsilon, n_1, \ldots, n_\nu, c^{ij}) = \hat{\mathcal{F}}(T, n_1, \ldots, n_\nu, c^{ij}) = \bar{\mathcal{F}}(T, y_1, \ldots, y_{\nu-1}, \rho, c^{ij}) = \acute{\mathcal{F}}(T, y_1, \ldots, y_{\nu-1}, C^{ij}) \,, \tag{49}$$

and define the *chemical potential* μ_α as:

$$\mu_\alpha \overset{(\mathrm{def})}{=} \frac{\partial \hat{\mathcal{F}}}{\partial n_\alpha} \,. \tag{50}$$

Moreover, the LEGENDRE transform as outlined in Appendix B yields:

$$\frac{\partial \tilde{\mathcal{S}}}{\partial n_\alpha} = -\frac{1}{T}\frac{\partial \hat{\mathcal{F}}}{\partial n_\alpha} = -\frac{\mu_\alpha}{T} \,. \tag{51}$$

By additionally applying the mass conservation of Eq. $(16)_3$, $j_\nu^i = -\sum_{\beta=1}^{\nu-1} \frac{m_\beta}{m_\nu} j_\beta^i$, the following form of Eq.

(48) is obtained:

$$q^i \frac{\partial 1/T}{\partial x^i} + \sum_{\alpha=1}^{\nu} j^i_\alpha \frac{\partial}{\partial x^i}\left(\frac{\partial \tilde{\mathcal{S}}}{\partial n_\alpha}\right) = q^i \frac{\partial 1/T}{\partial x^i} + \sum_{\beta=1}^{\nu-1} j^i_\beta \frac{\partial \left(\frac{m_\beta}{m_\nu}\mu_\nu - \mu_\beta\right)/T}{\partial x^i}$$
$$= q^i \frac{\partial 1/T}{\partial x^i} + \sum_{\beta=1}^{\nu-1} m_\beta j^i_\beta \frac{\partial \left(\frac{\mu_\nu}{m_\nu} - \frac{\mu_\beta}{m_\beta}\right)/T}{\partial x^i} \quad \geq \quad 0\,. \tag{52}$$

The simplest way to achieve a non-negative expression for the right hand side of Eq. $(52)_{1,2}$ is to choose q^i, $\sigma^{ij}_{\text{diss}}$, 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 thermo-diffusion coupling (Ludwig-Soret and Dufour effect, *cf.*, de Groot (1960)) is neglected we put:

$$j^i_\beta = \sum_{\delta=1}^{\nu-1} M^{ij}_{\beta\delta} \frac{\partial \left(\frac{m_\delta}{m_\nu}\mu_\nu - \mu_\delta\right)/T}{\partial x^j} \quad , \quad J^i_\beta = \sum_{\delta=1}^{\nu-1} B^{ij}_{\beta\delta} \frac{\partial \left(\mu^*_\nu - \mu^*_\delta\right)/T}{\partial x^j} \quad , \quad q^i = \kappa^{ij} \frac{\partial 1/T}{\partial x^j}\,, \tag{53}$$

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

$$\mu^*_\alpha = \frac{\partial \hat{\tilde{\mathcal{F}}}(T, \rho_1, \ldots, \rho_\nu, c^{ij})}{\partial \rho_\alpha} = \frac{1}{m_\alpha}\frac{\partial \hat{\mathcal{F}}}{\partial n_\alpha} \quad , \quad \alpha = \{1, \ldots, \nu\}\,. \tag{54}$$

Note that the material-specific, *positive definite diagonal* matrices $M^{ij}_{\beta\delta}$, $B^{ij}_{\beta\delta}$ and κ^{ij} in Eq. (53) are *not* necessarily constant and, in general, can depend on the same arguments used in the Eqs. (40/49).

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. $(53)_3$ 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. $(53)_{1,2}$ 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*.

4.2.2 ***Mechanical Constitutive Equations.*** In order to determine the pressure and the stress tensor we consider the condition $\mathsf{P} = 0$ in Eq. (47). The trace of σ^{ij} defines the pressure. One obtains from Eq. (45):

$$p = -\frac{1}{3}\sigma^{kk} = \frac{1}{3}J^{-2/3}T\left(F^{mk}F^{ml} + F^{ml}F^{mk}\right)\frac{\partial \tilde{\mathcal{S}}}{\partial c^{kl}} + T\left(\rho\eta - \frac{\rho\epsilon}{T} - \sum_{\alpha=1}^{\nu} n_\alpha \frac{\partial \tilde{\mathcal{S}}}{\partial n_\alpha} - \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial \tilde{\mathcal{S}}}{\partial c^{kl}}\right). \tag{55}$$

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 $\partial\tilde{\mathcal{S}}/\partial c^{kl}$ vanish and it follows by means of Eqs. (B6) and $(C6)_2$ in Appendix B,C:

$$\begin{aligned} p &= -\rho\varphi - T\sum_{\alpha=1}^{\nu} n_\alpha \frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha} \\ &\overset{\text{(App. B)}}{=} -\rho\varphi + \sum_{\alpha=1}^{\nu} n_\alpha \frac{\partial\hat{\mathcal{F}}}{\partial n_\alpha} \overset{\text{(App. C)}}{=} -\rho\varphi + \sum_{\alpha=1}^{\nu} n_\alpha m_\alpha \frac{\partial\bar{\mathcal{F}}}{\partial\rho} + \underbrace{\sum_{\alpha=1}^{\nu}\sum_{\beta=1}^{\nu-1} y_\alpha \frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}\left(\delta^{\alpha\beta} - \frac{n_\beta}{n}\right)}_{=0} \qquad (56) \\ &= -\rho\varphi + \rho\frac{\partial\bar{\mathcal{F}}}{\partial\rho} = \rho^2\frac{\partial\bar{\varphi}}{\partial\rho} \, . \qquad (57) \end{aligned}$$

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 and analyze the constraint $\mathsf{P} = 0$ with respect to Eq. (45):

$$\begin{aligned} t^{ij} &= J(F^{im})^{-1}\sigma^{mn}(F^{jn})^{-1} \\ &= -J^{1/3}T\left[\delta^{jk}\delta^{il} + \delta^{jl}\delta^{ik}\right]\frac{\partial\tilde{\mathcal{S}}}{\partial c^{kl}} - JT\underbrace{(F^{in})^{-1}(F^{jn})^{-1}}_{=(C^{ij})^{-1}}\left(\tilde{\mathcal{S}} - \frac{\rho\epsilon}{T} - \sum_{\alpha=1}^{\nu} n_\alpha\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha} - \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial\tilde{\mathcal{S}}}{\partial c^{kl}}\right) \\ &= -2J^{1/3}T\frac{\partial\tilde{\mathcal{S}}}{\partial c^{ij}} + J(C^{ij})^{-1}\left(\rho\varphi + T\sum_{\alpha=1}^{\nu} n_\alpha\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha} + \frac{2}{3}J^{-2/3}TC^{kl}\frac{\partial\tilde{\mathcal{S}}}{\partial c^{kl}}\right). \qquad (58) \end{aligned}$$

This equation can be further simplified by successively applying the Legendre transforms of Appendix B, C and D. One obtains:

$$\begin{aligned} t^{ij} &\overset{\text{(App. B,C)}}{=} 2J^{1/3}\frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}} + J(C^{ij})^{-1}\left(\rho\varphi - \rho\frac{\bar{\mathcal{F}}}{\partial\rho} - \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial\bar{\mathcal{F}}}{\partial c^{kl}}\right) \\ &\overset{\text{(App. D)}}{=} 2J^{1/3}\frac{\partial\acute{\mathcal{F}}}{\partial C^{kl}}\left(\frac{\rho_0}{\rho}\right)^{2/3} + J(C^{ij})^{-1}\left(\rho\varphi + \frac{2}{3}J^{2/3}c^{kl}\frac{\partial\acute{\mathcal{F}}}{\partial C^{kl}} - \frac{2}{3}C^{kl}\frac{1}{2}(\delta^{mk}\delta^{nl} + \delta^{nk}\delta^{ml})\frac{\partial\acute{\mathcal{F}}}{\partial C^{mn}}\right) \\ &= 2J\frac{\partial\acute{\mathcal{F}}}{\partial C^{ij}} + J(C^{ij})^{-1}(\rho\varphi) = 2J\frac{\partial\rho}{\partial C^{ij}}\varphi + 2J\rho\frac{\partial\acute{\varphi}}{\partial C^{ij}} + J(C^{ij})^{-1}(\rho\varphi) \\ &= 2J\rho\frac{\partial\acute{\varphi}}{\partial C^{ij}} = 2\rho_0\frac{\partial\acute{\varphi}}{\partial C^{ij}} \, . \qquad (59) \end{aligned}$$

For the last step in Eq. (59) we used the relation $\partial\rho/\partial C^{ij} = \frac{\partial}{\partial C^{ij}}\left(\frac{\rho_0}{(\det\mathbf{C})^{1/2}}\right) = -\frac{\rho_0}{2}(\det\mathbf{C})^{-3/2}\frac{\partial}{\partial C^{ij}}(\det\mathbf{C}) = -\frac{\rho_0}{2}(\det\mathbf{C})^{-1/2}(C^{ij})^{-1} = -\frac{\rho}{2}(C^{ij})^{-1}$.

4.2.3 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. $(56)_2$:

$$\frac{p}{\rho} + \varphi = \frac{1}{\rho}\sum_{\alpha=1}^{\nu} n_\alpha\frac{\partial\hat{\mathcal{F}}}{\partial n_\alpha} = \frac{1}{\rho}\sum_{\alpha=1}^{\nu} n_\alpha\mu_\alpha \, , \quad \text{(Gibbs-Duhem equation)} \, . \qquad (60)$$

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

$$\mathrm{d}(\rho\varphi) = \frac{\partial\hat{\mathcal{F}}}{\partial T}\,\mathrm{d}T + \sum_{\alpha=1}^{\nu}\frac{\partial\hat{\mathcal{F}}}{\partial n_\alpha}\,\mathrm{d}n_\alpha + \frac{\partial\hat{\mathcal{F}}}{\partial c^{ij}}\,\mathrm{d}c^{ij}\ . \tag{61}$$

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 B, C and D; it follows:

$$\frac{\partial\hat{\mathcal{F}}}{\partial T} \;=\; \frac{\partial}{\partial T}\left(\hat{\mathcal{E}} - T\hat{S}\right) \overset{\text{(App. B)}}{=} -\rho\eta \quad , \quad \frac{\partial\hat{\mathcal{F}}}{\partial n_\alpha} = \mu_\alpha \quad , \tag{62}$$

$$\frac{\partial\hat{\mathcal{F}}}{\partial c^{ij}} \overset{\text{(App. C)}}{=} \frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}} \;=\; \rho\frac{\partial\varphi}{\partial c^{ij}} \overset{\text{(App. D)}}{=} \rho J^{2/3}\frac{\partial\varphi}{\partial C^{ij}} \overset{(59)}{=} \frac{1}{2}J^{-1/3}t^{ij}\ . \tag{63}$$

In particular Eq. $(63)_2$ holds since ρ and c^{ij} are independent arguments within $\bar{\mathcal{F}}$. Thus we can finally write:

$$\mathrm{d}(\rho\varphi) = -\rho\eta\,\mathrm{d}T + \frac{1}{2}J^{-1/3}t^{ij}\,\mathrm{d}c^{ij} + \sum_{\alpha=1}^{\nu}\mu_\alpha\,\mathrm{d}n_\alpha\ , \quad \text{(GIBBS equation)}\ . \tag{64}$$

Eq. (64) 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 $\det c^{ij} = 1 \Leftrightarrow (c^{ij})^{-1}\mathrm{d}c^{ij} = 0$ holds. For the identification of the pressure and the 2nd Piola-Kirchhoff tensor one needs the Gibbs equation - according to Eqs. (57) and (59) - in terms of $\bar{\varphi}$ and $\acute{\varphi}$. Here a straightforward calculation yields the *two alternative forms* of the GIBBS equation:

$$\begin{aligned}\mathrm{d}\bar{\mathcal{F}} = \rho\mathrm{d}\bar{\varphi} + \bar{\varphi}\mathrm{d}\rho = \frac{\partial\bar{\mathcal{F}}}{\partial T}\mathrm{d}T + \frac{\partial\bar{\mathcal{F}}}{\partial\rho}\mathrm{d}\rho + \frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}}\mathrm{d}c^{ij} + \sum_{\beta}^{\nu-1}\frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}\mathrm{d}y_\beta \\ \Leftrightarrow \mathrm{d}\bar{\varphi} = -\eta\mathrm{d}T + \frac{p}{\rho^2}\mathrm{d}\rho + \frac{1}{\rho}\frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}}\mathrm{d}c^{ij} + \frac{1}{\rho}\sum_{\beta}^{\nu-1}\frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}\mathrm{d}y_\beta\ ,\end{aligned} \tag{65}$$

and

$$\begin{aligned}\mathrm{d}\acute{\mathcal{F}} = \rho\mathrm{d}\acute{\varphi} + \acute{\varphi}\mathrm{d}\rho = \frac{\partial\acute{\mathcal{F}}}{\partial T}\mathrm{d}T + \frac{\partial\acute{\mathcal{F}}}{\partial C^{ij}}\mathrm{d}C^{ij} + \sum_{\beta}^{\nu-1}\frac{\partial\acute{\mathcal{F}}}{\partial y_\beta}\mathrm{d}y_\beta \\ \Leftrightarrow \mathrm{d}\acute{\varphi} = -\eta\mathrm{d}T + \frac{1}{2\rho_0}t^{ij}\mathrm{d}C^{ij} + \frac{1}{\rho}\sum_{\beta}^{\nu-1}\frac{\partial\acute{\mathcal{F}}}{\partial y_\beta}\mathrm{d}y_\beta\ .\end{aligned} \tag{66}$$

Eqs. (65) and (66) allow for a direct identification of p and t^{ij} as partial derivatives of $\bar{\varphi}$ or $\acute{\varphi}$, respectively. However, the prize we pay is loss of the closed form for the chemical potential μ_α. Furthermore Eqs. (64, 65) can be used for the *liquid* matter, where for purely volumetric deformations $c^{ij} = \delta^{ij} \Leftrightarrow \mathrm{d}c^{ij} = 0$ holds. Consequently, one obtains from (64) for mixtures: $\mathrm{d}(\rho\varphi) = -\rho\eta\mathrm{d}T + \sum\mu_\alpha\mathrm{d}n_\alpha$ and from (65) for pure liquids: $\mathrm{d}\varphi = -\eta\mathrm{d}T + (p/\rho^2)\mathrm{d}\rho$, which matches the classical results of thermodynamics, *cf.*, Müller (1985*c*).

4.2.4 ***Splitting of the Free Energy into a Mechanical and a Chemical Part*[1].** 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. (50,54), which are necessary during calculation of the diffusion fluxes j^i_α or J^i_α in Eq. $(53)_{1,2}$.

(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 $\beta = \{1, 2, \ldots, \nu - 1\}$. These states are specified by the settings indicated in Table 2.

Table 2.: Specification of the three states required for the distinction between inelastic and elastic deformations in a multi-component thermo-elastic, diffusive solid.

	reference state S_0	intermediate state S_*	current state S
temperature T	T_0	$T_* = T$	T
composition y_β	y^0_β	$y^*_\beta = y_\beta$	y_β
deformation gradient F^{ij}	$F^{ij}_0 = \delta^{ij}$	F^{ij}_*	F^{ij}

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 1:

$$\sigma^{ij} \begin{cases} = -\bar{p}\delta^{ij} \stackrel{!}{=} \text{const.}\,, & \text{for } \mathsf{S}_0 \to \mathsf{S}_* \\ \neq -\bar{p}\delta^{ij}\,, & \text{for } \mathsf{S}_* \to \mathsf{S} \end{cases} \quad \text{and} \quad F^{ij} \begin{cases} = F^{ij}_*\,, & \text{for } \mathsf{S}_0 \to \mathsf{S}_* \\ = F^{ij}_{\mathrm{el}}\,, & \text{for } \mathsf{S}_* \to \mathsf{S} \end{cases}, \tag{67}$$

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^{ij}_{el} contains the pure elastic deformation. It is important to note that neither the concentration, *i.e.*, the distribution of the constituents over the lattice sites, nor the temperature do change for $\mathsf{S}_* \to \mathsf{S}$, *cf.*, Figure 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 $\mathsf{S}_0 \to \mathsf{S}_*$.

(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):

$$\rho_0 = m_H \cdot n_0 \cdot M(y^0_\alpha) \quad , \quad \rho_* = m_H \cdot n_* \cdot M(y_\alpha) \quad , \quad \rho = m_H \cdot n \cdot M(y_\alpha) \tag{68}$$

[1] This paragraph is based on preliminary considerations by Dreyer & Duderstadt (2004).

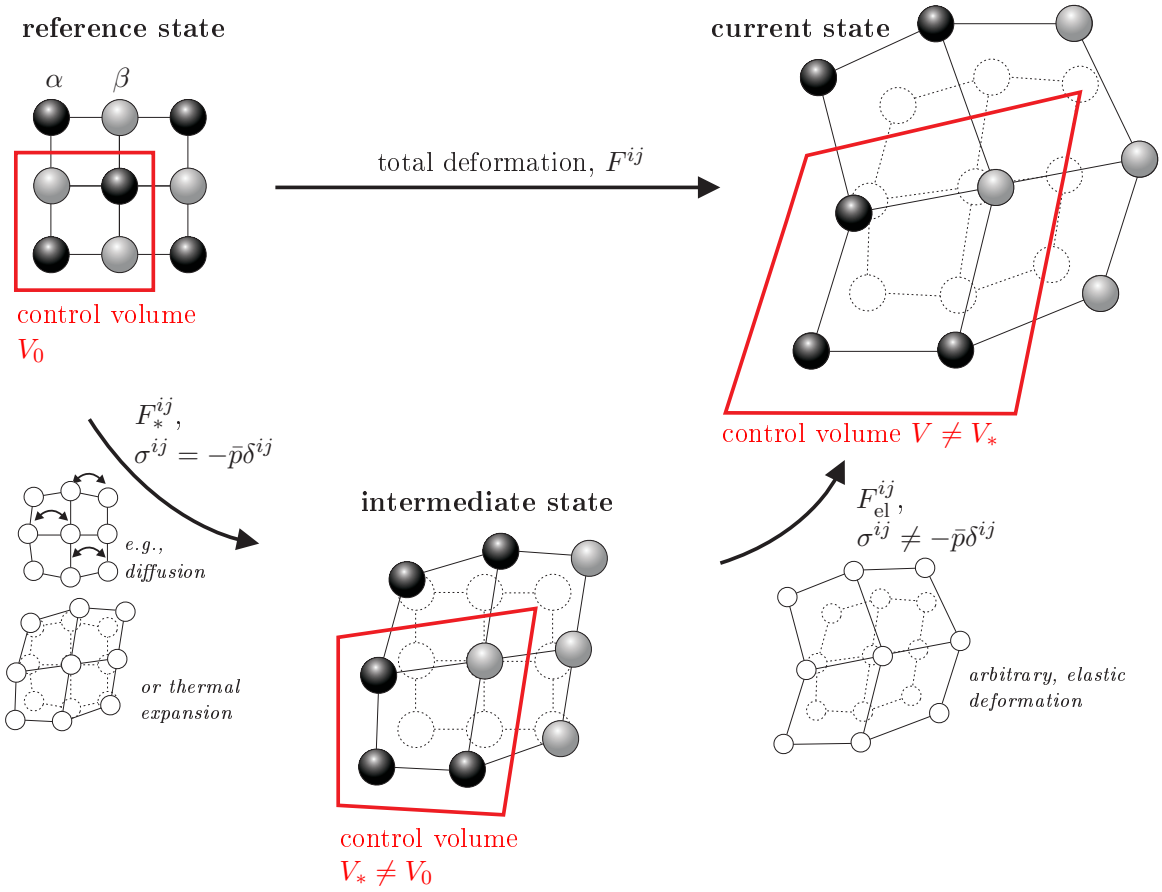

Figure 1.: Three states of a multi-component thermo-elastic diffusive solid. (a) The reference state S_0 with the reference temperature T, the reference composition y^0_β, and the reference (undeformed) strain state described by $F^{ij}_0 = \delta^{ij}$. (b) The intermediate state S_* with $T_* = T$, $y^*_\beta = y_\beta$, and F^{ij}_* for $\mathsf{S}_0 \to \mathsf{S}_*$. (c) The current state S with T, y_β, and F^{ij} for $\mathsf{S}_0 \to \mathsf{S}$ and $F^{ij}_{\rm el}$ for $\mathsf{S}_* \to \mathsf{S}$.

and the calculations of the Jacobians yields:

$$J_* \overset{\rm (def)}{=} \det F^{ij}_* = \frac{\rho_0}{\rho_*} = \underbrace{\frac{M(y^0_\alpha)}{M(y_\alpha)}}_{\overset{\rm (def)}{=}\nu(y_\alpha)} \frac{n_0}{n_*} \quad , \quad J_{\rm el} \overset{\rm (def)}{=} \det F^{ij}_{\rm el} = \frac{\rho_*}{\rho} = \frac{n_*}{n} \quad , \quad J \overset{\rm (def)}{=} \det F^{ij} = \frac{\rho_0}{\rho} = \nu(y_\alpha)\frac{n_0}{n} \, . \tag{69}$$

>From Eq. (69) the *multiplicative decomposition* of the Jacobian J directly follows:

$$J = J_{\rm el} J_* \, . \tag{70}$$

(III) Relations between the deformation gradients. In addition to Eq. (70) there is a corresponding decomposition of the total deformation gradient F^{ij}. If the concept of the three introduced states S_0, S_*, and S is accepted then we have

$$F^{ij} = F^{ik}_{\rm el} F^{kj}_* . \tag{71}$$

The proof of Eq. (71) directly follows from the three motions of the body (see Section 3.1):

$$x^i = \chi^i(t, X^j) \quad , \quad X^i_* = \chi^i_*(t, X^j) \quad , \quad x^i = \chi^i_{\rm el}(t, X^j_*) \, , \tag{72}$$

so that by virtue of the chain rule we may write

$$F^{ij} = \frac{\partial \chi^i}{\partial X^j} = \underbrace{\frac{\partial \chi^i_{\rm el}}{\partial X^k_*}}_{=F^{ik}_{\rm el}} \underbrace{\frac{\partial \chi^k_*}{\partial X^j}}_{=F^{kj}_*} \, . \tag{73}$$

(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.*, James *et al.* (2001), or Pignatiello *et al.* (2007). In this case we may write

$$J_* = \underbrace{\nu(y_\beta)}_{=1} \frac{n_0}{n_*} = \frac{n_0}{n_*} = \frac{V_*}{V_0} = [1 + \alpha(T - T_0)]^3 \, , \tag{74}$$

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

$$J_* = \det F^{ij}_* = \nu(y_\beta) \frac{n_0}{n_*} = \nu(y_\beta) \frac{V_*}{V_0} = \nu(y_\beta) \left[1 + \alpha(T - T_0)\right]^3 \, . \tag{75}$$

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

$$F^{ij}_* = \nu(y_\beta)^{1/3} \left[\delta^{ij} + \alpha^{ij}(T - T_0)\right] \, . \tag{76}$$

(V) Two second* Piola-Kirchhoff *&* Cauchy *stress tensors. According to Section 2 the Cauchy stress tensor can be written as:

$$\sigma^{ij} = \frac{1}{J} F^{im} F^{jn} t^{mn} \quad , \quad \sigma^{ij} = \frac{1}{J_{\rm el}} F^{im}_{\rm el} F^{jn}_{\rm el} z^{mn} \, , \tag{77}$$

where t^{ij} refers to the reference state S_0 and z^{ij} to the intermediate state S_*. A combination of Eq. $(77)_{1,2}$ yields the relation:

$$t^{ij} = J_* (F^{-1}_*)^{im} (F^{-1}_*)^{jn} z^{mn} \, . \tag{78}$$

(VI)* St. Venant-Kirchhoff *law. The St. Venant-Kirchhoff law relates a second Piola-Kirchhoff stress tensor to the elastic strains, *cf.*, Truesdell & Noll, (1965*a*). Since for the case illustrated in Figure 1 the elastic deformation starts at S_* and ends in S, we have to formulate that law for z^{ij}. It reads:

$$z^{ij} = -\bar{p} J_{\rm el} (C^{-1}_{\rm el})^{ij} + \frac{1}{2} \bar{K}^{ijkl}(T, y_\beta) \left(C^{kl}_{\rm el} - \delta^{kl}\right) \quad \text{with} \quad C^{kl}_{\rm el} = F^{mk}_{\rm el} F^{ml}_{\rm el} \, , \tag{79}$$

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. (59), we also need to know the second PIOLA-KIRCHHOFF stress tensor t^{ij}. By inserting Eq. (79) into Eq. (78) we find after some rearrangements of terms:

$$t^{ij} = -\bar{p}J(C^{-1})^{ij} + \frac{1}{2}K^{ijkl}(T, y_\beta)\left(C^{kl} - C_*^{kl}(T, y_\beta)\right) \tag{80}$$

with the definitions:

$$C_*^{kl} = F_*^{mk}F_*^{ml} \quad , \quad C^{kl} = F^{mk}F^{ml} \quad \text{and} \quad K^{ijkl} = J_*(F_*^{-1})^{im}(F_*^{-1})^{jn}(F_*^{-1})^{kp}(F_*^{-1})^{lq}\bar{K}^{mnpq}\,. \tag{81}$$

The Jacobian J_* as well as the deformation gradient F_*^{ij} depend on temperature T and on the concentrations y_β, *cf.*, Eqs. $(76)_2$ and (75), 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.

(VII) Chemical and mechanical part of the free energy. According to the decomposition of the deformation gradient in Eq. (71) we now present a decomposition of the HELMHOLTZ free energy into a *chemical part* and into a *mechanical part*, which refers, in this context, to the elastic deformations. We assume that the HELMHOLTZ free energy can be represented by two additive contributions

$$\varphi = \varphi^{\text{mech}} + \varphi^{\text{chem}}. \tag{82}$$

If the total HELMHOLTZ free energy is given, we identify those two contributions by the definitions:

$$\varphi^{\text{chem}} \overset{\text{(def)}}{=} \acute{\varphi}\left(T, y_1, \dots, y_{\nu-1}, C^{ij} = C_*^{ij}\right) \quad , \quad \varphi^{\text{mech}} \overset{\text{(def)}}{=} \acute{\varphi}\left(T, y_1, \dots, y_{\nu-1}, C^{ij}\right) - \varphi^{\text{chem}}\,. \tag{83}$$

The chemical part of the HELMHOLTZ free energy is typically obtained from measurements of phase equilibria 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 $\mathsf{S}_* \to \mathsf{S}$, is calculated from a given stress-strain relation, which is here given by Eq. (59). To this end recall that Eq. (80) depends on the variables $\{T, y_1, \dots, y_{\nu-1}, C^{ij}\}$ using the relation $J = \acute{J}(C^{kl}) = \sqrt{\det C_{kl}}$. Therefore we can insert Eq. (80) into Eq. (59) and integrate the result w.r.t. C^{ij}. We obtain

$$\acute{\varphi}(T, y_\beta, C^{ij}) = \frac{K^{ijkl}(T, y_\beta)}{8\rho_0}\big(C^{ij} - C_*^{ij}\big)\big(C^{kl} - C_*^{kl}\big) - \frac{\bar{p}}{\rho_0}\big[J_*(T, y_\beta) - \acute{J}\big] + \mathcal{K}(T, y_\beta)\,, \tag{84}$$

in which $\mathcal{K}$ and $\bar{p}J_*/\rho_0$ denote integration "constants" because they depend exclusively on the variables $\{T, y_1, \dots, y_{\nu-1}\}$. 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 $\rho\varphi$:

$$\acute{\mathcal{F}} = \frac{K^{ijkl}(T, y_\beta)}{8\acute{J}}\big(C^{ij} - C_*^{ij}\big)\big(C^{kl} - C_*^{kl}\big) - \bar{p}\left(\frac{J_*(T, y_\beta)}{\acute{J}} - 1\right) + \acute{\rho}\mathcal{K}(T, y_\beta)\,, \tag{85}$$

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

$$\rho\varphi^{\text{mech}} = \acute{\mathcal{F}}^{\text{mech}} = \frac{K^{ijkl}(T, y_\beta)}{8\acute{J}}\big(C^{ij} - C_*^{ij}\big)\big(C^{kl} - C_*^{kl}\big) - \bar{p}\left(\frac{J_*(T, y_\beta)}{\acute{J}} - 1\right)\,, \tag{86}$$

$$\rho\varphi^{\text{chem}} = \acute{\mathcal{F}}^{\text{chem}} = \acute{\rho}\mathcal{K}(T, y_\beta)\,. \tag{87}$$

In order to calculate the chemical potentials, μ_α, according to Eq. (50), we have to rewrite $\acute{\mathcal{F}}^{\text{mech/chem}}$ in

terms of $\{T, n_\alpha, c^{ij}\}$ with $\alpha = \{1, \dots, \nu\}$. By means of the relations

$$\rho = \hat{\rho}(n_\alpha) = \sum_\alpha m_\alpha n_\alpha \quad , \quad J = \hat{J}(n_\alpha) = \frac{\rho_0}{\sum_\alpha m_\alpha n_\alpha} \quad , \tag{88}$$

$$C^{ij} = \hat{J}^{2/3} c^{ij} \quad , \quad y_\beta = \hat{y}_\beta(n_\alpha) = \frac{n_\beta}{\sum_\alpha n_\alpha} \quad , \tag{89}$$

we reformulate Eq. (85) as follows:

$$\begin{aligned} \hat{\mathcal{F}} &= \hat{\mathcal{F}}^{\text{mech}} + \hat{\mathcal{F}}^{\text{chem}} = \\ &= \frac{K^{ijkl}(T, \hat{y}_\beta)}{8\hat{J}} \Big(\hat{J}^{2/3} c^{ij} - C_*^{ij}(T, \hat{y}_\beta) \Big) \Big(\hat{J}^{2/3} c^{kl} - C_*^{kl}(T, \hat{y}_\beta) \Big) + \hat{\rho} \mathcal{K}(T, \hat{y}_\beta) - \bar{p} \left(\frac{J_*(T, \hat{y}_\beta)}{\hat{J}} - 1 \right), \end{aligned} \tag{90}$$

which now may be differentiated w.r.t. n_α. As a result we find for the chemical potentials:

$$\begin{aligned} \mu_\alpha \overset{\text{(def)}}{=} \frac{\partial \hat{\mathcal{F}}}{\partial n_\alpha} &= \frac{(K^{ijkl})'}{8J} \frac{\partial \hat{y}_\beta}{n_\alpha} \big(C^{ij} - C_*^{ij}\big)\big(C^{kl} - C_*^{kl}\big) + \frac{K^{ijkl} m_\alpha}{8\rho_0} \big(C^{ij} - C_*^{ij}\big)\big(C^{kl} - C_*^{kl}\big) \\ &\quad + \frac{K^{ijkl}}{8J} \left(-\frac{2}{3} \frac{m_\alpha}{\rho} C^{ij} - (C_*^{ij})' \frac{\partial \hat{y}_\beta}{\partial n_\alpha} \right) \big(C^{kl} - C_*^{kl}\big) \\ &\quad + \frac{K^{ijkl}}{8J} \left(-\frac{2}{3} \frac{m_\alpha}{\rho} C^{kl} - (C_*^{kl})' \frac{\partial \hat{y}_\beta}{\partial n_\alpha} \right) \big(C^{ij} - C_*^{ij}\big) \\ &\quad - \bar{p} \left(\frac{J_*'}{J} \frac{\partial \hat{y}_\beta}{\partial n_\alpha} + J_* \frac{m_\alpha}{\rho_0} \right) + m_\alpha \mathcal{K} + \rho \mathcal{K}' \frac{\partial \hat{y}_\beta}{\partial n_\alpha} \, , \end{aligned} \tag{91}$$

where the symbol $(\Diamond)'$ stands for the derivative $\partial \Diamond / \partial y_\beta$. Furthermore we have $\partial \hat{y}_\beta / \partial n_\alpha = \frac{1}{n}(\delta^{\alpha\beta} - y_\beta)$, which follows directly from Eq. $(89)_2$.

4.3 *Comparison with the Literature:* Gibbs *and* Helmholtz *Free Energy, Specific Strain Energy, Complementary Strain Energy, and Theorems of* Castigliano

Finally we compare some of the derived equations with the literature. We specialize to *compressible pure substances* and start with the corresponding alternative form of the Gibbs relation in Eq. (66):

$$\mathrm{d}\varphi = -\eta \mathrm{d}T + \frac{1}{2\rho_0} t^{ij} \mathrm{d}C^{ij} \tag{92}$$

$$\Leftrightarrow \mathrm{d}w^\star = -\eta \mathrm{d}T - \frac{1}{2\rho_0} C^{ij} \mathrm{d}t^{ij} \quad \text{with} \quad w^\star \overset{\text{(def)}}{=} \varphi - \frac{1}{2\rho_0} t^{ij} C^{ij} \, , \tag{93}$$

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

Note that Eq. (93) - in which we *temporarily* call the introduced quantity $w^\star$ the *strain potential* - holds solely, if the stress strain relation is invertible[1]. Furthermore Eq. (92) and (93) imply the following *hyper-elastic* relations for the stresses and strains:

$$2\rho_0 \frac{\partial \tilde{\varphi}}{\partial C^{ij}} = t^{ij} \quad , \quad 2\rho_0 \frac{\partial \hat{w}^\star}{\partial t^{ij}} = -C^{ij} \, . \tag{94}$$

[1] A popular counter-example are rubber balloons, *cf.*, Müller & Strehlow (2004).

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

$$p^{ij} \overset{(\mathrm{def})}{=} J\sigma^{ik}(F^{-1})^{jk} \tag{95}$$

and the differentiation rule $\mathrm{d}C^{ij} = (\mathrm{d}F^{ki})F^{kj} + F^{ki}\mathrm{d}F^{kj}$. Then one obtains from Eq. (92):

$$\mathrm{d}\varphi = -\eta \mathrm{d}T + \frac{1}{\rho_0} p^{ij}\mathrm{d}F^{ij} \tag{96}$$

$$\Leftrightarrow \mathrm{d}w^\star = -\eta \mathrm{d}T - \frac{1}{\rho_0} F^{ij}\mathrm{d}p^{ij} \quad \text{with} \quad w^\star \overset{(\mathrm{def})}{=} \varphi - \frac{1}{\rho_0} p^{ij}F^{ij} \ , \tag{97}$$

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

$$\rho_0 \frac{\partial \bar{\varphi}}{\partial F^{ij}} = p^{ij} \quad , \quad \rho_0 \frac{\partial\, \widehat{w}^{\,\star}}{\partial p^{ij}} = -F^{ij} \ . \tag{98}$$

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, *cf.*, Colemann & Noll (1963). 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 & Lifschitz (1966) used a third form of the GIBBS relations to be obtained with the linearization $\mathrm{d}C^{ij} \approx \mathrm{d}(2\varepsilon^{ij} + \delta^{ij}) = 2\mathrm{d}\varepsilon^{ij}$ and $t^{ij} = \sigma^{ij}$ in Eq. (92). Consequently they found (in our notation):

$$\mathrm{d}\varphi = -\eta \mathrm{d}T + \frac{1}{\rho_0} \sigma^{ij}\mathrm{d}\varepsilon^{ij} \tag{99}$$

$$\Leftrightarrow \mathrm{d}w^\star = -\eta \mathrm{d}T - \frac{1}{\rho_0} \varepsilon^{ij}\mathrm{d}\sigma^{ij} \quad \text{with}^1 \quad w^\star \overset{(\mathrm{def})}{=} \varphi - \frac{1}{\rho_0} \sigma^{ij}\varepsilon^{ij} \ , \tag{100}$$

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

$$\rho_0 \frac{\partial \breve{\varphi}}{\partial \varepsilon^{ij}} = \sigma^{ij} \quad , \quad \rho_0 \frac{\partial \acute{w}^\star}{\partial \sigma^{ij}} = -\varepsilon^{ij} \ . \tag{101}$$

The energetic formulations for the stresses and strains in Eqs. (94,98,101) are frequently found in literature, *e.g.*, Truesdell & Noll (1965*b*), and can be interpreted as the continuum mechanical version of the *first* and *second theorem of* CASTIGLIANO, *cf.*, Becker & Bürger (1975). The quantities φ and $w^\star$ are typically called the (mass-)*specific strain energy*[2] and the *complementary specific strain energy*.

In this context we point out that there is a considerable confusion about the meaning of $w^\star$ in the literature. So, for instance, Landau & Lifschitz (1966), Becker & Bürger (1975) and Truedsell & Toupin (1960*b*) *wrongly* identify the complementary specific strain energy $w^\star$ with the GIBBS free energy ψ. In turn, Landau & Lifschitz (1966) are puzzled 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.*:

$$\psi = \varphi + \frac{p}{\rho} \qquad \text{with} \qquad p = -\frac{\sigma^{kk}}{3} = -\frac{1}{3J} t^{ij}C^{ij} = -\frac{1}{3J} p^{ij}F^{ij} \ . \tag{102}$$

[1] Note that the definitions of $w^\star$ in Eq. $(100)_2$ is not equivalent to the ones in Eqs. $(97,93)_2$ due to the performed linearization. This is evident replacing in, *e.g.*, Eq. $(93)_2$ the term $t^{ij}C^{ij}$ by the linearized form $\sigma^{ij}(2\varepsilon^{ij} + \delta^{ij})$.

[2] Another notation frequently found is *specific stored energy*.

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. (92,93), (96,97) and (99,100).

5 Multiphase Mixtures

5.1 *Exploitation of the 2nd Law by Considering Higher Gradients*

In this section we consider materials that consist of different phases. *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 ($\tau^n_\alpha = 0$ and $\sigma^{ij} = \sigma^{ij}_{\rm el}$). Consequently the occurring phases differ in its composition, *i.e.*, in the partial particle densities $n_1, \dots, n_\nu$. Therefore we must incorporate phase boundaries containing considerable gradients $\nabla_i n_\alpha$, $\nabla_{ij} n_\alpha$, ... etc. ($\alpha = \{1, \dots, \nu\}$), and we modify the functional representation of $\rho\eta$ according to Eq. (40) as follows:

$$\begin{aligned}\rho\eta &= \tilde{\mathbb{S}}(\rho\epsilon, n_\alpha, \nabla_i n_\alpha, \nabla_{ij} n_\alpha, c^{ij}) = \hat{\mathbb{S}}(T, n_\alpha, \nabla_i n_\alpha, \nabla_{ij} n_\alpha, c^{ij}) = \\ &= \bar{\mathbb{S}}(T, y_\beta, \nabla_i y_\beta, \nabla_{ij} y_\beta, \nabla_i \rho, \nabla_{ij}\rho, \rho, c^{ij}) = \acute{\mathbb{S}}(T, y_\beta, \nabla_i y_\beta, \nabla_{ij} y_\beta, \nabla_i \rho, \nabla_{ij}\rho, C^{ij}) \,. \end{aligned} \tag{103}$$

The index $\alpha = \{1, ..., \nu\}$ and $\beta = \{1, ..., \nu - 1\}$ were used as abbreviations. The expressions A and B of the dissipation inequality, Eq. (41), are now re-written analogously to Eqs. $(42)_{1,2}$:

$$\frac{\partial \tilde{\mathbb{S}}}{\partial t} = \frac{\partial \tilde{\mathbb{S}}}{\partial \rho\epsilon}\frac{\partial \rho\epsilon}{\partial t} + \frac{\partial \tilde{\mathbb{S}}}{\partial c^{ij}}\frac{\partial c^{ij}}{\partial t} + \sum_{\alpha=1}^{\nu}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial t} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_i n_\alpha}\frac{\partial \nabla_i n_\alpha}{\partial t} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{ij} n_\alpha}\frac{\partial \nabla_{ij} n_\alpha}{\partial t}\right) \tag{104}$$

$$\frac{\partial \tilde{\mathbb{S}}}{\partial x^i} = \frac{\partial \tilde{\mathbb{S}}}{\partial \rho\epsilon}\frac{\partial \rho\epsilon}{\partial x^i} + \frac{\partial \tilde{\mathbb{S}}}{\partial c^{kl}}\frac{\partial c^{kl}}{\partial x^i} + \sum_{\alpha=1}^{\nu}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial x^i} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha}\frac{\partial \nabla_k n_\alpha}{\partial x^i} + \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}\frac{\partial \nabla_{kl} n_\alpha}{\partial x^i}\right) \tag{105}$$

The terms $\partial\rho\epsilon/\partial t$ and $\partial n_\alpha/\partial t$ are substituted in the same manner as in Section 4.1, namely by the right hand sides of Eqs. (10,17). 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. (17), *viz.*:

$$\begin{aligned}\frac{\partial \nabla_k n_\alpha}{\partial t} &= -\frac{\partial}{\partial x^k}\left[v^i\frac{\partial n_\alpha}{\partial x^i} + n_\alpha\frac{\partial v^i}{\partial x^i} + \frac{\partial j^i_\alpha}{\partial x^i}\right] \\ &= -\frac{\partial v^i}{\partial x^k}\frac{\partial n_\alpha}{\partial x^i} - v^i\frac{\partial^2 n_\alpha}{\partial x^i \partial x^k} - \frac{\partial n_\alpha}{\partial x^k}\frac{\partial v^i}{\partial x^i} - n_\alpha\frac{\partial^2 v^i}{\partial x^i \partial x^k} - \frac{\partial^2 j^i_\alpha}{\partial x^i \partial x^k} \,, \end{aligned} \tag{106}$$

$$\begin{aligned}\frac{\partial \nabla_{kl} n_\alpha}{\partial t} &= -\frac{\partial^2 v^i}{\partial x^k \partial x^l}\frac{\partial n_\alpha}{\partial x^i} - 2\frac{\partial v^i}{\partial x^k}\frac{\partial^2 n_\alpha}{\partial x^i \partial x^l} - v^i\frac{\partial^3 n_\alpha}{\partial x^i \partial x^k \partial x^l} - \frac{\partial^2 n_\alpha}{\partial x^k \partial x^l}\frac{\partial v^i}{\partial x^i} \\ &\quad -2\frac{\partial n_\alpha}{\partial x^k}\frac{\partial^2 v^i}{\partial x^i \partial x^l} - n_\alpha\frac{\partial^3 v^i}{\partial x^i \partial x^k \partial x^l} - \frac{\partial^3 j^i_\alpha}{\partial x^i \partial x^k \partial x^l} \,. \end{aligned} \tag{107}$$

Note, that Eq. (104) 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 3.4. Here the occurring temporal derivatives of Eq. (104) occur due to Statement 1 of the Entropy Principle, proposed in Section 3.4, and depend on the choice of the arguments in Eq. $(103)_1$.

By inserting Eqs. (10, 17, 106, 107) into Eq. (104) one obtains for the entropy production ζ according to Eq. (41):

$$
\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{\mathbb{S}}}{\partial n_\alpha}\right] + 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{\mathbb{S}}}{\partial n_\alpha}\right) \\
&+ \frac{\partial v^i}{\partial x^j}\left[\frac{\sigma^{ij}_{\mathrm{el}}}{T} + J^{-2/3}(F^{jk}F^{il} + F^{ik}F^{jl})\frac{\partial \tilde{\mathbb{S}}}{\partial c^{kl}} - \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}\Bigg(\underbrace{\frac{\partial v^i}{\partial x^k}\frac{\partial n_\alpha}{\partial x^i}}_{=\mathsf{a}} + \underbrace{\frac{\partial n_\alpha}{\partial x^k}\frac{\partial v^i}{\partial x^i}}_{=\mathsf{b}} + \underbrace{n_\alpha \frac{\partial^2 v^i}{\partial x^i \partial x^k}}_{=\mathsf{c}} + \underbrace{\frac{\partial^2 j^i_\alpha}{\partial x^i \partial x^k}}_{=\mathsf{d}} \Bigg) \\
&- \sum_{\alpha=1}^{\nu} \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}\Bigg(\underbrace{\frac{\partial^2 v^i}{\partial x^k \partial x^l}\frac{\partial n_\alpha}{\partial x^i}}_{=\mathsf{e}} + \underbrace{2\frac{\partial v^i}{\partial x^k}\frac{\partial^2 n_\alpha}{\partial x^i \partial x^l}}_{=\mathsf{f}} + \underbrace{\frac{\partial^2 n_\alpha}{\partial x^k \partial x^l}\frac{\partial v^i}{\partial x^i}}_{=\mathsf{g}} \\
&+ \underbrace{2\frac{\partial n_\alpha}{\partial x^k}\frac{\partial^2 v^i}{\partial x^i \partial x^l}}_{=\mathsf{h}} + \underbrace{n_\alpha \frac{\partial^3 v^i}{\partial x^i \partial x^k \partial x^l}}_{=\mathsf{i}} + \underbrace{\frac{\partial^3 j^i_\alpha}{\partial x^i \partial x^k \partial x^l}}_{=\mathsf{j}} \Bigg) . \qquad (108)
\end{aligned}
$$

The first four summands correspond to the result in Eq. (45). In what follows one has to include the HG-terms $\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha}(\mathsf{a}+\ldots+\mathsf{d})$ and $\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}(\mathsf{e}+\ldots+\mathsf{j})$ "suitably" into the first three rows of Eq. (108), 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^i_α 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:

$$
\begin{aligned}
-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha}(\mathsf{d}) &= \frac{\partial}{\partial x^i}\left[j^i_\alpha \frac{\partial}{\partial x^k}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha}\right) - \frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_i n_\alpha}\frac{\partial j^k_\alpha}{\partial x^k}\right] - j^i_\alpha \frac{\partial}{\partial x^i}\left[\frac{\partial}{\partial x^k}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha}\right)\right] , \qquad (109) \\
-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}(\mathsf{j}) &= \frac{\partial}{\partial x^i}\Bigg[- j^i_\alpha \frac{\partial^2}{\partial x^k \partial x^l}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}\right) + \frac{\partial j^l_\alpha}{\partial x^l}\frac{\partial}{\partial x^k}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{ki} n_\alpha}\right) - \frac{\partial}{\partial x^k}\left(\frac{\partial j^l_\alpha}{\partial x^l}\right)\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{ki} n_\alpha}\Bigg] \\
&\quad + j^i_\alpha \frac{\partial}{\partial x^i}\left[\frac{\partial^2}{\partial x^k \partial x^l}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}\right)\right] . \qquad (110)
\end{aligned}
$$

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

$$
\begin{aligned}
-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha}(\mathsf{a}+\mathsf{b}+\mathsf{c}) &= n_\alpha \frac{\partial v^i}{\partial x^i}\frac{\partial}{\partial x^k}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha}\right) - \frac{\partial v^i}{\partial x^k}\frac{\partial n_\alpha}{\partial x^i}\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_k n_\alpha} - \frac{\partial}{\partial x^i}\left[n_\alpha \frac{\partial v^k}{\partial x^k}\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_i n_\alpha}\right] , \qquad (111) \\
-\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}(\mathsf{e}+\mathsf{f}) &= \frac{\partial v^i}{\partial x^k}\left[\frac{\partial n_\alpha}{\partial x^i}\frac{\partial}{\partial x^l}\left(\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}\right) - \frac{\partial^2 n_\alpha}{\partial x^i \partial x^l}\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{kl} n_\alpha}\right] - \frac{\partial}{\partial x^i}\left(\frac{\partial v^k}{\partial x^l}\frac{\partial n_\alpha}{\partial x^k}\frac{\partial \tilde{\mathbb{S}}}{\partial \nabla_{li} n_\alpha}\right) , \qquad (112)
\end{aligned}
$$

$$-\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{kl}n_\alpha}(\mathsf{g}+\mathsf{h}+\mathsf{i}) = \frac{\partial}{\partial x^i}\left[n_\alpha\frac{\partial v^k}{\partial x^k}\frac{\partial}{\partial x^l}\left(\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{il}n_\alpha}\right) - \frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{ki}n_\alpha}\frac{\partial}{\partial x^k}\left(n_\alpha\frac{\partial v^l}{\partial x^l}\right)\right] - n_\alpha\frac{\partial v^i}{\partial x^i}\frac{\partial^2}{\partial x^k\partial x^l}\left(\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{kl}n_\alpha}\right) . \tag{113}$$

Eq. (109-113) can be substituted into Eq. (108). By means of the Euler-Lagrange derivative:

$$\frac{\delta\lozenge}{\delta n_\alpha} \overset{(\mathrm{def})}{=} \frac{\partial\lozenge}{\partial n_\alpha} - \nabla_k\cdot\frac{\partial\lozenge}{\partial\nabla_k n_\alpha} + \nabla_{kl}\cdot\frac{\partial\lozenge}{\partial\nabla_{kl}n_\alpha} \tag{114}$$

and the partial particle balance in the form:

$$\dot{n}_\alpha \overset{(\mathrm{def})}{=} \frac{\partial n_\alpha}{\partial t} + v^i\frac{\partial n_\alpha}{\partial x^i} \overset{(17)}{=} -n_\alpha\frac{\partial v^i}{\partial x^i} - \frac{\partial j^i_\alpha}{\partial x^i} . \tag{115}$$

we finally write for the **entropy production** ζ:

$$\begin{aligned}\zeta =& \frac{\partial}{\partial x^i}\left\{\phi^i - \frac{q^i}{T} - \sum_\alpha^\nu j^i_\alpha\frac{\delta\tilde{\mathbb{S}}}{\delta n_\alpha} + \sum_\alpha^\nu\dot{n}_\alpha\left[\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_i n_\alpha} - \frac{\partial}{\partial x^l}\left(\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{li}n_\alpha}\right)\right]\right.\\ &\left. + \sum_\alpha^\nu\frac{\partial\dot{n}_\alpha}{\partial x^l}\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{li}n_\alpha} - \sum_\alpha^\nu\frac{\partial v^l}{\partial x^k}\frac{\partial n_\alpha}{\partial x^l}\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{ki}n_\alpha}\right\}\\ &+ q^i\frac{\partial 1/T}{\partial x^i} + \sum_\alpha^\nu j^i_\alpha\frac{\partial}{\partial x^i}\left(\frac{\delta\tilde{\mathbb{S}}}{\delta n_\alpha}\right)\\ &+ \frac{\partial v^i}{\partial x^j}\left\{\frac{\sigma^{ij}_{\mathrm{el}}}{T} + J^{-2/3}(F^{jk}F^{il}+F^{ik}F^{jl})\frac{\partial\tilde{\mathbb{S}}}{\partial c^{kl}} - \sum_\alpha^\nu\frac{\partial n_\alpha}{\partial x^i}\left[\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_j n_\alpha} - \frac{\partial}{\partial x^l}\left(\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{jl}n_\alpha}\right)\right]\right.\\ &\left. - \sum_\alpha^\nu\frac{\partial^2 n_\alpha}{\partial x^i\partial x^l}\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{jl}n_\alpha} - \delta^{ij}\left[\frac{\rho\epsilon}{T} - \tilde{\mathbb{S}} + \sum_\alpha^\nu n_\alpha\frac{\delta\tilde{\mathbb{S}}}{\delta n_\alpha} + \frac{2}{3}J^{-2/3}C^{kl}\frac{\partial\tilde{\mathbb{S}}}{\partial c^{kl}}\right]\right\} \geq 0 .\end{aligned} \tag{116}$$

Indeed, the calculations leading to Eqs. (109-113) are lengthy but easily reproducible. In particular the divergence term of Eq. (113) was arranged in this form because of the last two summands of the divergence term in Eq. (110) and keeping the partial particle balance of Eq. (115) in mind. In the same manner one can combine the last term of Eq. (111) and the second part of the divergence term in Eq. (109).

5.2 *Entropy, Heat and Diffusion Flux and Mechanical Constitutive Equations*

Eq. (116) can now be exploited in the same manner as in Section 4.1. First, we define the entropy flux such that the divergence term of the first two rows vanishes:

$\lozenge$ *Entropy flux*:

$$\phi^i = \frac{q^i}{T} + \sum_\alpha^\nu j^i_\alpha\frac{\delta\tilde{\mathbb{S}}}{\delta n_\alpha} - \sum_\alpha^\nu\dot{n}_\alpha\left[\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_i n_\alpha} - \frac{\partial}{\partial x^l}\left(\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{li}n_\alpha}\right)\right] - \sum_\alpha^\nu\frac{\partial\dot{n}_\alpha}{\partial x^l}\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{li}n_\alpha} + \sum_\alpha^\nu\frac{\partial v^l}{\partial x^k}\frac{\partial n_\alpha}{\partial x^l}\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{ki}n_\alpha} . \tag{117}$$

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

$$q^i\frac{\partial 1/T}{\partial x^i}+\sum_\alpha^\nu j^i_\alpha\frac{\partial}{\partial x^i}\left(\frac{\delta\tilde{\mathbb{S}}}{\delta n_\alpha}\right)\geq 0\,, \tag{118}$$

$$-\frac{\sigma^{ij}_{\mathrm{el}}}{T}=J^{-2/3}(F^{jk}F^{il}+F^{ik}F^{jl})\frac{\partial\tilde{\mathbb{S}}}{\partial c^{kl}}-\sum_\alpha^\nu\frac{\partial n_\alpha}{\partial x^i}\left[\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_j n_\alpha}-\frac{\partial}{\partial x^l}\left(\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{jl}n_\alpha}\right)\right]-\sum_\alpha^\nu\frac{\partial^2 n_\alpha}{\partial x^i\partial x^l}\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla_{jl}n_\alpha}$$
$$-\delta^{ij}\left[\frac{\rho\epsilon}{T}-\tilde{\mathbb{S}}+\sum_\alpha^\nu n_\alpha\frac{\delta\tilde{\mathbb{S}}}{\delta n_\alpha}+\frac{2}{3}J^{-2/3}C^{kl}\frac{\partial\tilde{\mathbb{S}}}{\partial c^{kl}}\right]\,. \tag{119}$$

Eq. (118) and (119) represent important results which allow to derive the constitutive equations for the *heat flux*, the *diffusion flux* and for the *stresses* in *multi-component*, *multi-phase* solid mixtures. The partial derivatives of $\tilde{\mathbb{S}}$ must be substituted using the different functional representations of the Helmholtz free energy ($\alpha=1,\dots,\nu$ and $\beta=1,\dots,\nu-1$):

$$\begin{aligned}\rho\varphi&=\tilde{\mathbb{F}}(\rho\epsilon,n_\alpha,\nabla_i n_\alpha,\nabla_{ij}n_\alpha,c^{ij})=\hat{\mathbb{F}}(T,n_\alpha,\nabla_i n_\alpha,\nabla_{ij}n_\alpha,c^{ij})\\&=\bar{\mathbb{F}}(T,y_\beta,\nabla_i y_\beta,\nabla_{ij}y_\beta,\nabla_i\rho,\nabla_{ij}\rho,\rho,c^{ij})=\acute{\mathbb{F}}(T,y_\beta,\nabla_i y_\beta,\nabla_{ij}y_\beta,\nabla_i\rho,\nabla_{ij}\rho,C^{ij})\end{aligned} \tag{120}$$

and applying the Legendre transforms of Appendix E - G.

As an example we consider the heat and the diffusion flux in Eq. (118). To this end we define the *chemical potential* μ_α in multi-phase mixtures according to Eq. (50) and (54) as:

$$\frac{\mu_\alpha}{T}\overset{(\mathrm{def})}{=}\frac{\delta\hat{\mathbb{F}}/T}{\delta n_\alpha}\qquad\text{or}\qquad\frac{\mu^*_\alpha}{T}\overset{(\mathrm{def})}{=}\frac{\delta\hat{\bar{\mathbb{F}}}/T}{\delta\rho_\alpha}=\frac{1}{m_\alpha}\frac{\delta\hat{\mathbb{F}}/T}{\delta n_\alpha} \tag{121}$$

with the alternative functional representation of the Helmholtz free energy $\rho\varphi=\hat{\bar{\mathbb{F}}}(T,\rho_\alpha,\nabla_i\rho_\alpha,\nabla_{ij}\rho_\alpha,c^{ij})$ and the Euler-Lagrange derivative introduced in Eq. (114).

In order to guarantee a non-negative entropy production in Eq. (118) we choose j^i_α and q^i such that quadratic expressions result, *cf.*, Section 4.2. The Legendre transform in Appendix E yields $\delta\tilde{\mathbb{S}}/\delta n_\alpha=-\delta(\hat{\mathbb{F}}/T)/\delta n_\alpha$. Therefore we find (without thermo-diffusion coupling):

$\Diamond$ *Diffusion flux*:

$$j^i_\beta=\sum_{\delta=1}^{\nu-1}M^{ij}_{\beta\delta}\frac{\partial\frac{1}{T}\left(\frac{m_\delta}{m_\nu}\mu_\nu-\mu_\delta\right)}{\partial x^j}\quad\text{and}\quad J^i_\beta=\sum_{\delta=1}^{\nu-1}B^{ij}_{\beta\delta}\frac{\partial\frac{1}{T}\left(\mu^*_\nu-\mu^*_\delta\right)}{\partial x^j}\,, \tag{122}$$

$\Diamond$ *Heat flux*:

$$q^i=\kappa^{ij}\frac{\partial 1/T}{\partial x^j}\qquad(\text{Fourier's law})\,, \tag{123}$$

where the symbols $M^{ij}_{\beta\delta}$, $B^{ij}_{\beta\delta}$ 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 $j^i_\nu=-\sum_{\beta=1}^{\nu-1}\frac{m_\beta}{m_\nu}j^i_\beta$ or $J^i_\nu=-\sum_{\beta=1}^{\nu-1}J^i_\beta$, respectively.

Note that the higher gradients do not enter the classical Fourier's law in Eq. (123) 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. (121).

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 4.2, *i.e.*, from the exploitation of Eq. (119) and the LEGENDRE transforms examined in the Appendices E - G .

5.3 *An Instructive Example: Isothermal Diffusion in Binary Mixtures*

5.3.1 ***Preliminary Remarks 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 $\delta\bar{\mathbb{F}}/\delta y_\beta$ or $\delta\bar{\bar{\mathbb{F}}}/\delta c_\beta$, respectively. To this end we consider the LEGENDRE transform in Appendix F and write for the case of *isothermal diffusion* (*i.e.*, $T = \text{const}$):

$$\mu_\alpha \overset{(121)_1}{=} \frac{\delta\hat{\mathbb{F}}}{\delta n_\alpha} \overset{\text{(App. F)}}{=} m_\alpha \frac{\delta\bar{\mathbb{F}}}{\delta\rho} + \sum_{\lambda=1}^{\nu-1} \frac{\delta\bar{\mathbb{F}}}{\delta y_\lambda}\left(\frac{\delta_{\alpha\lambda}}{n} - \frac{n_\lambda}{n^2}\right) . \tag{124}$$

Thus one obtains for the difference term in Eq. $(122)_1$:

$$\frac{m_\delta}{m_\nu}\mu_\nu - \mu_\delta \;=\; \frac{m_\delta}{m_\nu}\sum_{\lambda=1}^{\nu-1}\frac{\delta\bar{\mathbb{F}}}{\delta y_\lambda}\left(\frac{\delta_{\nu\lambda}}{n} - \frac{n_\lambda}{n^2}\right) - \sum_{\lambda=1}^{\nu-1}\frac{\delta\bar{\mathbb{F}}}{\delta y_\lambda}\left(\frac{\delta_{\delta\lambda}}{n} - \frac{n_\lambda}{n^2}\right) . \tag{125}$$

Note that the calculation of Eq. $(124)_2$ directly follows by applying the relations of Eqs. (H13-H15) to the three summands of the EULER-LAGRANGE derivative defined in Eq. (114).

For the consideration of the alternative definition of the chemical potential μ^*_α in Eq. $(121)_2$ one needs the LEGENDRE transform between the following functional representations of $\rho\varphi$:

$$\rho\varphi = \hat{\bar{\mathbb{F}}}(T, \rho_\alpha, \nabla_i\rho_\alpha, \nabla_{ij}\rho_\alpha, c^{ij}) = \bar{\bar{\mathbb{F}}}(T, c_\beta, \nabla_i c_\beta, \nabla_{ij}c_\beta, \nabla_i\rho, \nabla_{ij}\rho, \rho, c^{ij}) , \tag{126}$$

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

$$\mu^*_\alpha \overset{(121)_2}{=} \frac{\delta\hat{\bar{\mathbb{F}}}}{\delta\rho_\alpha} \overset{\text{(App. H)}}{=} \frac{\delta\bar{\bar{\mathbb{F}}}}{\delta\rho} + \sum_{\lambda=1}^{\nu-1}\frac{\delta\bar{\mathbb{F}}}{\delta c_\lambda}\left(\frac{\delta_{\alpha\lambda}}{\rho} - \frac{\rho_\lambda}{\rho^2}\right) , \tag{127}$$

and for the difference term in Eq. $(122)_2$:

$$\mu^*_\nu - \mu^*_\delta \;=\; \sum_{\lambda=1}^{\nu-1}\frac{\delta\bar{\bar{\mathbb{F}}}}{\delta c_\lambda}\left(\frac{\delta_{\nu\lambda}}{\rho} - \frac{\rho_\lambda}{\rho^2}\right) - \sum_{\lambda=1}^{\nu-1}\frac{\delta\bar{\bar{\mathbb{F}}}}{\delta c_\lambda}\left(\frac{\delta_{\delta\lambda}}{\rho} - \frac{\rho_\lambda}{\rho^2}\right) = -\sum_{\lambda=1}^{\nu-1}\frac{\delta\bar{\bar{\mathbb{F}}}}{\delta c_\lambda}\frac{\delta_{\delta\lambda}}{\rho} = -\frac{1}{\rho}\frac{\delta\bar{\bar{\mathbb{F}}}}{\delta c_\delta} . \tag{128}$$

Note that the variational derivatives $\delta\bar{\mathbb{F}}/\delta\rho$ and $\delta\bar{\bar{\mathbb{F}}}/\delta\rho$ vanish in the difference of the chemical potentials in Eqs. (125, 128).

5.3.2 ***Particle Diffusion Flux.*** In what follows we specify to a binary mixture **A-B** characterized by the following relations:

$$n = n_\mathrm{A} + n_\mathrm{B} \quad , \quad y_\mathrm{B} = 1 - y_\mathrm{A} . \tag{129}$$

For the case of isothermal diffusion as defined before, Eq. $(122)_1$ reduces to:

$$j^i_\mathrm{A} = \frac{M^{ij}_\mathrm{AA}}{T}\frac{\partial\left(\frac{m_\mathrm{A}}{m_\mathrm{B}}\mu_\mathrm{B} - \mu_\mathrm{A}\right)}{\partial x^j} \quad \text{and} \quad j^i_\mathrm{B} = -\frac{m_\mathrm{A}}{m_\mathrm{B}}j^i_\mathrm{A} . \tag{130}$$

The difference of the chemical potentials reads according to Eq. (125):

$$\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}}\mu_{\mathrm{B}} - \mu_{\mathrm{A}} = \frac{m_{\mathrm{A}}}{m_{\mathrm{B}}}\frac{\delta\hat{\mathbb{F}}}{\delta n_{\mathrm{B}}} - \frac{\delta\hat{\mathbb{F}}}{\delta n_{\mathrm{A}}} \overset{(125)}{=} \frac{m_{\mathrm{A}}}{m_{\mathrm{B}}}\frac{\delta\bar{\mathbb{F}}}{\delta y_{\mathrm{A}}}\Bigg(\underbrace{\frac{\delta_{\mathrm{BA}}}{n}}_{=0} - \frac{n_{\mathrm{A}}}{n^2}\Bigg) - \frac{\delta\bar{\mathbb{F}}}{\delta y_{\mathrm{A}}}\left(\frac{\delta_{\mathrm{AA}}}{n} - \frac{n_{\mathrm{A}}}{n^2}\right)$$

$$= -\frac{1}{n}\frac{\delta\bar{\mathbb{F}}}{\delta y_{\mathrm{A}}}\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}}y_{\mathrm{A}} + y_{\mathrm{B}}\right) . \tag{131}$$

Thus a combination of Eq. (131) and $(130)_1$ yields for the *particle diffusion flux* of component **A**:

$$j^i_{\mathrm{A}} = -\frac{M^{ij}_{\mathrm{AA}}}{T}\nabla^j\left[\frac{1}{n}\frac{\delta\bar{\mathbb{F}}}{\delta y_{\mathrm{A}}}\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}}y_{\mathrm{A}} + y_{\mathrm{B}}\right)\right] \overset{(\mathrm{App.\,G})}{=} -\frac{M^{ij}_{\mathrm{AA}}}{T}\nabla^j\left[\frac{1}{n}\frac{\delta\bar{\mathbb{F}}}{\delta y_{\mathrm{A}}}\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}}y_{\mathrm{A}} + y_{\mathrm{B}}\right)\right] , \tag{132}$$

in which the diffusion flux of component **B** is determined by the relation of Eq. $(130)_2$.

5.3.3 ***Mass Diffusion Flux.*** Analogously to Eq. (129) and (130) we write for the total mass density, the mass concentrations and the mass diffusion flux of component **A**:

$$\rho = \rho_{\mathrm{A}} + \rho_{\mathrm{B}} \quad , \quad c_{\mathrm{A}} = 1 - c_{\mathrm{B}} \tag{133}$$

and with $(122)_2$

$$J^i_{\mathrm{A}} = \frac{B^{ij}_{\mathrm{AA}}}{T}\frac{\partial\left(\mu^*_{\mathrm{B}} - \mu^*_{\mathrm{A}}\right)}{\partial x^j} \quad \text{with} \quad J^i_{\mathrm{B}} = -J^i_{\mathrm{A}} . \tag{134}$$

By using the relation of Eq. (128) the difference of the chemical potentials reduces to:

$$\mu^*_{\mathrm{B}} - \mu^*_{\mathrm{A}} = \frac{\delta\widehat{\bar{\mathbb{F}}}}{\delta\rho_{\mathrm{B}}} - \frac{\delta\widehat{\bar{\mathbb{F}}}}{\delta\rho_{\mathrm{A}}} \overset{(128)}{=} \frac{\delta\bar{\bar{\mathbb{F}}}}{\delta c_{\mathrm{A}}}\Bigg(\underbrace{\frac{\delta_{\mathrm{BA}}}{\rho}}_{=0} - \frac{\rho_{\mathrm{A}}}{\rho^2}\Bigg) - \frac{\delta\bar{\bar{\mathbb{F}}}}{\delta c_{\mathrm{A}}}\left(\frac{\delta_{\mathrm{AA}}}{\rho} - \frac{\rho_{\mathrm{A}}}{\rho^2}\right) = -\frac{1}{\rho}\frac{\delta\bar{\bar{\mathbb{F}}}}{\delta c_{\mathrm{A}}} . \tag{135}$$

Hence we finally obtain from Eq. (134) and (135) and the LEGENDRE transforms in Appendix G and H:

$$J^i_{\mathrm{A}} = -\frac{B^{ij}_{\mathrm{AA}}}{T}\nabla^j\left(\frac{1}{\rho}\frac{\delta\overset{\diamond}{\mathbb{F}}}{\delta c_{\mathrm{A}}}\right) \quad \text{and} \quad J^i_{\mathrm{B}} = -\frac{B^{ij}_{\mathrm{AA}}}{T}\nabla^j\left(\frac{1}{\rho}\frac{\delta\overset{\diamond}{\mathbb{F}}}{\delta c_{\mathrm{B}}}\right) , \tag{136}$$

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

Eq. (136) implies that, in contrast to the 'multiphase-field approach' of Eiken *et al.* (2006), the relation $\rho(\mu^*_{\mathrm{B}} - \mu^*_{\mathrm{A}}) = \delta\overset{\diamond}{\mathbb{F}}/\delta c_{\mathrm{B}} = -\delta\overset{\diamond}{\mathbb{F}}/\delta c_{\mathrm{A}}$ holds *exclusively*, if the mass concentration c_β is used, otherwise the relations in Eq. (132) must be considered.

5.3.4 ***Expansion of the Free Energy Density.*** In order to investigate Eq. (136) in more detail the question arise, how $\overset{\diamond}{\mathbb{F}}$ depends on the higher gradients, *e.g.*, $\nabla_i c_{\mathrm{B}}$, $\nabla_{ij} c_{\mathrm{B}}$, $\nabla_i\rho$, and $\nabla_{ij}\rho$. To this end we follow the strategy of Cahn & Hilliard (1958) and expand the HELMHOLTZ free energy into a TAYLOR series

around the homogeneous (*i.e.*, no gradients) state[1]:

$$\mathbb{F} = \mathbb{F}_0(T, c_\mathrm{B}, C^{ij}) + \underbrace{\frac{\partial \mathbb{F}_0}{\partial \nabla_k c_\mathrm{B}}}_{\overset{(\mathrm{def})}{=} l^k} \cdot \nabla_k c_\mathrm{B} + \underbrace{\frac{\partial \mathbb{F}_0}{\partial \nabla_{kl} c_\mathrm{B}}}_{\overset{(\mathrm{def})}{=} -a^{kl}} \cdot \nabla_{kl} c_\mathrm{B} + \frac{1}{2} \underbrace{\frac{\partial^2 \mathbb{F}_0}{\partial \nabla_k c_\mathrm{B} \partial \nabla_l c_\mathrm{B}}}_{\overset{(\mathrm{def})}{=} 2\, b^{kl}} \cdot \nabla_k c_\mathrm{B} \cdot \nabla_l c_\mathrm{B} + \dots \,, \tag{137}$$

where the introduced so-called *Higher Gradient Coefficients* (HGCs) depend on the temperature T, the (homogeneous) composition c_B, and the strain tensor C^{ij}, *i.e.*, $l^k = l^k(T, c_\mathrm{B}, C^{ij})$, $a^{kl} = a^{kl}(T, c_\mathrm{B}, C^{ij})$, and $b^{kl} = b^{kl}(T, c_\mathrm{B}, C^{ij})$. Furthermore we neglect in Eq. (137) the higher gradients $\nabla_i \rho$ and $\nabla_{ij} \rho$, since they do not enter the diffusion flux in Eq. (136).

The HGCs in Eq. (137) characterize the (smoothly) changing composition within the phase boundaries and are directly linked to the surface tensions between the different phases, *cf.*, Dreyer & Wagner (2005). Moreover, they can be *exactly* determined by means of microscopic theories taking interatomic potentials into account, *e.g.*, Lennard-Jones potentials (*cf.*, Dreyer & Müller (2003)) or Embedded-Atom-Method potentials (*cf.*, Böhme *et al.* (2007)). 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*: $\mathbb{F}_0 = \mathbb{F}_0^{\mathrm{chem}} + \mathbb{F}_0^{\mathrm{mech}}$, *cf.*, Section 4.2.4. The chemical part can be found from phase equilibrium data, typically provided by thermodynamical databases, *e.g.*, MTdata (1998). 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 4.2.4.

5.3.5 ***Extended Diffusion Equation.*** For the investigation of the temporal and spatial evolution of the mass concentration field $c_\mathrm{B} = c(x^i, t)$ within a non-reacting elastic solid mixture we rewrite Eq. (14) by means of the relation $\rho_\alpha = c_\alpha \rho$ as follows:

$$\rho \frac{\mathrm{d}c}{\mathrm{d}t} + \frac{\partial J^i}{\partial x^i} = 0 \qquad \text{(partial mass balance)} \,, \tag{138}$$

where we put $J^i_\mathrm{B} = J^i$ and used the total temporal derivative $\mathrm{d}_t c = \partial_t c + v^i(\nabla_i c)$. In order to calculate the Euler-Lagrange derivative $\delta\mathbb{F}/\delta c$ in Eq. (136) we obtain by means of Eq. (137) and $l^k = 0$:

$$\frac{\partial \mathbb{F}}{\partial c} = \frac{\partial \mathbb{F}_0}{\partial c} - \frac{\partial a^{kl}}{\partial c} \frac{\partial^2 c}{\partial x^k \partial x^l} + \frac{\partial b^{kl}}{\partial c} \frac{\partial c}{\partial x^k} \frac{\partial c}{\partial x^l} \quad , \quad \frac{\partial \mathbb{F}}{\partial (\partial c / \partial x^m)} = 2 b^{ml} \frac{\partial c}{\partial x^l} \quad , \quad \frac{\partial \mathbb{F}}{\partial (\partial^2 c / \partial x^m \partial x^n)} = -a^{kl} \,. \tag{139}$$

Thus it follows by virtue of the chain rule:

$$\frac{\partial}{\partial x^m} \left(\frac{\partial \mathbb{F}}{\partial (\partial c / \partial x^m)} \right) = 2 \frac{\partial b^{ml}}{\partial c} \frac{\partial c}{\partial x^m} \frac{\partial c}{\partial x^l} + 2 \frac{\partial b^{ml}}{\partial C^{rs}} \frac{\partial C^{rs}}{\partial x^m} \frac{\partial c}{\partial x^l} + 2 b^{ml} \frac{\partial^2 c}{\partial x^m \partial x^l} \,, \tag{140}$$

$$\begin{aligned} \frac{\partial^2}{\partial x^m \partial x^n} \left(\frac{\partial \mathbb{F}}{\partial (\partial^2 c / \partial x^m \partial x^n)} \right) = & - \frac{\partial^2 a^{mn}}{\partial c^2} \frac{\partial c}{\partial x^m} \frac{\partial c}{\partial x^n} - \frac{\partial a^{mn}}{\partial c} \frac{\partial^2 c}{\partial x^m \partial x^n} - 2 \frac{\partial^2 a^{mn}}{\partial c \partial C^{rs}} \frac{\partial C^{rs}}{\partial x^m} \frac{\partial c}{\partial x^n} \\ & - \frac{\partial^2 a^{mn}}{\partial C^{op} C^{rs}} \frac{\partial C^{op}}{\partial x^m} \frac{\partial C^{rs}}{\partial x^n} - \frac{\partial a^{mn}}{\partial C^{rs}} \frac{\partial^2 C^{rs}}{\partial x^m \partial x^n} \,. \end{aligned} \tag{141}$$

[1] In the following we write by convenience $\mathbb{F} = \overset{\diamond}{\mathbb{F}}$.

The relation $(139)_1$-(140)+(141) defines the variational derivative $\delta\mathbb{F}/\delta c$. Consequently one obtains for the diffusion flux in Eq. $(136)_2$ by using the abbreviation $A^{ij} = \frac{\partial a^{ij}}{\partial c} + b^{ij}$:

$$J^i = -\frac{B^{ij}_{\mathrm{AA}}}{T}\nabla^j\Bigg[\frac{1}{\rho}\Bigg(\frac{\partial \mathbb{F}_0}{\partial c} - 2A^{kl}\frac{\partial^2 c}{\partial x^k \partial x^l} - \frac{\partial A^{kl}}{\partial c}\frac{\partial c}{\partial x^k}\frac{\partial c}{\partial x^l} - 2\frac{\partial A^{kl}}{\partial C^{mn}}\frac{\partial c}{\partial x^k}\frac{\partial C^{mn}}{\partial x^l} - \frac{\partial^2 a^{kl}}{\partial C^{op}C^{mn}}\frac{\partial C^{op}}{\partial x^k}\frac{\partial C^{mn}}{\partial x^l} - \frac{\partial a^{kl}}{\partial C^{mn}}\frac{\partial^2 C^{mn}}{\partial x^k \partial x^l}\Bigg)\Bigg]\,. \tag{142}$$

Eq. (138) and Eq. (142) 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 equation.

5.3.6 *Numerical Example: Spinodal Decomposition and* Ostwald *Ripening in Eutectic Ag-Cu.*

Assumptions and Restrictions. In order to reduce the computational effort we restrict in what follows to linear elastic solids subjected to *small deformations* and use for the functional representations the linearized strains ε^{ij} instead of the right Cauchy-Green strain tensor C^{ij}, *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 $A^{kl} = A^{kl}(T, c, \varepsilon^{ij})$. Moreover, corresponding to small deformations we approximate the first and second Piola-Kirchhoff tensor, p^{ij} and t^{ij}, by the Cauchy stress tensor, σ^{ij}, which implies that the differences between the reference configuration and the current configuration are ignored. By using a Lagrangeian description, *cf.*, Section 3.1, the *primary variables* are the *concentration field* $c(X^j, t)$ and the *displacements* $U^i(X^j, t)$, which are determined by:

$$\rho_0\frac{\mathrm{d}c}{\mathrm{d}t} + \frac{\partial J^i}{\partial X^i} = 0 \quad \text{(partial mass balance)} \quad , \quad \frac{\partial p^{ij}}{\partial X^j} = 0 \quad \text{(static momentum balance)} \tag{143}$$

and for which the following constitutive equations hold:

$$J^i = -\rho_0\mathcal{M}^{ij}(T)\nabla^j\Bigg[\frac{\partial(\mathbb{F}_0^{\mathrm{chem}} + \mathbb{F}_0^{\mathrm{mech}})}{\partial c} - 2A^{kl}\frac{\partial^2 c}{\partial X^k \partial X^l} - \frac{\partial A^{kl}}{\partial c}\frac{\partial c}{\partial X^k}\frac{\partial c}{\partial X^l} - 2\frac{\partial A^{kl}}{\partial \varepsilon^{mn}}\frac{\partial c}{\partial X^k}\frac{\partial \varepsilon^{mn}}{\partial X^l} - \frac{\partial^2 a^{kl}}{\partial \varepsilon^{op}\varepsilon^{mn}}\frac{\partial \varepsilon^{op}}{\partial X^k}\frac{\partial \varepsilon^{mn}}{\partial X^l} - \frac{\partial a^{kl}}{\partial \varepsilon^{mn}}\frac{\partial^2 \varepsilon^{mn}}{\partial X^k \partial X^l}\Bigg]\,, \tag{144}$$

$$p^{ij} \approx \sigma^{ij} \approx \frac{\partial \mathbb{F}}{\partial \varepsilon^{ij}} = \sigma^{ij}_{\mathrm{local}} - \frac{\partial a^{kl}}{\partial \varepsilon^{ij}}\frac{\partial^2 c}{\partial X^k \partial X^l} + \frac{\partial b^{kl}}{\partial \varepsilon^{ij}}\frac{\partial c}{\partial X^k}\frac{\partial c}{\partial X^l}\,, \tag{145}$$

with $\sigma^{ij}_{\mathrm{local}} \overset{(\mathrm{Hooke})}{=} K^{ijkl}(T,c)\left(\varepsilon^{kl} - \alpha^{kl}\Delta T\right)$, $\mathbb{F}_0^{\mathrm{mech}} = \frac{1}{2}\sigma^{ij}\left(\varepsilon^{ij} - \alpha^{ij}\Delta T\right)$ and $\varepsilon^{ij} = \frac{1}{2}(\partial U^i/\partial X^j + \partial U^j/\partial X^i$. Moreover, the alternatively introduced mobility $\mathcal{M}^{ij}$ is given by the redefinition $\rho_0^2\mathcal{M}^{ij}(T) = B^{ij}_{\mathrm{AA}}/T$ with $[\mathcal{M}^{ij}] = [\mathrm{m}^5/\mathrm{Js}]$. In order to solve the PDE system (143–145) for the unknown variables c and U^i numerically we restrict the simulations to three cases:

a) 1D-simulations without local thermo-mechanical strains, *i.e.*, $\varepsilon^{kl}_{\mathrm{elast}} = \varepsilon^{kl} - \alpha^{kl}\Delta T = 0$, $\forall\,\{k,l\}$.
b) 1D-simulations under the presence of one-dimensional local thermo-mechanical strains[1] ("line strains"), *i.e.*, $\varepsilon^{11}_{\mathrm{elast}} = \varepsilon_{\mathrm{elast}} \neq 0 \wedge \varepsilon^{kl}_{\mathrm{elast}} = 0$, $\forall\{k,l\} = \{k,l \mid k \cdot l > 0\}$.
c) 2D-simulations without local thermo-mechanical strains.

The restriction to line strains according to Case **b)** requires overestimated stresses 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 $\varepsilon_{\mathrm{elast}} = \varepsilon_{\mathrm{elast}}(X,t)$ with $X \equiv X^1$. To this end we assume *linearity* for the stiffness K^{ijkl} and

[1] This strain state denotes the one-dimensional equivalent to the two-dimensional case of *plane strains*.

for the thermal expansion coefficient α^{kl} within the smoothly changing phase boundary between the two equilibrium phase α and β, *viz.*:

$$\Xi(c) = (1-\Theta(c))\,\Xi_\alpha + \Theta(c)\Xi_\beta \quad , \quad \Xi_{\alpha/\beta} = \{K^{ijkl}_{\alpha/\beta}, \alpha^{kl}_{\alpha/\beta}\} \quad , \quad \Theta(c) = \frac{c_\beta - c(X,t)}{c_\beta - c_\alpha}\,. \tag{146}$$

For cubic lattice structures (as given for Ag, Cu and Ag-Cu) all elements of the stiffness matrix vanish except for $K^{11} = K^{22} = K^{33}$, $K^{12} = K^{13} = K^{23}$, and $K^{44} = K^{55} = K^{66}$ (VOIGT notation), *cf.*, Table 4. By assuming in Eq. (145) $\sigma^{ij}_{\text{local}}$ to be the leading term one obtains from HOOKE's law:

$$\sigma^{11} = \left[K^{11}_\beta - \Theta(c)(K^{11}_\beta - K^{11}_\alpha)\right](\varepsilon^{11} - \alpha^{11}\Delta T)\,, \tag{147}$$

$$\sigma^{22} = \left[K^{12}_\beta - \Theta(c)(K^{12}_\beta - K^{12}_\alpha)\right](\varepsilon^{11} - \alpha^{11}\Delta T)\,, \tag{148}$$

$$\sigma^{33} = \left[K^{13}_\beta - \Theta(c)(K^{13}_\beta - K^{13}_\alpha)\right](\varepsilon^{11} - \alpha^{11}\Delta T) \qquad \text{and} \qquad \sigma^{12} = \sigma^{13} = \sigma^{23} = 0\,. \tag{149}$$

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

$$\frac{\mathrm{d}\sigma^{11}}{\mathrm{d}X} = 0 \quad \Rightarrow \quad \sigma^{11} = \sigma_0 = \text{const.} \tag{150}$$

and consequently for the elastic strains, *cf.*, Eq. (147) and for the mechanical part of the HELMHOLTZ free energy:

$$\varepsilon^{11}_{\text{elast}} = \frac{\sigma_0}{K^{11}_\beta - \frac{c_\beta - c(X,t)}{c_\beta - c_\alpha}(K^{11}_\beta - K^{11}_\alpha)} \qquad , \qquad \mathbb{F}^{\text{mech}}_0 = \frac{1}{2}\frac{\sigma_0^2}{K^{11}_\beta - \frac{c^\beta - c(X,t)}{c_\beta - c_\alpha}(K^{11}_\beta - K^{11}_\alpha)}\,. \tag{151}$$

Eqs. $(151)_{1,2}$ can be directly used to substitute the $\mathbb{F}^{\text{mech}}_0$- and the ε^{ij}-terms in Eq. (144). In order to solve the resulting EDE one needs reliable material data, in particular for (i) the chemical part of the HELMHOLTZ free energy $\mathbb{F}^{\text{chem}}_0$, (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 $c \equiv c_{\text{Cu}}$.

***Materials Data I. Chemical Part of the Free Energy*[1].** In order to determine $\mathbb{F}^{\text{chem}}_0$ we use the commercial MTdata$^{\text{TM}}$ database, MTdata (1998), which provides a field of discrete values $\mathbb{F}^{\text{chem}}_0(c_i)$, $c_i = \{0, 0.01, 0.02, \ldots, 0.99, 1\}$ from phase equilibrium measurements. In order to obtain a closed functional form of these data required for computation and for the encoding we simply perform a polynomial fit according to the MARGULES-ansatz

$$\mathbb{F}^{\text{chem}}_0(c) = (1-c)g_{\text{a}} + cg_{\text{b}} + g_{\text{c}}RT\,[c\ln c + (1-c)\ln(1-c)] + c(1-c)\,[\chi_{\text{I}}c + \chi_{\text{II}}(1-c)]\,, \tag{152}$$

where $R = 8.314$ [J/(mol K)] stands for the universal gas constant. The fit parameters g_a, g_b, g_c, χ_I, and χ_{II} have no physical meaning and are compiled in Table 3 together with the resulting equilibrium concentrations, $c_{\alpha/\beta}$, following from the common tangent rule and the spinodal concentrations, $c^{\text{sp}}_{1/2}$, resulting from the roots of $\partial^2\mathbb{F}^{\text{chem}}_0/\partial c^2$. The corresponding curves are displayed in Figure 2.

Materials Data II. Mobility, Stiffness, and Thermal Expansion Coefficient. By comparing the first and second Fick's law, *i.e.*, $\mathrm{d}_t c = -\partial J^i/\partial X^i$ with $J^i = -D^{ij}(\partial c/\partial X^j)$ with the EDE for the limit case

[1] Note that the most databases, *e.g.*, MTdata (1998), make no difference between the HELMHOLTZ and the GIBBS free energy.

Table 3.: Fit parameters according to the MARGULES-ansatz and characteristic concentrations.

$g_{\mathrm{a}}\ \left[\frac{\mathrm{GJ}}{\mathrm{m}^3}\right]$	$g_{\mathrm{b}}\ \left[\frac{\mathrm{GJ}}{\mathrm{m}^3}\right]$	$g_{\mathrm{c}}\ \left[\frac{\mathrm{mole}}{\mathrm{m}^3}\right]$	$\chi_{\mathrm{I}}\ \left[\frac{\mathrm{GJ}}{\mathrm{m}^3}\right]$	$\chi_{\mathrm{II}}\ \left[\frac{\mathrm{GJ}}{\mathrm{m}^3}\right]$	c_{eut}	c_α	c_β	c_1^{sp}	c_2^{sp}
-7.27	-5.20	$1.11 \cdot 10^5$	2.97	3.01	0.29	0.063	0.945	0.19	0.79

Table 4.: Stiffness matrix of pure silver and copper in GPa and VOIGT notation, Source: Kittel (1962).

$K_{ij}^{kl}\big\vert_{\mathrm{Ag}}$	11	22	33	23	31	12	$K_{ij}^{kl}\big\vert_{\mathrm{Cu}}$	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 5.: Diffusion, mobility, and thermal expansion coefficients for the pure substances Ag and Cu Source: Brandes & Brook (1992), MTdata (1998), Winter (2007).

D_α [m^2/s]	D_β [m^2/s]	M_α [m^5/Js]	M_β [m^5/Js]	α_α^{11} [10^-6/K]	α_β^{11} [10^{-6}/K]
1.01×10^{-14}	4.09×10^{-15}	7.25×10^{-25}	3.65×10^{-25}	18.9	16.5

c and ε^{ij}, Böhme *et al.* (2007). In particular it is shown that the HCGs take the form:

$$a^{kl}(c,\varepsilon^{ij}) = -k(c)\frac{\partial y}{\partial c}\cdot\mathcal{H}^{kl}(c,\varepsilon^{ij}) \quad , \quad b^{kl}(c,\varepsilon^{ij}) = k(c)\frac{\partial^2 y}{\partial c^2}\cdot\mathcal{H}^{kl}(c,\varepsilon^{ij}) \quad , \quad A^{kl} \overset{\text{(def)}}{=} \frac{\partial a^{kl}}{\partial c} + b^{kl} \, , \tag{155}$$

$$\mathcal{H}^{kl}(c,\varepsilon^{ij}) = \Phi_0^{kl}(c) + \varepsilon^{mn}\Phi_1^{mnkl}(c) + \varepsilon^{mn}\varepsilon^{pq}\Phi_2^{mnpqkl}(c) \, , \tag{156}$$

where the functions Φ_0^{kl}, Φ_1^{mnkl}, and Φ_2^{mnpqkl} 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, $\mathcal{H}^{kl}$ 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 distinguish between the effects of compressive and tensile loadings during the diffusion simulations. Figure 3 (first row) shows the HGCs a^{11}, b^{11}, and A^{11} calculated from the EAM approach for the 'line strain' case $\varepsilon^{ij} = \varepsilon\cdot\delta^{ij}\delta^{1i}\delta^{1j}$.

The functions used for the calculations of the curves in Figure 3 are very lengthy and extremely time-consuming. In order to optimize the computation time we perform a bilinear interpolation of the form:

$$\Xi(c,\varepsilon) = k_\varepsilon^\Xi\cdot\varepsilon + k_c^\Xi\cdot c + k_{c\varepsilon}^\Xi\cdot\varepsilon\cdot c + k_0^\Xi \quad \text{with} \quad \Xi = \left\{a^{11}, b^{11}, A^{11}\right\} . \tag{157}$$

in which the fitting procedure must be performed separately for positive and negative strains. To this end we use the atomistically calculated HGCs of Figure 3 (first row) at the *ad hoc chosen* points $(c,\varepsilon) = \{(c_\alpha,0),(c_\beta,0),(c_\alpha,\pm 0.2),(c_\beta,\pm 0.2)\}$. Figure 3 (second row) displays the according interpolated functions. The fit parameters introduced in Eq. (157) are compiled in Table 6.

Brief Remarks on the Numerical Realization. For the numerical treatment we, first, transformed 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.*, Li & Müller (2001):

$$\tilde{X}^i = \frac{X^i}{L} \quad , \quad \tilde{\mathbb{F}}_0 = \frac{\mathbb{F}_0}{\Psi_0} \quad , \quad \tilde{t} = \frac{\Psi_0 M_\beta}{L^2(c_\beta - c_\alpha)} = \frac{t}{t_0} \, , \tag{158}$$

in which the factors L, Ψ_0, and t_0 must be "appropriately" chosen. Table 7 shows the corresponding values that were used during the simulations.

The resulting dimensionless EDE is implemented in a FORTRAN 90 program. Moreover, the spatial

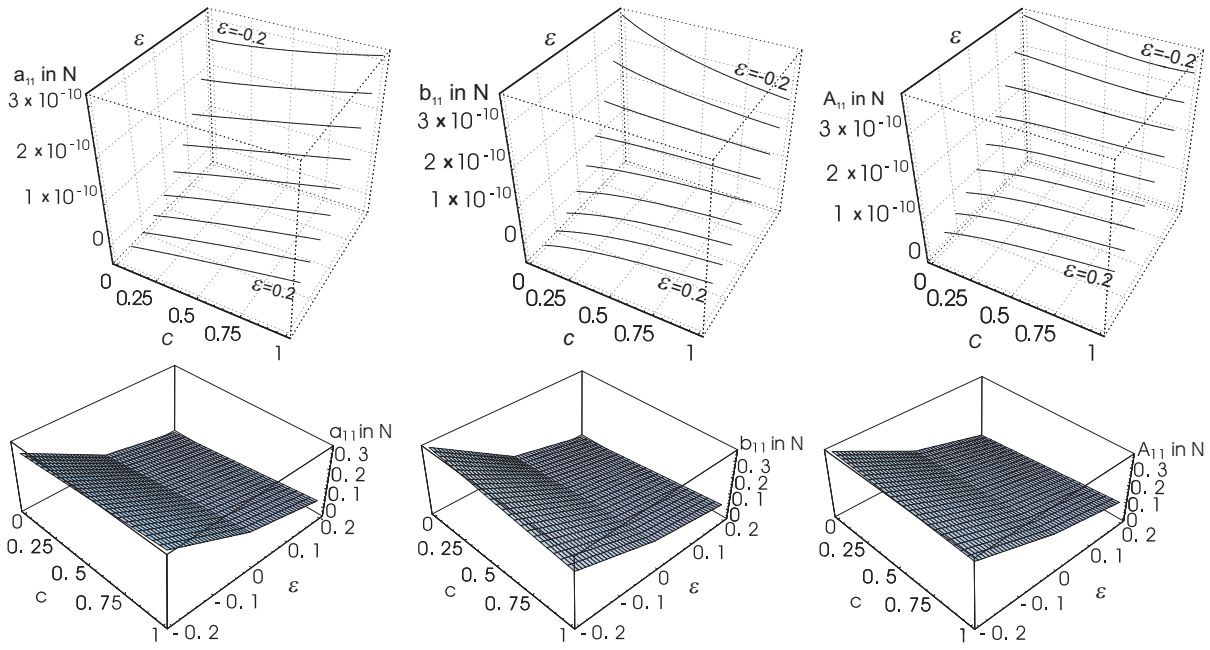

Figure 3.: 1st Row: Various HGCs calculated by means of the embedded-atom-method, *cf.*, Böhme *et al.* (2007). 2nd Row: Interpolated HGCs.

Table 6.: Interpolated coefficients for the HGCs as bilinear functions of c and ε.

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)				
a^{11}	$-3.79 \cdot 10^{-10}$	$8.74 \cdot 10^{-11}$	$-6.40 \cdot 10^{-11}$	$4.04 \cdot 10^{-11}$
b^{11}	$-5.22 \cdot 10^{-10}$	$4.72 \cdot 10^{-11}$	$1.64 \cdot 10^{-10}$	$5.84 \cdot 10^{-11}$
A^{11}	$-5.74 \cdot 10^{-10}$	$3.74 \cdot 10^{-11}$	$1.50 \cdot 10^{-10}$	$1.53 \cdot 10^{-10}$
$\varepsilon < 0$ (pressure loading)				
a^{11}	$-1.11 \cdot 10^{-9}$	$8.74 \cdot 10^{-11}$	$1.91 \cdot 10^{-10}$	$4.04 \cdot 10^{-11}$
b^{11}	$-1.52 \cdot 10^{-9}$	$4.72 \cdot 10^{-11}$	$7.77 \cdot 10^{-10}$	$5.84 \cdot 10^{-11}$
A^{11}	$-1.10 \cdot 10^{-9}$	$3.74 \cdot 10^{-11}$	$3.80 \cdot 10^{-10}$	$1.53 \cdot 10^{-10}$

derivatives are discretized by finite differences (with N grid points in 1D and $N \times N$ grid points in 2D, *cf.*, Table 7) and replaced by an algebraic expression in FOURIER space, *cf.*, Dreyer & Müller (2000). For the required discrete FOURIER transforms we use the free available FFTPACK5 package, *cf.*, Hairer & Wanner (2002). The time integration is performed by means of an explicit EULER method with the constant time step $\Delta\tilde{t}$ and, partially, by an implicit and time adaptive RUNGE-KUTTA procedure using the free available RADAU package, *cf.*, Schwarztrauber & Valent (2004).

1D-Simulations. Figures 4-6 display the spinodal decomposition and coarsening process along a "line" in Ag-Cu at 1000 Kelvin. We started with an eutectic homogeneous concentration profile ($c_{\text{eut}} = 0.29$) 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 ones identify the spinodal concentrations, *cf.*, Table 3. Obviously, the system immediately begins to decompose for small simulation times. When the whole mixture reaches the equilibrium concentrations coarsening proceeds such that the bigger phases grow at the expense of the smaller ones.

Table 7.: Numerical parameters used during the simulations.

Simulations	Ψ_0 in GJ/m^3	$2\pi L$ in μm	t_0 in sec	N ($N \times N$)	$\Delta\tilde{t}$
1D (strain-free)	0.1	0.06	2.105	256	$0.04 \cdot 10^{-6}$
1D (5000 MPa)	0.1	0.06	2.105	256	$0.04 \cdot 10^{-6}$
1D (-5000 MPa)	0.1	0.06	2.105	256	$0.02 \cdot 10^{-6}$
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	—

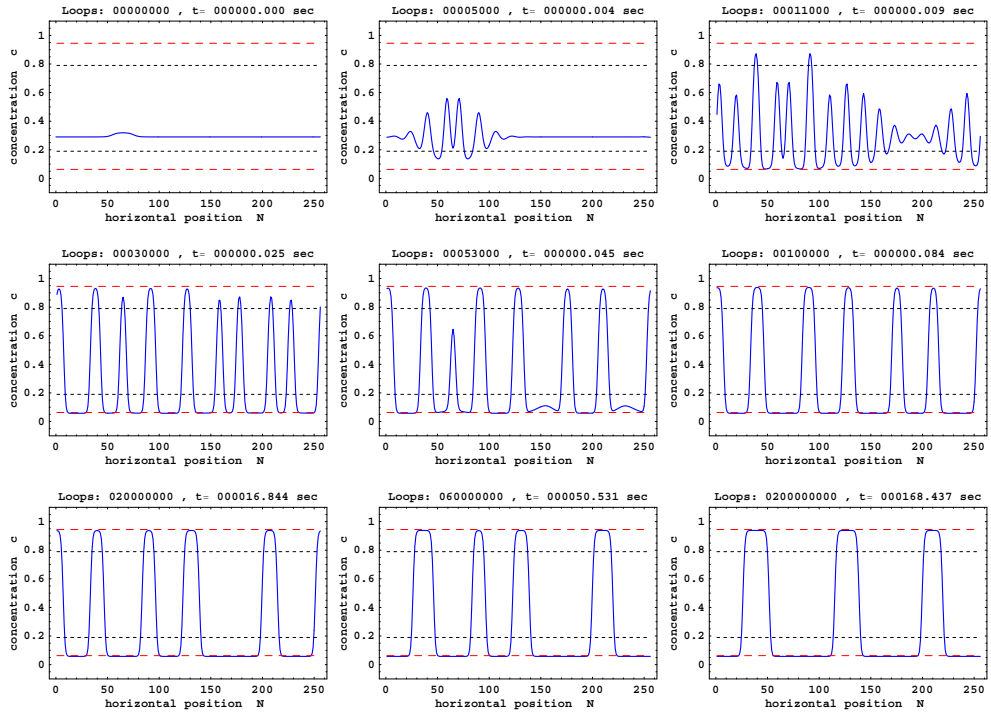

Figure 4.: One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 K (strain-free case).

At this point it is worth mentioning that the total simulation times are in the range of some minutes, which is notedly shorter w.r.t. the experimental observations of these phenomena, *cf.*, Müller & Böhme (2006). The reason for that are the *extremely small HGCs* used during the simulations. In fact, typical values found in literature are much larger, *cf.*, Ubachs *et al.* (2004)[1], which is more convenient from the numerical point-of-view and results in greater time steps $\Delta\tilde{t}$. However, in some rare cases there are also similarly small HGC values reported in the literature, *cf.*, Küpper & Masbaum (1994),[2] in which the simulation times are also extremely short.

Furthermore smaller HGCs result in a sharper phase boundary width and, consequently, the discretization N must be chosen sufficiently large, whereas the simulated volume element $2\pi L$ must be chosen small in

[1]Here the authors used a constant value of $\gamma_{\mathrm{CH}} = \kappa\lambda^2 = 1 \cdot 10^{-5}$ N (in their notation).
[2]Within this work the authors considered an Al-In system and chose a constant HGC of $\gamma = 2 \cdot 10^{-10}$ N (in their notation).

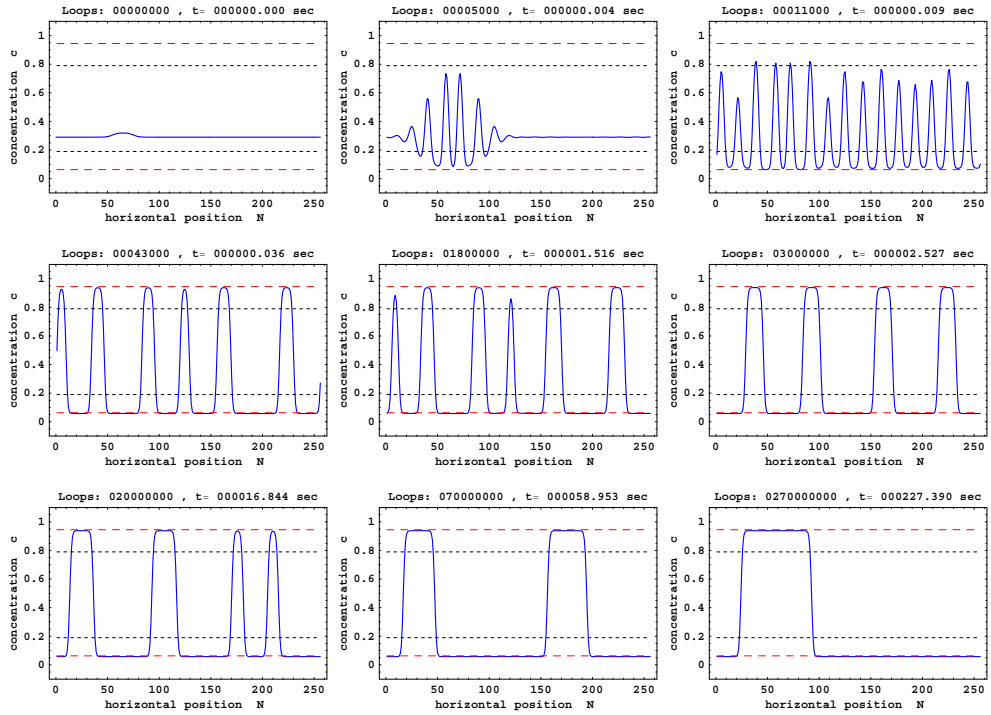

Figure 5.: One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 K (tensile loading of $\sigma_0 = 5000$ MPa).

order to model the interface boundary realistically,[3] *cf.*, Table 7. In particular, the discretization of $N = 256$ yields approximately 9 grid points within the phase boundary as illustrated in Figure 7 (second row, left). From this fact we calculate:

$$256\,\text{grid points} = 0.06\,\mu\text{m} \quad \Leftrightarrow \quad 9\,\text{grid points} = 2.1\,\text{nm} = 21\,\mathring{\text{A}}\,, \tag{159}$$

which corresponds to approximately 7 atomic distances ($r_{\text{Ag}} = 2.88\ \mathring{\text{A}}$) and reflects a realistically sharp interface boundary.

The impact of the HGCs on the interface width is illustrated in Figure 7 (second row), in which we varied the magnitude of A^{11} under the constraint of $\partial A^{11}/\partial c = \text{const}$. The corresponding coarsening behavior is displayed in Figure 7 (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.

Finally the application of very large loading regimes during the simulations illustrated in the Figure 5 and 6 is noticeable. This was done in order to investigate the effect of thermo-mechanical stresses within manageable computational times. Indeed, tensile and compressive stresses increase the coarsening rate. In particular, it seems that pressure loading has a stronger influence on coarsening than tensile loading.

2D-Simulations. For the two-dimensional simulations we start with a eutectic homogeneous concentration profile disturbed by one, two and 18 fluctuations as indicated in Figure 8. We use a spatial discretization of $N \times N = 128 \times 128$ so that approximately 4–5 grid points are within the phase boundary. Figure 9 and 10 displays 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 in the one-dimensional simulations – an explicit EULER method for the time integration.

[3] See also Brandmair (2007) for a detailed study of the different numerical parameters.

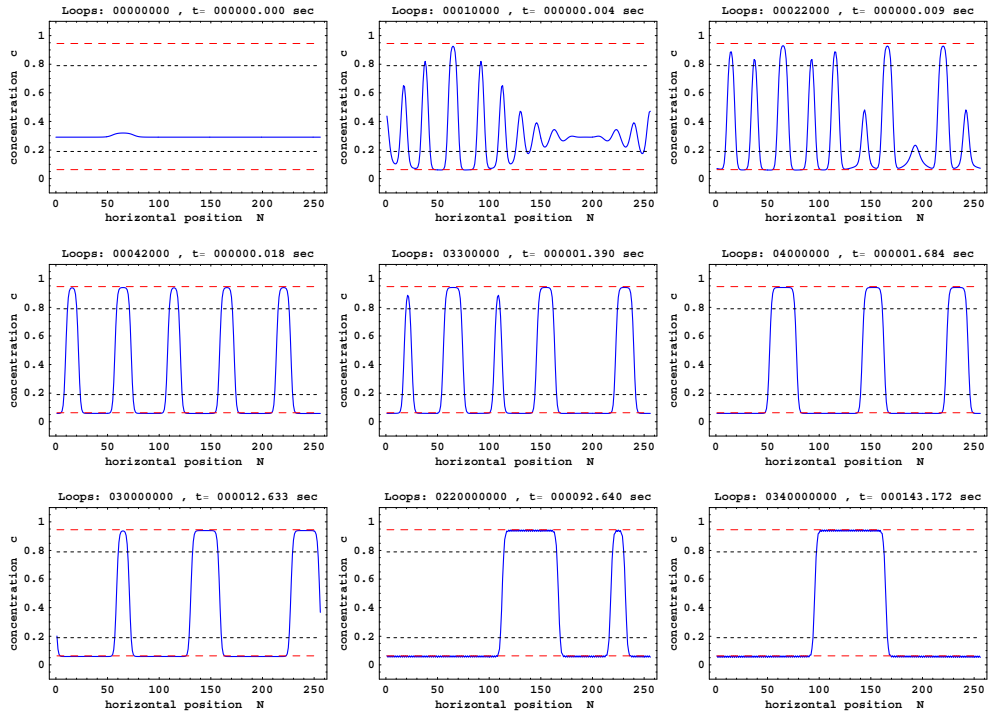

Figure 6.: One-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 K (pressure loading of $\sigma_0 = -5000$ MPa).

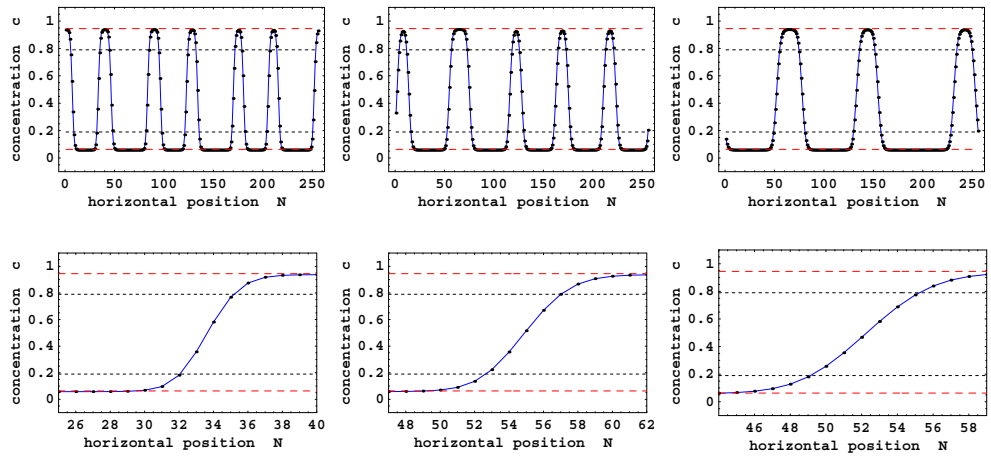

Figure 7.: The impact of the magnitude of the HGCs on the phase boundary width and on the coarsening rate. 1st Row: Coarsening stages after 20000 loops (strain-free case) using a HGC of $A^{11} = A^{11}_{\mathrm{EAM}}$, $A^{11} = 2 \cdot A^{11}_{\mathrm{EAM}}$, and $A^{11} = 4 \cdot A^{11}_{\mathrm{EAM}}$. 2nd Row: According zoomed interface areas.

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 RADAU routine, *cf.*, Hairer & Wanner (2002). The corresponding simulations are illustrated in Figure 11. Unfortunately the complex IRK procedure increase the computational time considerably, which cannot be compensated by the larger time steps $\Delta\tilde{t}$. Therefore the investigated coarsening stages are much smaller than the corresponding ones in Figure 9 and 10. In particu-

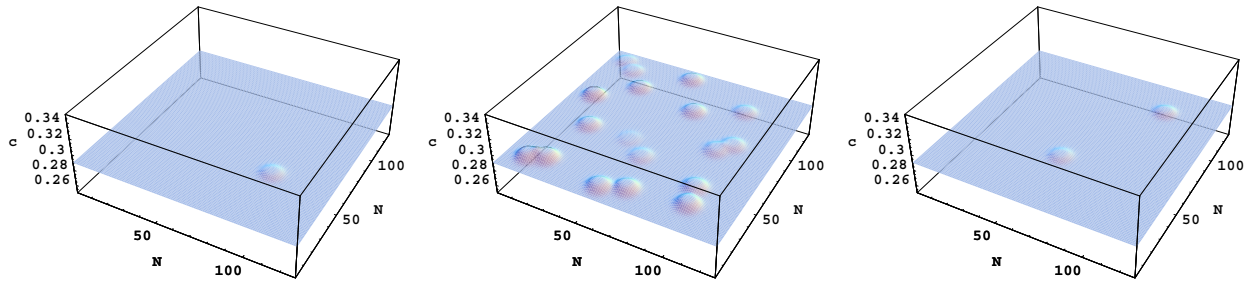

Figure 8.: Initial concentration profiles used for the two-dimensional simulations.

lar the final stage in Figure 11 corresponds approximately to the right graph of the first row in Figure 9 and 10. Finally, Figure 12 documents the adaptive time steps adjusted by the RADAU routine. Obviously $\Delta\tilde{t}$ continuously decreases during the spinodal decomposition process and remains relatively constant during coarsening with $\Delta\tilde{t} \approx 1.4 \cdot 10^{-6}$. From the numerical point-of-view this fact may be interesting since it eventually allows some conclusion about the impact of the different terms of the EDE.

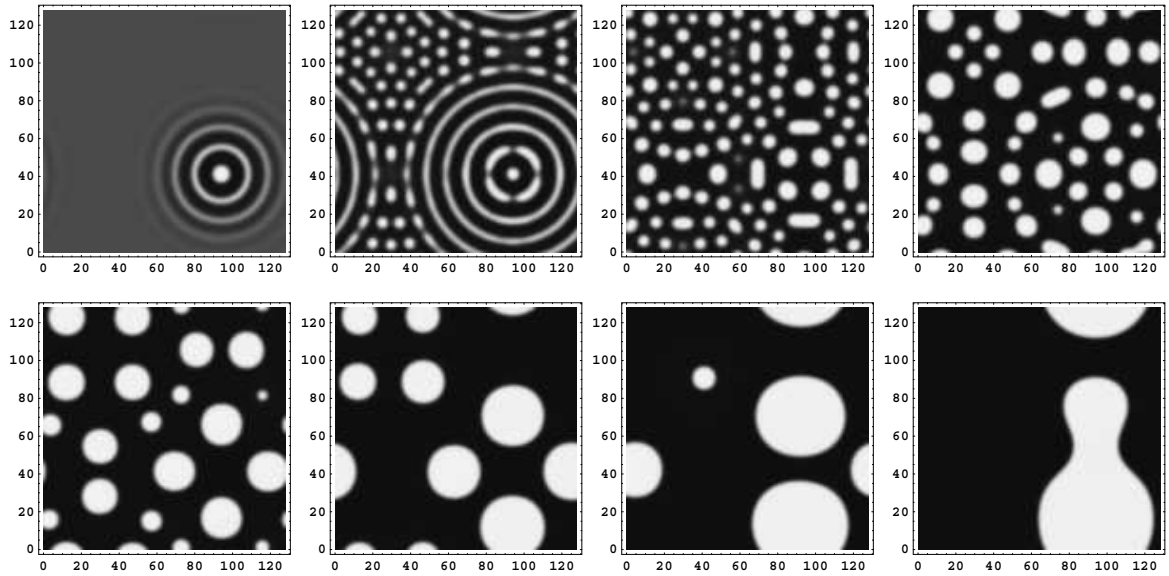

Figure 9.: Two-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 K without thermo-mechanical loading by using the explicit EULER method (one initial fluctuation). *From upper left to lower right*: after $\tilde{t} = 0.005$; 0.01; 0.015; 0.035; 0.1; 1; 2.1; 4.9.

6 Conclusion and Outlook

In this work a thermodynamically consistent theory was presented, which allows modeling of diffusion processes in multicomponent (solid) materials and the accompanying phenomena of phase transition and phase evolution, in particular under the presence of local thermo-mechanical strain fields.

We started with a brief historical overview about the development of diffusion theories and discuss existing shortcomings and open questions within the models and approaches. In particular we pointed out that the existing entropy principles - such as Liu's method of LAGRANGE multipliers - yield non-unique or questionable relations for the entropy flux ϕ^i. Due to these arguments we presented five statements for an entropy principle, which form the undisputed elements of the existing principles.

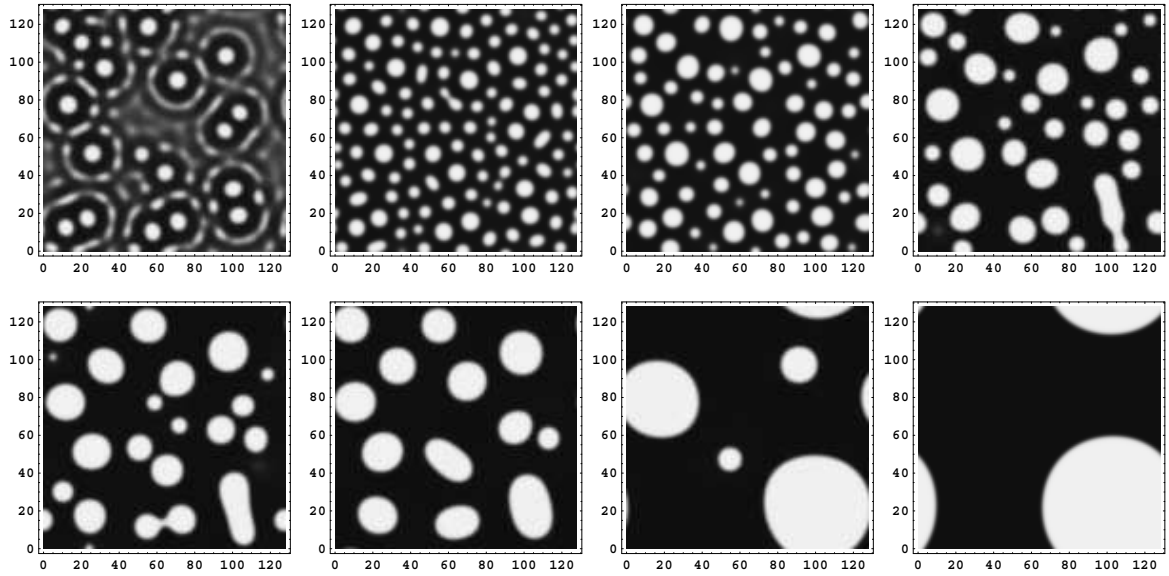

Figure 10.: Two-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 K without thermo-mechanical loading by using the explicit EULER method (16 initial fluctuation). *From upper left to lower right*: after $\tilde{t} = 0.004$; 0.006; 0.015; 0.04; 0.06; 0.1; 1.5; 4.3.

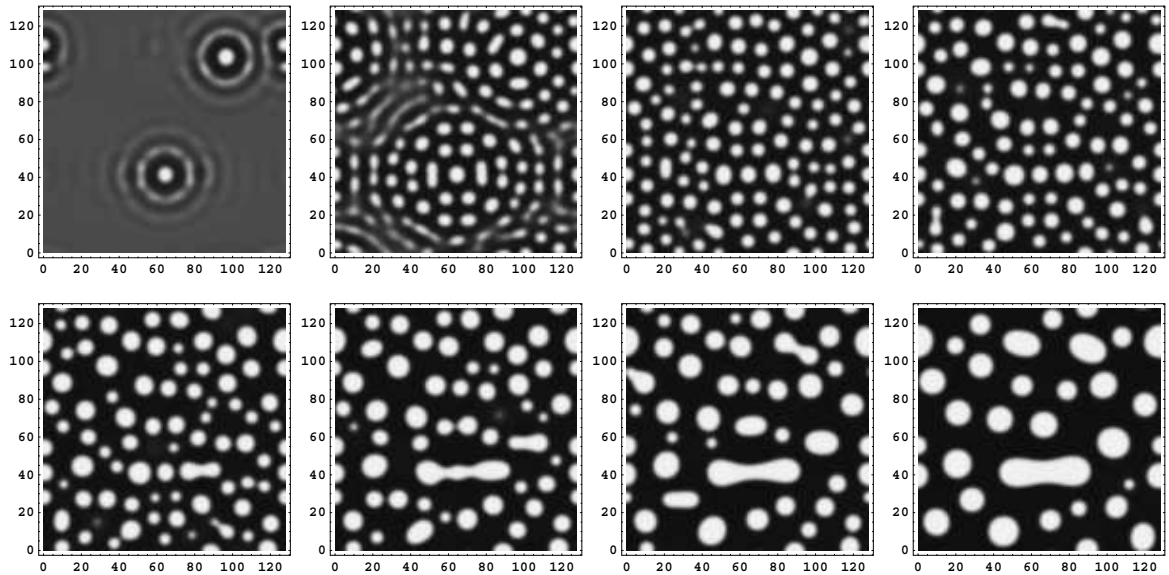

Figure 11.: Two-dimensional simulation of spinodal decomposition and coarsening in Ag-Cu at 1000 K without thermo-mechanical loading by using the time adaptive implicit RUNGE-KUTTA method provided by the RADAU routine (two initial fluctuation). *From upper left to lower right*: after $\tilde{t} = 0.0038$; 0.0077; 0.0088; 0.0131; 0.0163; 0.0217; 0.0307; 0.0486.

In order to stress the feasibility of the principle we, first, investigated a single phase, which corresponds to the case of classical mixtures, and derived the constitutive equations for the entropy, heat, and diffusion flux as well as for the pressure and the second PIOLA-KIRCHHOFF stress tensor. Moreover, we also derived a GIBBS-DUHEM and various GIBBS relations and demonstrated the consistency with the results of classical thermodynamics of fluid mixtures. Furthermore the additive decomposition of the HELMHOLTZ free energy $\varphi = \varphi^{\text{mech}} + \varphi^{\text{chem}}$ and of the chemical potential $\mu = \mu^{\text{mech}} + \mu^{\text{chem}}$ was introduced, motivated by the

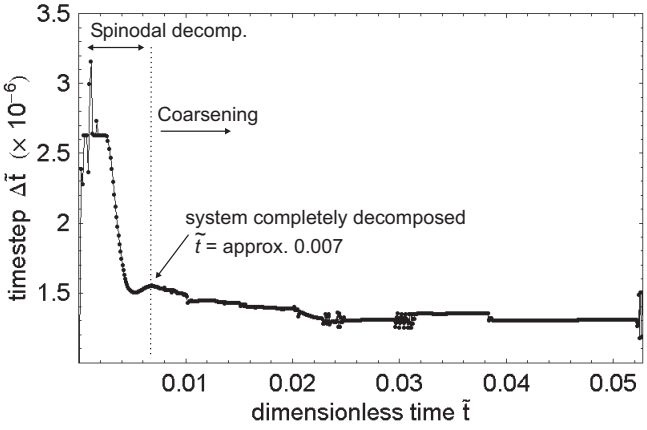

Figure 12.: The time step adaption of the RADAU routine during the simulation illustrated in Figure 11.

observation that the mass density ρ within a diffusive solid mixture can change by two independent effects: (a) elastic lattice deformations (mechanical effect) and (b) redistribution of atoms by diffusion (chemical effect).

Second, we exploited the entropy principle for multi-phase mixtures by means of the incorporation of so-called higher gradients. In particular, we turned the attention to the diffusion flux and derived an extended diffusion equation, which represents - in combination with the partial mass balance - a generalization of the well-established Cahn-Hilliard equation. The HGCs depend here on the concentration and the local thermo-mechanical strains, which lead to additional contributions to the diffusion flux. Finally we specified to the binary case and exemplarily presented numerical studies w.r.t. the brazing solder alloy Ag-Cu.

The introduced thermodynamical approach can be used as a general framework in order to obtain the constitutive relations for different classes of materials. We specified to non-reacting ($\tau_\alpha^{\rho/n} = 0$) mixtures and to the elastic case ($\sigma_{\text{diss}}^{ij} = 0$). However, an extension to reacting materials under, *e.g.*, plastic deformations can be performed by considering the production term $\tau_\alpha^{\rho/n}$ and the dissipative term $\sigma_{\text{diss}}^{ij}$ during the exploitation of the 2nd law. In particular, $\sigma_{\text{diss}}^{ij}$ contributes the the entropy production, *cf.*, Eq. (37), and, thus, it can be treated analogously to the diffusion flux or the heat flux. Furthermore the numerical investigation of mechanical loading to the two-dimensional case as well as three-dimensional simulations are planned for future studies.

Acknowledgements

We thank Prof. H. W. Alt for many valuable discussions. Furthermore we grateful acknowledge assistance of A. Brandmair during the numerical implementations and support by the Deutsche Bundesstiftung Umwelt (DBU). Finally it is a great pleasure to mention the fruitful discussions between Prof. W.H. Müller and Prof. B.D. Colemann about the entropy principle during the informal talks at the CMDS-11 conference.

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Appendix A: Proof of Equation (44)

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:

$$\dot{c}^{kl} = \frac{\mathrm{d}}{\mathrm{d}t}\left(J^{-2/3}C^{kl}\right) = -\frac{2}{3}J^{-5/3}\dot{J}C^{kl} + J^{-2/3}\dot{C}^{kl} \ . \tag{A1}$$

Moreover we have the identity:

$$\dot{J} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\det F^{ij}\right) = \left[\frac{\partial}{\partial F^{kl}}\left(\det F^{ij}\right)\right]\dot{F}^{kl} = \left[(\det F^{ij})(F^{-1})^{lk}\right]\frac{\partial v^k}{\partial X^l} = J\frac{\partial v^k}{\partial x^k} \tag{A2}$$

and

$$\begin{aligned}\dot{C}^{kl} &= \frac{\mathrm{d}}{\mathrm{d}t}\left(F^{mk}F^{ml}\right) = \dot{F}^{mk}F^{ml} + F^{mk}\dot{F}^{ml} = \frac{\partial v^m}{\partial X^k}F^{ml} + \frac{\partial v^m}{\partial X^l}F^{mk} \\ &= \frac{\partial v^m}{\partial x^s}\frac{\partial x^s}{\partial X^k}F^{ml} + \frac{\partial v^m}{\partial x^s}\frac{\partial x^s}{\partial X^l}F^{mk} = \frac{\partial v^i}{\partial x^j}\left(F^{jk}F^{il} + F^{jl}F^{ik}\right) \ .\end{aligned} \tag{A3}$$

The result of Eqs. (A3) and (A2) can be inserted into Eq. (A1). We finally find:

$$\dot{c}^{kl} = -\frac{2}{3}J^{-2/3}\frac{\partial v^i}{\partial x^i}C^{kl} + J^{-2/3}\frac{\partial v^i}{\partial x^j}\left(F^{jk}F^{il} + F^{jl}F^{ik}\right) \ . \tag{A4}$$

□

Appendix B: Legendre Transform between $\tilde{\mathcal{S}}$ and $\hat{\mathcal{S}}$

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

$$\mathrm{d}(\rho\eta) = \mathrm{d}\tilde{\mathcal{S}} = \frac{\partial\tilde{\mathcal{S}}}{\partial\rho\epsilon}\,\mathrm{d}(\rho\epsilon) + \sum_{\alpha=1}^{\nu}\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha}\,\mathrm{d}n_\alpha + \frac{\partial\tilde{\mathcal{S}}}{\partial c^{ij}}\,\mathrm{d}c^{ij} \tag{B1}$$

$$= \mathrm{d}\hat{\mathcal{S}} = \frac{\partial\hat{\mathcal{S}}}{\partial T}\,\mathrm{d}T + \sum_{\alpha=1}^{\nu}\frac{\partial\hat{\mathcal{S}}}{\partial n_\alpha}\,\mathrm{d}n_\alpha + \frac{\partial\hat{\mathcal{S}}}{\partial c^{ij}}\,\mathrm{d}c^{ij}\ , \tag{B2}$$

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

$$\mathrm{d}(\rho\epsilon) = \mathrm{d}\hat{\mathcal{E}} = \frac{\partial\hat{\mathcal{E}}}{\partial T}\,\mathrm{d}T + \sum_{\alpha=1}^{\nu}\frac{\partial\hat{\mathcal{E}}}{\partial n_\alpha}\,\mathrm{d}n_\alpha + \frac{\partial\hat{\mathcal{E}}}{\partial c^{ij}}\,\mathrm{d}c^{ij}\ . \tag{B3}$$

The term $\mathrm{d}(\rho\epsilon)$ in Eq. (B1) can now be substituted by the left hand side of Eq. (B3). By means of the definition of the absolute temperature, Eq. (36), one obtains:

$$\mathrm{d}(\rho\eta) = \underbrace{\frac{1}{T}\frac{\partial\hat{\mathcal{E}}}{\partial T}}_{=\frac{\partial\hat{\mathcal{S}}}{\partial T}}\mathrm{d}T + \sum_{\alpha=1}^{\nu}\underbrace{\left(\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha} + \frac{1}{T}\frac{\partial\hat{\mathcal{E}}}{\partial n_\alpha}\right)}_{=\frac{\partial\hat{\mathcal{S}}}{\partial n_\alpha}}\mathrm{d}n_\alpha + \underbrace{\left(\frac{\partial\tilde{\mathcal{S}}}{\partial c^{ij}} + \frac{1}{T}\frac{\partial\hat{\mathcal{E}}}{\partial c^{ij}}\right)}_{=\frac{\partial\hat{\mathcal{S}}}{\partial c^{ij}}}\mathrm{d}c^{ij} \tag{B4}$$

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

$$\frac{\partial\hat{\mathcal{S}}}{\partial T} = \frac{1}{T}\frac{\partial\hat{\mathcal{E}}}{\partial T} \quad , \quad \frac{\partial\hat{\mathcal{S}}}{\partial n_\alpha} = \frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha} + \frac{1}{T}\frac{\partial\hat{\mathcal{E}}}{\partial n_\alpha} \quad , \quad \frac{\partial\hat{\mathcal{S}}}{\partial c^{ij}} = \frac{\partial\tilde{\mathcal{S}}}{\partial c^{ij}} + \frac{1}{T}\frac{\partial\hat{\mathcal{E}}}{\partial c^{ij}}\ . \tag{B5}$$

Since the variables T and n_α *are independent* within the domain of $\hat{\mathcal{S}}$ one can, in particular, find from Eq. $(\mathrm{B5})_2$ the relation ($\beta \neq \alpha$):

$$\frac{\partial\tilde{\mathcal{S}}}{\partial n_\alpha} = -\frac{1}{T}\left(\frac{\partial\hat{\mathcal{E}}}{\partial n_\alpha} - T\frac{\partial\hat{\mathcal{S}}}{\partial n_\alpha}\right) = -\frac{1}{T}\frac{\partial\hat{\mathcal{F}}}{\partial n_\alpha} = -\frac{1}{T}\frac{\partial(\rho\varphi)}{\partial n_\alpha}\bigg|_{T,n_\beta,c^{ij}}\ . \tag{B6}$$

Appendix C: Legendre Transform between $\hat{\mathcal{F}}$ and $\bar{\mathcal{F}}$

Recall the functional representations shown in Eq. $(49)_{2,3}$. Consequently we can write:

$$\mathrm{d}(\rho\varphi) = \ \mathrm{d}\hat{\mathcal{F}} = \frac{\partial\hat{\mathcal{F}}}{\partial T}\,\mathrm{d}T + \sum_{\alpha=1}^{\nu}\frac{\partial\hat{\mathcal{F}}}{\partial n_\alpha}\,\mathrm{d}n_\alpha + \frac{\partial\hat{\mathcal{F}}}{\partial c^{ij}}\,\mathrm{d}c^{ij}\ , \tag{C1}$$

$$= \ \mathrm{d}\bar{\mathcal{F}} = \frac{\partial\bar{\mathcal{F}}}{\partial T}\,\mathrm{d}T + \sum_{\beta=1}^{\nu-1}\frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}\,\mathrm{d}y_\beta + \frac{\partial\bar{\mathcal{F}}}{\partial\rho}\,\mathrm{d}\rho + \frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}}\,\mathrm{d}c^{ij}\ . \tag{C2}$$

Obviously the transfer from $\bar{\mathcal{F}}$ to $\hat{\mathcal{F}}$ requires the substitution of $\mathrm{d}y_\beta$ and $\mathrm{d}\rho$ by $\mathrm{d}n_\alpha$. For this reason we calculate:

$$\rho(n_1,\dots,n_\nu)=\sum_{\alpha=1}^{\nu} m_\alpha n_\alpha \Rightarrow \mathrm{d}\rho=\sum_{\alpha=1}^{\nu}\frac{\partial\rho}{\partial n_\alpha}\mathrm{d}n_\alpha=\sum_{\alpha=1}^{\nu} m_\alpha \mathrm{d}n_\alpha \tag{C3}$$

$$y_\beta(n_1,\dots,n_\nu)=\frac{n_\beta}{\sum_{\alpha=1}^{\nu} n_\alpha}\Rightarrow \mathrm{d}y_\beta=\sum_{\alpha=1}^{\nu}\frac{\partial y_\beta}{\partial n_\alpha}\mathrm{d}n_\alpha=\sum_{\alpha=1}^{\nu}\left(\frac{\delta^{\alpha\beta}}{n}-\frac{n_\beta}{n^2}\right)\mathrm{d}n_\alpha\,. \tag{C4}$$

Eqs. (C3) and (C4) can be inserted into Eq. (C2). We obtain:

$$\mathrm{d}(\rho\varphi)=\frac{\partial\bar{\mathcal{F}}}{\partial T}\,\mathrm{d}T+\sum_{\alpha=1}^{\nu}\left[m_\alpha\frac{\partial\bar{\mathcal{F}}}{\partial\rho}+\sum_{\beta=1}^{\nu-1}\frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}\left(\frac{\delta^{\alpha\beta}}{n}-\frac{n_\beta}{n^2}\right)\right]\mathrm{d}n_\alpha+\frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}}\,\mathrm{d}c^{ij}\,. \tag{C5}$$

By comparing the coefficients between Eqs. (C1) and (C5) results:

$$\frac{\partial\hat{\mathcal{F}}}{\partial T}=\frac{\partial\bar{\mathcal{F}}}{\partial T}\quad,\quad \frac{\partial\hat{\mathcal{F}}}{\partial n_\alpha}=m_\alpha\frac{\partial\bar{\mathcal{F}}}{\partial\rho}+\sum_{\beta=1}^{\nu-1}\frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}\left(\frac{\delta^{\alpha\beta}}{n}-\frac{n_\beta}{n^2}\right)\quad,\quad \frac{\partial\hat{\mathcal{F}}}{\partial c^{ij}}=\frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}}\,. \tag{C6}$$

Appendix D: Legendre Transform between $\bar{\mathcal{F}}$ and $\acute{\mathcal{F}}$

According to Eq. $(49)_{3,4}$ we write:

$$\mathrm{d}(\rho\varphi)=\ \mathrm{d}\bar{\mathcal{F}}=\frac{\partial\bar{\mathcal{F}}}{\partial T}\,\mathrm{d}T+\sum_{\beta=1}^{\nu-1}\frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}\,\mathrm{d}y_\beta+\frac{\partial\bar{\mathcal{F}}}{\partial\rho}\,\mathrm{d}\rho+\frac{\partial\bar{\mathcal{F}}}{\partial c^{ij}}\,\mathrm{d}c^{ij} \tag{C2}$$

$$=\ \mathrm{d}\acute{\mathcal{F}}=\frac{\partial\acute{\mathcal{F}}}{\partial T}\,\mathrm{d}T+\sum_{\beta=1}^{\nu-1}\frac{\partial\acute{\mathcal{F}}}{\partial y_\beta}\,\mathrm{d}y_\beta++\frac{\partial\acute{\mathcal{F}}}{\partial C^{ij}}\,\mathrm{d}C^{ij}\,. \tag{D1}$$

Hence we have to substitute $\mathrm{d}\rho$ and $\mathrm{d}c^{ij}$ by means of $\mathrm{d}C^{ij}$. For this reason we find:

$$C^{ij}(c^{ij},\rho)=J^{2/3}c^{ij}=c^{ij}\left(\frac{\rho_0}{\rho}\right)^{2/3}\quad\Rightarrow\quad \mathrm{d}C^{ij}=\frac{\partial C^{ij}}{\partial c^{kl}}\mathrm{d}c^{kl}+\frac{\partial C^{ij}}{\partial\rho}\mathrm{d}\rho\,, \tag{D2}$$

$$\text{with}\quad \frac{\partial C^{ij}}{\partial c^{kl}}\ \overset{(C^{ij}=C^{ji})}{=}\ \frac{1}{2}\frac{\partial}{\partial c^{kl}}(C^{ij}+C^{ji})=\frac{1}{2}\left(\frac{\rho_0}{\rho}\right)^{2/3}(\delta^{ik}\delta^{jl}+\delta^{jk}\delta^{il}) \tag{D3}$$

$$\text{and}\quad \frac{\partial C^{ij}}{\partial\rho}\ =\ -\frac{2}{3}\frac{c^{ij}}{\rho}\left(\frac{\rho_0}{\rho}\right)^{2/3}\,. \tag{D4}$$

Insertion of Eqs. $(D2)_2$, (D3) and (D4) into Eq. (D1) results in:

$$\mathrm{d}(\rho\varphi)=\frac{\partial\acute{\mathcal{F}}}{\partial T}\,\mathrm{d}T+\sum_{\beta=1}^{\nu-1}\frac{\partial\acute{\mathcal{F}}}{\partial y_\beta}\,\mathrm{d}y_\beta+\frac{\partial\acute{\mathcal{F}}}{\partial C^{ij}}\left[\frac{1}{2}\left(\frac{\rho_0}{\rho}\right)^{2/3}(\delta^{ik}\delta^{jl}+\delta^{jk}\delta^{il})\mathrm{d}c^{kl}-\frac{2}{3}\frac{c^{ij}}{\rho}\left(\frac{\rho_0}{\rho}\right)^{2/3}\mathrm{d}\rho\right]. \tag{D5}$$

Comparison of Eqs. (C2) and (D5) yields for the coefficients:

$$\frac{\partial\bar{\mathcal{F}}}{\partial T}=\frac{\partial\acute{\mathcal{F}}}{\partial T}\quad,\quad\frac{\partial\bar{\mathcal{F}}}{\partial y_\beta}=\frac{\partial\acute{\mathcal{F}}}{\partial y_\beta}\quad,\quad\frac{\partial\bar{\mathcal{F}}}{\partial\rho}=-\frac{2}{3}\frac{c^{ij}}{\rho}\left(\frac{\rho_0}{\rho}\right)^{2/3}\frac{\partial\acute{\mathcal{F}}}{\partial C^{ij}}\quad,$$
$$\frac{\partial\bar{\mathcal{F}}}{\partial c^{kl}}=\frac{1}{2}\frac{\partial\acute{\mathcal{F}}}{\partial C^{ij}}\left(\frac{\rho_0}{\rho}\right)^{2/3}(\delta^{ik}\delta^{jl}+\delta^{jk}\delta^{il})\,. \tag{D6}$$

Appendix E: Legendre Transform between $\tilde{\mathbb{S}}$ and $\hat{\mathbb{S}}$

According to the functional representations in Eq. $(103)_{1,2}$ the following total differentials are formulated ($\alpha=1,\dots,\nu$):

$$\mathrm{d}(\rho\eta)=\mathrm{d}\tilde{\mathbb{S}}=\frac{\partial\tilde{\mathbb{S}}}{\partial\rho\epsilon}\mathrm{d}(\rho\epsilon)+\frac{\partial\tilde{\mathbb{S}}}{\partial n_\alpha}\mathrm{d}n_\alpha+\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^i n_\alpha}\mathrm{d}(\nabla^i n_\alpha)+\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^{ij}n_\alpha}\mathrm{d}(\nabla^{ij}n_\alpha)+\frac{\partial\tilde{\mathbb{S}}}{\partial c^{ij}}\mathrm{d}c^{ij} \tag{E1}$$
$$=\mathrm{d}\hat{\mathbb{S}}=\frac{\partial\hat{\mathbb{S}}}{\partial T}\mathrm{d}T+\frac{\partial\hat{\mathbb{S}}}{\partial n_\alpha}\mathrm{d}n_\alpha+\frac{\partial\hat{\mathbb{S}}}{\partial\nabla^i n_\alpha}\mathrm{d}(\nabla^i n_\alpha)+\frac{\partial\hat{\mathbb{S}}}{\partial\nabla^{ij}n_\alpha}\mathrm{d}(\nabla^{ij}n_\alpha)+\frac{\partial\hat{\mathbb{S}}}{\partial c^{ij}}\mathrm{d}c^{ij}\,, \tag{E2}$$

with the definition of the absolute temperature $\frac{\partial\tilde{\mathcal{S}}}{\partial\rho\epsilon}=1/T$. The total differential of the internal energy density $\rho\epsilon=\hat{\mathbb{E}}(T,n_\alpha,\nabla^i n_\alpha,\nabla^{ij}n_\alpha,c^{ij})$ in Eq. (E1) can be replaced by means of:

$$\mathrm{d}(\rho\epsilon)=\mathrm{d}\hat{\mathbb{E}}=\frac{\partial\hat{\mathbb{E}}}{\partial T}\mathrm{d}T+\frac{\partial\hat{\mathbb{E}}}{\partial n_\alpha}\mathrm{d}n_\alpha+\frac{\partial\hat{\mathbb{E}}}{\partial\nabla^i n_\alpha}\mathrm{d}(\nabla^i n_\alpha)+\frac{\partial\hat{\mathbb{E}}}{\partial\nabla^{ij}n_\alpha}\mathrm{d}(\nabla^{ij}n_\alpha)+\frac{\partial\hat{\mathbb{E}}}{\partial c^{ij}}\mathrm{d}c^{ij}\,. \tag{E3}$$

Hence it follows from Eq. (E1):

$$\begin{aligned}\mathrm{d}\tilde{\mathbb{S}}=&\frac{1}{T}\frac{\partial\hat{\mathbb{E}}}{\partial T}\mathrm{d}T+\left(\frac{1}{T}\frac{\partial\hat{\mathbb{E}}}{\partial n_\alpha}+\frac{\partial\tilde{\mathbb{S}}}{\partial n_\alpha}\right)\mathrm{d}n_\alpha+\left(\frac{1}{T}\frac{\partial\hat{\mathbb{E}}}{\partial\nabla^i n_\alpha}+\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^i n_\alpha}\right)\mathrm{d}(\nabla^i n_\alpha)\\&+\left(\frac{1}{T}\frac{\partial\hat{\mathbb{E}}}{\partial\nabla^{ij}n_\alpha}+\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^{ij}n_\alpha}\right)\mathrm{d}(\nabla^{ij}n_\alpha)+\left(\frac{1}{T}\frac{\partial\hat{\mathbb{E}}}{\partial c^{ij}}+\frac{\partial\tilde{\mathbb{S}}}{\partial c^{ij}}\right)\mathrm{d}c^{ij}\,.\end{aligned} \tag{E4}$$

Since T and n_α are independent arguments within the functional representations $\hat{\mathbb{E}}$ and $\hat{\mathbb{S}}$ we identify:

$$\begin{aligned}&\frac{\partial\hat{\mathbb{S}}}{\partial T}=\frac{1}{T}\frac{\partial\hat{\mathbb{E}}}{\partial T}\quad,\quad-T\frac{\partial\tilde{\mathbb{S}}}{\partial n_\alpha}=\frac{\partial\hat{\mathbb{F}}}{\partial n_\alpha}\quad,\quad-T\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^i n_\alpha}=\frac{\partial\hat{\mathbb{F}}}{\partial\nabla^i n_\alpha}\\&-T\frac{\partial\tilde{\mathbb{S}}}{\partial\nabla^{ij}n_\alpha}=\frac{\partial\hat{\mathbb{F}}}{\partial\nabla^{ij}n_\alpha}\quad,\quad-T\frac{\partial\tilde{\mathbb{S}}}{\partial c^{ij}}=\frac{\partial\hat{\mathbb{F}}}{\partial c^{ij}}\,,\end{aligned} \tag{E5}$$

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 $\rho\varphi$.

Appendix F: Legendre Transform between $\hat{\mathbb{F}}$ and $\bar{\mathbb{F}}$

Using the representations in Eq. (120) we find the following total differentials ($\alpha = 1, \dots, \nu$ and $\beta = 1, \dots, \nu - 1$):

$$d(\rho\varphi) = \mathrm{d}\hat{\mathbb{F}} = \frac{\partial\hat{\mathbb{F}}}{\partial T}\mathrm{d}T + \frac{\partial\hat{\mathbb{F}}}{\partial n_\alpha}\mathrm{d}n_\alpha + \frac{\partial\hat{\mathbb{F}}}{\partial\nabla^i n_\alpha}\mathrm{d}(\nabla^i n_\alpha) + \frac{\partial\hat{\mathbb{F}}}{\partial\nabla^{ij} n_\alpha}\mathrm{d}(\nabla^{ij} n_\alpha) + \frac{\partial\hat{\mathbb{F}}}{\partial c^{ij}}\mathrm{d}c^{ij} \tag{F1}$$

$$= \mathrm{d}\bar{\mathbb{F}} = \frac{\partial\bar{\mathbb{F}}}{\partial T}\mathrm{d}T + \frac{\partial\bar{\mathbb{F}}}{\partial y_\beta}\underline{\mathrm{d}y_\beta} + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i y_\beta}\underline{\mathrm{d}(\nabla^i y_\beta)} + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\underline{\mathrm{d}(\nabla^{ij} y_\beta)} + \frac{\partial\bar{\mathbb{F}}}{\partial\rho}\underline{\mathrm{d}\rho}$$

$$+ \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i\rho}\underline{\mathrm{d}(\nabla^i\rho)} + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho}\underline{\mathrm{d}(\nabla^{ij}\rho)} + \frac{\partial\bar{\mathbb{F}}}{\partial c^{ij}}\mathrm{d}c^{ij} \ . \tag{F2}$$

Now the terms with brackets must be "suitably" replaced by expressions of $\mathrm{d}n_\alpha$, $\mathrm{d}(\nabla^i n_\alpha)$ and $\mathrm{d}(\nabla^{ij} n_\alpha)$. For this reason we write as follows:

$$\rho = \sum_\alpha m_\alpha n_\alpha \quad \Rightarrow \quad \mathrm{d}\rho = \sum_\alpha m_\alpha \mathrm{d}n_\alpha \ , \tag{F3}$$

$$\nabla^i\rho = \sum_\alpha m_\alpha \nabla^i n_\alpha \quad \Rightarrow \quad \mathrm{d}(\nabla^i\rho) = \sum_\alpha m_\alpha \mathrm{d}(\nabla^i n_\alpha) \ , \tag{F4}$$

$$\nabla^{ij}\rho = \sum_\alpha m_\alpha \nabla^{ij} n_\alpha \quad \Rightarrow \quad \mathrm{d}(\nabla^{ij}\rho) = \sum_\alpha m_\alpha \mathrm{d}(\nabla^{ij} n_\alpha) \ . \tag{F5}$$

Furthermore holds:

$$y_\beta = \frac{n_\beta}{\sum_\alpha n_\alpha} \quad \Rightarrow \quad y_\beta = \hat{\mathbb{Y}}_\beta(n_\alpha) \ , \tag{F6}$$

$$\nabla^i y_\beta = \nabla^i\left(\frac{n_\beta}{\sum_\alpha n_\alpha}\right) \quad \Rightarrow \quad \nabla^i y_\beta = \hat{\mathbb{Y}}^i_\beta(n_\alpha, \nabla^i n_\alpha) \ , \tag{F7}$$

$$\nabla^{ij} y_\beta = \nabla^{ij}\left(\frac{n_\beta}{\sum_\alpha n_\alpha}\right) \quad \Rightarrow \quad \nabla^{ij} y_\beta = \hat{\mathbb{Y}}^{ij}_\beta(n_\alpha, \nabla^i n_\alpha, \nabla^{ij} n_\alpha) \tag{F8}$$

and after a straightforward calculation:

$$\mathrm{d}y_\beta = \sum_\alpha \frac{\partial\hat{\mathbb{Y}}_\beta}{\partial n_\alpha}\mathrm{d}n_\alpha = \sum_\alpha\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right)\mathrm{d}n_\alpha \tag{F9}$$

$$\mathrm{d}(\nabla^i y_\beta) = \sum_\alpha \frac{\partial\hat{\mathbb{Y}}^i_\beta}{\partial n_\alpha}\mathrm{d}n_\alpha + \sum_\alpha \frac{\partial\hat{\mathbb{Y}}^i_\beta}{\partial\nabla^i n_\alpha}\mathrm{d}(\nabla^i n_\alpha) = \sum_\alpha \nabla^i\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right)\mathrm{d}n_\alpha + \sum_\alpha\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right)\mathrm{d}(\nabla^i n_\alpha) \tag{F10}$$

$$\mathrm{d}(\nabla^{ij} y_\beta) = \sum_\alpha \frac{\partial\hat{\mathbb{Y}}^{ij}_\beta}{\partial n_\alpha}\mathrm{d}n_\alpha + \sum_\alpha \frac{\partial\hat{\mathbb{Y}}^{ij}_\beta}{\partial\nabla^k n_\alpha}\mathrm{d}(\nabla^k n_\alpha) + \sum_\alpha \frac{\partial\hat{\mathbb{Y}}^{ij}_\beta}{\partial\nabla^{kl} n_\alpha}\mathrm{d}(\nabla^{kl} n_\alpha)$$

$$= \sum_\alpha \nabla^{ij}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right)\mathrm{d}n_\alpha + 2\sum_\alpha \nabla^j\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right)\mathrm{d}(\nabla^i n_\alpha) + \sum_\alpha\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right)\mathrm{d}(\nabla^{ij} n_\alpha) \ . \tag{F11}$$

Substituting the underbracket terms in Eq. (F2) by the results in Eqs. (F3-F5) and (F9-F11) yields:

$$
\begin{aligned}
\mathrm{d}\bar{\mathbb{F}} = & \frac{\partial\bar{\mathbb{F}}}{\partial T}\mathrm{d}T + \frac{\partial\bar{\mathbb{F}}}{\partial c^{ij}}\mathrm{d}c^{ij} + \\
& + \sum_\alpha \left\{ m_\alpha \frac{\partial\bar{\mathbb{F}}}{\partial\rho} + \sum_\beta \left[\frac{\partial\bar{\mathbb{F}}}{\partial y_\beta}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i y_\beta}\nabla^i\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\nabla^{ij}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) \right] \right\} \mathrm{d}n_\alpha \\
& + \sum_\alpha \left\{ m_\alpha \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i\rho} + \sum_\beta \left[\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i y_\beta}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) + 2\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\nabla^j\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) \right] \right\} \mathrm{d}(\nabla^i n_\alpha) \\
& + \sum_\alpha \left\{ m_\alpha \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho} + \sum_\beta \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) \right\} \mathrm{d}(\nabla^{ij} n_\alpha) \ . \qquad \text{(F12)}
\end{aligned}
$$

and we identify with $\mathrm{d}\bar{\mathbb{F}} = \mathrm{d}\hat{\mathbb{F}}$:

$$
\frac{\partial\hat{\mathbb{F}}}{\partial T} = \frac{\partial\bar{\mathbb{F}}}{\partial T} \quad , \quad \frac{\partial\hat{\mathbb{F}}}{\partial c^{ij}} = \frac{\partial\bar{\mathbb{F}}}{\partial c^{ij}} \ , \qquad \text{(F13)}
$$

$$
\frac{\partial\hat{\mathbb{F}}}{\partial n_\alpha} = m_\alpha \frac{\partial\bar{\mathbb{F}}}{\partial\rho} + \sum_\beta \left[\frac{\partial\bar{\mathbb{F}}}{\partial y_\beta}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i y_\beta}\nabla^i\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\nabla^{ij}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) \right] , \qquad \text{(F14)}
$$

$$
\frac{\partial\hat{\mathbb{F}}}{\partial\nabla^i n_\alpha} = m_\alpha \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i\rho} + \sum_\beta \left[\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i y_\beta}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) + 2\frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\nabla^j\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) \right] , \qquad \text{(F15)}
$$

$$
\frac{\partial\hat{\mathbb{F}}}{\partial\nabla^{ij} n_\alpha} = m_\alpha \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho} + \sum_\beta \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\left(\frac{\delta^{\alpha\beta}}{n} - \frac{n_\beta}{n^2}\right) \ . \qquad \text{(F16)}
$$

Appendix G: Legendre Transform between $\bar{\mathbb{F}}$ and $\acute{\mathbb{F}}$

This calculation is similar to that one of Appendix D. We start with the total differentials for $\bar{\mathbb{F}}$ and $\acute{\mathbb{F}}$, *viz*:

$$
\begin{aligned}
d(\rho\varphi) = \mathrm{d}\bar{\mathbb{F}} = \mathrm{d}\acute{\mathbb{F}} = & \\
= & \frac{\partial\bar{\mathbb{F}}}{\partial T}\mathrm{d}T + \frac{\partial\bar{\mathbb{F}}}{\partial y_\beta}\mathrm{d}y_\beta + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i y_\beta}\mathrm{d}(\nabla^i y_\beta) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\mathrm{d}(\nabla^{ij} y_\beta) + \frac{\partial\bar{\mathbb{F}}}{\partial\rho}\mathrm{d}\rho \\
& + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i\rho}\mathrm{d}(\nabla^i\rho) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho}\mathrm{d}(\nabla^{ij}\rho) + \frac{\partial\bar{\mathbb{F}}}{\partial c^{ij}}\mathrm{d}c^{ij} \qquad \text{(G1)} \\
= & \frac{\partial\bar{\mathbb{F}}}{\partial T}\mathrm{d}T + \frac{\partial\bar{\mathbb{F}}}{\partial y_\beta}\mathrm{d}y_\beta + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i y_\beta}\mathrm{d}(\nabla^i y_\beta) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij} y_\beta}\mathrm{d}(\nabla^{ij} y_\beta) \\
& + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^i\rho}\mathrm{d}(\nabla^i\rho) + \frac{\partial\bar{\mathbb{F}}}{\partial\nabla^{ij}\rho}\mathrm{d}(\nabla^{ij}\rho) + \frac{\partial\bar{\mathbb{F}}}{\partial C^{ij}}\underbrace{\mathrm{d}C^{ij}} \quad . \qquad \text{(G2)}
\end{aligned}
$$

The term with the bracket, *i.e.*, $\mathrm{d}C^{ij}$, can be substituted by the relation

$$
\mathrm{d}C^{ij} = \frac{1}{2}\left(\frac{\rho_0}{\rho}\right)^{2/3}(\delta^{ik}\delta^{jl} + \delta^{jk}\delta^{il})\mathrm{d}c^{kl} - \frac{2}{3}\frac{c^{ij}}{\rho}\left(\frac{\rho_0}{\rho}\right)^{2/3}\mathrm{d}\rho \qquad \text{(G3)}
$$

following the calculations shown in Eqs. (D2-D4). The resulting total differential for $\mathrm{d}\bar{\mathbb{F}}$ 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:

$$\frac{\partial\bar{\mathbb{F}}}{\partial\Xi} = \frac{\partial\acute{\mathbb{F}}}{\partial\Xi} \quad , \quad \Xi = \{T, y_\beta, \nabla^i y_\beta, \nabla^{ij} y_\beta, \nabla^i\rho, \nabla^{ij}\rho\} \tag{G4}$$

and

$$\frac{\partial\bar{\mathbb{F}}}{\partial\rho} = -\frac{2}{3}\frac{C^{ij}}{\rho}\frac{\partial\acute{\mathbb{F}}}{\partial C^{ij}} \quad , \quad \frac{\partial\bar{\mathbb{F}}}{\partial c^{kl}} = \frac{1}{2}\left(\frac{\rho_0}{\rho}\right)^{\frac{2}{3}}(\delta^{ik}\delta^{jl} + \delta^{il}\delta^{kj})\frac{\partial\acute{\mathbb{F}}}{\partial C^{ij}} \, . \tag{G5}$$

Appendix H: Legendre Transform between $\widehat{\widehat{\mathbb{F}}}$ and $\overline{\overline{\mathbb{F}}}$

According to the functional representations introduced in Eq. (126) we write for the total differentials of $\rho\varphi$ ($\alpha = 1, \ldots, \nu$ and $\beta = 1, \ldots, \nu - 1$):

$$d(\rho\varphi) = \mathrm{d}\widehat{\widehat{\mathbb{F}}} = \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial T}\mathrm{d}T + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial\rho_\alpha}\mathrm{d}\rho_\alpha + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial\nabla^i\rho_\alpha}\mathrm{d}(\nabla^i\rho_\alpha) + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial\nabla^{ij}\rho_\alpha}\mathrm{d}(\nabla^{ij}\rho_\alpha) + \frac{\partial\widehat{\widehat{\mathbb{F}}}}{\partial c^{ij}}\mathrm{d}c^{ij} \tag{H1}$$

$$\begin{aligned} = \mathrm{d}\overline{\overline{\mathbb{F}}} = {} & \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial T}\mathrm{d}T + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial c_\beta}\underline{\mathrm{d}c_\beta} + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^i c_\beta}\underline{\mathrm{d}(\nabla^i c_\beta)} + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^{ij}c_\beta}\underline{\mathrm{d}(\nabla^{ij}c_\beta)} \\ & + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^i\rho}\underline{\mathrm{d}(\nabla^i\rho)} + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\nabla^{ij}\rho}\underline{\mathrm{d}(\nabla^{ij}\rho)} + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial\rho}\underline{\mathrm{d}\rho} + \frac{\partial\overline{\overline{\mathbb{F}}}}{\partial c^{ij}}\mathrm{d}c^{ij} \, . \end{aligned} \tag{H2}$$

The highlighted terms must be substituted by the expressions $\mathrm{d}\rho_\alpha$, $\mathrm{d}(\nabla^i\rho_\alpha)$ and $\mathrm{d}(\nabla^{ij}\rho_\alpha)$. Analogously to the Eqs. (F3-F5) and (F6-F8) one finds:

$$\rho = \sum_\alpha \rho_\alpha \quad \Rightarrow \quad \mathrm{d}\rho = \sum_\alpha \mathrm{d}\rho_\alpha \, , \tag{H3}$$

$$\nabla^i\rho = \sum_\alpha \nabla^i\rho_\alpha \quad \Rightarrow \quad \mathrm{d}(\nabla^i\rho) = \sum_\alpha \mathrm{d}(\nabla^i\rho_\alpha) \, , \tag{H4}$$

$$\nabla^{ij}\rho = \sum_\alpha m_\alpha\nabla^{ij}n_\alpha \quad \Rightarrow \quad \mathrm{d}(\nabla^i\rho) = \sum_\alpha \mathrm{d}(\nabla^{ij}\rho_\alpha) \, , \tag{H5}$$

and

$$c_\beta = \frac{\rho_\beta}{\sum_\alpha \rho_\alpha} \quad \Rightarrow \quad c_\beta = \widehat{\widehat{\mathbb{C}}}_\beta(\rho_\alpha) \, , \tag{H6}$$

$$\nabla^i c_\beta = \nabla^i\left(\frac{\rho_\beta}{\sum_\alpha \rho_\alpha}\right) \quad \Rightarrow \quad \nabla^i c_\beta = \widehat{\widehat{\mathbb{C}}}^i_\beta(\rho_\alpha, \nabla^i\rho_\alpha) \, , \tag{H7}$$

$$\nabla^{ij} c_\beta = \nabla^{ij}\left(\frac{\rho_\beta}{\sum_\alpha \rho_\alpha}\right) \quad \Rightarrow \quad \nabla^{ij} c_\beta = \widehat{\widehat{\mathbb{C}}}^{ij}_\beta(\rho_\alpha, \nabla^i\rho_\alpha, \nabla^{ij}\rho_\alpha) \, . \tag{H8}$$

Thus we derive in the same manner as in the Eqs. (F9-F11):

$$\mathrm{d}c_\beta = \sum_\alpha \frac{\partial \widehat{\widehat{\mathbb{C}}}_\beta}{\partial \rho_\alpha} \mathrm{d}\rho_\alpha = \sum_\alpha \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \mathrm{d}\rho_\alpha \; , \tag{H9}$$

$$\mathrm{d}(\nabla^i c_\beta) = \sum_\alpha \frac{\partial \widehat{\widehat{\mathbb{C}}}^i_\beta}{\partial \rho_\alpha} \mathrm{d}\rho_\alpha + \sum_\alpha \frac{\partial \widehat{\widehat{\mathbb{C}}}^i_\beta}{\partial \nabla^i \rho_\alpha} \mathrm{d}(\nabla^i \rho_\alpha) = \sum_\alpha \nabla^i \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \mathrm{d}\rho_\alpha + \sum_\alpha \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \mathrm{d}(\nabla^i \rho_\alpha) \; , \tag{H10}$$

$$\begin{aligned} \mathrm{d}(\nabla^{ij} c_\beta) &= \sum_\alpha \frac{\partial \widehat{\widehat{\mathbb{C}}}^{ij}_\beta}{\partial \rho_\alpha} \mathrm{d}\rho_\alpha + \sum_\alpha \frac{\partial \widehat{\widehat{\mathbb{C}}}^{ij}_\beta}{\partial \nabla^k \rho_\alpha} \mathrm{d}(\nabla^k \rho_\alpha) + \sum_\alpha \frac{\partial \widehat{\widehat{\mathbb{C}}}^{ij}_\beta}{\partial \nabla^{kl} \rho_\alpha} \mathrm{d}(\nabla^{kl} \rho_\alpha) \\ &= \sum_\alpha \nabla^{ij} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \mathrm{d}\rho_\alpha + 2 \sum_\alpha \nabla^j \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \mathrm{d}(\nabla^i \rho_\alpha) + \sum_\alpha \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \mathrm{d}(\nabla^{ij} \rho_\alpha) \; . \end{aligned} \tag{H11}$$

Eqs. (H3-H11) can be inserted into Eq. (H2). A following comparison of the coefficients between the Eqs. (H1) and (H2) allows to identify the final relations:

$$\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial T} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial T} \quad , \quad \frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial c^{ij}} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c^{ij}} \quad , \tag{H12}$$

$$\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \rho_\alpha} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \rho} + \sum_\beta \left[\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial c_\beta} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) + \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^i c_\beta} \nabla^i \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) + \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{ij} c_\beta} \nabla^{ij} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \right] \quad , \tag{H13}$$

$$\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \nabla^i \rho_\alpha} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^i \rho} + \sum_\beta \left[\frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^i c_\beta} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) + 2 \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{ij} c_\beta} \nabla^j \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \right] \quad , \tag{H14}$$

$$\frac{\partial \widehat{\widehat{\mathbb{F}}}}{\partial \nabla^{ij} \rho_\alpha} = \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{ij} \rho} + \sum_\beta \frac{\partial \overline{\overline{\mathbb{F}}}}{\partial \nabla^{ij} c_\beta} \left(\frac{\delta^{\alpha\beta}}{\rho} - \frac{\rho_\beta}{\rho^2} \right) \; . \tag{H15}$$