Weierstraß-Institut
für Angewandte Analysis und Stochastik

im Forschungsverbund Berlin e.V.

Preprint ISSN 0946 – 8633

On the modelling of semi-insulating GaAs including surface tension and bulk stresses

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submitted: 22th December 2004

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No. 995
Berlin 2004

2000 *Mathematics Subject Classification.* 74N20, 74A15, 74N05, 74B99.

Key words and phrases. thermodynamics, phase transitions, phase diagrams, precipitates, surface stress, deviatoric stress, chemical potentials, elasticity, GaAs.

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Abstract

Necessary heat treatment of single crystal semi-insulating Gallium Arsenide (GaAs), which is deployed in micro- and opto-electronic devices, generates undesirable liquid precipitates in the solid phase [24, 27, 26, 30, 29]. The appearance of precipitates is influenced by surface tension at the liquid/solid interface and deviatoric stresses in the solid.

The central quantity for the description of the various aspects of phase transitions is the chemical potential, which can be additively decomposed into a chemical and a mechanical part. In particular the calculation of the mechanical part of the chemical potential is of crucial importance. We determine the chemical potential in the framework of the St. Venant–Kirchhoff law, which gives an appropriate stress/strain relation for many solids in the small strain regime [33]. We establish criteria, which allow the correct replacement of the St. Venant–Kirchhoff law by the simpler Hooke law.

The main objectives of this study are: (*i*) We develop a thermo-mechanical model that describes diffusion and interface motion, which both are strongly influenced by surface tension effects and deviatoric stresses. (*ii*) We give an overview and outlook on problems that can be posed and solved within the framework of the model. (*iii*) We calculate non-standard phase diagrams for GaAs above 786°C, i.e. those that take into account surface tension and non-deviatoric stresses, and we compare the results with classical phase diagrams without these phenomena.

1 Introduction

Phase transitions in solids are usually strongly influenced by surface tension and non-isotropic stresses which give rise to nonzero stress deviators. An important example regards the nucleation and growth of liquid droplets in semi-insulating gallium arsenide (GaAs) [27, 26, 30, 29]. These processes are accompanied by deviatoric stresses resulting from the liquid/solid misfit [15, 4]. In the classical treatment the nucleation barrier is determined by surface tension of the droplet [32, 14, 35]. However, due to deviatoric stresses in the neighborhood of the droplet, and in particular at the liquid/solid interface, the nucleation barrier may be decreased.

A further mechanism that controls the evolution of liquid droplets in semi-insulating GaAs is diffusion in the vicinity of the droplet [8]. The diffusion flux results from a competition of chemical and mechanical driving forces.

The quantity of central importance for the description of all these phenomena is the chemical potential. Its calculation in the presence of mechanical stresses is among the subjects of this study. We determine the chemical potential in the framework of the St.Venant–Kirchhoff law, which gives an appropriate stress/strain relation for many solids in the small strain regime [33]. Subtle problems concerning the chemical potentials appear in the limiting case, where the St.Venant–Kirchhoff law is approximated by the classical Hooke law.

In a series of studies we develop a thermodynamical model for the description of liquid/solid phase transitions that are accompanied by deviatoric stresses, diffusion and chemical reactions. The model is especially designed to describe phenomena, which arise during heat treatments of GaAs wafer at elevated temperatures above the right eutectic line. However, a generalisation of the model to other materials with dynamic precipitation phenomena may be undertaken. An example is the formation of cementit in steel.

This paper starts a series of studies with the formulation of the model and the description of various settings for the following tasks: 1. Calculation of non-standard phase diagrams in the presence of surface tension and deviatoric stresses. 2. Diffusional processes in the presence of surface tension and deviatoric stresses [8]. 3. Determination of the size distributions of droplets by a generalised Becker/Döring model that takes mechanical stresses into account [6].

We have organised the paper as follows:

We describe in Chapter 2 the constitution of the phases of GaAs, and in particular the semi-insulating solid phase. The central fact is the description of the sublattice structure with three sublattices. Experiments and preliminary theoretical considerations have motivated a special distribution of the constituents of GaAs on the sublattices that we will call the Freiberg model [11], see also [19, 28].

Chapter 3 reminds the reader to some basic thermodynamics for fluids and solids with special emphasis on a correct description of strains and stresses within the nonlinear theory of elasticity. In this chapter we define the chemical potentials for the constituents, and we give rules for their calculation within a quite general framework.

In Chapter 4 we restrict ourselves to thermodynamic processes at constant and uniform temperature and at constant external pressure. For such processes we derive and exploit the thermodynamic inequality, which determines the dynamics of thermodynamic processes. The inequality serves here for various purposes. These consist of: (i) Establishment of relations between driving forces and thermodynamic fluxes. Among these there are driving forces that induce diffusion fluxes and interface motion. (ii) Identification of mechanical, chemical, diffusional and phase equilibria and the determination of possible equilibrium states.

Chapter 5 is addressed to the special constitutive laws that we will use for the description of semi-insulating GaAs. We decompose the constitutive quantities into chemical and mechanical parts. The chemical parts rely on the well established sublattice model, which was formulated by Oates, Wenzl et al [25, 37, 36]. The mechanical parts rely on the St.Venant–Kirchhoff law which relates the Green strain tensor to the second Piola-Kirchhoff stress tensor. The mechanical parts of the chemical potentials are calculated here for the first time, and for this reason an extensive discussion and a comparison with those chemical potentials that appear in the literature is included.

In Chapter 6 we solve the mechanical boundary value problem for a misfitting liquid sphere in a solid surrounding.

Chapter 7 contains the first important application of the proposed model, viz. the calculation of phase diagrams in the presence of surface tension and stress deviators. A detailed comparison with standard phase diagrams is included.

In Chapter 8 we give a short summarise and we pose two further problems that can be treated by the model equations.

We conclude the paper with two appendices, which contain 1. technical proves of some statements of the main text and 2. certain material data regarding standard phase diagrams.

2 Constitution of the three phases of GaAs

2.1 Chemical constitution of semi-insulating solid GaAs

Semi-insulating gallium arsenide (GaAs) is a single crystal solid with the major substances gallium (Ga) and arsenic (As). The stoichiometric solid, i.e. equal amounts of Ga and As, has zinc-blend structure with two fcc sublattices, α and β, which are completely occupied by Ga-atoms and As-atoms, respectively. In order to fabricate semi-insulating GaAs, a small amount of excess As-atoms and further trace elements are added. Among these may be Oxygen (O), Silicon (Si), Bor (B) and Carbon (C) in very small quantities. The constituents of semi-insulating GaAs are found either on α and β sublattice sites or on interstitial sites, which form a third fcc sublattice, γ. The major substance of the sublattice γ are vacancies (V). However, vacancies may also be found on the two other sublattices. A serious description of the physical and chemical properties of semi-insulating GaAs also needs to consider charged states of the introduced constituents and additionally free electrons and holes [3, 13, 17, 18, 37, 36].

Sublattice α :	Ga_α	$\mathrm{As}_\alpha^{(0)}$	$\mathrm{As}_\alpha^{(+)}$	$\mathrm{V}_\alpha^{(0)}$	$\mathrm{V}_\alpha^{(3-)}$	$\mathrm{B}_\alpha^{(0)}$	$\mathrm{Si}_\alpha^{(+)}$
Sublattice β :	As_β	$\mathrm{V}_\beta^{(0)}$	$\mathrm{O}_\beta^{(0)}$	$\mathrm{O}_\beta^{(-)}$	$\mathrm{O}_\beta^{(+)}$	$\mathrm{C}_\beta^{(-)}$	
Sublattice γ :	$\mathrm{As}_\gamma^{(0)}$	$\mathrm{V}_\gamma^{(0)}$					
free charges :	e	h					

Table 1: Species of the complete Freiberg model.

The so called *Freiberg model* gives a complete list of the possible distribution of all constituents on the three sublattices for semi-insulating GaAs as it is fabricated at Freiberg *Compound Materials* (FCM), [12]. The notion Freiberg model refers in particular to the fact that Ga-atoms exclusively live on the sublattice α [11], see also [19, 28].

In fact we have used this model to calibrate the various material parameters, which appear in the model equations [7].

However, for a simplified description of semi-insulating GaAs, a reduced chemical model is possible, which is described by the following table:

Sublattice α :	Ga_α	As_α	V_α
Sublattice β :	As_β	V_β	
Sublattice γ :	As_γ	V_γ	

Table 2: Species of the reduced model.

The reduced model embodies qualitatively the essential properties of the Freiberg model: (i) Ga atoms reside exclusively on sublattice α. (ii) The antisite As_α controls the semi-insulating behaviour of GaAs. (iii) Vacancies are taken into account. (iv) There is interstitial arsenic, As_γ, which drives the diffusion processes.

In summary, the solid GaAs of this study consists of seven chemically reacting substances. Their distribution on the sublattices is described by the mole densities n_{Ga_α}, n_{As_α}, n_{V_α}, n_{As_β}, n_{V_β}, n_{As_γ} and n_{V_γ}.

2.2 Chemical constitution of the liquid and gaseous phases of GaAs

The solid phase of GaAs can coexist with a liquid phase and a gas phase, respectively. The liquid phase consists of Ga and As, with mole densities $n_{\mathrm{Ga_L}}$, $n_{\mathrm{As_L}}$ in the liquid. The gaseous phase has four constituents, namely the molecules Ga, As, As_2, As_4. However, in the interesting range between 0.001 bar and 20 bar, the appearance of Ga and mon-atomic As can be ignored, so that we may deal with a gas phase that consists exclusively of As_2 and As_4 with mole densities n_{As_2} and n_{As_4}, see also [2, 31].

3 Some piece of thermodynamics of mixtures

This chapter reminds the reader to some basic facts of thermodynamics of mixtures, see [20, 21], for an extensive treatment. Furthermore we present some simple generalisations regarding solid mixtures. The general thermodynamic relations are formulated so that they can be applied to solids as well as to liquids and gases. However, the gaseous phase will not be considered here explicitly. It is introduced in [7], where we rely on experiments, involving the gaseous phase, in order to determine the needed material data.

3.1 The basic variables of the solid and liquid phases of GaAs

We consider a body $\Omega = \Omega_{\mathrm{S}} \cup \Omega_{\mathrm{L}}$, which may consist of solid and liquid phases, denoted by Ω_{S}, and Ω_{L}, respectively. At any time $t \geq 0$, the thermodynamic state of the body Ω is described by a certain number of variables, which may be functions of space $x = (x^1, x^2, x^3) \in \Omega$. In general they are thus given by fields.

The variables of the solid phase are the seven mole densities

$$n_a(t,x), \qquad a \in a_{\mathrm{S}} = \{\mathrm{Ga}_\alpha, \mathrm{As}_\alpha, \mathrm{V}_\alpha, \mathrm{As}_\beta, \mathrm{V}_\beta, \mathrm{As}_\gamma, \mathrm{V}_\gamma\}, \tag{1}$$

and the mechanical displacement field

$$u(t,x) = \big(u^1(t,x), u^2(t,x), u^3(t,x)\big). \tag{2}$$

In the liquid phase, the variables are the two mole densities

$$n_a(t,x), \qquad a \in a_{\mathrm{L}} = \{\mathrm{Ga}_{\mathrm{L}}, \mathrm{As}_{\mathrm{L}}\}, \tag{3}$$

which determine the thermodynamic state of the liquid.

There are thus 7+3+2 unknowns, whose determination for given temperature T and given outer pressure p_0 is the main objective of this study.

3.2 Detailed description of the constitution of the solid and liquid phases

In this section we introduce further quantities that describe various aspects of the constitution of solid and liquid phases.

Mass densities: The mole densities can be used to define the mass densities of the phases:

$$\rho_{\mathrm{S}} = \sum_{a \in a_{\mathrm{S}}} M_a n_a, \quad \rho_{\mathrm{L}} = \sum_{a \in a_{\mathrm{L}}} M_a n_a. \tag{4}$$

The quantities M_a are the constant molecular weights of the constituents, viz. $M_{\mathrm{As}_\alpha} = M_{\mathrm{As}_\beta} = M_{\mathrm{As}_\gamma} = M_{\mathrm{As}}$ and $M_{\mathrm{Ga}_\alpha} = M_{\mathrm{Ga}}$.

Conservation law of mass: The mass density ρ satisfies the local conservation law of mass, which reads in each of the phases

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v^i}{\partial x^i} = 0. \tag{5}$$

The newly introduced quantity v^i denotes the barycentric velocity of the mixture.

Vacancies: We assume that the vacancies are carrier of energy and entropy, but they have no mass, i.e. we set $M_{\mathrm{V}_\alpha} = M_{\mathrm{V}_\beta} = M_{\mathrm{V}_\gamma} = 0$.

Mole fractions and lattice occupancies in the solid phase: The solid phase is a crystal with three fcc sublattices α, β, γ, which have the same number of lattice sites. We introduce now their common mole density, n_{G}, and lattice occupancies according to

$$n_{\mathrm{G}} = \frac{1}{3}\sum_{a\in a_{\mathrm{S}}} n_a \quad \text{and} \quad Y_a = \frac{n_a}{n_{\mathrm{G}}}. \tag{6}$$

The original 7 variables n_a, with $a \in a_{\mathrm{S}}$, may be substituted by the 7 variables n_{G} and Y_b with $b \in b_{\mathrm{S}} = a_{\mathrm{S}}\backslash\{\mathrm{Ga}_\alpha\}$. There holds

$$n_b = Y_b n_{\mathrm{G}} \quad \text{for} \quad b \in b_{\mathrm{S}} \quad \text{and} \quad n_{\mathrm{Ga}_\alpha} = \left(3 - \sum_{b\in b_{\mathrm{S}}} Y_b\right) n_{\mathrm{G}}. \tag{7}$$

We indicate this transformation by

$$n_a = \check{n}_a(Y_{b_{\mathrm{S}}}, n_{\mathrm{G}}) \quad \text{with} \quad Y_{b_{\mathrm{S}}} = \bigcup_{b\in b_{\mathrm{S}}} \{Y_b\}. \tag{8}$$

The distribution of the constituents on the lattice sites according to Table 2 implies that the total amounts of lattice occupancies for the three groups of constituents are given by

$$Y_{\mathrm{Ga}} = Y_{\mathrm{Ga}_\alpha}, \quad Y_{\mathrm{As}} = Y_{\mathrm{As}_\alpha} + Y_{\mathrm{As}_\beta} + Y_{\mathrm{As}_\gamma} \quad \text{and} \quad Y_{\mathrm{V}} = Y_{\mathrm{V}_\alpha} + Y_{\mathrm{V}_\beta} + Y_{\mathrm{V}_\gamma}. \tag{9}$$

The density of the solid phase can now be written

$$\rho_{\mathrm{S}} = \sum_{a\in a_{\mathrm{S}}} M_a \check{n}_a(Y_{b_{\mathrm{S}}}, n_{\mathrm{G}}) = (M_{\mathrm{Ga}}Y_{\mathrm{Ga}} + M_{\mathrm{As}}Y_{\mathrm{As}})n_{\mathrm{G}} = \check{\rho}_{\mathrm{S}}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}, n_{\mathrm{G}}). \tag{10}$$

Note that the ratio of ρ_{S} and n_{G} does only depend on Y_{Ga} and Y_{As}. We express this fact by the definition of a mean molecular weight of the solid:

$$\mathfrak{M}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}) = \frac{\check{\rho}_{\mathrm{S}}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}, n_{\mathrm{G}})}{2n_{\mathrm{G}}}. \tag{11}$$

It is often useful to represent the mole densities of the lattice sites and of the constituents, respectively, by the functions

$$n_{\mathrm{G}} = \widehat{n}_{\mathrm{G}}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}, \rho_{\mathrm{S}}) \quad \text{and} \quad n_a = \widehat{n}_a(Y_{b_{\mathrm{S}}}, \rho_{\mathrm{S}}). \tag{12}$$

Furthermore we need mole fractions of the material constituents of the solid phase. These are defined by

$$X_{\mathrm{S}a} = \frac{n_a}{n_{\mathrm{S}}} = \frac{Y_a}{Y_{\mathrm{Ga}} + Y_{\mathrm{As}}} = \frac{Y_a}{3 - Y_{\mathrm{V}}}. \quad \text{with} \quad n_{\mathrm{S}} = \sum_{a\in a_{\mathrm{S}}} n_a - n_{\mathrm{V}_\alpha} - n_{\mathrm{V}_\beta} - n_{\mathrm{V}_\gamma}. \tag{13}$$

Mole fractions in the liquid phase: In the liquid phase we change the variables from $n_{\mathrm{Ga_L}}$ and $n_{\mathrm{As_L}}$ to the total mole density of the liquid, n_{L}, and to the mole fraction X_{L} of the arsenic. We thus introduce

$$n_{\mathrm{L}} = n_{\mathrm{Ga_L}} + n_{\mathrm{As_L}} \quad \text{and} \quad X_{\mathrm{L}} = \frac{n_{\mathrm{As_L}}}{n_{\mathrm{L}}}. \tag{14}$$

There follows

$$n_{\mathrm{As_L}} = X_{\mathrm{L}} n_{\mathrm{L}} \quad \text{and} \quad n_{\mathrm{Ga_L}} = (1 - X_{\mathrm{L}}) n_{\mathrm{L}}, \tag{15}$$

which can also be written as

$$n_a = \check{n}_a(X_{\mathrm{L}}, n_{\mathrm{L}}). \tag{16}$$

The liquid mass density $(4)_2$ can now be written

$$\rho_{\mathrm{L}} = \sum_{a \in a_{\mathrm{L}}} M_a \check{n}_a(X_{\mathrm{L}}, n_{\mathrm{L}}) = \check{\rho}_{\mathrm{L}}(X_{\mathrm{L}}, n_{\mathrm{L}}). \tag{17}$$

Note that the ratio $\rho_{\mathrm{L}}/n_{\mathrm{L}}$ does only depend on X_{L} but not on n_{L}. We define the mean molecular weight of the liquid by

$$\mathcal{M}(X_{\mathrm{L}}) = \frac{\check{\rho}_{\mathrm{L}}(X_{\mathrm{L}}, n_{\mathrm{L}})}{n_{\mathrm{L}}} = M_{\mathrm{Ga}}(1 - X_{\mathrm{L}}) + M_{\mathrm{As}} X_{\mathrm{L}}. \tag{18}$$

The following representations will become useful in the next subsections:

$$n_{\mathrm{L}} = \widehat{n}_{\mathrm{L}}(X_{\mathrm{L}}, \rho_{\mathrm{L}}), \qquad n_a = \widehat{n}_a(X_{\mathrm{L}}, \rho_{\mathrm{L}}), \qquad \check{\rho}_{\mathrm{L}}(X_{\mathrm{L}}, n_{\mathrm{L}}) = \mathcal{M}(X_{\mathrm{L}}) n_{\mathrm{L}}. \tag{19}$$

3.3 Detailed description of motion and strain in the solid phase

In this section we relate the displacement field to motion and strain of a solid phase. We start with the introduction of a reference state in order to measure the motion of a material point of the solid phase.

Let $X = (X^1, X^2, X^3)$ be the location of a material point in a reference state, whose location at time t is given by $x = (x^1, x^2, x^3)$. The location x is determined by the function

$$x = \chi(t, X) = \big(\chi^1(t, X), \chi^2(t, X), \chi^3(t, X)\big). \tag{20}$$

We call $\chi^i(t, X)$ the motion of the material points of the solid phase. The motion can be used to calculate the barycentric velocity of the mixture, $\hat{v}^i(t, X) = \partial \chi^i(t, X)/\partial t$. The displacement of a material point is defined by

$$U^i(t, X) = \chi^i(t, X) - X^i. \tag{21}$$

The gradients of $\chi^i(t, X)$ and $U^i(t, X)$ are called deformation gradient and displacement gradient, respectively:

$$F^{ij} = \frac{\partial \chi^i}{\partial X^j}, \qquad H^{ij} = \frac{\partial U^i}{\partial X^j}, \quad \text{thus} \quad F^{ij} = \delta^{ij} + H^{ij}. \tag{22}$$

The Jacobian of F^{ij} is denoted by J. If we assume that $J > 0$, we may invert the motion $x^i = \chi^i(t, X)$ at any time t with respect to the coordinates X^i. We write

$$X^i = (\chi^{-1})^i(t, x). \tag{23}$$

We are now able to identify the displacement field u^i, that was introduced as a variable in the last section, by

$$u^i(t, x) = U^i(t, \chi^{-1}(t, x)). \tag{24}$$

This is a typical example for the representation of mechanical quantities with respect to actual coordinates. We call this representation the Euler or the spatial description, whereas the representation with respect to the reference coordinates is called the Lagrange or material description.

The barycentric velocity $\hat{v}^i(t, X)$ can likewise be given with respect to the coordinates x^i. We define $v^i(t, x) = \hat{v}^i(t, \chi^{-1}(t, x))$, and this quantity has already appeared in the local conservation law for the mass density (5).

A similar definition for the mass density, viz. $\rho(t, x) = \hat{\rho}(t, \chi^{-1}(t, x))$, is useful to integrate (5) to obtain

$$J = \det(F) = \frac{\rho^{\mathrm{R}}}{\rho}, \tag{25}$$

where ρ_R is the mass density for $F^{ij} = \delta^{ij}$.

In this study we prefer the Euler representation, and to this end we introduce the spatial displacement gradient and the inverse deformation gradient according to

$$h^{ij} = \frac{\partial u^i}{\partial x^j} \quad \text{and} \quad (F^{-1})^{ij} = \frac{\partial (\chi^{-1})^i}{\partial x^j}. \tag{26}$$

We have then the relations

$$(F^{-1})^{ij} = \delta^{ij} - h^{ij}, \quad H^{ij} = h^{ik}((I - h)^{-1})^{kj}. \tag{27}$$

Further important objects for the description of the stretch are the right and the left Cauchy-Green tensor, C^{ij} and B^{ij}, and for the description of the strain we define the Green strain tensor G^{ij}:

$$C^{ij} = F^{mi} F^{mj}, \quad B^{ij} = F^{im} F^{jm}, \quad G^{ij} = \frac{1}{2}(C^{ij} - \delta^{ij}). \tag{28}$$

These quantities may also easily be given with respect to the spatial representation.

Finally we decompose the stretch of a body into a part, which gives pure volume changes of the body and the complementary part, which describes pure changes of its shape. Pure changes of the volume are obviously given by the Jacobian J, whereas the unimodular tensor

$$c^{ij} = J^{-2/3} C^{ij} \quad \text{with} \quad \det(\boldsymbol{c}) = 1 \tag{29}$$

represents changes of the shape of a body. For details see [22].

3.4 Notations regarding free energy, chemical potentials and stresses

In order to describe the various mentioned thermodynamic processes in GaAs, we need to introduce further quantities. These are the specific internal energy u, the specific entropy s, the specific free energy $\psi = u - Ts$, and the chemical potential of the constituents μ_a with $a \in a_{\mathrm{L}} \cup a_{\mathrm{S}}$. Furthermore we need to introduce two measures of stress: the Cauchy stress σ^{ij} and the second Piola-Kirchhoff stress t^{ik}. There holds

$$\sigma^{ij} = \sigma^{ji}, \quad t^{ij} = J(F^{-1})^{im}(F^{-1})^{jn}\sigma^{mn}. \tag{30}$$

The isotropic part of the Cauchy stress is related to the pressure p, which is defined by

$$p = -\frac{1}{3}\sigma^{mm}, \quad \text{so that} \quad \sigma^{ij} = -p\,\delta^{ij} + \sigma^{\langle ij \rangle}. \tag{31}$$

Here the angle brackets indicate the stress deviator, which represent the stress due to pure changes of the shape of a solid, whereas the pressure is related to pure changes of the volume of a body.

3.5 Constitutive model, Part 1: General constitutive equations

The constitutive model establishes equations that allow to calculate quantities which are not among the list of variables that were introduced in Section 3.1.

The general constitutive model that we use for the description of the solid and the liquid phases of GaAs starts from a free energy density $\rho\psi$, which we assume here to be given by the constitutive function

$$\rho\psi = \rho\psi(T, n_a, \boldsymbol{c}), \tag{32}$$

for $a \in a_{\mathrm{S}}$ and $a \in a_{\mathrm{L}}$ in the solid and liquid phase, respectively. In liquids there is no dependence of the free energy density on $\boldsymbol{c}$ because there is no change of shape during deformations of liquids.

Entropy, stresses and chemical potentials are related to the free energy via the Gibbs equation, which reads

$$d(\rho\psi) = -\rho s\ dT + \frac{1}{2}J^{-1/3}t^{ji}dc^{ij} + \sum_a \mu_a dn_a. \tag{33}$$

Furthermore we have the Gibbs-Duhem equation

$$\frac{p}{\rho} + \psi = \frac{1}{\rho}\sum_a \mu_a n_a. \tag{34}$$

The proof of the Gibbs equation and of the Gibbs-Duhem equation for fluid mixtures and for solids consisting of a pure substance is given in [20]. The extension to the corresponding equation (33) can be carried out along the same strategies that are explained in detail by I. Müller in [20].

The quantity $g = \psi + p/\rho$ is called the specific Gibbs free energy and Mg is identical to the chemical potential of a pure substance with the molecular weight M. The Gibbs equation implies

$$\rho s = -\frac{\partial \rho\psi}{\partial T}, \quad \text{and} \quad \mu_a = \frac{\partial \rho\psi}{\partial n_a}, \tag{35}$$

which can be read directly off from (33).

In order to relate the stress and the pressure to the free energy density we change at first the variables.

In the solid we substitute $T, n_{a_\mathrm{S}}, \boldsymbol{c}$ by $T, Y_{b_\mathrm{S}}, \rho_\mathrm{S}, \boldsymbol{c}$. By means of $(12)_2$ we obtain

$$\psi_\mathrm{S}(T, n_{a_\mathrm{S}}, \boldsymbol{c}) = \psi_\mathrm{S}(T, \widehat{n}_{a_\mathrm{S}}(Y_{b_\mathrm{S}}, \rho_\mathrm{S}), \boldsymbol{c}) = \widehat{\psi}_\mathrm{S}(T, Y_{b_\mathrm{S}}, \rho_\mathrm{S}, \boldsymbol{c}) = \check{\psi}_\mathrm{S}(T, Y_{b_\mathrm{S}}, n_\mathrm{G}, \boldsymbol{c}). \tag{36}$$

In the liquid we change from T, n_{a_L} to $T, X_\mathrm{L}, \rho_\mathrm{L}$. By means of $(19)_2$ we obtain

$$\psi_\mathrm{L}(T, n_{a_\mathrm{L}}) = \psi_\mathrm{L}(T, \widehat{n}_{a_\mathrm{L}}(X_\mathrm{L}, \rho_\mathrm{L})) = \widehat{\psi}_\mathrm{L}(T, X_\mathrm{L}, \rho_\mathrm{L}) = \check{\psi}_\mathrm{L}(T, X_\mathrm{L}, n_\mathrm{L}). \tag{37}$$

Insertion of $(35)_2$ into (34) leads both for solids and liquid to

$$p = \rho^2 \frac{\partial \widehat{\psi}}{\partial \rho}. \tag{38}$$

We prove this statement in two steps:

At first we insert $(35)_2$ in (34) and carry out the indicated differentiations to obtain

$$p = \rho \sum_a \frac{\partial \psi}{\partial n_a}\, n_a. \tag{39}$$

According to (36) and (37) we calculate

$$\sum_{a \in a_\mathrm{L}} \frac{\partial \psi_\mathrm{L}}{\partial n_a}\, n_a = \frac{\partial \widehat{\psi}_\mathrm{L}}{\partial X_\mathrm{L}} \sum_{a \in a_\mathrm{L}} \frac{\partial X_\mathrm{L}}{\partial n_a}\, n_a + \frac{\partial \widehat{\psi}_\mathrm{L}}{\partial \rho_\mathrm{L}} \sum_{a \in a_\mathrm{L}} \frac{\partial \rho_\mathrm{L}}{\partial n_a}\, n_a. \tag{40}$$

and

$$\sum_{a \in a_\mathrm{S}} \frac{\partial \psi_\mathrm{S}}{\partial n_a} n_a = \sum_{a \in a_\mathrm{S}} \sum_{b \in b_\mathrm{S}} \frac{\partial \widehat{\psi}_\mathrm{S}}{\partial Y_b} \frac{\partial Y_b}{\partial n_a}\, n_a + \sum_{a \in a_\mathrm{S}} \frac{\partial \widehat{\psi}_\mathrm{S}}{\partial \rho_\mathrm{S}} \frac{\partial \rho_\mathrm{S}}{\partial n_a} n_a. \tag{41}$$

By means of the identities

$$\sum_{a \in a_\mathrm{L}} \frac{\partial X_\mathrm{L}}{\partial n_a} n_a = 0, \qquad \sum_{a \in a_\mathrm{S}} \frac{\partial Y_b}{\partial n_a} n_a = 0, \quad \sum_a \frac{\partial \rho}{\partial n_a} n_a = \rho, \tag{42}$$

we finally obtain from (39) the proposition (38).

In the liquid phase, the pressure is the only contribution to the stress, so that we may write here

$$t^{ij}_{\mathrm{L}} = -p_{\mathrm{L}} J (C^{-1})^{ij} \quad \text{and} \quad \sigma^{ij}_{\mathrm{L}} = -p_{\mathrm{L}} \delta^{ij}. \tag{43}$$

In the solid phase there is an extra contribution to the stress that we calculate now. We read off from (36), (25), (28) and (29) the representation

$$\widehat{\psi}_{\mathrm{S}}(T, Y_{b_{\mathrm{S}}}, \rho_{\mathrm{S}}, \boldsymbol{c}) = \widehat{\psi}_{\mathrm{S}}(T, Y_{b_{\mathrm{S}}}, \tilde{\rho}_{\mathrm{S}}(T, Y_{b_{\mathrm{S}}}, C), C/\sqrt[3]{\det C}) = \tilde{\psi}_{\mathrm{S}}(T, Y_{b_{\mathrm{S}}}, C), \tag{44}$$

and we rewrite the Gibbs equation (33) as a total differential for $\tilde{\psi}$, which implies by means of (34) the familiar result

$$t^{ij} = 2\rho^{\mathrm{R}} \frac{\partial \tilde{\psi}}{\partial C^{ij}}. \tag{45}$$

Thus the knowledge of the free energy density $\rho\psi(T, n_a, \boldsymbol{c})$ is sufficient to calculate all quantities that were introduced in the last section.

In order to illustrate the similarity between solid and liquid, we introduce in analogy to (44) for the liquid phase the representation

$$\psi_{\mathrm{L}}(T, n_{a_{\mathrm{L}}}) = \widehat{\psi}_{\mathrm{L}}(T, X_{\mathrm{L}}, \rho_{\mathrm{L}}) = \tilde{\psi}_{\mathrm{L}}(T, X_{\mathrm{L}}, J_{\mathrm{L}}), \tag{46}$$

instead of (37). Herein J_{L} is defined by $\rho^{\mathrm{R}}_{\mathrm{L}}/\rho_{\mathrm{L}}$.

In Section 5 we will introduce an explicit constitutive model for GaAs. This model will turn out to describe appropriately the various phenomena in GaAs which were listed in the introduction.

4 The approach of a thermodynamic system to equilibrium

4.1 The Global Laws of Energy and Entropy

Our objective is to study phase transitions for various systems with the common feature, that their temperature is homogeneous and constant and that the total system is subjected to a constant outer pressure, for example see Figure 2 and Figure 3. For the derivation of the relevant thermodynamic inequality, it is sufficient to consider the generic system, which is shown in Figure 1. The adjustment of the results to the special systems is trivial and left to the reader.

The body Ω of the generic system consists of a solid phase Ω_{S} and a liquid phase Ω_{L}, which are separated by the interface I. The volume of Ω can be decomposed as $V(t) = V_{\mathrm{S}}(t) + V_{\mathrm{L}}(t)$. The outer surfaces $\partial\Omega_{\mathrm{S}} \backslash I$ and $\partial\Omega_{\mathrm{L}} \backslash I$ are considered as

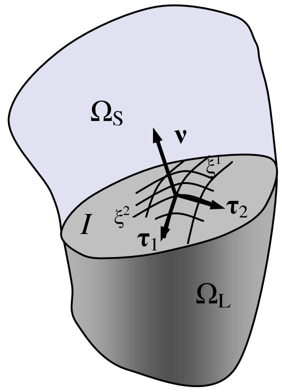

Figure 1: Liquid and solid phases, Ω_L and Ω_S, connected by the interface I.

material surfaces, i.e. they move with the barycentric velocity of the mixture, υ, so that there are no mass fluxes through $\partial\Omega_S\backslash I$ and $\partial\Omega_L\backslash I$.

The interface I is parametrised by any two Gauss parameters (ξ^1, ξ^2), and a point $x \in I$ is determined by the function $x_I^i(t, \xi^1, \xi^2)$, see for example [34] or [1]. We choose the parametrisation so that its speed is given by $w^i = w_\nu \nu^i$. The unit normal of the interface, ν^i, points into the solid phase. The tangent vectors, i.e. the ξ derivatives of $x_I^i(t, \xi^1, \xi^2)$, are denoted by τ_α^i, $\alpha \in \{1, 2\}$. The mean curvature of the interface is denoted by k_M.

We study exclusively processes at constant outer pressure p_0 and constant outer temperature T_0. Furthermore we assume that the temperature T within Ω is constant with $T = T_0$.

We now apply the global balance laws of total energy E and entropy S to this system:

$$\frac{dE}{dt} + p_0 \frac{dV}{dt} = \dot{Q}, \quad \text{and} \quad \frac{dS}{dt} \geq \frac{\dot{Q}}{T_0}. \tag{47}$$

The quantity $\dot{Q}$ denotes the heat power, which may enter, $\dot{Q} > 0$, or leave, $\dot{Q} < 0$, the system, so that a constant temperature T_0 is guaranteed. The equality sign of $(47)_2$ holds in equilibrium, while in non-equilibrium, the variation of the entropy is greater than the ratio of supplied heat and temperature. This statement expresses Clausius version of the second law of thermodynamics, [5].

Elimination of the heat power leads to the thermodynamic inequality

$$\frac{d\mathcal{A}}{dt} \leq 0 \quad \text{with the definition} \quad \mathcal{A} = E - T_0 S + p_0 V. \tag{48}$$

The newly defined quantity $\mathcal{A}$ is called the available free energy or availability. We conclude that for arbitrary thermodynamic processes that run at constant outer pressure, constant temperature and constant total mass, the availability must always decrease and assumes its minimum in thermodynamic equilibrium.

The availability contains the combination $\Psi = E - T_0 S$. The total energy E is the sum of internal energy and kinetic energy. In the following we will neglect the kinetic energy, which implies that Ψ is identical with the Helmholtz free energy. Note however, that $\mathcal{A} = \Psi + p_0 V$ is not the Gibbs free energy G of the system. The available free energy coincides with the Gibbs free energy only if there is an overall constant pressure $p = p_0$ in the interior of the volume V. However, in general we will not meet this case here.

The free energy may be additively decomposed into three contributions which refer to the two phases and the interface. The volume is the sum of the solid and the liquid volume:

$$\Psi = \Psi_{\mathrm{S}} + \Psi_{\mathrm{L}} + \Psi_{\mathrm{I}} \quad \text{and} \quad V = V_{\mathrm{S}} + V_{\mathrm{L}}. \tag{49}$$

The three contributions to the free energy can be represented by volume and surface integrals, viz.

$$\Psi_{\mathrm{S}} = \int\limits_{\Omega_{\mathrm{S}}} \rho_{\mathrm{S}} \psi_{\mathrm{S}} dV, \quad \Psi_{\mathrm{L}} = \int\limits_{\Omega_{\mathrm{L}}} \rho_{\mathrm{L}} \psi_{\mathrm{L}} dV \quad \text{and} \quad \Psi_{\mathrm{I}} = \int\limits_{I} \sigma da. \tag{50}$$

The density of the interfacial free energy, which is also called surface tension, is denoted by σ. We assume that the surface tension depends only on temperature, and thus is a constant here.

The inequality (48) can now be written

$$\frac{d\mathcal{A}}{dt} = \frac{d}{dt}\left(\int\limits_{\Omega_{\mathrm{S}}} \rho_{\mathrm{S}} \psi_{\mathrm{S}} dV + \int\limits_{\Omega_{\mathrm{L}}} \rho_{\mathrm{L}} \psi_{\mathrm{L}} dV + \sigma \int\limits_{I} da + p_0 (V_{\mathrm{S}} + V_{\mathrm{L}}) \right) \leq 0, \tag{51}$$

and is valid for arbitrary thermodynamic processes in Ω, that, however, are subjected to (i) constant temperature in Ω, (ii) constant outer pressure on $\partial\Omega$, (iii) constant mass in Ω, and several further side conditions, which will be introduced and discussed in the next section.

4.2 Side conditions

In this section we consider various side conditions of different origin. They concern the sublattice structure of the solid phase, which restricts possible chemical reactions, and diffusion in the solid phase. Further side conditions result from the conservation of mass during the thermodynamic processes.

1. Equal number of lattice sites of the three sublattices: The three fcc sublattices α, β, γ of solid GaAs have the the same number of lattice sites. This implies two restrictions on the seven mole densities in the solid, viz.

$$n_{\mathrm{Ga}_\alpha} + n_{\mathrm{As}_\alpha} + n_{\mathrm{V}_\alpha} = n_{\mathrm{As}_\beta} + n_{\mathrm{V}_\beta} \quad \text{and} \quad n_{\mathrm{As}_\gamma} + n_{\mathrm{V}_\gamma} = n_{\mathrm{As}_\beta} + n_{\mathrm{V}_\beta}, \tag{52}$$

and there are thus only five independent mole densities in the solid phase.

2. Balance of particle numbers including chemical reactions: Let us start from the mole number balance for the constituent a:

$$\frac{\partial n_a}{\partial t} + \frac{\partial n_a \upsilon_a^k}{\partial x^k} = \tau_a. \tag{53}$$

The quantity υ_a^k is the velocity of constituent a, and τ_a denote its chemical production rate.

An alternative form of (53), which is more suitable for our purposes, results by introducing the diffusion flux $j_a^k = n_a(\upsilon_a^k - \upsilon^k)$ and the material time derivative $()^{\cdot} = \partial/\partial t + \upsilon^k \partial/\partial x^k$:

$$\dot{n}_a - \frac{n_a}{\rho}\dot{\rho} + \frac{\partial j_a^k}{\partial x^k} = \tau_a. \tag{54}$$

In Section 3.2 we have already introduced the barycentric velocity υ of the mixture. Here we note, that υ can be calculated from the velocities υ_a^k of the constituents by

$$\rho \upsilon^k = \sum_a M_a n_a \upsilon_a^k. \tag{55}$$

According to its definition, the weighted diffusion fluxes $J_a^k = M_a j_a^k$ sum up to zero. Multiplication of the balance (54) by the molecular weights M_a yields that the sum of the weighted productions rates $M_a \tau_a$ gives also zero:

$$\sum_a M_a j_a^k = 0 \quad \text{and} \quad \sum_a M_a \tau_a = 0. \tag{56}$$

Chemical reactions concern here the transfer of constituents between the three sublattices. According to the *Freiberg* model, the Ga-Atoms cannot leave the sublattice α. Consequently there are only two independent chemical reactions $r \in \{1, 2\}$, viz.

$$\mathrm{As}_\alpha + \mathrm{V}_\beta = \mathrm{As}_\beta + \mathrm{V}_\alpha \quad \text{and} \quad \mathrm{As}_\gamma + \mathrm{V}_\beta = \mathrm{As}_\beta + \mathrm{V}_\gamma. \tag{57}$$

The stoichiometric coefficients, γ_a^r, can be read off from (57):

$$\begin{aligned} &\gamma_2^1 = 1, \gamma_3^1 = -1, \gamma_6^1 = 1, \gamma_5^1 = -1, \\ &\gamma_4^2 = 1, \gamma_6^2 = 1, \gamma_3^2 = -1, \gamma_7^2 = -1, \gamma_a^r = 0. \end{aligned} \tag{58}$$

Thus we may introduce production rates Γ^r, which measure per unit volume the number of reactions per second, and we write

$$\tau_a = \sum_r \Gamma^r \gamma_a^r. \tag{59}$$

According to (52) we require in Ω_{S}

$$j_{\mathrm{Ga}_\alpha}^k + j_{\mathrm{As}_\alpha}^k + j_{\mathrm{V}_\alpha}^k = j_{\mathrm{As}_\beta}^k + j_{\mathrm{V}_\beta}^k \quad \text{and} \quad j_{\mathrm{As}_\gamma}^k + j_{\mathrm{V}_\gamma}^k = j_{\mathrm{As}_\beta}^k + j_{\mathrm{V}_\beta}^k, \tag{60}$$

which guarantees, that there are only five independent mole balances in the solid phase for five independent mole densities as variables.

3. Conservation of mass flux through the interface: The one-sided mass fluxes through the interface I are defined by

$$\dot{m}_{\pm} = \rho^{\pm}(\upsilon_{\nu}^{\pm} - w_{\nu}), \tag{61}$$

where the " + " and " − " indicate the limiting values of any quantity approaching the interface from the solid, +, and the liquid phase, −, respectively.

The conservation of total mass implies

$$\dot{m}_{+} = \dot{m}_{-} = \dot{m}. \tag{62}$$

4. Conservation of material mole flux across the interface: The one-sided mole fluxes across the interface are defined by

$$\dot{\mathcal{N}}_a = \frac{\dot{m}}{\rho^{+/-}} n_a^{\pm} + (j_a^k)^{\pm}\nu^k, \quad \text{with} \quad \sum_{a \in a_{S/L}} M_a \dot{\mathcal{N}}_a = \dot{m}_{\pm}. \tag{63}$$

The conservation of the mole numbers of Ga and As when they cross the interface implies

$$\dot{\mathcal{N}}_{\mathrm{Ga}_\alpha} = \dot{\mathcal{N}}_{\mathrm{Ga_L}} \quad \text{and} \quad \dot{\mathcal{N}}_{\mathrm{As}_\alpha} + \dot{\mathcal{N}}_{\mathrm{As}_\beta} + \dot{\mathcal{N}}_{\mathrm{As}_\gamma} = \dot{\mathcal{N}}_{\mathrm{As_L}}. \tag{64}$$

The four classes of side conditions will now be used to exploit the inequality (51).

4.3 Intermediate representation of the thermodynamic inequality

In Appendix A we take care for all side conditions and evaluate the time derivative of available free energy, which appear in inequality (51). We obtain a quite explicit form, which is best suited for a further evaluation.

In this section we change from the general system shown in Figure 1 to the single droplet system which is shown in Figure 3, so that there is no boundary $\partial\Omega_{\mathrm{L}} \backslash I$. Furthermore, from now on we ignore diffusion in the liquid droplet.

Proposition:

$$
\begin{aligned}
\frac{d\mathcal{A}}{dt} = &-\int\limits_{\Omega_\mathrm{S}} \frac{\partial \sigma^{ij}}{\partial x^j} \upsilon^i dV + \int\limits_{\Omega_\mathrm{L}} \frac{\partial p}{\partial x^i} \upsilon^i dV + \int\limits_{\partial\Omega_\mathrm{S}\setminus I} (\sigma^{ij} + p_0 \delta^{ij}) \upsilon^i da^j \\
&- \int\limits_I (\sigma_\mathrm{S}^{ij} \nu^i \nu^j + p_\mathrm{L} + 2\sigma k_\mathrm{M}) w_\nu da - \int\limits_I \sigma^{ij} \tau_\alpha^i \nu^j \upsilon_\tau^\alpha da \\
&+ \int\limits_{\Omega_\mathrm{S}} \big(\Gamma^1(\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{As}_\beta} + \mu_{\mathrm{V}_\beta}) + \Gamma^2(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As}_\beta} + \mu_{\mathrm{V}_\beta})\big)\, dV \\
&+ \int\limits_{\Omega_\mathrm{S}} \left(\frac{\partial}{\partial x^j} \left(\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \frac{M_\mathrm{As}}{M_\mathrm{Ga}} (\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha}) \right) \right) j^j_{\mathrm{As}_\alpha} dV \\
&+ \int\limits_{\Omega_\mathrm{S}} \left(\frac{\partial}{\partial x^j} \left(\mu_{\mathrm{As}_\beta} - \mu_{\mathrm{V}_\beta} - \frac{M_\mathrm{As}}{M_\mathrm{Ga}} (\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha}) \right) \right) j^j_{\mathrm{As}_\beta} dV \\
&+ \int\limits_{\Omega_\mathrm{S}} \left(\frac{\partial}{\partial x^j} \left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \frac{M_\mathrm{As}}{M_\mathrm{Ga}} (\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha}) \right) \right) j^j_{\mathrm{As}_\gamma} dV \\
&+ \int\limits_{\Omega_\mathrm{S}} \left(\frac{\partial}{\partial x^j} (\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma}) \right) (j^j_{\mathrm{As}_\gamma} + j^j_{\mathrm{V}_\gamma}) dV - \int\limits_{\partial\Omega_\mathrm{S}\setminus I} \sum_{a \in a_\mathrm{S}} \mu_a j_a^j da^j \\
&+ \int\limits_I \left(\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{Ga}_\mathrm{L}} - \frac{M_\mathrm{Ga}}{\rho_+} \sigma_+^{\langle ij \rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{Ga}_\alpha} da \\
&+ \int\limits_I \left(\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{As}_\mathrm{L}} - \frac{M_\mathrm{As}}{\rho_+} \sigma_+^{\langle ij \rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{As}_\alpha} da \\
&+ \int\limits_I \left(\mu_{\mathrm{As}_\beta} - \mu_{\mathrm{V}_\beta} - \mu_{\mathrm{As}_\mathrm{L}} - \frac{M_\mathrm{As}}{\rho_+} \sigma_+^{\langle ij \rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{As}_\beta} da \\
&+ \int\limits_I \left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As}_\mathrm{L}} - \frac{M_\mathrm{As}}{\rho_+} \sigma_+^{\langle ij \rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{As}_\gamma} da \\
&+ \int\limits_I (\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma}) (\dot{\mathcal{N}}_{\mathrm{As}_\gamma} + \dot{\mathcal{N}}_{\mathrm{V}_\gamma}) da \leq 0. \qquad (65)
\end{aligned}
$$

This representation of the thermodynamic inequality will be derived in Appendix A.

Inspection of the inequality (65) reveals four mechanisms that drive the system to thermodynamic equilibrium. The first two lines represent mechanical processes. The third line describes the two chemical reactions between the constituents of the three sublattices. The lines four to eight represent diffusion within the sublattices, and the remaining lines nine to thirteen represent mole fluxes across the interface, which drive the system to phase equilibrium.

There are thus four different contributions to $d\mathcal{A}/dt$. We write

$$\frac{d\mathcal{A}}{dt} = \dot{\mathcal{A}}^{\mathrm{mech}} + \dot{\mathcal{A}}^{\mathrm{chem}} + \dot{\mathcal{A}}^{\mathrm{diff}} + \dot{\mathcal{A}}^{\mathrm{I}} \tag{66}$$

in order to indicate the different processes. The identification of the newly introduced quantities may be easily read off from (65).

4.4 Necessary conditions for equilibrium, Part 1: Mechanical equilibrium

The integrands that contribute to $\dot{\mathcal{A}}^{\mathrm{mech}}$ are linear in the baricentric and in the interface velocity. Galileian invariance of the inequality requires that the corresponding coefficients of the velocities must vanish in order to avoid the possibility to violate the inequality. This leads to the conditions

$$\begin{aligned}
&\frac{\partial \sigma_{\mathrm{S}}^{ij}}{\partial x^j} = 0 \quad \text{in } \Omega_{\mathrm{S}} \quad \text{and} \quad \frac{\partial p_{\mathrm{L}}}{\partial x^i} = 0 \quad \text{in } \Omega_{\mathrm{L}},\\
&\sigma_{\mathrm{S}}^{ij}\nu^j + p_0\nu^i = 0 \quad \text{on } \partial\Omega_{\mathrm{S}}\backslash I,\\
&\sigma_{\mathrm{S}}^{ij}\nu^i\nu^j + p_{\mathrm{L}} + 2\sigma k_{\mathrm{M}} = 0 \quad \text{and} \quad \sigma_{\mathrm{S}}^{ij}\tau_\alpha^i\nu^j = 0 \quad \text{on } I.
\end{aligned} \tag{67}$$

We identify these conditions as the well known necessary conditions for mechanical equilibrium. Insertion of the constitutive laws for σ_{S}^{ij} and p_{L}, will lead to an elliptic boundary value problem, that will be solved explicitly in Section 6, where we consider the problem of a spherical liquid droplet within a solid matrix.

Note that the reasoning that has lead to the conditions (67) were also valid in non-equilibrium, so that the same conditions arise in non-equilibrium. At first glance, this is a surprising result. However, it is due to the fact that we had already ignored the kinetic energy of the mechanical motion, which restricts us to the case of quasi-static mechanical equilibrium. In other words: The neglect of the kinetic energy is equivalent to the assumption that mechanical equilibrium is established with zero relaxation time.

4.5 General structure of the thermodynamic inequality and its exploitation

We proceed to discuss the remaining three contributions to the main inequality (65), viz.

$$\frac{d\mathcal{A}}{dt} = \dot{\mathcal{A}}^{\mathrm{chem}} + \dot{\mathcal{A}}^{\mathrm{diff}} + \dot{\mathcal{A}}^{\mathrm{I}}. \tag{68}$$

At first we restrict ourselves to boundary conditions at $\partial\Omega_{\mathrm{S}}\backslash I$ so that the surface integral vanishes, i.e.

$$\int\limits_{\partial\Omega_{\mathrm{S}}\backslash I}\sum_{a\in a_{\mathrm{S}}}\mu_a j_a^j da^j = 0. \tag{69}$$

In other words we consider here the case that the solid is in contact with an inert gas so that Neumann conditions result. A different consideration is necessary if the solid is in contact with the gaseous Phase of GaAs. We consider this case in [7] and [8].

An inspection of the explicit form of the right hand side of (68) reveals that it consists of volume and surface integrals, respectively, with sums of binary products as integrands. The factors of these products are called fluxes and driving forces. The fluxes are $F_\alpha^{\mathrm{C}} = (\Gamma^1, \Gamma^2)$, $\alpha \in \{1, 2\}$, $F_\alpha^{\mathrm{D}} = (j^k_{\mathrm{As}_\alpha}, j^k_{\mathrm{As}_\beta}, j^k_{\mathrm{As}_\gamma}, j^k_{\mathrm{As}_\gamma} + j^k_{\mathrm{V}_\gamma})$, $\alpha \in \{1, 2, ..., 12\}$, and $F_\alpha^{\mathrm{I}} = (\dot{\mathcal{N}}_{\mathrm{Ga}_\alpha}, \dot{\mathcal{N}}_{\mathrm{As}_\alpha}, \dot{\mathcal{N}}_{\mathrm{As}_\beta}, \dot{\mathcal{N}}_{\mathrm{As}_\gamma}, \dot{\mathcal{N}}_{\mathrm{As}_\gamma} + \dot{\mathcal{N}}_{\mathrm{V}_\gamma})$, $\alpha \in \{1, 2, ..., 5\}$, whereas the corresponding factors are the driving forces D_α^{C}, D_α^{D} and D_α^{I}.

The generic form of the three contributions to (68) thus reads

$$\dot{\mathcal{A}}^{\mathrm{chem}} = \int\limits_{\Omega_{\mathrm{S}}}\sum_{\alpha=1}^{2} F_\alpha^{\mathrm{C}} D_\alpha^{\mathrm{C}} \qquad \dot{\mathcal{A}}^{\mathrm{diff}} = \int\limits_{\Omega_{\mathrm{S}}}\sum_{\alpha=1}^{12} F_\alpha^{\mathrm{D}} D_\alpha^{\mathrm{D}} \qquad \dot{\mathcal{A}}^{\mathrm{I}} = \int\limits_{\Omega_{\mathrm{S}}}\sum_{\alpha=1}^{5} F_\alpha^{\mathrm{D}} D_\alpha^{\mathrm{D}}. \tag{70}$$

The fluxes are the independent variations of an equilibrium state, where $\dot{\mathcal{A}}_{|\mathrm{eq}} = 0$. We conclude that the necessary conditions for equilibrium are given by

$$D^{\mathrm{C}}_{\alpha|\mathrm{eq}} = 0 \qquad D^{\mathrm{D}}_{\alpha|\mathrm{eq}} = 0 \qquad D^{\mathrm{I}}_{\alpha|\mathrm{eq}} = 0. \tag{71}$$

In non-equilibrium $\dot{\mathcal{A}}$ is negative, so that its equilibrium value, which is zero, establishes a minimum of $\mathcal{A}$. Let us now assume that the fluxes are given as functions of the driving forces, i.e.

$$F_\alpha^a = \hat{F}_\alpha^a(D_\beta^b, y) \quad \text{for} \quad a, b \in \{\mathrm{C,\ D,\ I}\}, \quad \alpha, \beta \in \{1, 2, ..., 15\}, \tag{72}$$

where y denote quantities which are not among the driving forces. It follows that

$$D^a_{\alpha|\mathrm{eq}} = 0 \Leftrightarrow F^a_{\alpha|\mathrm{eq}} = 0. \tag{73}$$

See Gurtin and Vorhees [16] for a similar consideration.

The simplest ansatz that satisfies (73) is the assumption that driving forces and fluxes are proportional to each other. The proportionality factors are called mobilities. In particular, if we ignore cross effects, the ansatz simply reads

$$F_\alpha^{\mathrm{C}} = -M_\alpha^{\mathrm{C}} D_\alpha^{\mathrm{C}} \qquad F_\alpha^{\mathrm{D}} = -M_\alpha^{\mathrm{D}} D_\alpha^{\mathrm{D}} \qquad F_\alpha^{\mathrm{I}} = -M_\alpha^{\mathrm{I}} D_\alpha^{\mathrm{I}}, \tag{74}$$

with positive mobilities M_α^{C}, M_α^{D}, M_α^{I}.

4.6 Assumptions on relaxation times

The mobilities are inversely proportional to the relaxation times of the three different processes, which drive the system to chemical, diffusional and phase equilibria. We denote these by τ^{C},τ^{D} and τ^{I}, respectively. Mechanical processes play a special role in our treatment, because it is by far the fastest process, so that we implicitly already had set the mechanical relaxation time equal to zero. We proceed to discuss the the relaxation times of the other processes.

Chemical reactions concern here the transfer of atoms between the three sublattices, and due to the high temperature range, that we are considering, we assume that these processes run at the same time scale as mechanical processes, i.e. we set $\tau^{\mathrm{C}} = 0$.

Within the sublattices there is diffusion of Ga_α, the three arsenic constituents As_α, As_β, As_γ, and of the vacancies V_α, V_β, V_γ. There are thus seven diffusional relaxation times $\tau^{\mathrm{D}} \in \{\tau_{\mathrm{Ga}_\alpha}, \tau_{\mathrm{As}_\alpha}, \tau_{\mathrm{As}_\beta}, \tau_{\mathrm{As}_\gamma}, \tau_{\mathrm{V}_\alpha}, \tau_{\mathrm{V}_\beta}, \tau_{\mathrm{V}_\gamma}\}$. We assume that diffusion of the material constituents runs at a much slower time scale than mechanical and chemical processes, whereas diffusional equilibria of the vacancies are reached almost as fast as mechanical and chemical equilibria are reached. Accordingly, the mobilities of the material constituents have finite values. Regarding the vacancies we consider only the limiting case of infinite mobilities.

These assumptions rely on careful discussions and interpretations of existing experiments [11]. The situation of the time scale of interface motion, which regards here the evolution of liquid droplets, is different. We do not know, whether interface motion is diffusion controlled, i.e. $\tau^{\mathrm{I}} = 0$, or interface controlled, i.e. $\tau^{\mathrm{I}} \neq 0$. For that reason we will consider both cases separately, so that a later comparison of the corresponding results with experiments might decide.

4.7 Necessary conditions for equilibrium, Part 2: Chemical equilibrium

The contribution of chemical reactions to the inequality (65) reads

$$\dot{\mathcal{A}}^{\mathrm{diff}} = \int\limits_{\Omega_{\mathrm{S}}} \Big(\Gamma^1(\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{As}_\beta} + \mu_{\mathrm{V}_\beta}) + \Gamma^2(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As}_\beta} + \mu_{\mathrm{V}_\beta})\Big)\, dV. \quad (75)$$

In equilibrium we have $\dot{\mathcal{A}}^{\mathrm{diff}} = 0$ and

$$\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{As}_\beta} + \mu_{\mathrm{V}_\beta} = 0, \quad \mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{As}_\beta} + \mu_{\mathrm{V}_\beta} = 0. \quad (76)$$

The conditions (76) are necessary conditions for equilibrium and give two algebraic equations for the determination of the equilibrium mole densities of the constituents after the mechanical problem has been solved according to the mechanical boundary value problem from subsection 4.4.

4.8 Necessary conditions for equilibrium, Part 3: Diffusional equilibrium

The contribution of diffusion processes to the inequality (65) reads

$$
\begin{aligned}
\dot{\mathcal{A}}^{\text{chem}} = & \int\limits_{\Omega_{\text{S}}} \left(\frac{\partial}{\partial x^j} \left(\mu_{\text{As}_\alpha} - \mu_{\text{V}_\alpha} - \frac{M_{\text{As}}}{M_{\text{Ga}}} (\mu_{\text{Ga}_\alpha} - \mu_{\text{V}_\alpha}) \right) \right) j^j_{\text{As}_\alpha} dV \\
& + \int\limits_{\Omega_{\text{S}}} \left(\frac{\partial}{\partial x^j} (\mu_{\text{As}_\beta} - \mu_{\text{V}_\beta} - \frac{M_{\text{As}}}{M_{\text{Ga}}} (\mu_{\text{Ga}_\alpha} - \mu_{\text{V}_\alpha})) \right) j^j_{\text{As}_\beta} dV \\
& + \int\limits_{\Omega_{\text{S}}} \left(\frac{\partial}{\partial x^j} \left(\mu_{\text{As}_\gamma} - \mu_{\text{V}_\gamma} - \frac{M_{\text{As}}}{M_{\text{Ga}}} (\mu_{\text{Ga}_\alpha} - \mu_{\text{V}_\alpha}) \right) \right) j^j_{\text{As}_\gamma} dV \\
& + \int\limits_{\Omega_{\text{S}}} \left(\frac{\partial}{\partial x^j} (\mu_{\text{V}_\alpha} + \mu_{\text{V}_\beta} + \mu_{\text{V}_\gamma}) \right) (j^j_{\text{As}_\gamma} + j^j_{\text{V}_\gamma}) dV.
\end{aligned}
\tag{77}
$$

In equilibrium we have $\dot{\mathcal{A}}^{\text{chem}} = 0$ and

$$
\begin{aligned}
& \mu_{\text{As}_\alpha} - \mu_{\text{V}_\alpha} - \frac{M_{\text{As}}}{M_{\text{Ga}}} (\mu_{\text{Ga}_\alpha} - \mu_{\text{V}_\alpha}) = c_{\text{As}_\alpha}, \\
& \mu_{\text{As}_\beta} - \mu_{\text{V}_\beta} - \frac{M_{\text{As}}}{M_{\text{Ga}}} (\mu_{\text{Ga}_\alpha} - \mu_{\text{V}_\alpha}) = c_{\text{As}_\beta}, \\
& \mu_{\text{As}_\gamma} - \mu_{\text{V}_\gamma} - \frac{M_{\text{As}}}{M_{\text{Ga}}} (\mu_{\text{Ga}_\alpha} - \mu_{\text{V}_\alpha}) = c_{\text{As}_\gamma}, \\
& \mu_{\text{V}_\alpha} + \mu_{\text{V}_\beta} + \mu_{\text{V}_\gamma} = c_{\text{V}}.
\end{aligned}
\tag{78}
$$

The quantities c_{As_α}, c_{As_β}, c_{As_γ} and c_{V} are constants which can be calculated from the boundary conditions.

4.9 Necessary conditions for equilibrium, Part 4: Interfacial equilibrium

The contribution of interface motion to the inequality (65) reads

$$\begin{aligned}
\dot{\mathcal{A}}^{\mathrm{I}} = & \int_I \left(\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{Ga_L}} - \frac{M_{\mathrm{Ga}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right)\dot{\mathcal{N}}_{\mathrm{Ga}_\alpha} da \\
& + \int_I \left(\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right)\dot{\mathcal{N}}_{\mathrm{As}_\alpha} da \\
& + \int_I \left(\mu_{\mathrm{As}_\beta} - \mu_{\mathrm{V}_\beta} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right)\dot{\mathcal{N}}_{\mathrm{As}_\beta} da \\
& + \int_I \left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right)\dot{\mathcal{N}}_{\mathrm{As}_\gamma} da \\
& + \int_I (\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma})(\dot{\mathcal{N}}_{\mathrm{As}_\gamma} + \dot{\mathcal{N}}_{\mathrm{V}_\gamma}) da.
\end{aligned} \tag{79}$$

In equilibrium we have $\dot{\mathcal{A}}^{\mathrm{I}} = 0$ and

$$\begin{aligned}
& \mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{Ga_L}} - \frac{M_{\mathrm{Ga}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j = 0, \\
& \mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j = 0, \\
& \mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma} = 0.
\end{aligned} \tag{80}$$

There follow only three independent conditions from (79) because the conditions for chemical equilibrium (76) imply $\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} = \mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma}$ and $\mu_{\mathrm{As}_\beta} - \mu_{\mathrm{V}_\beta} = \mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma}$. The conditions (80) are necessary conditions for equilibrium and give three further algebraic equations for the determination of the equilibrium values of the mole densities after the mechanical problem has been solved according to the mechanical boundary value problem from subsection 4.4.

4.10 The diffusion law

In this section we establish the diffusion law in the solid phase for non-equilibrium processes. In principle, according to subsection 4.8 we could read off four diffusion laws from (77) for the fluxes $F_\alpha^{\mathrm{D}} = (j^k_{\mathrm{As}_\alpha}, j^k_{\mathrm{As}_\beta}, j^k_{\mathrm{As}_\gamma}, j^k_{\mathrm{As}_\gamma} + j^k_{\mathrm{V}_\gamma})$. However, due to our assumption that equilibrium of chemical reactions and diffusion of vacancies is immediately established, there is only one independent diffusion law, which we formulate for the total arsenic flux:

$$j^k = j^k_{\mathrm{As}_\alpha} + j^k_{\mathrm{As}_\beta} + j^k_{\mathrm{As}_\gamma} = -\frac{B}{RT}\frac{\partial}{\partial x^k}\left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \frac{M_{\mathrm{As}}}{M_{\mathrm{Ga}}}(\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha})\right). \tag{81}$$

The bulk mobility $B \geq 0$ can be related to the diffusion constant, which may be determined from measurements of diffusion of interstitial As_γ, see [8] for details.

Note that we have started with seven unknown mole densities in the solid phase. Due to the various side conditions from Section 4.2 and to the assumptions regarding the relaxation times, six mole densities can be related to a single remaining unknown mole density, say n_{As_γ}, by algebraic equations. Thus we have to solve only the diffusional initial and boundary value problem for the interstitial As_γ, see [8] for details.

There are two regimes with different laws that determine the motion of the solid/liquid interface.

The interface motion is called diffusion controlled, if the interface is in local equilibrium, so that the three conditions (80) hold. Having solved the diffusional initial and boundary value problem we may use the conservation law $(64)_2$ for the determination of the normal speed w_ν of the interface. For high numerical accuracy it is necessary to take into account the barycentric velocity, which appears in $(64)_2$. Its calculation relies on the time dependent density of total mass, that is due to the quasistatic evolution of the mechanical deformations according to (25). We refer to [8] for the details of a subtle discussion of this point. However, for completeness we give already here the result, which reads

$$\left(\frac{\rho_{\mathrm{L}}}{\rho_{\mathrm{S}}} - \frac{n_{\mathrm{As_L}}}{n_{\mathrm{As}_\alpha} + n_{\mathrm{As}_\beta} + n_{\mathrm{As}_\gamma}}\right) w_\nu + \left(\frac{\dot{\rho}_{\mathrm{L}}}{\rho_{\mathrm{S}}} - \frac{\dot{n}_{\mathrm{AsL}}}{n_{\mathrm{As}_\alpha} + n_{\mathrm{As}_\beta} + n_{\mathrm{As}_\gamma}}\right) \frac{V_{\mathrm{L}}}{O_{\mathrm{L}}} = \frac{j^k_{\mathrm{As}} \nu^k}{n_{\mathrm{As}_\alpha} + n_{\mathrm{As}_\beta} + n_{\mathrm{As}_\gamma}}. \tag{82}$$

Herein V_L and O_L denote the Volume, respectively, the surface of a homogeneous liquid droplet in a solid matrix.

The interface motion is called interface controlled if its normal speed w_ν is determined by the driving forces. According to $(74)_3$, which expresses the assumption of linear relations between fluxes and driving forces without cross effects, we have at first

$$\begin{aligned}
\dot{\mathcal{N}}_{\mathrm{Ga}_\alpha} &= -\frac{B^{\mathrm{I}}_{\mathrm{Ga}}}{RT}\left(\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{Ga_L}} - \frac{M_{\mathrm{Ga}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right), \\
\dot{\mathcal{N}}_{\mathrm{As_S}} &= -\frac{B^{\mathrm{I}}_{\mathrm{As}}}{RT}\left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right), \\
\dot{\mathcal{N}}_{\mathrm{As}_\gamma} + \dot{\mathcal{N}}_{\mathrm{V}_\gamma} &= -\frac{B^{\mathrm{I}}_{\mathrm{V}}}{RT}\left(\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma}\right).
\end{aligned} \tag{83}$$

The positive quantities $B^{\mathrm{I}}_{\mathrm{Ga}}, B^{\mathrm{I}}_{\mathrm{As}}$ and $B^{\mathrm{I}}_{\mathrm{V}}$ are the interface mobilities.

Likewise to our assumption in the bulk, we consider at the interface the limiting case of $B^{\mathrm{I}}_{\mathrm{V}} \to \infty$, so that $\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma} = 0$ holds at any time at the interface, and the equation $(83)_3$ cannot be used anymore to calculate the flux $\dot{\mathcal{N}}_{\mathrm{As}_\gamma} + \dot{\mathcal{N}}_{\mathrm{V}_\gamma}$.

By means of similar arguments that has lead to (82) we conclude from (63) $\dot{\mathcal{N}}_{\mathrm{Ga_L}} = -w_\nu n_{\mathrm{Ga_L}} - \dot{n}_{\mathrm{GaL}}\frac{V_\mathrm{L}}{O_\mathrm{L}}$ and $\dot{\mathcal{N}}_{\mathrm{As_L}} = -w_\nu n_{\mathrm{As_L}} - \dot{n}_{\mathrm{AsL}}\frac{V_\mathrm{L}}{O_\mathrm{L}}$. With (64) and $(83)_{1,2}$ we thus obtain the equation

$$\begin{aligned}\frac{B^{\mathrm{I}}_{\mathrm{Ga}}}{n_{\mathrm{Ga_L}}RT}&\left(\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{Ga_L}} - \frac{M_{\mathrm{Ga}}}{\rho_\mathrm{S}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right) + \frac{\dot{n}_{\mathrm{GaL}}}{n_{\mathrm{GaL}}}\frac{V_\mathrm{L}}{O_\mathrm{L}} \\ &= \frac{B^{I}_{\mathrm{As}}}{n_{\mathrm{As_L}}RT}\left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_\mathrm{S}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right) + \frac{\dot{n}_{\mathrm{AsL}}}{n_{\mathrm{AsL}}}\frac{V_\mathrm{L}}{O_\mathrm{L}}, \qquad (84)\end{aligned}$$

which is supplemented by the single growth law

$$w_\nu = \frac{B^{\mathrm{I}}_{\mathrm{As}}}{n_{\mathrm{As_L}}RT}\left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_\mathrm{S}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right) + \frac{\dot{n}_{\mathrm{AsL}}}{n_{\mathrm{AsL}}}\frac{V_\mathrm{L}}{O_\mathrm{L}}. \qquad (85)$$

We refer again to [8] for the details.

It remains the determination of the interface mobilities $B^{\mathrm{I}}_{\mathrm{As}}$, $B^{\mathrm{I}}_{\mathrm{Ga}}$. In principle this can be done by experiments. However, there exists a case, where a kinetic reasoning leads to an explicit theoretical expression for the interface mobilities. If a liquid droplet is in contact with its vapour, the growth of the droplet due to the incoming gas particles with mole density n and molecular weight M is given by the number of hits of the droplet per time unit and surface unit. It follows in this case $B = n\sqrt{RT/(2\pi M)}$. This result can be transferred as a guess to the solid/liquid interface for the case at hand. We set

$$B^{\mathrm{I}}_{\mathrm{As}} = n_{\mathrm{As_L}}\sqrt{\frac{RT}{2\pi\mathcal{M}(X_\mathrm{L})}} \quad \text{and} \quad B^{\mathrm{I}}_{\mathrm{Ga}} = n_{\mathrm{Ga_L}}\sqrt{\frac{RT}{2\pi\mathcal{M}(X_\mathrm{L})}}. \qquad (86)$$

5 Explicit constitutive model for GaAs

In this section we will formulate explicit constitutive laws for solid and liquid GaAs. These laws regard the dependence of free energy densities, chemical potentials and stresses to the variables and on temperature dependent quantities that refer to special reference states, which will be introduced next.

5.1 Reference systems and reference configurations

We consider at first the situation which is depicted in Figure 2: A solid phase is in contact with a liquid phase and a gas. The order of the phases ought to indicate that the solid is under hydrostatic pressure. Moreover there are no curved interfaces, so that no capillary forces appear and the three phases live under the same common pressure, which is equal to the outer pressure p_0.

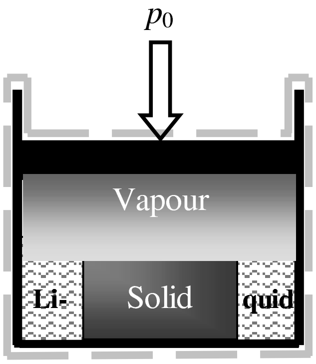

Figure 2: Standard system: All phases are under hydrostatic stress, which is equal to the outer pressure p_0.

If the gas is an inert gas, that does not take part during phase changes between the liquid and solid phases, we call this system the *standard system*.

If the gas consists of Ga and As constituents, which may cross the interfaces, a triple phase equilibrium under the vapour pressure $p_0 = \bar{p}(T)$ may be established. In this case we call the system of Figure 2 the *reference standard system*. The detailed introduction and the exploitation of the reference standard system is found in [7].

In this study the free energy densities and the chemical potentials will be given with respect to the reference standard system. On the other hand the stress/strain relations will be formulated with respect to a reference configuration, which is defined as follows: A liquid/solid body of GaAs is free of strain, i.e.

$$C^{ij} = C_{\mathrm{R}}^{ij} = \delta^{ij}, \; n_{\mathrm{G}} = n_{\mathrm{G}}^{\mathrm{R}} = \bar{n}_{\mathrm{G}} \quad \text{in the solid, and} \quad \varrho_{\mathrm{L}} = \varrho_{\mathrm{L}}^{\mathrm{R}} = \bar{\varrho}_{\mathrm{L}} \quad \text{in the liquid,} \tag{87}$$

if the body (i) is under uniform pressure $\bar{p}(T)$ and (ii) has the composition $\bar{Y}_{b_S}$ in the solid and $\bar{X}_L$ in the liquid. The bar indicates that the corresponding quantity is measured in the *reference standard system*.

According to the representations (11) and (18) for the solid and liquid mass densities we define

$$\begin{aligned} \bar{\rho}_{\mathrm{S}} &= 2\bar{n}_{\mathrm{G}}\mathfrak{M}(\bar{Y}_{\mathrm{Ga}}, \bar{Y}_{\mathrm{As}}) = \check{\rho}_{\mathrm{S}}(\bar{Y}_{\mathrm{Ga}}, \bar{Y}_{\mathrm{As}}, \bar{n}_{\mathrm{G}}), \qquad && \bar{\rho}_{\mathrm{L}} = \bar{n}_{\mathrm{L}}\mathcal{M}(\bar{X}_{\mathrm{L}}) = \check{\rho}_{\mathrm{L}}(\bar{X}_{\mathrm{L}}, \bar{n}_{\mathrm{L}}), \\ \rho_{\mathrm{S}}^{*} &= 2n_{\mathrm{G}}^{\mathrm{R}}\mathfrak{M}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}) = \check{\rho}_{\mathrm{S}}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}, \bar{n}_{\mathrm{G}}) \quad \text{and} && \rho_{\mathrm{L}}^{*} = \bar{n}_{\mathrm{L}}\mathcal{M}(X_{\mathrm{L}}) = \check{\rho}_{\mathrm{L}}(X_{\mathrm{L}}, \bar{n}_{\mathrm{L}}). \end{aligned} \tag{88}$$

Note that ρ_S^* gives the mass density of a solid, whose lattice coincides with the lattice of the reference configuration, but the distribution of particles over the lattice sides is different from the distribution in the reference configuration. This state of the solid is needed for the description of elastic deformations, which are reversible deformations, and these are not accompanied by a redistribution of atoms over the lattice sites.

The changes of mass densities due to elastic deformations are thus given by

$$
\begin{aligned}
J &= \frac{\bar{\rho}_{\mathrm{S}}}{\rho_{\mathrm{S}}} = \tilde{J}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}, n_{\mathrm{G}}), \\
J^* &= \tilde{J}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}, n_{\mathrm{G}}^{\mathrm{R}}) = \frac{\mathfrak{M}(\bar{Y}_{\mathrm{Ga}}, \bar{Y}_{\mathrm{As}})}{\mathfrak{M}(Y_{\mathrm{Ga}}, Y_{\mathrm{As}})} = \tilde{J}^*(Y_{\mathrm{Ga}}, Y_{\mathrm{As}}), \\
J_{\mathrm{L}} &= \frac{\bar{\rho}_{\mathrm{L}}}{\rho_{\mathrm{L}}} = \tilde{J}_{\mathrm{L}}(X_{\mathrm{L}}, n_{\mathrm{L}}) \quad \text{and } J_{\mathrm{L}}^* = \tilde{J}_{\mathrm{L}}(X_{\mathrm{L}}, \bar{n}_{\mathrm{L}}) = \frac{\mathcal{M}(\bar{X}_{\mathrm{L}})}{\mathcal{M}(X_{\mathrm{L}})} = \tilde{J}_{\mathrm{L}}^*(X_{\mathrm{L}}). \qquad (89)
\end{aligned}
$$

The mole densities in the reference configuration may be read off from the corresponding data tables that can be found in the literature, for details see [7].

5.2 Decomposition of the free energy and chemical potentials into chemical and mechanical parts

We start from the general constitutive model as it was described in subsection 3.5 of this study. At first we show that the introduction of a strain free reference state implies a decomposition of the specific free energy and the chemical potentials into chemical and mechanical parts:

$$\rho\psi = \rho\psi^{\mathrm{chem}} + \rho\psi^{\mathrm{mech}}, \quad \mu_a = \mu_a^{\mathrm{chem}} + \mu_a^{\mathrm{mech}}. \qquad (90)$$

The proof of validity of this decomposition starts from the equations (37), (36), (46) and (44):

$$\psi_{\mathrm{L}} = \tilde{\psi}_{\mathrm{L}}(T, X_{\mathrm{L}}, J_{\mathrm{L}}) \quad \text{and} \quad \psi_{\mathrm{S}} = \tilde{\psi}_{\mathrm{S}}(T, Y_{b_{\mathrm{S}}}, C) \qquad (91)$$

Correspondingly we write the chemical potentials as

$$\mu_{a_{\mathrm{L}}} = \tilde{\mu}_{a_{\mathrm{L}}}(T, X_{\mathrm{L}}, J_{\mathrm{L}}) \quad \text{and} \quad \mu_{a_{\mathrm{S}}} = \tilde{\mu}_{a_{\mathrm{S}}}(T, Y_{b_{\mathrm{S}}}, C) \qquad (92)$$

We define now the chemical parts of these quantities by setting $n_{\mathrm{L}} = \bar{n}_{\mathrm{L}}$, $n_{\mathrm{G}} = \bar{n}_{\mathrm{G}}$ and $c^{ij} = \delta^{ij}$, which characterizes a state of the body with $\sigma^{ij} = -\bar{p}(T)\delta_{ij}$ and $p_L = \bar{p}(T)$:

$$\psi_{\mathrm{L}}^{\mathrm{chem}}(T, X_{\mathrm{L}}) = \check{\psi}_{\mathrm{L}}(T, X_{\mathrm{L}}, \bar{n}_{\mathrm{L}}) \quad \text{and} \quad \psi_{\mathrm{S}}^{\mathrm{chem}}(T, Y_{b_{\mathrm{S}}}) = \check{\psi}_{\mathrm{S}}(T, Y_{b_{\mathrm{S}}}, \bar{n}_{\mathrm{G}}, I), \qquad (93)$$

$$\mu_{a_{\mathrm{L}}}^{\mathrm{chem}}(T, X_{\mathrm{L}}) = \check{\mu}_{a_{\mathrm{L}}}(T, X_{\mathrm{L}}, \bar{n}_{\mathrm{L}}) \quad \text{and} \quad \mu_{a_{\mathrm{S}}}^{\mathrm{chem}}(T, Y_{b_{\mathrm{S}}}) = \check{\mu}_{a_{\mathrm{S}}}(T, Y_{b_{\mathrm{S}}}, \bar{n}_{\mathrm{G}}, I). \qquad (94)$$

Consequently, the mechanical parts of the specific free energies result from

$$
\begin{aligned}
\psi_{\mathrm{L}}^{\mathrm{mech}}(T, Y_{b_{\mathrm{S}}}, J_{\mathrm{L}}) &= \check{\psi}_{\mathrm{L}}(T, X_{\mathrm{L}}, n_{\mathrm{L}}) - \psi_{\mathrm{L}}^{\mathrm{chem}}(T, X_{\mathrm{L}}) \quad \text{and} \\
\psi_{\mathrm{S}}^{\mathrm{mech}}(T, Y_{b_{\mathrm{S}}}, C) &= \check{\psi}_{\mathrm{S}}(T, Y_{b_{\mathrm{S}}}, n_{\mathrm{G}}, \boldsymbol{c}) - \psi_{\mathrm{S}}^{\mathrm{chem}}(T, Y_{b_{\mathrm{S}}}). \qquad (95)
\end{aligned}
$$

In analogy we define

$$
\begin{aligned}
\mu_{a_{\mathrm{L}}}^{\mathrm{mech}}(T, X_{\mathrm{L}}, J_{\mathrm{L}}) &= \tilde{\mu}_{a_{\mathrm{L}}}(T, X_{\mathrm{L}}, J_{\mathrm{L}}) - \mu_{a_{\mathrm{L}}}^{\mathrm{chem}}(T, X_{\mathrm{L}}) \quad \text{and} \\
\mu_{a_{\mathrm{S}}}^{\mathrm{mech}}(T, Y_{b_{\mathrm{S}}}, C) &= \tilde{\mu}_{a_{\mathrm{S}}}(T, Y_{b_{\mathrm{S}}}, C) - \mu_{a_{\mathrm{S}}}^{\mathrm{chem}}(T, Y_{b_{\mathrm{S}}}). \qquad (96)
\end{aligned}
$$

Recall that elastic deformations result from deviations from the state $C^{ij} = (J^*)^{\frac{2}{3}}\delta^{ij}$ and $J_{\mathrm{L}} = J_{\mathrm{L}}^*$, which thus may be called a reference state for elastic deformations. This treatment guarantees that the chemical composition is not related to elastic deformations.

5.3 Constitutive model, Part 2: The chemical parts of the chemical potentials for the solid and liquid phases of GaAs

The modelling of the solid phase relies on the sublattice model, which is introduced and described by Oates, Wenzl, Hurle et al [25, 37, 36, 17, 18]. Furthermore we assume that there are exclusively entropic contributions to the chemical potentials. Due to the sublattice structure, these are not given in terms of the mole fractions X_a, see (14), but by lattice occupancies Y_a which are defined by (6).

Recall that the three sublattices have equal number of lattice sites, so that the Y_a give the mole densities per sublattice site.

The reason to consider only entropic contributions, is due to the fact that currently no data are available for the material constants of the energetic contributions. In this case we write

$$\mu_a^{\text{chem}} = \bar{\mu}_a(T) + RT \ln\left(\frac{Y_a}{\bar{Y}_a(T)}\right), \quad a \in a_{\text{S}}. \tag{97}$$

The quantities $\bar{\mu}_a(T)$ refer to the equilibrium of the triple phase system of Figure 2, where surface tension is ignored and exclusively hydrostatic stresses may appear. We have called this system the reference standard system, and we have chosen the thermodynamic equilibrium states of this system as the reference states of the chemical parts. Accordingly we denote the minimisers of the available free energy for the reference standard system by $\bar{Y}_a(T)$. The exploitation and determination of all quantities that refer to the reference standard system is found in [7].

In the liquid phase we consider entropic and energetic contributions to the chemical potentials of the two constituents As_L and Ga_L. We use the arsenic mole fraction X_L, see (14), to represent the chemical potentials of the two constituents of the liquid phase. These read for Ga_L:

$$\begin{aligned}\mu_{\text{Ga}_\text{L}}^{\text{chem}}(T, X_\text{L}) = {} & \bar{\mu}_{\text{Ga}_\text{L}}(T) + RT \ln\left(\frac{1-X_\text{L}}{1-\bar{X}_\text{L}(T)}\right) \\ & + \big(L_0(T) + L_1(T)(3-4X_\text{L})\big){X_\text{L}}^2 \\ & - \Big(L_0(T) + L_1(T)\big(3-4\bar{X}_\text{L}(T)\big)\Big)\bar{X}_\text{L}(T)^2,\end{aligned} \tag{98}$$

and for As_L:

$$\begin{aligned}\mu_{\text{As}_\text{L}}^{\text{chem}}(T, X_\text{L}) = {} & \bar{\mu}_{\text{As}_\text{L}}(T) + RT \ln\left(\frac{X_\text{L}}{\bar{X}_\text{L}(T)}\right) \\ & + \big(L_0(T) + L_1(T)(1-4X_\text{L})\big)(1-X_\text{L})^2 \\ & - \Big(L_0(T) + L_1(T)\big(1-4\bar{X}_\text{L}(T)\big)\Big)(1-\bar{X}_\text{L}(T))^2 .\end{aligned} \tag{99}$$

As above, the functions $\bar{\mu}_{\text{Ga}_\text{L}}(T)$ and $\bar{\mu}_{\text{As}_\text{L}}(T)$ refer to the reference standard system, and $\bar{X}_\text{L}(T)$ represents the arsenic mole fraction, that minimises the available free energy of the reference standard system. Data for these quantities can be read off from [7]. The constitutive laws (98) and (99) are given by Oates, Wenzl and Erikson [25].

5.4 Constitutive model, Part 3: The St. Venant–Kirchhoff law for the stresses and the mechanical parts of free energy and chemical potentials of the solid phase

While the chemical parts of the chemical potentials for the solid phase rely on the well established sublattice model, their mechanical parts are introduced here for the first time in order to model and simulate the problem of the appearance and evolution of As-rich droplets in solid GaAs. The procedure is as follows: We first formulate the stress-strain relation according to the St. Venant–Kirchhoff law, see for example [33]. Next we calculate the free energy density by an integration which rely on the general law (45). Finally we obtain the mechanical parts of the chemical potentials by differentiation of the free energy density with respect to the mole densities according to $(35)_2$.

The St. Venant–Kirchhoff law assumes that the stress, which results for small elastic strains $(C^{ij} - J^{*\frac{2}{3}}\delta^{ij})/2$, are given by a linear representation for the second Piola-Kirchhoff stress. The special form of this representation, which will be given below, is suited to describe the response of GaAs to elastic deformations.

$$t^{ij} = \frac{1}{2}K^{ijkl}\left(\left(\frac{\bar{n}_{\mathrm{G}}}{n_{\mathrm{G}}}\right)^{\frac{2}{3}} c^{kl} - \delta^{kl}\right) - \bar{p}(C^{-1})^{ij}J. \tag{100}$$

This version of the St. Venant–Kirchhoff law relies on the assumption that elastic deformations describe here exclusively deformations of the crystal lattice, so that in particular the volumetric part is given by the ratio $\frac{\bar{n}_{\mathrm{G}}}{n_{\mathrm{G}}}$. Furthermore there is no misfit strain due to a rearrangement of the Ga and As atoms on the lattice sites. If we were to allow that Ga atoms may occupy the β and γ sublattices such a misfit strain would appear, because the lattice sites of both sublattices offer less space than the lattice sites of the α lattice. Finally we mention that the absence of misfit strain due to thermal expansion results from the chosen reference state. In other words, thermal expansion is already included in $\bar{p}(T)$ and the temperature dependent stiffness matrix K^{ijkl}.

By means of (89) we may rewrite (100) as

$$t^{ij} = \frac{1}{2J^{*\frac{2}{3}}}K^{ijkl}\left(C^{kl} - J^{*\frac{2}{3}}\delta^{kl}\right) - \bar{p}(C^{-1})^{ij}J. \tag{101}$$

The St. Venant–Kirchhoff law is appropriate in the small strain regime. The reference pressure is introduced here, so that the homogeneous deformation $F^{ij} = J^{*1/3}\delta^{ij}$ leads to $\sigma^{ij} = -\bar{p}(T)\delta^{ij}$. The complete linearisation of the St.Venant-Kirchhoff law with respect to the spatial displacement gradient h^{ij} gives the spatial version of the classical Hooke law. The linearisation of the Green strain $(C^{ij}-\delta^{ij})/2$ gives the strain $e^{ij}=(h^{ij}+h^{ji})/2$.

We insert now (101) into the left hand site of (45) and calculate the free energy density $\tilde{\psi}_{\mathrm{S}}(T,Y_{b_{\mathrm{S}}},C)$ by integration. Next we rewrite the function $\tilde{\psi}_{\mathrm{S}}(T,Y_{b_{\mathrm{S}}},C)$ according to (44) and obtain the following representation of the mechanical part of the free energy density:

$$
\begin{aligned}
&\rho\hat{\psi}^{\mathrm{mech}}(T,Y_{b_{\mathrm{S}}},J,\boldsymbol{c})\\
&\quad=\frac{1}{8\big(\tilde{J}^{*}(Y_{b_{\mathrm{S}}})\big)^{\frac{2}{3}}J}\left(J^{2/3}c^{ij}-\big(\tilde{J}^{*}(Y_{b_{\mathrm{S}}})\big)^{\frac{2}{3}}\delta^{ij}\right)K^{ijkl}(T)\big(J^{2/3}c^{kl}-\big(\tilde{J}^{*}(Y_{b_{\mathrm{S}}})\big)^{\frac{2}{3}}\delta^{kl}\big)\\
&\qquad-\bar{p}(T)\left(1-\frac{\tilde{J}^{*}(Y_{b_{\mathrm{S}}})}{J}\right). \qquad (102)
\end{aligned}
$$

We add this function to the chemical part of the free energy density in order to calculate the chemical potentials by differentiating with respect to the mole densities according $(35)_2$. Note that the dependence on the mole densities is contained in J and J^{*} via the functions from Section 5.1 and (6).

We start the calculation of the chemical potentials with the Gibbs-Duhem equation (34), which reads in the elastic strain free configuration $C^{ij}=J^{*2/3}\delta^{ij}$

$$
\psi^{\mathrm{chem}}=-\frac{\bar{p}}{\rho^{*}}+\frac{1}{\rho^{*}}\sum_{a}\mu_a^{\mathrm{chem}}n_a^{\mathrm{R}}. \qquad (103)
$$

Multiplying this equation by ρ yields

$$
\rho\psi^{\mathrm{chem}}=-\bar{p}\frac{\rho}{\rho^{*}}+\frac{\rho}{\rho^{*}}\sum_{a}\mu_a^{\mathrm{chem}}n_a^{\mathrm{R}}=-\bar{p}\frac{J^{*}}{J}+\sum_{a}\mu_a^{\mathrm{chem}}n_a, \qquad (104)
$$

and with (102) and $(90)_1$ we obtain

$$
\rho\psi=\frac{1}{8J^{*2/3}J}\Big(J^{2/3}c^{ij}-J^{*2/3}\delta^{ij}\Big)K^{ijkl}(T)\Big(J^{2/3}c^{kl}-J^{*2/3}\delta^{kl}\Big)-\bar{p}+\sum_{a}\mu_a^{\mathrm{chem}}n_a. \qquad (105)
$$

Next we use $(35)_2$ to obtain the chemical potentials by differentiation. There results

$$
\begin{aligned}
\mu_a&=\frac{\partial(\rho\psi)}{\partial n_a}\\
&=\mu_a^{\mathrm{chem}}+\frac{1}{24J^{*2/3}}K^{ijkl}(C^{kl}-J^{*2/3}\delta^{kl})\\
&\qquad\left(2\frac{J^{*}}{J}(C^{ij}+J^{*2/3}\delta^{ij})\frac{\partial J^{*-1}}{\partial n_a}-(C^{ij}+3J^{*2/3}\delta^{ij})\frac{\partial J^{-1}}{\partial n_a}\right) \qquad (106)
\end{aligned}
$$

and

$$
\mu_a^{\mathrm{mech}}=\frac{K^{ijkl}(C^{kl}-J^{*\frac{2}{3}}\delta^{kl})}{24J^{*\frac{2}{3}}}\left(2\frac{J^{*}}{J}(C^{ij}+J^{*\frac{2}{3}}\delta^{ij})\frac{\partial J^{*-1}}{\partial n_a}-(C^{ij}+3J^{*\frac{2}{3}}\delta^{ij})\frac{\partial J^{-1}}{\partial n_a}\right). \qquad (107)
$$

The calculation of $\partial J^{-1}/\partial n_a$ relies on (89) where $n_{\rm G}$ is given by (6) and with $\bar n_{\rm G}(T)$. There results

$$\frac{\partial J^{-1}}{\partial n_a} = \frac{M_a}{2\mathfrak{M}(\bar Y_{\rm Ga}, \bar Y_{\rm As})}\frac{1}{n_{\rm G}^{\rm R}} \quad \text{and} \quad \frac{\partial J^{*-1}}{\partial n_a} = \frac{\partial\left(J^{-1}\frac{n_{\rm G}^{\rm R}}{n_{\rm G}}\right)}{\partial n_a} = \frac{3M_a - 2\mathfrak{M}(Y_{\rm Ga}, Y_{\rm As})}{6\mathfrak{M}(\bar Y_{\rm Ga}, \bar Y_{\rm As})}\frac{1}{n_{\rm G}}, \tag{108}$$

so that we finally obtain

$$\mu_a^{\rm mech} = -\frac{K^{ijkl}(C^{kl} - J^{*2/3}\delta^{kl})}{72 J^{*2/3}} \left(2J^{*-1}(C^{ij} + J^{*2/3}\delta^{ij}) - \frac{3}{2}(C^{ij} - J^{*2/3}\delta^{ij})\frac{M_a}{\mathfrak{M}(\bar Y_{\rm Ga}, \bar Y_{\rm As})}\right)\frac{1}{\bar n_{\rm G}}. \tag{109}$$

There are two significant differences of the current representation for $\mu_a^{\rm mech}$ to the corresponding representation that is usually used in the literature. For a comparison it is sufficient to discuss a pure substance with molecular weight M, where the chemical potential μ reduces to the specific free enthalpy $g = M\mu$.

The first difference of (109) to the literature is due to the appearance of the reference pressure in the St. Venant-Kirchhoff law (101), which is usually ignored there. Here, the solid phase couples to a liquid phase, and at the common interface between solid and liquid, mechanical equilibrium can only be established if the reference pressure is taken into account.

However, for a discussion and an easy comparison of the second difference of (109) to the literature, let us ignore the reference pressure, i.e. we set $\bar p(T) = 0$ for a while. In this case and for $J^* = 1$ (107) may be written as

$$\bar\rho_{\rm S}(T) g^{\rm mech} = t^{ij}(C^{ij} - \delta^{ij})/4 - t^{ij}C^{ij}/3 = -t^{ij}(C^{ij} - \delta^{ij})/12 - t^{ii}/3, \tag{110}$$

and we will compare this representation with the most cited corresponding representation $g^{\rm LL}$, which is found in Landau/Lifschitz [23]. The authors write without any justification

$$\bar\rho_{\rm S}(T) g^{\rm LL} = t^{ij}(C^{ij} - \delta^{ij})/4 - t^{ij}(C^{ij} - \delta^{ij})/2 = -t^{ij}(C^{ij} - \delta^{ij})/4 \tag{111}$$

where the Green strain $(C^{ij} - \delta^{ij})/2$ has been replaced by its linearisation with respect to H^{ij}:

$$(C^{ij} - \delta^{ij})/2 = (H^{ij} + H^{ji})/2. \tag{112}$$

If we assume now a linear dependence between the stress t^{ij} and the strain $(C^{ij} - \delta^{ij})/2$, we state two important differences to (110): (i) The Landau/Lifschitz result (111) contains exclusively quadratic contributions in the strain $(C^{ij} - \delta^{ij})/2$, whereas the correct result (110) additionally contains linear contributions. (ii) The quadratic terms appear in (111) with the factor 1/4, whereas the correct result shows that the factor should be 1/12.

We proceed to give the representation of the chemical potentials, which is correct up to terms of third order.

To this end we calculate $\overset{-1}{(C)}{}^{ij}$ in terms of the actual displacement gradient h^{ij} and obtain

$$\overset{-1}{(C)}{}^{ij} = \delta^{ij} - h^{ij} - h^{ji} + h^{im}h^{jm}. \tag{113}$$

We consider $\|h\|$ as a small quantity, so that there results

$$C^{ij} = \delta^{ij} + h^{ij} + h^{ji} + h^{mi}h^{jm} + h^{im}h^{mj} + h^{jm}h^{mi} + \mathrm{O}(\|h\|^3). \tag{114}$$

Let us now calculate $\big(p_\mathrm{S} - \bar{p}(T)\big)\frac{M_a}{\rho} = -(t^{ij}C^{ij} + 3\bar{p}J)\frac{M_a}{3\bar{\rho}}$ within the same order of approximation. We obtain

$$\begin{aligned}\big(p_\mathrm{S} - \bar{p}(T)\big)\frac{M_a}{\rho} = -\frac{M_a}{6\bar{\rho}}K^{iimn}(h^{mn} + h^{nm} + h^{mk}h^{kn} + h^{nk}h^{km} + h^{mk}h^{nk}) \\ -\frac{2M_a}{3\bar{\rho}}h^{ik}K^{kimn}h^{mn} + \mathrm{O}(\|h\|^3).\end{aligned} \tag{115}$$

The mechanical parts of the chemical potentials thus read within the quadratic approximation

$$\mu_a^\mathrm{mech} = \big(p_\mathrm{S} - \bar{p}(T)\big)\frac{M_a}{\rho} + \frac{M_a}{2\bar{\rho}}h^{ij}K^{ijkl}h^{kl} + \mathrm{O}(\|h\|^3). \tag{116}$$

We conclude that if $(p_\mathrm{S} - \bar{p}(T)\big)\frac{M_a}{\rho}$ were known within the quadratic approximation, linear elasticity is sufficient to calculate μ_a^mech. On the other hand, if we calculate $(p_\mathrm{S} - \bar{p}(T)\big)\frac{M_a}{\rho}$ by means of (115) we obtain

$$\begin{aligned}\mu_a^\mathrm{mech} = -\frac{M_a}{6\bar{\rho}}K^{iikl}(T)(h^{kl} + h^{lk} + h^{km}h^{ml} + h^{lm}h^{mk} + h^{lm}h^{km}) \\ -\frac{M_a}{6\bar{\rho}}h^{ij}K^{ijkl}h^{kl} + \mathrm{O}(\|h\|^3).\end{aligned} \tag{117}$$

A calculation that relies on (117) thus needs the non-linear theory of elasticity.

Note again that the linear terms do not appear in the Landau/Lifschitz model. The consequences of this fact are as follows. The linear theory of elasticity is only sufficient to calculate the chemical potentials if the quadratic terms in (117) can be neglected. In case that the quadratic terms are needed, we have to solve the elastic boundary value problem up to second order in order to calculate the linear terms of (117) consistently to the quadratic contributions.

5.5 Constitutive model, Part 4: Pressure and the mechanical parts of free energy and chemical potentials for the liquid phase

We describe the liquid phase as a compressible liquid which is linear in $J_\mathrm{L}^{-1} = \rho_\mathrm{L}/\bar{\rho}_\mathrm{L}$ and whose strain free state is realised under the pressure $\bar{p}(T)$. We write

$$p = \bar{p}(T) + \frac{\bar{\varrho}_\mathrm{L}(T, \bar{X}_\mathrm{L})}{\varrho_\mathrm{L}^*}\tilde{k}_\mathrm{L}(T, X_\mathrm{L})\left(\frac{\varrho_\mathrm{L}}{\bar{\varrho}_\mathrm{L}(T, \bar{X}_\mathrm{L})} - \frac{\varrho_\mathrm{L}^*}{\bar{\varrho}_\mathrm{L}(T, \bar{X}_\mathrm{L})}\right).$$

The newly introduced function $\tilde{k}_{\rm L}(T, X_{\rm L}) > 0$ denotes the bulk modulus of the liquid.

The problem that we consider exclusively in this study, regards the formation and evolution of liquid droplets in semi-insulating GaAs. Due to this application we may restrict ourselves to liquid GaAs mixtures with an arsenic mole fraction $X_{\rm L} > 0.9$. Thus for simplification and due due to lack of data for the function $\tilde{k}_{\rm L}(T, X_{\rm L})$, we set $X_{\rm L} = 1$ within $\tilde{k}_{\rm L}$ and write

$$
\begin{aligned}
p_{\rm L} &= \bar{p}(T) + k_{\rm L}(T)\frac{\mathcal{M}(\bar{X}_{\rm L})}{\mathcal{M}(X_{\rm L})}\left(\frac{\varrho_{\rm L}}{\varrho_{\rm L}^{\rm R}(T,\bar{X}_{\rm L})} - \frac{\mathcal{M}(X_{\rm L})}{\mathcal{M}(\bar{X}_{\rm L})}\right) = \widehat{p}_{\rm L}(T, X_{\rm L}, \varrho_{\rm L}) \\
&= \bar{p}(T) + \tilde{J}_{\rm L}^{*}(X_{\rm L})k_{\rm L}(T)\left(J_{\rm L}^{-1} - \tilde{J}_{\rm L}^{*-1}(X_{\rm L})\right) \qquad = \tilde{p}_{\rm L}(T, X_{\rm L}, J_{\rm L}).
\end{aligned}
\tag{118}
$$

Thermal expansion of the liquid is included in this law and represented by means of the dependence of $n_{\rm L}^{\rm R}$ and $k_{\rm L}$ on temperature, see [7] for details.

Similarly to the solid phase, we calculate the mechanical part of the free energy density of the liquid by integration of (38), and afterwards we obtain by means of $(35)_2$ the mechanical part of the chemical potential:

$$
\mu_a^{\rm mech}(T, X_{\rm L}, J_{\rm L}) = k_{\rm L}(T)\ln\left(\frac{\tilde{J}_{\rm L}^{*}(X_{\rm L})}{J_{\rm L}}\right)\frac{\partial\left(\frac{\tilde{J}_{\rm L}^{*}(X_{\rm L})}{J_{\rm L}}\right)}{\partial n_a}. \tag{119}
$$

The calculation of $\partial(J_{\rm L}^{*}/J_{\rm L})/\partial n_a$ relies on $(4)_2$ and $(89)_2$, which may be written as

$$
\frac{J_{\rm L}^{*}}{J_{\rm L}} = \frac{n_{\rm L}}{\bar{n}_{\rm L}} \tag{120}
$$

and we obtain

$$
\frac{\partial\left(\frac{\tilde{J}_{\rm L}^{*}(X_{\rm L})}{J_{\rm L}}\right)}{\partial n_a} = \frac{1}{\bar{n}_{\rm L}(T)}. \tag{121}
$$

The chemical part of the chemical potentials thus read in the liquid phase

$$
\mu_a^{\rm mech}(T, X_{\rm L}, J_{\rm L}) = \frac{k_{\rm L}(T)}{\bar{n}_{\rm L}(T)}\ln\left(\frac{\tilde{J}_{\rm L}^{*}(X_{\rm L})}{J_{\rm L}}\right). \tag{122}
$$

In order to exhibit the similarity between the mechanical constitutive laws for the liquid and solid phases, we introduce in the liquid a quantity $h_{\rm L}$ that may be interpreted as a strain, if it is defined by $J_{\rm L}^{-1} = (1 - h_{\rm L})^3$. In the same manner, we define $J_{\rm L}^{*-1} = (1 - h_{\rm L}^{*})^3$. Likewise as in the solid, there result constitutive laws for the liquid within the second order approximation in $h_{\rm L}$ and $h_{\rm L}^{*}$:

$$
p_{\rm L} = \bar{p}(T) - 3k_{\rm L}(T)(h_{\rm L}(1 - h_{\rm L}) - h_{\rm L}^{*}(1 - h_{\rm L}^{*}) + 3h_{\rm L}^{*}(h_{\rm L} - h_{\rm L}^{*})), \tag{123}
$$

$$
\mu_a^{\rm mech} = -3\frac{k_{\rm L}(T)}{n_{\rm L}^{\rm R}(T)}(h_{\rm L} - h_{\rm L}^{*})\left(1 + \frac{1}{2}(h_{\rm L} - h_{\rm L}^{*})\right). \tag{124}
$$

6 Strains and stresses induced by an evolving liquid droplet in a solid phase

Phase transitions in solid semi-insulating GaAs may lead to small liquid droplets that induce strains and stresses in their surrounding, because the liquid phase of GaAs has a lower density than the solid phase and thus needs more space than solid GaAs. We consider a distribution of liquid droplets in solid GaAs, whose radii are much smaller than their mean distance, which is about 1μm - 2μm. This fact motivates the reduction of the mechanical problem to the calculation of strains and stresses for a single spherical liquid droplet within an infinite solid matrix as it is indicated in Figure 3.

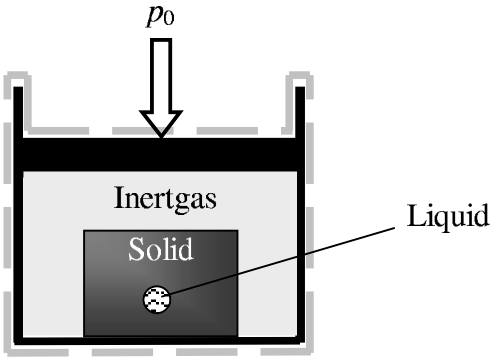

Figure 3: Single liquid droplet in a solid matrix, which is subjected to a hydrostatic pressure p_0.

The cubic anisotropy of GaAs is quite small, see [9], and this gives rise to a further simplification: We approximate the stiffness tensor by an isotropic representation that contains the two material parameters bulk and the shear modulus, which we denote by $k_\mathrm{S}(T)$ and $G_\mathrm{S}(T)$, respectively. In this case the St.Venant-Kirchhoff law (101) for the second Piola-Kirchhoff stress implies the following representation for the Cauchy stress:

$$\begin{aligned}
\sigma^{ij} &= -\bar{p}(T)\delta^{ij} + \frac{B^{ik}K^{kjmn}(B^{mn} - J^{*\frac{2}{3}}\delta^{mn})}{2J^{*\frac{2}{3}}\sqrt{\det(B)}} \\
\text{with} \qquad & K^{ijkl}(T) = k_\mathrm{S}(T)\delta^{ij}\delta^{kl} + G_\mathrm{S}(T)\left(\delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk} - \frac{2}{3}\delta^{ij}\delta^{kl}\right) \\
\text{and} \qquad & J^{*-1} = (1-h^*)^3. \qquad (125)
\end{aligned}$$

At first we study the mechanical problem up to second order in the displacement gradient $h^{ij} = \partial u^i/\partial x^j$. To this end we calculate the left Cauchy-Green tensor

$$\begin{aligned}
B^{ij} &= \delta^{ij} + h^{ij} + h^{ji} + h^{ik}h^{kj} + h^{jk}h^{ki} + h^{ik}h^{jk} + \mathrm{O}(\|h\|^3) \\
\text{and} \quad J^{*\frac{2}{3}} &= 1 + 2h^* + 3h^{*2} + \mathrm{O}(|h^*|^3), \qquad (126)
\end{aligned}$$

and insert the result into the representation (125) for the Cauchy stress

$$\sigma^{ij} = -\bar{p}(T)\delta^{ij} + \frac{1}{2}K^{ijmn}((h^{mn}+h^{nm})(1-2h^*) + h^{mk}h^{kn} + h^{nk}h^{km} + h^{mk}h^{nk} - 2h^*\delta^{mn} + h^{*2}\delta^{mn}) + \frac{1}{2}(h^{ik}+h^{ki}-h^{ll}\delta^{ik})K^{kjmn}(h^{mn}+h^{nm}-2h^*\delta^{mn}) + \mathrm{O}(\|h\|^3). \tag{127}$$

Next we introduce the expected spherical symmetry of the solution. We assume that the displacement vector in spherical coordinates is given by

$$(u^r, u^\varphi, u^\vartheta) = (u(r), 0, 0), \quad \text{so that there holds} \quad h^{rr} = \frac{\partial u}{\partial r}, \quad h^{\vartheta\vartheta} = h^{\varphi\varphi} = \frac{u}{r}, \tag{128}$$

and $h^{ij} = 0$ otherwise.

¿From (125) we obtain $\sigma^{r\vartheta} = \sigma^{r\varphi} = \sigma^{\varphi\vartheta} = 0$, $\sigma^{\vartheta\vartheta} = \sigma^{\varphi\varphi}$, and

$$\begin{aligned}\begin{pmatrix}\sigma^{rr}\\ \sigma^{\varphi\varphi}\end{pmatrix} = {}& -\bar{p}\begin{pmatrix}1\\1\end{pmatrix} + \left(\left(k_\mathrm{S} - \frac{2}{3}G_\mathrm{S}\right)(h^{rr}+2h^{\varphi\varphi}) - 3k_\mathrm{S}h^*\right)\begin{pmatrix}1\\1\end{pmatrix}\\ & + 2G_\mathrm{S}\begin{pmatrix}h^{rr}\\ h^{\varphi\varphi}\end{pmatrix} + 7G_\mathrm{S}\begin{pmatrix}(h^{rr})^2\\ (h^{\varphi\varphi})^2\end{pmatrix}\\ & + \left(k_\mathrm{S} + \frac{4}{3}G_\mathrm{S}\right)(h^{rr}+2h^{\varphi\varphi})h^*\begin{pmatrix}1\\1\end{pmatrix}\\ & +2\left(\left(k_\mathrm{S} - \frac{5}{3}G_\mathrm{S}\right)(h^{rr}+2h^{\varphi\varphi}) - (3k_\mathrm{S}+2G_\mathrm{S})h^*\right)\begin{pmatrix}h^{rr}\\ h^{\varphi\varphi}\end{pmatrix}\\ & + \left(\left(\frac{3}{2}k_\mathrm{S} - G_\mathrm{S}\right)((h^{rr})^2 + 2(h^{\varphi\varphi})^2) + \frac{3}{2}k_\mathrm{S}\,(h^*)^2\right)\begin{pmatrix}1\\1\end{pmatrix}\\ & - \left(k_\mathrm{S} - \frac{2}{3}G_\mathrm{S}\right)(h^{rr}+2h^{\varphi\varphi})^2\begin{pmatrix}1\\1\end{pmatrix} + \mathrm{O}(\|h\|^3).\end{aligned} \tag{129}$$

The resulting mechanical boundary value problem relies on the equilibrium condition (67), which reduces to

$$\frac{\partial\sigma^{rr}}{\partial r} + 2\frac{\sigma^{rr}-\sigma^{\varphi\varphi}}{r} = 0 \quad \text{in } \Omega_\mathrm{S} \quad \text{and} \quad \frac{\partial p_\mathrm{L}}{\partial r} = 0 \quad \text{in } \Omega_\mathrm{L}. \tag{130}$$

The conditions at the outer boundary $r = r_\mathrm{A}$ and at the interface $r = r_\mathrm{I}$ read

$$\lim_{r_A\to\infty}\sigma^{rr}(r_\mathrm{A}) = -p_0 \quad \text{and} \quad \sigma^{rr}(r_\mathrm{I}) + p_\mathrm{L} = \frac{2\sigma}{r_\mathrm{I}}. \tag{131}$$

We conclude from $(130)_2$ that the liquid pressure is constant, which implies a constant liquid mass density. Finally we insert the constitutive law (129) into $(130)_1$ to obtain an ODE for the displacement, viz.

$$
\begin{aligned}
u''(r) &+ \frac{2}{r}\left(u'(r) - \frac{u(r)}{r}\right) \\
&= u''(r)\left(\frac{12G_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}}\frac{u(r)}{r} - 5u'(r)\right) + 6\frac{3k_\mathrm{S}+G_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}}\frac{u^2(r)}{r^3} \\
&\quad - 2\frac{u'(r)}{r}\left(\frac{6k_\mathrm{S}+5G_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}}u'(r) + \frac{3k_\mathrm{S}-2G_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}}\frac{u(r)}{r}\right) \\
&\quad + h^{*\prime}(r)\left(\big(1-h^*(r)\big)\frac{9k_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}} + \frac{15k_\mathrm{S}+8G_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}}u'(r) - 2\frac{u(r)}{r}\right) \\
&\quad\quad + \frac{15k_\mathrm{S}+8G_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}}h^*(r)\left(u''(r) + 2\left(\frac{u'(r)}{r} - \frac{u(r)}{r^2}\right)\right). \qquad (132)
\end{aligned}
$$

The solution reads in the first order approximation

$$
u(r) = \left(a + b_\mathrm{I}\left(\frac{r_\mathrm{I}}{r}\right)^3 + \frac{3k_\mathrm{S}}{3k_\mathrm{S}+4G_\mathrm{S}}\left(h^*(r) - \frac{1}{r^3}\int_{r_\mathrm{I}}^{r} z^3 h^{*\prime}(z)\, dz\right)\right) r. \qquad (133)
$$

The parameter a describes the stress contribution due to changes of the volume of the solid phase, whereas b determine the deviatoric stress components due to changes of its shape. a and b depend via the boundary conditions on the droplet radius r_I and on the liquid density ρ_L. Next we discuss the determination of r_I and ρ_L.

There are three different points of view to determine the interfacial radius r_I: (*i*) If we are interested in the possible equilibria of solid/liquid phase transitions, where the liquid appears as a small droplet, we have to establish special phase diagrams, whose calculation needs the determination of the possible equilibrium values for the droplet radius as minimiser of the available free energy. (*ii*) The description and simulation of nucleation and growth of small droplets requires the determination of critical radii, which will turn out as maximisers of the available free energy. Both cases are discussed in detail in Section 7. (*iii*) The diffusional problem in the vicinity of an evolving liquid droplet leads to a free boundary problem which yields among other things the temporal development of the droplet radius. This case is exploited in [8].

The determination of the liquid density ρ_L relies on an assumption regarding the deformation during the phase transition. The assumption will now be described by means of a thought experiment.

At first we consider the current state of a two phase sphere with a liquid sphere of radius r_I in the center. According to $(19)_3$, the density of the liquid is given by $\rho_\mathrm{L} = M(X_\mathrm{L})n_\mathrm{L}$. Next we we simulate a phase transition that changes at constant mass and constant mole fraction X_L the liquid sphere into a solid sphere. During this process, we assume that the occupancies of lattice sites of the outer solid sphere, Y_a, remain unchanged. In particular, the occupancy of vacancies at the interface, $Y_\mathrm{V}^\mathrm{I} := Y_{\mathrm{V}_\alpha}^\mathrm{I} + Y_{\mathrm{V}_\beta}^\mathrm{I} + Y_{\mathrm{V}_\gamma}^\mathrm{I}$ remains unchanged. Furthermore we assume homogeneous occupancies of lattice sites of the new inner solid sphere where the occupancy of vacancies is given by $Y_{\mathrm{V}}^{\mathrm{I}}$.

We denote the current density of sublattices by n_{GL}, so that the current mass density ρ_{SL} of the new solid sphere reads

$$\rho_{\mathrm{SL}} = n_{\mathrm{GL}}(3 - Y_{\mathrm{VI}})M(X_{\mathrm{L}}). \tag{134}$$

The common boundary between the two spheres is denoted by r_{ISL}. Thus we have

$$\rho_{\mathrm{L}} r_{\mathrm{I}}^3 = \rho_{\mathrm{SL}}(r_{\mathrm{ISL}})^3. \tag{135}$$

Next we introduce the reference states of the two spheres. As the reference state of the outer sphere we choose a homogeneous strain state with the reference mass density $\bar{\rho}_{\mathrm{S}} = \bar{n}_{\mathrm{G}}(3-\bar{Y}_{\mathrm{V}})M(\bar{X}_{\mathrm{S}})$. The reference state of the inner sphere is likewise assumed to be homogeneous with the reference mass density $\bar{\rho}_{\mathrm{SL}} = \bar{n}_{\mathrm{G}}(3-\bar{Y}_{\mathrm{V}})M(\bar{X}_{\mathrm{L}})$. Finally we assume that both solid spheres have a common boundary with radius R_{I} in the reference state.

These assumptions imply

$$\rho_{\mathrm{SL}}(r_{\mathrm{ISL}})^3 = \bar{\rho}_{\mathrm{SL}}(r_{\mathrm{I}} - u(r_{\mathrm{I}}))^3, \tag{136}$$

and we consider this condition as an equation for the determination of the liquid density n_{L}. Thus we may rewrite (135) as

$$n_{\mathrm{L}} = (3 - \bar{Y}_{\mathrm{V}}^{\mathrm{I}})\ \bar{n}_{\mathrm{G}}(T) \left(\frac{1 - \frac{u(r_{\mathrm{I}})}{r_{\mathrm{I}}}}{1 - h_{\mathrm{L}}^*} \right)^3 . \tag{137}$$

The equation (137) serves a third boundary condition, which is used in combination with the two other conditions $(131)_{1,2}$ to determine uniquely the mechanical boundary value problem.

We proceed to determine the mechanical problem within an approximation, which is of first order in the spatial displacement gradient h^{ij}. In order to exhibit the similarity between the mechanical constitutive laws for liquid and solid, we introduce in the liquid a quantity a_{L}, which is defined by $J_{\mathrm{L}}^{-1} = (1 - 3a_{\mathrm{L}})$.

We start from

$$\rho_{\mathrm{L}} = (1 - 3a_{\mathrm{L}})\ \bar{n}_{\mathrm{L}}\ \mathcal{M}(\bar{X}_{\mathrm{L}}) \tag{138}$$

and the first order approximation of $(129)_1$ by use of solution (133)

$$\begin{aligned} \sigma^{rr}(r_{\mathrm{A}}) = -\bar{p} + 3k_{\mathrm{S}} &\left(a - \widetilde{h^*} \frac{4G_{\mathrm{S}}}{3k_{\mathrm{S}} + 4G_{\mathrm{S}}} \right) \\ &- 4G_{\mathrm{S}} \left(\frac{r_{\mathrm{I}}}{r_{\mathrm{A}}} \right)^3 \left(b_{\mathrm{I}} + \frac{3k_{\mathrm{S}}}{3k_{\mathrm{S}} + 4G_{\mathrm{S}}} \left(h^*(r_{\mathrm{I}}) - \widetilde{h^*} \right) \right) \end{aligned} \tag{139}$$

with

$$\widetilde{h^*} = \frac{3}{r_{\mathrm{A}}^3 - r_{\mathrm{I}}^3} \int_{r_{\mathrm{I}}}^{r_{\mathrm{A}}} r^2 h^*(r) dr \quad \text{and} \quad \lim_{r_{\mathrm{A}} \to \infty} \widetilde{h^*} = h^*(r_{\mathrm{A}}). \tag{140}$$

Now we determine the quantities a, $b_{\rm I}$ and $a_{\rm L}$ by means of the three boundary conditions $(131)_{1,2}$ and (137). There results

$$3k_{\rm S}\left(a - h^*(r_{\rm A})\frac{4G_{\rm S}}{3k_{\rm S}+4G_{\rm S}}\right) - \bar{p} = -p_0,$$

$$3k_{\rm S}\left(a - h^*(r_{\rm I})\frac{4G_{\rm S}}{3k_{\rm S}+4G_{\rm S}}\right) - 4G_{\rm S}b_{\rm I} = 3k_{\rm L}(a_{\rm L} - h^*_{\rm L}) + \frac{2\sigma}{r_{\rm I}} \quad \text{and}$$

$$\sqrt[3]{\frac{n^{\rm R}_{\rm L}}{(3-\bar{Y}^{\rm I}_{\rm V})n^{\rm R}_{\rm G}}} - 1 - a_{\rm L} = -\frac{3k_{\rm S}}{3k_{\rm S}+4G_{\rm S}}h^*(r_{\rm I}) - a - b_{\rm I}. \quad (141)$$

In order to guarantee the applicability of the approximation we require

$$\kappa = \frac{2\sigma}{3k_{\rm L}r_{\rm I}} = {\rm O}(\|h\|) \quad \text{and} \quad \delta = \sqrt[3]{\frac{n^{\rm R}_{\rm L}}{(3-\bar{Y}^{\rm I}_{\rm V})n^{\rm R}_{\rm G}}} - 1 = {\rm O}(\|h\|). \quad (142)$$

We thus finally end up with

$$a = h^*(r_{\rm A})\frac{4G_{\rm S}}{3k_{\rm S}+4G_{\rm S}} + \frac{\bar{p}-p_0}{3k_{\rm S}}, \quad (143)$$

$$b_{\rm I} = \frac{3k_{\rm S}-3k_{\rm L}}{4G_{\rm S}+3k_{\rm L}}a - \frac{3k_{\rm L}}{4G_{\rm S}+3k_{\rm L}}(\kappa+\delta-h^*_{\rm L}) - \frac{3k_{\rm S}}{3k_{\rm S}+4G_{\rm S}}h^*(r_{\rm I}) \quad (144)$$

and

$$a_{\rm L} = \frac{4G_{\rm S}+3k_{\rm S}}{4G_{\rm S}+3k_{\rm L}}a - \frac{3k_{\rm L}}{4G_{\rm S}+3k_{\rm L}}(\kappa-h^*_{\rm L}) + \frac{4G_{\rm S}}{4G_{\rm S}+3k_{\rm L}}\delta. \quad (145)$$

These equations solve the mechanical boundary value problem if the interfacial radius $r_{\rm I}$, the outer radius $r_{\rm A}$, and the quantities $h^*_{\rm L}$ and $h^*(r)$ are given. In the diffusional equilibrium $h^*(r)$ is independent of r in the first order approximation. The determination of $r_{\rm I}$, $r_{\rm A}$, $h^*_{\rm L}$ and h^* for diffusional equilibrium is the subject of the next section.

The calculation of the chemical potentials within the first order approximation, which are needed in the next section, leads with (109) to

$$\begin{aligned} \mu_{a_{\rm S}} &= \mu^{\rm chem}_{a_{\rm S}} - k_{\rm S}\frac{a}{n^{\rm R}_{\rm G}} + k_{\rm S}\frac{4G_{\rm S}}{3k_{\rm S}+4G_{\rm S}}\frac{h^*(r)}{n^{\rm R}_{\rm G}} \\ &= \mu^{\rm chem}_{a_{\rm S}} + \frac{p_0-\bar{p}}{3n^{\rm R}_{\rm G}} + \frac{4\ G_{\rm S}\ k_{\rm S}}{3k_{\rm S}+4G_{\rm S}}\frac{h^*(r)-h^*(r_{\rm A})}{n^{\rm R}_{\rm G}} \end{aligned} \quad (146)$$

and with (122) to

$$\mu_{a_{\rm L}} = \mu^{\rm chem}_{a_{\rm L}} - 3k_{\rm L}\frac{a_{\rm L}-h^*_{\rm L}}{n^{\rm R}_{\rm L}}. \quad (147)$$

Moreover we calculate the stress deviator at $r = r_{\rm I}$, which is also needed in the next section. There results within the same approximation

$$\frac{M_a\sigma^{\langle rr\rangle}}{\rho_{\rm S}} = -b_{\rm I}\frac{4G_{\rm S}M_a}{\rho^{\rm R}_{\rm S}}. \quad (148)$$

7 Standard and non-standard phase diagrams

7.1 Statement of the problem

A phase diagram of a multiphase body is used to exhibit the existence regions of its different phases. There is diffusional equilibrium in each phase. The boundaries of the phases represent the extrema of the available free energy $\mathcal{A}$.

A *standard phase diagram* takes into account exclusively hydrostatic stresses and ignores surface tension and stress deviators. The extrema that can be read off from a standard phase diagram are minimisers of the available free energy.

We call a phase diagram a *non-standard phase diagram* if surface tension and stress deviators are incorporated, and if also maximisers of the available free energy, if there are any, are taken into account. The maximisers indicate the existence of critical phases.

In this section we apply the introduced model to calculate standard and non-standard phase diagrams, respectively. In both cases we consider exclusively liquid/solid systems. The important case of three coexisting phases, viz. liquid/solid /gas, is extensively described in [7]. Here it serves only as a reference system, which provides the reference values, respectively, of the chemical potentials $\overline{\mu}_a(T)$, lattice occupancies $\overline{Y}_a(T)$, liquid mole fraction $\overline{X}_{\mathrm{L}}(T)$ and the vapour pressure $\overline{p}(T)$.

The incorporation of surface tension and stress deviators presumes that the resulting phase diagram is assigned to a given morphology. We calculate a non-standard phase diagram for a single droplet system as it is indicated in Figure 3, whereas the calculation of a standard phase diagram refers to Figure 2.

The variables of a standard phase diagram for GaAs consist of (i) the seven lattice occupancies Y_{Ga_α}, Y_{As_α}, Y_{V_α}, Y_{As_β}, Y_{V_β}, Y_{As_γ}, Y_{V_γ}, which are the chemical variables of the solid phase, (ii) the mechanical variable n_{G} giving the mole density of lattice sites, (iii) the arsenic mole fraction of the liquid X_{L} and (iv) the total mole density of liquid particles, n_{L}. The arsenic mole fraction of the solid, X_{S}, can then be calculated from the variables according to

$$X_{\mathrm{S}} = \frac{Y_{\mathrm{As}_\alpha} + Y_{\mathrm{As}_\beta} + Y_{\mathrm{As}_\gamma}}{Y_{\mathrm{As}_\alpha} + Y_{\mathrm{As}_\beta} + Y_{\mathrm{As}_\gamma} + Y_{\mathrm{Ga}_\alpha}}. \tag{149}$$

Having determined these quantities we can prescribe the mean arsenic composition of the total system, X_0, in order to calculate the phase fraction, Z, from the equation

$$X_0 = Z X_{\mathrm{L}} + (1 - Z) X_{\mathrm{S}} \quad \text{with} \quad X_0 = \frac{N_{\mathrm{As}_0}}{N_0} \quad \text{and} \quad Z = \frac{N_{\mathrm{L}}}{N_0}. \tag{150}$$

The quantities N_0, N_{As_0} and N_{L} denote respectively the size of the system, i.e. the total mole number of atoms, the total mole number of the arsenic and the total mole number of liquid particles.

Note that the phase fraction must satisfy

$$0 \leq Z = \frac{X_0 - X_\mathrm{S}}{X_\mathrm{L} - X_\mathrm{S}} \leq 1, \tag{151}$$

which restricts the admissible equilibria states.

The same set as above is among the variables of a non-standard phase diagram for GaAs. However, here it turns out that the equations that determine the extrema of the available free energy contain additionally the radius r_I of the droplet. In other words: the phase fraction must now be calculated simultaneously with the other variables because there holds

$$N_\mathrm{L} = n_\mathrm{L}\frac{4\pi}{3}{r_\mathrm{I}}^3 \quad \text{which implies} \quad Z = \frac{1}{N_0}n_\mathrm{L}\frac{4\pi}{3}{r_\mathrm{I}}^3. \tag{152}$$

Thus the calculation of the extrema of the available free energy for a non standard phase diagram requires the prescription of the total number of moles N_0, and of the mean composition X_0 of the total system.

The total mole number, i.e. the size of the considered thermodynamic system, has no affect at all on standard phase diagrams, and it has negligible influence on the the size of the critical droplet. However, it significantly affects the size of the stable droplets but does not influence their composition.

For convenience we summarise here the relevant equations from Section 4.

(i) constraints on lattice occupancies

$$Y_{\mathrm{Ga}_\alpha} + Y_{\mathrm{As}_\alpha} + Y_{\mathrm{V}_\alpha} = 1, \quad Y_{\mathrm{As}_\beta} + Y_{\mathrm{V}_\beta} = 1 \quad \text{and} \quad Y_{\mathrm{As}_\gamma} + Y_{\mathrm{V}_\gamma} = 1. \tag{153}$$

(ii) necessary conditions for chemical equilibria

$$\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{As}_\gamma} + \mu_{\mathrm{V}_\gamma} = 0, \quad \mu_{\mathrm{As}_\beta} - \mu_{\mathrm{V}_\beta} - \mu_{\mathrm{As}_\gamma} + \mu_{\mathrm{V}_\gamma} = 0. \tag{154}$$

(iii) necessary conditions for interfacial equilibria

$$\begin{aligned} &\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha} - \mu_{\mathrm{Ga}_\mathrm{L}} - \frac{M_\mathrm{Ga}}{\rho_\mathrm{S}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j = 0, \\ &\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As}_\mathrm{L}} - \frac{M_\mathrm{As}}{\rho_\mathrm{S}}\sigma_+^{\langle ij\rangle}\nu^i\nu^j = 0, \\ &\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma} = 0. \end{aligned} \tag{155}$$

7.2 The reference standard system

The liquid/solid/gas equilibrium for a GaAs reference standard system is used in [7] to calibrate the various material data and to calculate the needed reference values $\overline{\mu}_a(T)$, $\overline{Y}_a(T)$, $\overline{X}_\mathrm{L}(T)$ and $\overline{p}(T)$. According to the Gibbs phase rule, this system has

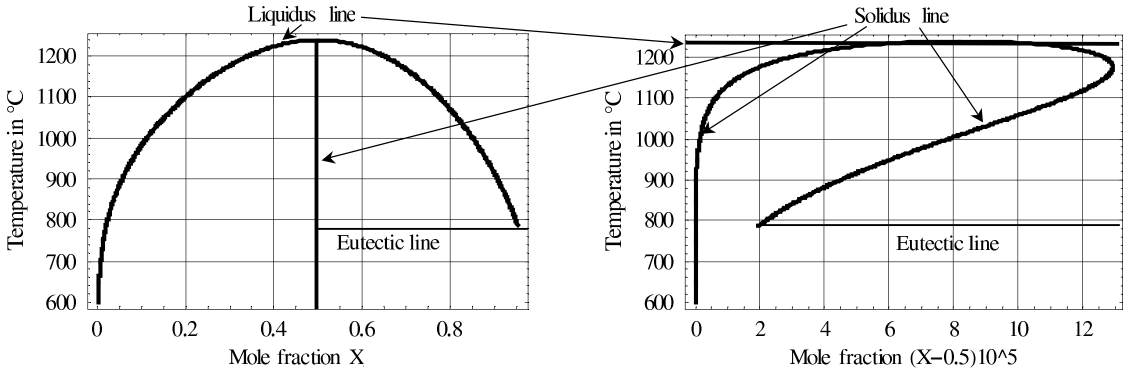

Figure 4: Phase diagram of the reference standard system (3-phase -equilibrium under vapour pressure). Left: total range of mole fraction X. Right: mole fraction in the vicinity of $X = 0.5$.

only one degree of freedom in equilibrium, viz. only a prescription of temperature is possible.

The Figures 4 and 5 refer to the reference standard system. The graphs are calculated in [7]. The resulting vapour pressure of the reference standard system is represented in Figure 5. Its calculation and the calculation of the graphs in Figure 4 are similar to the corresponding calculations of previous studies, see [37, 36, 17, 18, 31]. The liquidus lines of various authors do not differ significantly from each other. However, the shape of the solidus lines of the reference standard system depends strongly on the chemical model of the solid phase, that were differently proposed by different authors. The solidus line of Figure 4 relies on a composition of the solid phase, which is represented according to Table 2 on page 4, and the gas consists of As_2 and As_4. We have presented here Figure 4 in order to compare the current model with surface tension and thermomechanical coupling with corresponding results without these phenomena.

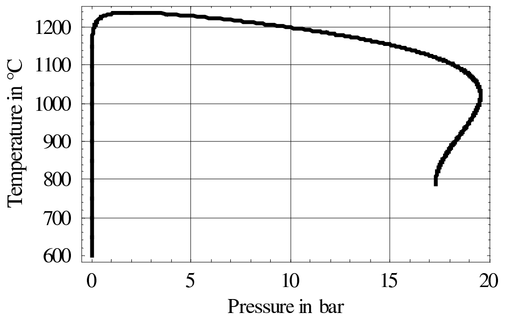

Figure 5: Vapour pressure of the reference standard system.

7.3 The standard system for various external pressures

In this section we consider a standard system that contains a liquid/solid body which is in contact with an inert gas under a prescribed pressure p_0. The minima of the available free energy rely on (i) the constraints (153), (ii) the necessary conditions for chemical equilibrium (154), and (iii) the necessary conditions for interfacial equilibrium (155). In these equations we set the stress deviators equal to zero and insert the constitutive laws from Section 5. We obtain eight algebraic equations for eight unknowns.

The resulting phase diagram is depicted in Figure 6. It turns out that in the range from $p_0 = 1$ bar to $p_0 = 100$ bar the resulting liquidus lines are indistinguishable from the liquidus line of the reference standard system, see Figure 4, and thus are not drawn again. The visible difference of the solidus lines for the two pressures is likewise negligible.

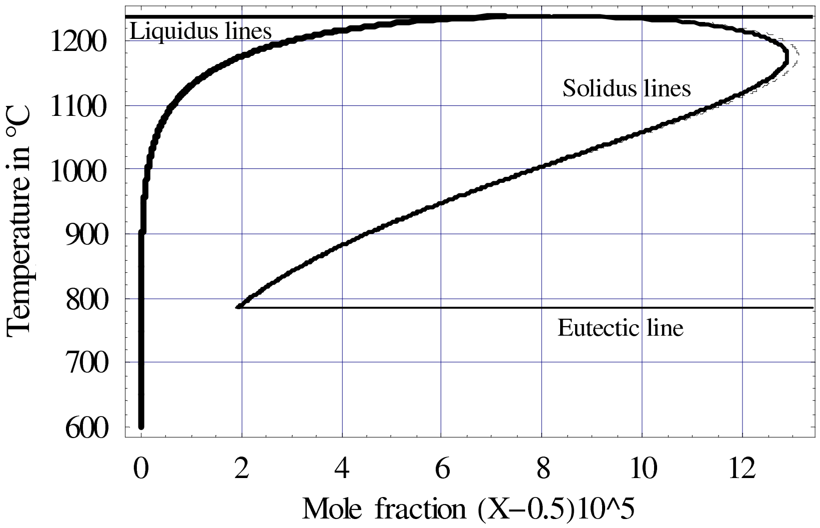

Figure 6: Phase diagrams for a standard system. Solid line: $p_0 = 1$ bar. Dashed line: $p_0 = 100$ bar.

Next we calculate the available free energy $\mathcal{A}$, which can be written as

$$\mathcal{A} = \Psi_\mathrm{L} + \Psi_\mathrm{S} + p_0 V = \sum_{a \in a_\mathrm{L} \cup a_\mathrm{S}} N_a \mu_a, \tag{156}$$

because both phases are in the diffusionial equilibrium homogeneous. Let us introduce $\mu_a^* = \mu_a - \bar{\mu}_a(T)$ to obtain after some elementary manipulations

$$\begin{aligned} \mathcal{A} &= \sum_{a \in a_\mathrm{L} \cup a_\mathrm{S}} N_a \bar{\mu}_a + \sum_{a \in a_\mathrm{L} \cup a_\mathrm{S}} N_a \mu_a^* \\ &= N_0 (X_0 \bar{\mu}_{\mathrm{As_L}} + (1 - X_0) \bar{\mu}_{\mathrm{Ga_L}}) + \sum_{a \in a_\mathrm{L} \cup a_\mathrm{S}} N_a \mu_a^* = \bar{\mathcal{A}} + \sum_{a \in a_\mathrm{L} \cup a_\mathrm{S}} N_a \mu_a^*. \end{aligned} \tag{157}$$

We will study now $\mathcal{A}$ for given parameters T, p_0, X_0 as a function of the single variable

$$y = \frac{Y_{\mathrm{As}}}{\bar{Y}_{\mathrm{As}}}, \tag{158}$$

depending on three possibilities to eliminate the other variables in the function $\mathcal{A}(T, p_0, X_0; Y_{\mathrm{Ga}_\alpha}, Y_{\mathrm{As}_\alpha}, Y_{\mathrm{V}_\alpha}, Y_{\mathrm{As}_\beta}, Y_{\mathrm{V}_\beta}, Y_{\mathrm{As}_\gamma}, Y_{\mathrm{V}_\gamma}, X_{\mathrm{L}})$.

The three constraints (153) are used to eliminate Y_{Ga_α}, Y_{As_β} and Y_{V_γ}. Next we assume that (i) chemical equilibria and (ii) equilibria of the vacancies at the interface are instantaneously established, so that we can use the equations (154) and $(155)_3$ to eliminate Y_{As_α}, Y_{V_α}, Y_{As_β} and Y_{V_β} to end up with the function $\mathcal{A}(T, p_0, X_0; y, X_{\mathrm{L}})$.

Finally we eliminate the liquid mole fraction X_{L}, and to this end we consider three different cases. 1. X_{L} will be eliminated by means of the interfacial condition $(155)_1$. 2. X_{L} will be eliminated by means of $(155)_2$. 3. We calculate the so called liquidus equation from (154) and (155), see [25, 37, 17]. The equation reads

$$\mu^*_{\mathrm{Ga_L}} + \mu^*_{\mathrm{As_L}} = \mu^*_{\mathrm{Ga}_\alpha} + \mu^*_{\mathrm{As}_\beta} + \mu^*_{\mathrm{V}_\gamma}. \tag{159}$$

In any case we end up with three different functions $\mathcal{A}(T, p_0, X_0; y)$ for the available free energy depending on a single variable.

We consider a total arsenic mole fraction $X_0 = \bar{X}_{\mathrm{S}}(T^{\max}) = 0.500082$. In this case the liquid phase only exists below $T = 1007.8°\mathrm{C}$, whereas $X_{\mathrm{S}} = X_0$ holds between $T = 1007.8°\mathrm{C}$ and the congruent melting point $T^{\max} = 1238.78°\mathrm{C}$.

The available free energies corresponding to the three considered cases, which obviously yield the same minimum, are now plotted in Figure 7 for $T = 926.85°\mathrm{C}$ and $p_0 = 100$ bar. Note that the deviation of the location of the minimum from $y = 1$, which would result for $p_0 = \bar{p}(T)$, exhibits the compressibilities of liquid and solid.

The three different curvatures in Figure 7 would become important in a dynamic calculation of the approach of a system, which is in partial equilibrium, to total equilibrium.

7.4 The non-standard phase diagram for the system with a single liquid droplet

In this section we consider the liquid/solid system from Figure 3 containing a liquid droplet with the interfacial radius r_{I}. The droplet is embedded in a solid GaAs matrix. The external pressure is adjusted by means of an inert gas.

Recall that we have already solved in Section 6 the mechanical part of the problem. The solution represents strains and stresses by explicit functions that depend on the parameters T and p_0 and on the variables X_{L} and r_{I}.

The remaining unknowns are thus given by the lattice occupancies Y_{Ga_α}, Y_{As_α}, Y_{V_α}, Y_{As_β}, Y_{V_β}, Y_{As_γ}, Y_{V_γ}, the liquid mole fraction X_{L} and the interfacial radius r_{I}. These

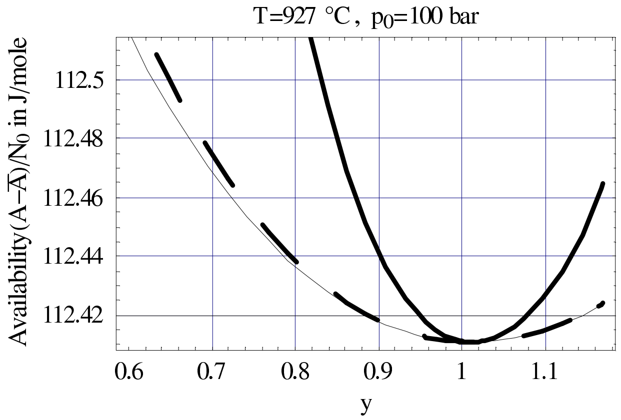

Figure 7: Available free energies for liquid/solid equilibrium. Both phases are under the common pressure $p_0 = 100$ bar. Thick line: Equilibrium condition $(155)_2$ is already established. Dashed Line: Equilibrium condition $(155)_1$ is already established. Thin line: Equilibrium condition (159) is already established.

unknowns are determined by the extrema of the available free energy. The arsenic mole fraction X_{S} of the solid is again given by (149).

The determination of the extrema relies as before on the necessary conditions for equilibrium (153), (154) and (155). Additionally we need the equation (152) for r_{I}, which reads explicitly

$$Z = \frac{4\pi}{3N_0}\bar{n}_{\mathrm{L}}(T)\Big(1 - 3\big(a_{\mathrm{L}}(T, p_0; X_{\mathrm{L}}, y, r_{\mathrm{I}}) - h^*_{\mathrm{L}}(T, X_{\mathrm{L}})\big)\Big)r_{\mathrm{I}}^3, \tag{160}$$

where a_{L} is given by (145). Furthermore h^*_{L} is given by $h^*_{\mathrm{L}} = (1-\mathcal{M}(X_{\mathrm{L}})/\mathcal{M}(\bar{X}_{\mathrm{L}}))/3$. Due to the appearance of the phase fraction Z in (160) we need furthermore the equation (150) for the determination of Z.

In summary, we conclude that a phase diagram can be calculated if the parameters T, p_0, X_0 and N_0 are given. It follows that the mean arsenic mole fraction and the total mole number of the system now do influence the phase diagram. This behaviour is in contrast to the case without surface tension and stress deviators. Furthermore note that the phase fraction is here among the variables that determine the extrema of the available free energy. This fact constitutes a main difference to the previous case, where the location of the extrema are independent of the phase fraction.

We proceed to calculate phase diagrams. The phase diagram of Figure 8 relies on the choice $p_0 = 1$bar, $X_0 = 0.500082$, $N_0 = 3.8\ 10^{-14}$mole.

We observe that in the temperature range, where two phases may coexist, there are two extrema for a given temperature. The parts of the current solidus and liquidus lines, which are located near to the solidus and liquidus lines of the standard phase diagram consists of minima of the available free energy. The remaining parts of the solidus and liquidus lines correspond to maxima of the available free energy. This

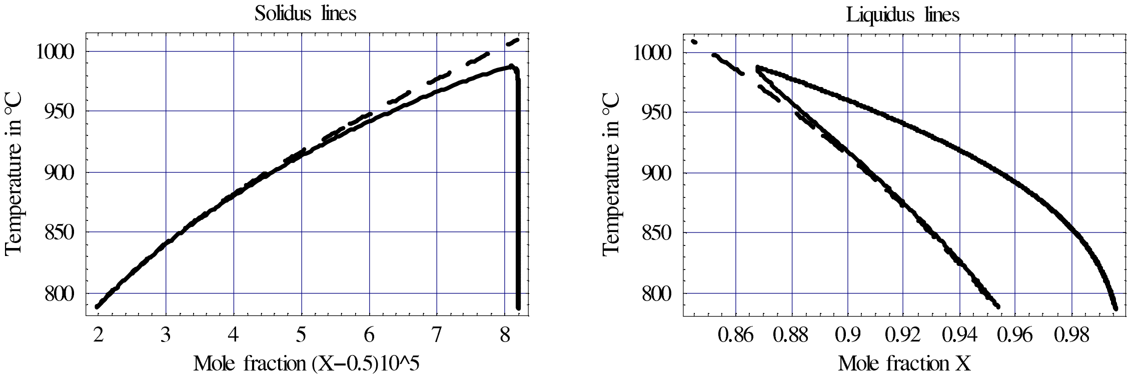

Figure 8: Phase diagram for $p_0 = 1$ bar, $N_0 = 3.810^{-14}$ mole. Left: solidus lines. Right: liquidus lines. Solid lines: Liquid droplet embedded in a solid phase. Dashed lines: Corresponding lines of the standard phase diagram.

proposition will be exhibited at the end of this section. Note that the location of the maxima of the solidus line are quite near to the total arsenic mole fraction X_0.

The minima describe stable droplets, whereas the maxima may be related to critical droplets in the following sense: A droplet that appears by fluctuation with a radius, which is smaller than the critical radius will disappear, whereas the droplet will further grow, if it has initially a radius which is larger than the critical radius.

A further difference to the standard phase diagram is a dependence of the non-standard phase diagram on the total mole number N_0 of atoms of the system. A doubling of N_0 increases the range of temperature, where both phases may coexist, by 5 K.

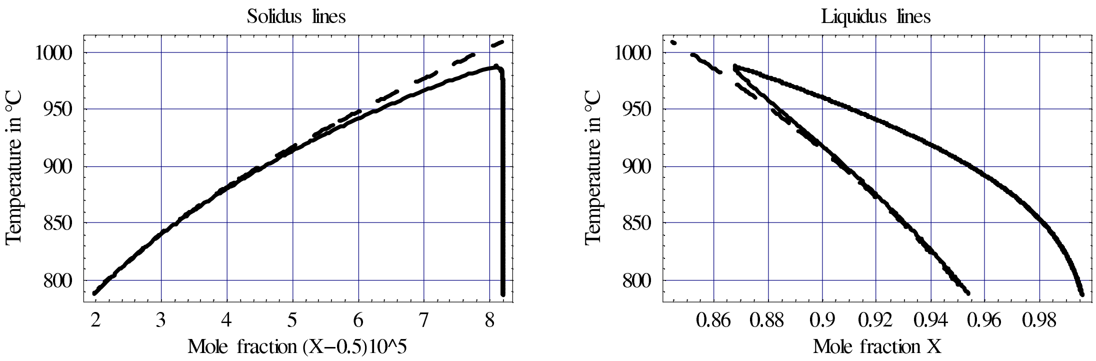

Figure 9: Phase diagram for $p_0 = 1$ bar, $N_0 = 10^{-14}$ mole. Left: solidus lines. Right: liquidus lines. Solid lines: Liquid droplet embedded in a solid phase. Dashed lines: Corresponding lines of the standard phase diagram.

¿From Figure 10 we may read off that the number of atoms in a stable droplet is proportional to the total mole number of the system, whereas the number of atoms in a critical droplet does not depend on the size of the system, i.e. on the total mole number.

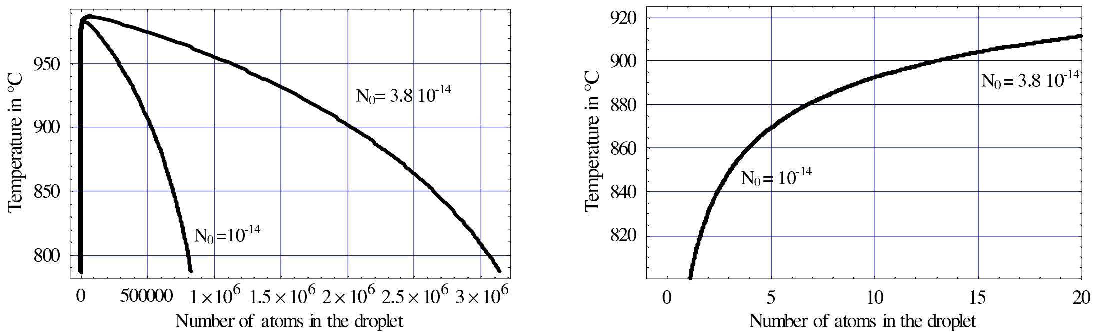

Figure 10: Number of atoms in a stable droplet for $p_0 = 1$bar, $N_0 = 10^{-14}$mole and $N_0 = 3.8\ 10^{-14}$mole, respectively. Left: Number of atoms in stable and critical droplets. Right: Zoom of the critical droplet from the left hand side. Here the curves for $N_0 = 10^{-14}$mole and $N_0 = 3.8\ 10^{-14}$mole are in fact indistinguishable.

However, the number of atoms in a critical droplet depends sensitively on the magnitude of surface tension. Unfortunately, there is a rare data basis for surface tension of liquid arsenic, so that we have used $\sigma = 0.075$ N/m for liquid water at 0°C as a guess. A doubling of this value has no influence at all. Not until we reduce the surface tension to 0.020 N/m, we observe a change of the phase diagram, because now the surface tension cannot compensate the misfit of the droplet, whereupon the liquid needs more space than the solid phase. A decrease from $\sigma = 0.075$ N/m to $\sigma = 0.020$ N/m increases the maximal temperature for coexistence by 21 K.

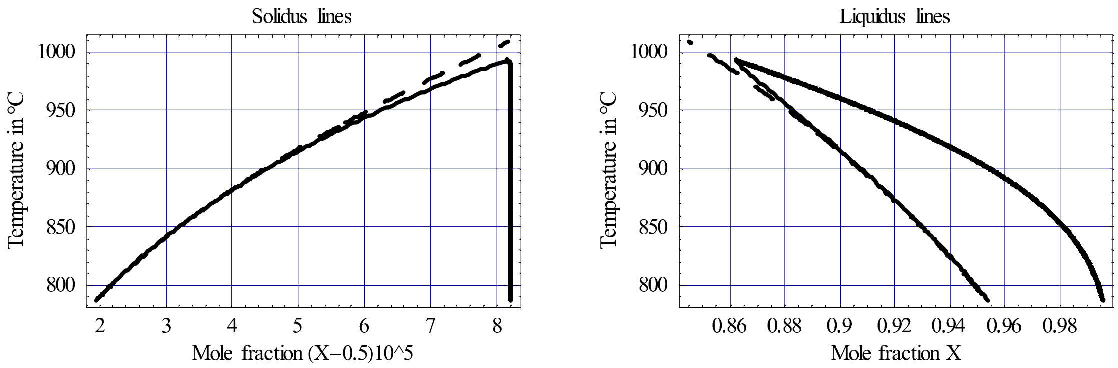

Figure 11: Phase diagrams for $p_0 = 1$ bar and $N_0 = 3.8\ 10^{-14}$ mole. $\sigma = 0.075$ N/m is replaced by $\sigma = 0.020$ N/m. Left: Solidus lines. Right: Liquidus lines. Solid lines: Liquid droplet embedded in a solid phase. Dashed lines: Corresponding lines of the standard phase diagram.

The number of atoms in a stable droplet is not influenced by a modification of the surface tension, whereas the number of atoms in a critical droplet decreases significantly, see Figure 12.

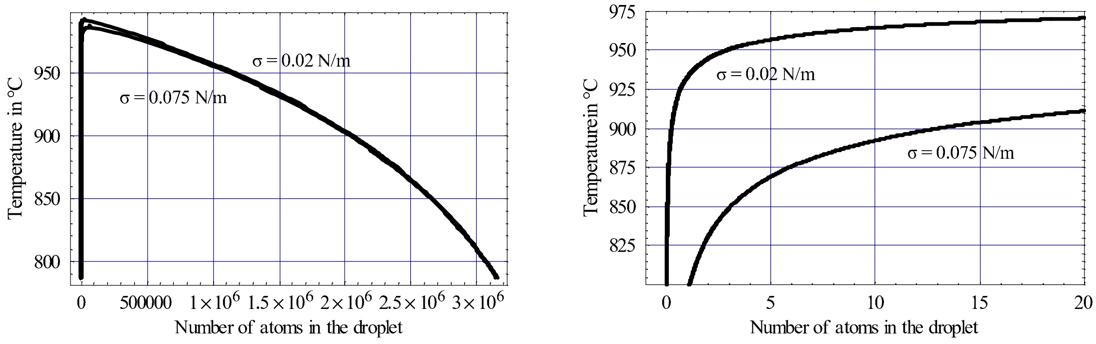

Figure 12: Number of atoms in a droplet for $p_0 = 1$ bar, $N_0 = 3.8\ 10^{-14}$mole. Left: Number of atoms for $\sigma = 0.020$ N/m. Right: Zoom of the critical droplet from the left hand side. Upper curve: $\sigma = 0.020$ N/m. Lower curve: $\sigma = 0.075$ N/m.

Finally we discuss again the available free energy as a function of a single variable, see the corresponding discussion in Subsection 7.3 for comparison. The generalisation of the expression (157), which is due to surface tension and stress deviators, reads

$$\begin{aligned}
\mathcal{A} &= \Psi_\mathrm{L} + \Psi_\mathrm{S} + 4\pi\sigma r_\mathrm{I}^2 + p_0 V \\
&= \sum_{a\in a_\mathrm{L}\cup a_\mathrm{S}} N_a \bar{\mu}_a + \sum_{a\in a_\mathrm{L}\cup a_\mathrm{S}} N_a \mu_a^* + \frac{4\pi\sigma r_\mathrm{I}^2}{3} + \frac{4\pi r_\mathrm{I}^3}{3}\sigma^{\langle rr\rangle} \qquad (161)\\
&= \bar{\mathcal{A}} + \sum_{a\in a_\mathrm{L}\cup a_\mathrm{S}} N_a \mu_a^* - \frac{N_0 Z}{n_\mathrm{L}^\mathrm{R}(T)}\Bigg(6G_\mathrm{S} b_\mathrm{I}(T,p_0;y,X_\mathrm{L},r_\mathrm{I}) \\
&\qquad -\frac{3}{2}\Big(k_\mathrm{S}(T)\big(a(T,p_0;y) - h^*(T,p_0;y)\big) \\
&\qquad - k_\mathrm{L}(T)\big(a_\mathrm{L}(T,p_0;y,X_\mathrm{L},r_\mathrm{I}) - h_\mathrm{L}^*(T,p_0;X_\mathrm{L})\big)\Big)\Bigg),
\end{aligned}$$

where the phase fraction Z is calculated according to (160).

As before we study $\mathcal{A}$ for given parameters T, p_0, X_0 as a function of the relative lattice occupancy y. To this end we use again the three constraints (153), and we assume, as before, that (i) chemical equilibria and (ii) equilibria of the vacancies at the interface are instantaneously established, so that we can use the equations (154) and $(155)_3$ to eliminate Y_{As_α}, Y_{V_α}, Y_{As_β} and Y_{V_β} to end up with the function $\mathcal{A}(T,p_0,X_0,N_0;y,X_\mathrm{L})$.

Regarding the elimination of the liquid mole fraction we repeat the discussion from page 40 of Subsection 7.3: We consider again the three alternatives to eliminate X_L. 1. X_L will be eliminated by means of the interfacial condition $(155)_1$. 2. X_L will be eliminated by means of $(155)_2$. 3. We use the liquidus equation, which reads now

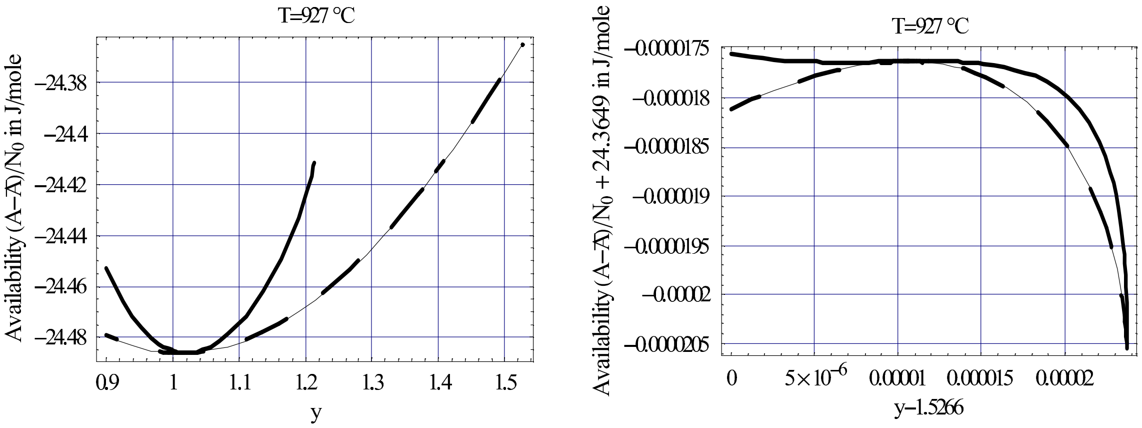

Figure 13: Available free energies for $X_0 = 0.500082$, $N_0 = 3.8\ 10^{-14}$ mole, $p_0 = 1$ bar. Left: Thick line: Equilibrium condition $(155)_2$ is already established. Dashed Line: Equilibrium condition $(155)_1$ is already established. Thin line: Equilibrium condition (162) is already established. Right: Zoom of the of the vicinity of $y = 1.522$. The usage of $(155)_2$ leads to an inflection point. In all three cases, for $y > 1.527$ there is no liquid phase anymore.

with mechanical terms

$$\mu^*_{\mathrm{Ga_L}}(T, p_0; X_\mathrm{L}) + \mu^*_{\mathrm{As_L}}(T, p_0; X_\mathrm{L}) = \mu^*_{\mathrm{Ga}_\alpha}(T, p_0; y) + \mu^*_{\mathrm{As}_\beta}(T, p_0; y) + \mu^*_{\mathrm{V}_\gamma}(T, p_0; y)$$
$$+ 4G\tilde{b}_\mathrm{I}(T, p_0, X_0, N_0; X_\mathrm{L}, y)\frac{M_\mathrm{Ga} + M_\mathrm{As}}{\bar{\rho}_\mathrm{S}(T)}. \quad (162)$$

Note that the function $\tilde{b}_\mathrm{I}(T, p_0, X_0, N_0; X_\mathrm{L}, y)$ results from the previous introduced function $b_\mathrm{I}(T, p_0; X_\mathrm{L}, r_\mathrm{I})$ by substituting at first the interfacial radius r_I by the phase fraction Z, see (160), and hereafter we replace the phase fraction by the relative lattice occupancy y, see (150) and (149).

There result three representations for the available free energy, see Figure 13, that have the following peculiarities. If the process of eliminations is carried out by $(155)_1$ and the liquidus equation (162), respectively, we have minima and maxima at the same location. On the other hand, if we use instead the equation $(155)_2$, the previous maximum changes to an inflection point, whereas the minimum remains. We conclude that there must be a new maximum between the minimum and the inflection point. However, it turns out, that in this region non-admissible solutions with $X_\mathrm{L} > 1$ appear, see Figure 14.

The physical reasoning of the discussed three possibilities to calculate the available free energy as a function of a single variable, $\mathcal{A}(T, p_0, X_0, N_0; y)$, relies on the assumption that the used necessary conditions for equilibrium are established with different relaxation times, that are much larger as the relaxation time of the non-used condition that finally determine the extrema of $\mathcal{A}$.

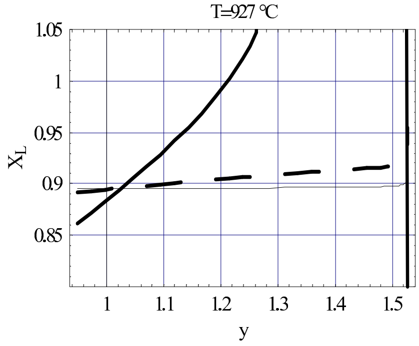

Figure 14: Liquid mole fraction. Data and details as in Figure 13. Note the non-admissible region $X_{\rm L} > 1$.

8 Summary and outlook

In this study we have proposed a model that is designed to simulate the appearance of liquid droplets in semi-insulating GaAs. The main part of the study regards the incorporation of mechanical stresses in the thermodynamic equations that describe phase transitions without surface tension and deviatoric stresses.

Section 7 contains as a first application the calculation of non-standard phase diagrams. An extensive comparison with classical phase diagrams are include here.

Further applications of the model regard (i) the diffusion problem of an evolving liquid droplet within a solid matrix, and (ii) the evolution of a many droplet system and, in particular, the determination of the size distributions of the droplets. These tasks are described in [8] and [6].

Appendix

A Proof of the thermodynamic inequality (65)

The proof of the fundamental inequality needs several steps. In this appendix we refer to the system of Figure 1. In the first step we calculate the time derivative of the free energy of the solid phase. Reynolds transport theorem gives

$$\frac{d\Psi_{\rm S}}{dt} = \int\limits_{\Omega_{\rm S}} \frac{\partial \rho_{\rm S}\psi_{\rm S}}{\partial t} dV + \oint\limits_{\partial\Omega_{\rm S}} \rho_{\rm S}\psi_{\rm S} W^i da^i \quad \text{with} \quad W^i = \begin{cases} v^i & \partial\Omega_{\rm S}\backslash I \\ & \text{on} \\ w^i & I \end{cases} \tag{163}$$

The surface integral can be rewritten due to the divergence theorem, and after some simple manipulations, we finally obtain

$$\frac{d\Psi_{\rm S}}{dt} = \int\limits_{\Omega_{\rm S}} \big((\rho_{\rm S}\psi_{\rm S})^{\cdot} - \psi_{\rm S}\dot{\rho}_{\rm S}\big) dV + \int\limits_{I} \psi_{\rm S}\dot{m}_{\rm S} da. \tag{164}$$

Next we use the Gibbs equation (33), the Gibbs-Duhem equation (34) and the identities

$$\dot{c}^{ij} = J^{(-2/3)}\left(\frac{2}{3}\frac{\dot{\rho}}{\rho}C^{ij} + \dot{C}^{ij}\right), \quad \frac{\dot{\rho}}{\rho} = -\frac{1}{2}(C^{-1})^{li}\dot{C}^{il} \quad \text{and} \quad t^{ij}\dot{C}^{ij} = 2J\sigma^{ij}\frac{\partial \upsilon^i}{\partial x^j} \tag{165}$$

to calculate the material time derivative $(\rho\psi)^{\cdot}$. There results

$$(\rho\psi)^{\cdot} = \sum_a \mu_a \dot{n}_a - \frac{p}{\rho}\dot{\rho} + \sigma^{ij}\frac{\partial \upsilon^i}{\partial x^j}. \tag{166}$$

Thus we may now write (164)

$$\frac{d\Psi_{\mathrm{S}}}{dt} = \int_{\Omega_{\mathrm{S}}} \left(\sum_{a\in a_{\mathrm{S}}} \mu_a \dot{n}_a - g\dot{\rho}\right) dV + \int_{\Omega_{\mathrm{S}}} \sigma^{ij}\frac{\partial \upsilon^i}{\partial x^j} dV + \int_I \psi^+ \dot{m}_{\mathrm{S}} da. \tag{167}$$

The second integral will be further exploited to give

$$\begin{aligned}\int_{\Omega_{\mathrm{S}}} \sigma^{ij}\frac{\partial \upsilon^i}{\partial x^j} dV &= \int_{\Omega_{\mathrm{S}}} \frac{\partial \sigma^{ij}\upsilon^i}{\partial x^j} dV - \int_{\Omega_{\mathrm{S}}} \frac{\partial \sigma^{ij}}{\partial x^j}\upsilon^i dV \\ &= \int_{\partial\Omega_{\mathrm{S}}\setminus I} \sigma^{ij}\upsilon^i da^j - \int_I (\upsilon^+)^i \sigma_+^{ij}\nu^j da - \int_{\Omega_{\mathrm{S}}} \frac{\partial \sigma^{ij}}{\partial x^j}\upsilon^i dV\,. \end{aligned} \tag{168}$$

Next we use the agreement $w^i = w_\nu \nu^i$ and the decomposition $(\upsilon^+)^i = (\upsilon^+)^\alpha_\tau\, \tau^i_\alpha + \upsilon^+_\nu \nu^i$ to give an alternative representation of the integral over the interface:

$$\int_I \sigma_+^{ij}\upsilon^i\nu^j da = \int_I \sigma_+^{ij}\nu^i\nu^j(\upsilon^+_\nu - w_\nu) da + \int_I \sigma_+^{\langle ij\rangle}\tau^i_\alpha\nu^j(\upsilon^+)^\alpha_\tau\, da + \int_I \sigma_+^{ij}\nu^i\nu^j w_\nu da. \tag{169}$$

Finally we insert (169) into (168) and introduce the result in (167). This yields

$$\begin{aligned}\frac{d\Psi_{\mathrm{S}}}{dt} =& -\int_{\Omega_{\mathrm{S}}} \frac{\partial \sigma_+^{ij}}{\partial x^j}\upsilon^i dV + \int_{\partial\Omega_{\mathrm{S}}\setminus I} \sigma^{ij}\upsilon^i da^j - \int_I \sigma_+^{\langle ij\rangle}\tau^i_\alpha\nu^j\upsilon^\alpha_\tau da - \int_I \sigma_+^{ij}\nu^i\nu^j w_\nu da \\ &+ \int_{\Omega_{\mathrm{S}}} \left(\sum_{a\in a_{\mathrm{S}}} \mu_a\dot{n}_a - g\dot{\rho}\right) dV + \int_I \left(g^+ - \frac{1}{\rho^+}\sigma_+^{\langle ij\rangle}\nu^i\nu^j\right)\dot{m}_{\mathrm{S}} da. \end{aligned} \tag{170}$$

A similar representation results for the time derivative of the free energy for the liquid phase:

$$\begin{aligned}\frac{d\Psi_{\mathrm{L}}}{dt} =& \int_{\Omega_{\mathrm{L}}} \frac{\partial p}{\partial x^i}\upsilon^i dV - \int_{\partial\Omega_{\mathrm{L}}\setminus I} p\upsilon^i da^i - \int_I p^- w_\nu da \\ &+ \int_{\Omega_{\mathrm{L}}} \left(\sum_{a\in a_{\mathrm{L}}} \mu_a\dot{n}_a - g\dot{\rho}\right) dV - \int_I g^-\dot{m}_{\mathrm{L}} da. \end{aligned} \tag{171}$$

In the second step we exploit the integrand of the fifth integral in (170). We replace $\dot{n}_a$ by the side conditions (54) and (59). By means of the Gibbs/Duhem equation (34) there results

$$\int\limits_{\Omega_{\mathrm{S}}} \left(\sum_{a\in a_{\mathrm{S}}} \mu_a \dot{n}_a - g\dot{\rho}\right) dV = \int\limits_{\Omega_{\mathrm{S}}} \left(-\sum_{a\in a_{\mathrm{S}}} \mu_a \frac{\partial j_a^i}{\partial x^i} + \sum_r \Gamma^r \left(\sum_{a\in a_{\mathrm{S}}} \gamma_a^r \mu_a\right)\right) dV$$
$$= \int\limits_{\Omega_{\mathrm{S}}} \sum_{a\in a_{\mathrm{S}}} j_a^i \frac{\partial \mu_a}{\partial x^i} dV - \int\limits_{\partial\Omega_{\mathrm{S}}\setminus I} \sum_{a\in a_{\mathrm{S}}} \mu_a j_a^i da^i + \int\limits_I \sum_{a\in a_{\mathrm{S}}} \mu_a j_a^i \nu^i da + \sum_r \int\limits_{\Omega_{\mathrm{S}}} \Gamma^r \left(\sum_{a\in a_{\mathrm{S}}} \gamma_a^r \mu_a\right) dV. \tag{172}$$

There are neither chemical reactions nor gradients of the mole densities in the liquid, so that the corresponding integral gives

$$\int\limits_{\Omega_{\mathrm{L}}} \left(\sum_{a\in a_{\mathrm{L}}} \mu_a \dot{n}_a - g\dot{\rho}\right) dV = -\int\limits_{\partial\Omega_{\mathrm{L}}\setminus I} \sum_{a\in a_{\mathrm{L}}} \mu_a j_a^i da^i - \int\limits_I \sum_{a\in a_{\mathrm{L}}} \mu_a j_a^i \nu^i da. \tag{173}$$

It remains to calculate the time derivatives of the volumes V_{S} and V_{L} and of the interface surface, which explicitly appear in the representation (65) of the free energy.

We have the transport theorems, see [1] and [20] for details, for volume and surface integrals:

$$\frac{dV_{\mathrm{S/L}}}{dt} = \oint\limits_{\partial\Omega_{\mathrm{S/L}}} W^i da^i = \int\limits_{\partial\Omega_{\mathrm{S/L}}\setminus I} \upsilon^i da^i \mp \int\limits_I w_\nu da, \tag{174}$$
$$\frac{d}{dt} \int\limits_I da = -2 \int\limits_I k_{\mathrm{M}} w_\nu \, da. \tag{175}$$

which are used for the calculation of $\partial\mathcal{A}/dt$. The following intermediate result uses all the identities of the above, and additionally the side condition (63). It follows

$$\frac{d\mathcal{A}}{dt} = -\int\limits_{\Omega_{\mathrm{S}}} \frac{\partial\sigma^{ij}}{\partial x^j} \upsilon^i dV + \int\limits_{\Omega_{\mathrm{L}}} \frac{\partial p_{\mathrm{L}}}{\partial x^i} \upsilon^i dV + \int\limits_{\partial\Omega_{\mathrm{S}}\setminus I} (\sigma^{ij} + p_0 \delta^{ij}) \upsilon^i da^j - \int\limits_{\partial\Omega_{\mathrm{L}}\setminus I} (p_{\mathrm{L}} - p_0) \upsilon^i da^i$$
$$- \int\limits_I (\sigma^{ij}\nu^i\nu^j + p_{\mathrm{L}} + 2\sigma k_{\mathrm{M}}) w_\nu da - \int\limits_I \sigma^{ij} \tau_\alpha^i \nu^j \upsilon_\tau^\alpha da$$
$$+ \int\limits_I \left(\sum_{a\in a_{\mathrm{S}}} \left(\mu_a - \frac{M_a}{\rho_{\mathrm{S}}} \sigma^{\langle ij\rangle} \nu^i \nu^j\right) \dot{\mathcal{N}}_a - \sum_{a\in a_{\mathrm{L}}} \mu_a \dot{\mathcal{N}}_a\right) da - \int\limits_{\partial\Omega_{\mathrm{L}}\setminus I} \sum_{a\in a_{\mathrm{L}}} \mu_a j_a^j da^j$$
$$- \int\limits_{\partial\Omega_{\mathrm{S}}\setminus I} \sum_{a\in a_{\mathrm{S}}} \mu_a j_a^j da^j + \int\limits_{\Omega_{\mathrm{S}}} \sum_{a\in a_{\mathrm{S}}} j_a^i \frac{\partial\mu_a}{\partial x^i} dV + \int\limits_{\Omega_{\mathrm{S}}} \sum_{r=1}^{2} \left(\sum_{a\in a_{\mathrm{S}}} \gamma_a^r \mu_a\right) \Gamma^r dV \le 0. \tag{176}$$

Next we rewrite the 7^{th} integral of (176), and to this end we take care for the side conditions (52), (60), (63) and (64):

$$\int_I \left(\sum_{a\in a_{\mathrm{S}}} \left(\mu_a - \frac{M_a}{\rho_{\mathrm{S}}} \sigma_+^{\langle ij\rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_a - \sum_{a\in a_{\mathrm{L}}} \mu_a \dot{\mathcal{N}}_a \right) da$$
$$= \int_I \left(\left(\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{Ga_L}} - \mu_{\mathrm{V}_\alpha} - \frac{M_{\mathrm{Ga}}}{\rho_{\mathrm{S}}} \sigma^{\langle ij\rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{Ga}_\alpha} \right.$$
$$+ \left(\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{As_L}} - \mu_{\mathrm{V}_\alpha} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}} \sigma^{\langle ij\rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{As}_\alpha}$$
$$+ \left(\mu_{\mathrm{As}_\beta} - \mu_{\mathrm{As_L}} - \mu_{\mathrm{V}_\beta} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}} \sigma^{\langle ij\rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{As}_\beta}$$
$$+ \left(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - \mu_{\mathrm{As_L}} - \frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}} \sigma^{\langle ij\rangle} \nu^i \nu^j \right) \dot{\mathcal{N}}_{\mathrm{As}_\gamma}$$
$$\left. + (\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma})(\dot{\mathcal{N}}_{\mathrm{V}_\gamma} + \dot{\mathcal{N}}_{\mathrm{As}_\gamma}) \right) da. \quad (177)$$

The 10^{th} integral of (176) is created in an analogues manner by inserting the side conditions (52), (56) and (60):

$$\int_{\Omega_{\mathrm{S}}} \sum_{a\in a_{\mathrm{S}}} j_a^i \frac{\partial \mu_a}{\partial x^i} dV = \int_{\Omega_{\mathrm{S}}} (j^i_{\mathrm{V}_\gamma} + j^i_{\mathrm{As}_\gamma}) \frac{\partial(\mu_{\mathrm{V}_\alpha} + \mu_{\mathrm{V}_\beta} + \mu_{\mathrm{V}_\gamma})}{\partial x^i} dV$$
$$+ \int_{\Omega_{\mathrm{S}}} j^i_{\mathrm{As}_\alpha} \frac{\partial(\mu_{\mathrm{As}_\alpha} - \mu_{\mathrm{V}_\alpha} - (\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha}) M_{\mathrm{As}}/M_{\mathrm{Ga}})}{\partial x^i} dV$$
$$+ \int_{\Omega_{\mathrm{S}}} j^i_{\mathrm{As}_\beta} \frac{\partial(\mu_{\mathrm{As}_\beta} - \mu_{\mathrm{V}_\beta} - (\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha}) M_{\mathrm{As}}/M_{\mathrm{Ga}})}{\partial x^i} dV$$
$$+ \int_{\Omega_{\mathrm{S}}} j^i_{\mathrm{As}_\gamma} \frac{\partial(\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma} - (\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha}) M_{\mathrm{As}}/M_{\mathrm{Ga}})}{\partial x^i} dV. \quad (178)$$

The identities (177) and (178) are now inserted in (176), and there results the proposition (65).

B Some data regarding the standard reference system

We have solved the objective to determine non-standard phase diagrams by the application of the current model. The needed material data are provided by references to the standard reference system. In other words we are able to calculate explicitly non-standard phase diagrams if the functions $\bar{p}(T)$, $\bar{X}_{\mathrm{L}}(T)$, $k_{\mathrm{L}}(T)$, $\bar{n}_{\mathrm{L}}(T)$, $L_0(T)$,

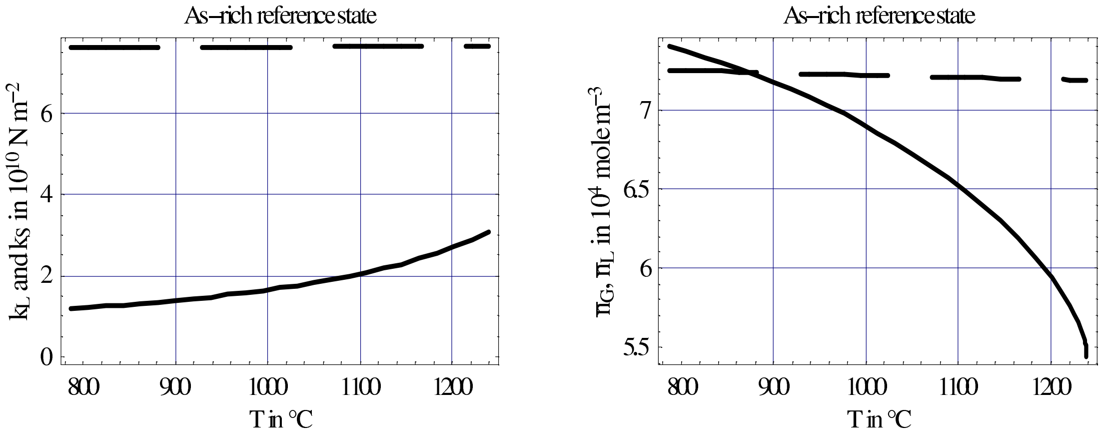

Figure 15: Material functions for the arsenic-rich region of the phase diagram. Left: Bulk moduli, dashed line: solid, solid line: liquid. Right: Mole densities, upper line: liquid arsenic, dashed line: liquid gallium, lower line: density of lattice sites in the solid.

$L_1(T)$ as well as $k_S(T), G_S(T), \bar{n}_G(T), \bar{Y}_{As_\alpha}(T), \bar{Y}_{V_\alpha}(T), \bar{Y}_{V_\beta}(T), \bar{Y}_{As_\gamma}(T)$, that refer to triple phase equilibria of the standard reference system, were known.

The functions $L_0(T)$ and $L_1(T)$ can be read off from Oates, Wenzl and Erikson [25]:

$$L_0(T) = (-25485 - 4.4T) \text{ J/mole} \quad \text{and} \quad L_1(T) = 5174.7 \text{ J/mole}. \tag{179}$$

The shear modulus within the isotropic approximation has been determined from cubic anisotropic data after [10]:

$$G_S(T) = 3.5364\ 10^{10} \text{ N m}^{-2}. \tag{180}$$

The functions $\bar{p}(T)$ and $\bar{X}_L(T)$, which result from the standard reference system, are already represented by Figures 4 and 5.

The remaining functions can be read of from Figures 15 and 16.

Acknowledgement

The presented model of semi-insulating GaAs at temperatures above the right eutectic line has been formulated in close collaboration with Stefan Eichler and Manfred Jurisch from FCM, and we are indebted for countless most fruitful discussions of various aspects of the model. The classical basis of the model has been established by Alan Oates and Heinrich Wenzl. Their comments and suggestions to our work are invaluable. This work was partly supported by BMBF grant under 03DRM3B5.

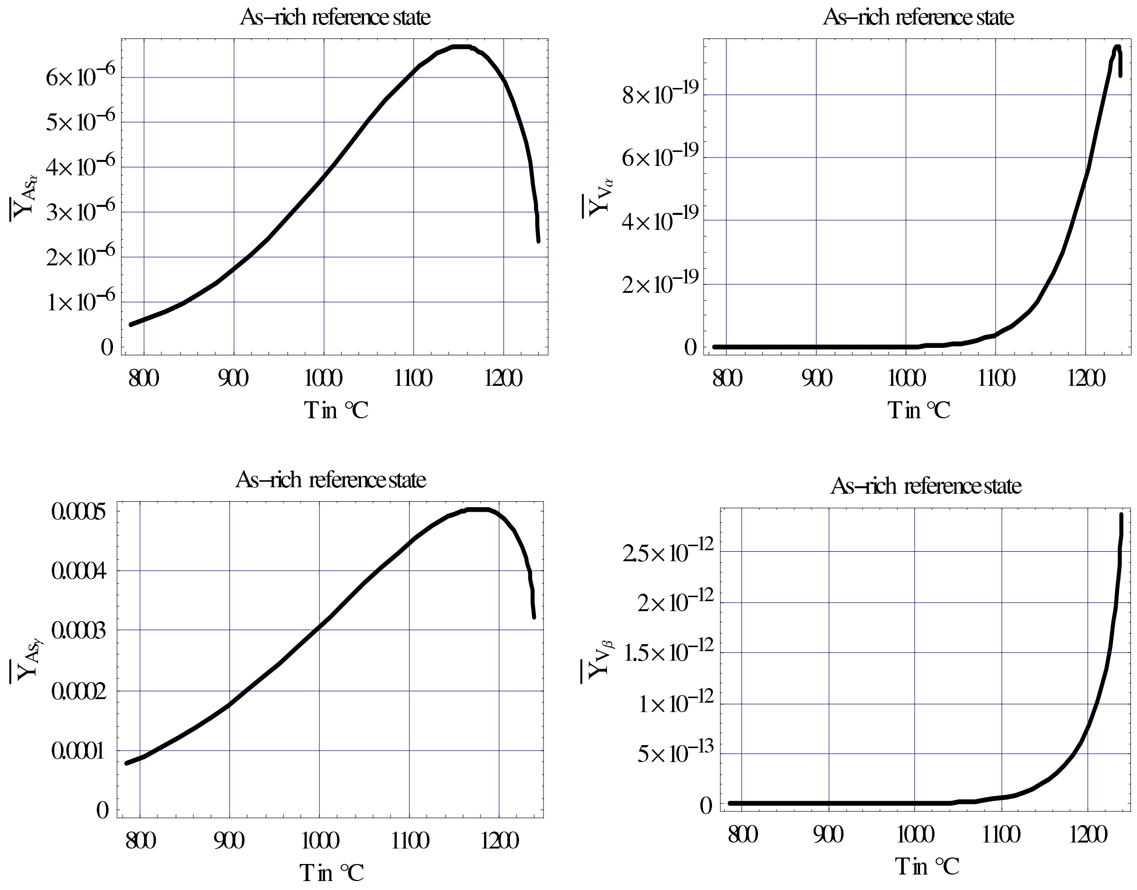

Figure 16: Lattice occupancies for the arsenic-rich region of the phase diagram.

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