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Diffusion in the vicinity of an evolving spherical arsenic droplet

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Abstract

We study the diffusion problem of liquid droplets in single crystal semi-insulating Gallium Arsenide (GaAs). This problem is posed by an industrial application, where the droplets, also called precipitates, appear during a necessary heat treatment of GaAs wafer. The subsequent dissolution of the droplets is mandatory, in order to use the wafer after the heat treatment as a substrate material for micro- and opto- electronic devices.

In this study we consider a single droplet in a solid matrix, which is in contact with an arsenic gas, so that the arsenic can cross the solid/gas interface. The model equations has been derived by the authors. They consist of a nonlinear diffusion equation with diffusion controlled and kinetic boundary conditions, respectively, at the liquid/solid interface. Furthermore we study at the solid/gas interface alternatively zero flux and Dirichlet conditions.

The latter appear due to different densities of liquid and solid GaAs. There is a large influence of these effects on diffusion, interface motion and phase diagrams, which are used to identify regions, where coexistence of liquid and solid phases is possible.

In order to study the evolution of the droplet, and in particular possibilities to enforce its dissolution, we solve several initial and boundary value problems for the diffusion system.

1 Introduction and setting of the problem

We consider an evolving phase transition between liquid and solid Gallium Arsenide, *GaAs*, at pressure p_0 and constant temperature T_0, where the liquid appears as small spherical droplets within a solid matrix. The droplets have radii on the nanometer scale, whereas their distances are between 1 and 2 μm. Our final objective is the determination of the size distribution of the droplets by means of a system of rate equations of the Becker/Döring type.

This task requires preliminary studies on non-standard phase diagrams that takes surface tension and mechanical stress fields into account. Moreover the diffusion problem of a single spherical droplet in a solid surrounding has to be solved.

The study on non-standard phase diagrams can be found in [1]. Among the various results we found the determination of critical radii r_{C}, so that a single droplet with $r_{\mathrm{I}} > r_{\mathrm{C}}$ growth further on, whereas it shrinks and finally disappears for $r_{\mathrm{I}} < r_{\mathrm{C}}$. The objective of the current study concerns the diffusion problem of a single droplet in a solid surrounding, which has initial radii below and above the critical radii.

To this end we consider a liquid sphere Ω_L with radius r_I which is surrounded by a solid sphere Ω_S with radius $r_\mathrm{O} > r_\mathrm{I}$. The liquid is a mixture of the two constituents of GaAs which we denote by $a_\mathrm{L} = \{\mathrm{Ga_L}, \mathrm{As_L}\}$. Their mole densities are $n_{\mathrm{Ga_L}}$ and $n_{\mathrm{As_L}}$. The solid phase is an ordered solid with three sublattices α, β, γ, respectively, with fcc symmetry and a common lattice constant. The sublattices thus have the same number of lattice sites, and they are occupied by the material constituents Ga and As and by vacancies V. According to the so called Freiberg model, As and V can be found on all sublattices, whereas Ga, due to its size, is only allowed to live on the sublattice α. Thus there are seven constituents in the solid, and we denote these by $a_\mathrm{S} = \{\mathrm{Ga}_\alpha, \mathrm{As}_\alpha, \mathrm{V}_\alpha, \mathrm{As}_\beta, \mathrm{V}_\beta, \mathrm{As}_\gamma, \mathrm{V}_\gamma\}$. Their mole densities are n_{Ga_α}, n_{As_α}, n_{V_α}, n_{As_β}, n_{V_β}, n_{As_γ}, n_{V_γ}.

For the description of the liquid and solid composition, we now introduce further quantities, that are commonly used in the literature. By means of the mole densities we define the mass densities of the phases:

$$\rho_\mathrm{S} = \sum_{a \in a_\mathrm{S}} M_a n_a, \quad \rho_\mathrm{L} = \sum_{a \in a_\mathrm{L}} M_a n_a. \tag{1}$$

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 $M_{\mathrm{Ga}_\alpha} = M_\mathrm{As}$.

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

Furthermore, with the total mole densities n_L, n_S and $n_{\mathrm{As_S}}$ we introduce the mole fractions of the material constituents, viz.

$$X_\mathrm{L} = \frac{n_{\mathrm{As_L}}}{n_{\mathrm{As_L}} + n_{\mathrm{Ga_L}}} = \frac{n_{\mathrm{As_L}}}{n_\mathrm{L}} \quad \text{and} \quad X_\mathrm{S} = \frac{n_{\mathrm{As}_\alpha} + n_{\mathrm{As}_\beta} + n_{\mathrm{As}_\gamma}}{n_{\mathrm{As}_\alpha} + n_{\mathrm{As}_\beta} + n_{\mathrm{As}_\gamma} + n_{\mathrm{Ga}_\alpha}} = \frac{n_{\mathrm{As_S}}}{n_\mathrm{S}}, \tag{2}$$

and for $a \in a_\mathrm{S}$ we introduce sublattice concentrations according to

$$Y_a = 3\frac{n_a}{n_{\mathrm{Ga}_\alpha} + n_{\mathrm{As}_\alpha} + n_{\mathrm{V}_\alpha} + n_{\mathrm{As}_\beta} + n_{\mathrm{V}_\beta} + n_{\mathrm{As}_\gamma} + n_{\mathrm{V}_\gamma}} = \frac{n_a}{n_\mathrm{G}}. \tag{3}$$

The quantity n_G gives the sublattice density. Recall that the sublattices have equal number of lattice sites, so that we have

$$Y_{\mathrm{Ga}_\alpha} + Y_{\mathrm{As}_\alpha} + Y_{\mathrm{V}_\alpha} = Y_{\mathrm{As}_\beta} + Y_{\mathrm{V}_\beta} = Y_{\mathrm{As}_\gamma} + Y_{\mathrm{V}_\gamma} = 1. \tag{4}$$

The phase transition of a piece of solid GaAs into liquid GaAs is accompanied by a change of its volume. Liquid GaAs needs more space than solid GaAs and for this reason, the liquid sphere is surrounded by a mechanical stress field with nonzero stress deviators. For the description of diffusion and the evolving liquid sphere, we are interested in a time scale, where mechanical equilibrium has already been established. Thus the stress can be calculated from the quasi-static momentum balance, where the time, t, appears only as a parameter.

We rely the determination of the stress on an isotropic elastic law, because the cubic anisotropy of the solid phase of GaAs is weak and will be ignored. In this case we may start from the symmetry assumption, that the displacement field has in in polar coordinates (r, ϑ, φ) the form $u^i = (u(t,r), 0, 0)$.

We conclude this Section by a summary. For any time $0 < t \leq t_f$, the objective of this study is the determination of

- the arsenic mole fraction and the mass density of the liquid:
$$X_{\rm L}(t,r), \quad \rho_{\rm L}(t,r) \quad \text{for} \quad 0 \leq r < r_{\rm I}(t), \tag{5}$$
- the sublattice concentrations and the the mass density of the solid:
$$Y_a(t,r), \quad a \in a_{\rm S}, \quad \rho_{\rm S}(t,r) \quad \text{for} \quad r_{\rm I}(t) \leq r \leq r_{\rm O}(t), \tag{6}$$
- the displacement field:
$$u(t,r) \quad \text{for} \quad r_{\rm I}(t) \leq r \leq r_{\rm O}(t), \tag{7}$$
- and the radius $r_{\rm I}(t)$ of the evolving liquid droplet.

For a solution of this problem we rely on further simplifying assumptions, which are partly motivated by experiments with semi-insulating GaAs at temperatures $T \gtrapprox 1100\text{K}$.

1. We assume that diffusional equilibrium in the liquid is much faster established than in the solid, so that the liquid densities are homogeneous in space.

2. There are chemical reactions in the solid that describe the transitions of the various constituents between the three sublattices, namely
$$\text{As}_\alpha + \text{V}_\beta = \text{As}_\beta + \text{V}_\alpha \quad \text{and} \quad \text{As}_\gamma + \text{V}_\beta = \text{As}_\beta + \text{V}_\gamma. \tag{8}$$
We assume, that local chemical equilibrium of these reactions is likewise much faster established than diffusional equilibrium in the solid.

3. We assume that the mobilities of the vacancies are much higher than the mobilities of the material constituents, and we consider the limiting case of local diffusional equilibrium of the vacancies.

4. The question whether the motion of the interface is *diffusion controlled* or *interface controlled* cannot be uniquely answered from existing experimental data. For this reason we have to study both regimes. However, in this paper we exclusively consider diffusion controlled motion of the interface.

These assumptions and the preceding setting will lead to the following mathematical structure of the problem: For a given distribution of atoms on the sublattices, we solve the mechanical problem of a liquid droplet with *misfit* in a solid surrounding. Hereafter we solve the diffusion problem where the coupling to the mechanical problem is given by explicit functions of the space variable r. The equations of the diffusion problem will consist of a single nonlinear diffusion equation and a set of nonlinear algebraic equations.

2 The mechanical boundary value problem

The mechanical boundary value problem concerns the variables u^i - displacement, ρ_{S} - mass density of the solid and ρ_{L} - mass density of the liquid.

If the displacement were known, we could determine ρ_S from to the well known geometric relation

$$\rho_S = \bar{\rho}_S(T) \det(\delta^{ij} - \frac{\partial u^i}{\partial x^j}) \approx \bar{\rho}_S(T)(1 - \frac{\partial u^k}{\partial x^k}). \tag{9}$$

The quantity $\bar{\rho}_S(T)$ is the temperature dependent density of a reference configuration. This is the state of a solid, where the strain

$$e^{ij} = \frac{1}{2}(\frac{\partial u^i}{\partial x^j} + \frac{\partial u^j}{\partial x^i}) \tag{10}$$

is zero. In this study we choose the triple phase equilibrium of GaAs under hydrostatic pressure $\bar{p}(T)$ as the reference state, see [1] for details.

The determination of the displacement relies on the quasi-static momentum balance for the cauchy stress σ^{ij}, which reads

$$\frac{\partial \sigma^{ij}}{\partial x^j} = 0. \tag{11}$$

We assume that the constitutive law for σ^{ij} in the liquid, respectively solid, is given by

$$\sigma^{ij} = \begin{cases} -p_{\mathrm{L}}(T, \rho_{\mathrm{L}})\delta^{ij} = -\Big(\bar{p}(T) + K_{\mathrm{L}}(T)\frac{\bar{\rho}_{\mathrm{L}}(T)}{\rho^*_{\mathrm{L}}}(\frac{\rho_{\mathrm{L}}}{\bar{\rho}_{\mathrm{L}}(T)} - \frac{\rho^*_{\mathrm{L}}}{\bar{\rho}_{\mathrm{L}}(T)})\Big)\,\delta^{ij} \\ \\ -\bar{p}(T)\delta^{ij} + K_{\mathrm{S}}(T)(\frac{\partial u^k}{\partial x^k} - 3h^*)\delta^{ij} + G_{\mathrm{S}}(T)(\frac{\partial u^i}{\partial x^j} + \frac{\partial u^j}{\partial x^i} - \frac{2}{3}\frac{\partial u^k}{\partial x^k}\delta^{ij}) \end{cases} \tag{12}$$

with

$$\rho^*_{\mathrm{L}} = \big(M_{\mathrm{Ga}}(1 - X_{\mathrm{L}}) + M_{\mathrm{As}}X_{\mathrm{L}}\big)\,\bar{n}_L \equiv M(X_{\mathrm{L}})\bar{n}_{\mathrm{L}} \tag{13}$$

and

$$h^* = 1 - \sqrt[3]{\frac{M_{\mathrm{Ga}}Y_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(Y_{\mathrm{As}_\alpha} + Y_{\mathrm{As}_\beta} + Y_{\mathrm{As}_\gamma})}{M_{\mathrm{Ga}}\bar{Y}_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(\bar{Y}_{\mathrm{AS}_\alpha} + \bar{Y}_{\mathrm{As}_\beta} + \bar{Y}_{\mathrm{As}_\gamma})}} \tag{14}$$

These laws describe a compressible liquid with bulk modulus K_{L}, and an isotropic elastic solid with bulk modulus K_{S} and shear modulus G_S.

For an illustration of the physical content of these laws we consider the liquid phase at first. Recall that a deformation of a liquid concerns a change of the mean distances of the atoms, which is obviously described by $n_{\mathrm{L}}/\bar{n}_{\mathrm{L}} - 1$. In terms of the liquid mass densities we have $\rho_{\mathrm{L}}/\bar{\rho}^*_{\mathrm{L}} - 1$, which can also be written as $\bar{\rho}_{\mathrm{L}}/\rho^*_{\mathrm{L}}(\rho_{\mathrm{L}}/\bar{\rho}_{\mathrm{L}} - \rho^*_{\mathrm{L}}/\bar{\rho}_{\mathrm{L}})$. The reasoning of the elastic law for the solid phase is the same, except that (12_2) results from a further linearization in the strain.

Next we consider the body Ω of Section 1 and assume spherical symmetry, i.e. $\rho_{\mathrm{L}} = \rho_L(t,r)$, $u^i = (u(t,r),0,0)$. The momentum balance yields

$$\frac{\partial p_L}{\partial r} = 0 \quad \text{in } \Omega_L \qquad \text{and} \qquad \frac{\partial \sigma^{rr}}{\partial r} + 2\frac{\sigma^{rr} - \sigma^{\varphi\varphi}}{r} = 0 \quad \text{in } \Omega_S. \tag{15}$$

Note that $\sigma^{\vartheta\vartheta} = \sigma^{\varphi\varphi}$, and σ^{rr} and $\sigma^{\varphi\varphi}$ are given by

$$\begin{aligned}
\sigma^{rr} &= -\bar{p}(T) + K_{\mathrm{S}}(T)\left(\frac{\partial u}{\partial r} + 2\frac{u}{r} - 3h^*\right) + \frac{4}{3}G_{\mathrm{S}}(T)\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right), \\
\sigma^{\varphi\varphi} &= -\bar{p}(T) + K_{\mathrm{S}}(T)\left(\frac{\partial u}{\partial r} + 2\frac{u}{r} - 3h^*\right) - \frac{2}{3}G_{\mathrm{S}}(T)\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right).
\end{aligned} \tag{16}$$

The field equations for ρ_{L} and u thus read

$$\frac{\partial \rho_L}{\partial r} = 0 \quad \text{in } \Omega_L, \qquad \text{and} \qquad \frac{\partial^2 u}{\partial r^2} + \frac{2}{r}\left(\frac{\partial u}{\partial r} - \frac{u}{r}\right) = \frac{\partial h^*}{\partial r}\frac{9K_S}{3K_S + 4G_S} \quad \text{in } \Omega_S. \tag{17}$$

Their solutions can be written as

$$\begin{aligned}
&\rho_L = \bar{\rho}_L(1 - 3a_L) \quad \text{in } \Omega_L \quad \text{and in } \Omega_S \\
&u(r) = \left(a + b_{\mathrm{I}}\left(\frac{r_{\mathrm{I}}}{r}\right)^3 + \frac{3k_{\mathrm{S}}}{3k_{\mathrm{S}} + 4G_{\mathrm{S}}}\left(h^*(r) - \frac{1}{r^3}\int_{r_{\mathrm{I}}}^{r} z^3 \frac{\partial h^*(z)}{\partial z}\, dz\right)\right) r.
\end{aligned} \tag{18}$$

The integration constants a_{L}, a and b_{I} may depend on time via the diffusion problem and they are determined by conditions at the outer boundary $r = r_{\mathrm{O}}$ and at the interface $r = r_{\mathrm{I}}$.

According to (9), the solution for the displacement yields

$$\rho_S = \bar{\rho}_S\left(1 - 3\left(a + \frac{3k_{\mathrm{S}}}{3k_{\mathrm{S}} + 4G_{\mathrm{S}}}h^*(r)\right)\right). \tag{19}$$

Due to this form we have chosen the integration constant for ρ_{L} by $(18)_1$ so that the similarity of both representations is exhibited.

The mechanical boundary conditions describe mechanical equilibrium, which is assumed to be established by a hydrostatic stress at the outer boundary and by the capillary force at the interface. Concerning the outer boundary we consider the limiting case $r_{\mathrm{O}} \to \infty$. The mechanical boundary conditions thus read

$$\lim_{r\to\infty} \sigma^{rr} = -p_0 \quad \text{on} \quad \partial\Omega_{\mathrm{S}} \backslash I \quad \text{and} \quad \sigma^{rr}(r_{\mathrm{I}}) + p_{\mathrm{L}} = \frac{2\sigma}{r_{\mathrm{I}}} \quad \text{on } I. \tag{20}$$

The quantity σ is the surface tension, which may depend on temperature. In (20) we insert

$$\begin{aligned}
\sigma^{rr} = -\bar{p} + 3K_{\mathrm{S}}&\left(a - \frac{4G_{\mathrm{S}}}{3K_{\mathrm{S}} + 4G_{\mathrm{S}}}h^*(r)\right) \\
&- 4G_{\mathrm{S}}\left(\frac{r_I}{r}\right)^3\left(b + \frac{3K_{\mathrm{S}}}{3K_{\mathrm{S}} + 4G_{\mathrm{S}}}\frac{1}{r_{\mathrm{I}}^3}\int_{r_{\mathrm{I}}}^{r} z^3 \frac{\partial h^*(z)}{\partial z}\, dz\right)
\end{aligned} \tag{21}$$

and p_L from (12) in order to obtain a and b in terms of ρ_L and r_I.

The determination of a_L, i.e. the liquid density ρ_L, relies on an assumption concerning the deformation during the phase transition. We introduce and motivate the assumption by means of a thought experiment.

We start from the current state of a solid sphere, which has a liquid phase with radius r_I and mass density $\rho_\mathrm{L} = M(X_\mathrm{L})n_\mathrm{L}$ at its center. Next we simulate a liquid-solid phase transition of the liquid sphere at constant mass, constant mole fraction X_L and fixed lattice occupancy Y_a in the solid phase. Due to the phase transition, the resulting solid sphere assumes the radius r_SL. Let the occupancies of vacancies at the radius r_SL be $Y_{\mathrm{V}_\mathrm{SL}} := (Y_{\mathrm{V}_\alpha} + Y_{\mathrm{V}_\beta} + Y_{\mathrm{V}_\gamma})_{r=r_\mathrm{SL}}$. Furthermore we assume that the original inner sphere has during its life as a solid phase, a homogeneous lattice occupancy of vacancies, which is given by $Y_{\mathrm{V}_\mathrm{SL}}$.

The current density of sublattice sites is denoted by n_GL implying a current mass density ρ_SL of the inner sphere according to

$$\rho_\mathrm{SL} = n_\mathrm{GL}(3 - Y_{\mathrm{V}_\mathrm{SL}})M(X_\mathrm{L}). \tag{22}$$

Due to conservation of mass we have

$$\rho_\mathrm{L} r_\mathrm{I}^3 = \rho_\mathrm{SL} r_\mathrm{SL}^3. \tag{23}$$

In its reference configuration, the outer sphere has zero strain and the reference mass density $\bar{\rho}_\mathrm{S} = \bar{n}_\mathrm{G}(3 - \bar{Y}_\mathrm{V})M(\bar{X}_\mathrm{S})$. The reference configuration of the inner sphere has zero strain with mass density $\bar{\rho}_\mathrm{SL} = \bar{n}_\mathrm{G}(3 - \bar{Y}_\mathrm{V})M(\bar{X}_\mathrm{L})$.

Moreover, we assume that both spheres have a common radius $R_\mathrm{I} = r_\mathrm{I} - u(r_\mathrm{I})$ in their reference states so that the right side of 23 can also be represented by

$$\rho_\mathrm{SL} r_\mathrm{SL}^3 = \bar{\rho}_\mathrm{SL}(r_\mathrm{I} - u(r_\mathrm{I}))^3. \tag{24}$$

Thus in combination with (23) we finally obtain the equation that allows the determination of the liquid density ρ_L.

In order to summarize the results we introduce the abbreviations

$$\kappa(T, r_\mathrm{I}) = \frac{2\sigma(T)}{3K_\mathrm{L}(T) r_\mathrm{I}} \qquad \delta(T) = \left(\frac{\bar{n}_\mathrm{L}(T)}{(3 - \bar{Y}_\mathrm{V}(T))\bar{n}_\mathrm{G}(T)}\right)^{1/3} - 1. \tag{25}$$

We obtain

$$\begin{aligned}
a &= \frac{\bar{p} - p_0}{3K_\mathrm{S}} + \frac{4G_\mathrm{S}}{3K_\mathrm{S} + 4G_\mathrm{S}}\, h^*\left(X_\mathrm{S}(r_\mathrm{O}), Y_\mathrm{V}(r_\mathrm{O})\right), \\
a_\mathrm{L} &= \frac{4G_S + 3K_S}{4G_S + 3K_\mathrm{L}} a - \frac{3K_\mathrm{L}}{4G_\mathrm{S} + 3K_\mathrm{L}} \left(\kappa(r_\mathrm{I}) - h_\mathrm{L}^*(X_\mathrm{L})\right) + \frac{4G_\mathrm{S}}{4G_\mathrm{S} + 3K_\mathrm{L}} \delta, \\
b &= \frac{3K_\mathrm{S} - 3K_\mathrm{L}}{4G_\mathrm{S} + 3K_\mathrm{L}} a - \frac{3K_\mathrm{L}}{4G_\mathrm{S} + 3K_\mathrm{L}} \left(\kappa(r_\mathrm{I}) + \delta - h_\mathrm{L}^*(X_\mathrm{L})\right) \\
&\quad - \frac{3K_\mathrm{S}}{3K_S + 4G_\mathrm{S}} h^*\left(X_\mathrm{S}(r_\mathrm{I}), Y_\mathrm{V}(r_\mathrm{I})\right).
\end{aligned} \tag{26}$$

After inserting these results into (21), we conclude that the resulting stress in the two-phase sphere is due to surface tension, misfit, a deviation of the outer pressure from the reference pressure and due to the radial dependence of the composition.

3 The diffusion problem

The objective of this chapter is the formulation of the diffusion problem for the considered two-phase system containing a liquid sphere with a free interface with radius $r_{\mathrm{I}}(t)$ at the center of a solid sphere with free outer radius $r_{\mathrm{O}}(t)$, see Figure 1.

The central thermodynamic quantities for the description of chemical reactions, diffusion and interface motion are the chemical potentials, μ_a, of the constituents. These result from the the free energy density function $\rho\psi(T, n_1, n_2, ..., c^{ij})$, which were calculated in [1], according to

$$\mu_a = \frac{\partial \rho\psi}{\partial n_a}.$$

Here the newly introduced quantity c^{ij} denotes the unimodular part of the right Cauchy-Green-tensor $C^{ij} \approx \delta_{ij} + 2e_{ij}$. The chemical potentials depend on temperature, on mole fractions, on sublattice concentrations and on the mechanical variables. Its explicit representation for the liquid and solid constituents, respectively, are given in the appendix. The diffusion model for the case at hand rely on the various assumptions that were stated in Section 1. Its exploitation is studied in detail by the authors in [1]. Here we cite only the results.

3.1 Reduction of the number of variables

Recall that the treatment of the mechanical problem ends up with representations for the displacement, the strain, the stress and the liquid and solid mass densities, which allows their calculation for given values of temperature, outer pressure, current liquid mole fraction, current lattice occupancies in the solid and interfacial and outer radius.

Next we reduce the seven lattice occupancies Y_a to a single one, say Y_{As_γ}, which serve as the single variable for which we have to formulate the diffusion equation.

This reduction relies on algebraic equations. The first three of them are the equations (4), which may be used to calculate the concentrations of the three dominant constituents as functions of the four minor constituents:

$$Y_{\mathrm{Ga}_\alpha} = 1 - Y_{\mathrm{As}_\alpha} - Y_{\mathrm{V}_\alpha}, \quad Y_{\mathrm{As}_\beta} = 1 - Y_{\mathrm{V}_\beta}, \quad Y_{\mathrm{As}_\gamma} = 1 - Y_{\mathrm{V}_\gamma}. \tag{27}$$

The second group of algebraic conditions concerns the transitions of constituents between the sublattices. We are only interested in elevated temperatures, where we appropriately may assume that the transition processes are in local equilibrium, so that they are characterized by two conditions for the chemical potentials. These have been derived in [1], and they read

$$\mu_{As_\alpha} - \mu_{V_\alpha} = \mu_{As_\gamma} - \mu_{V_\gamma}, \quad \mu_{As_\beta} - \mu_{V_\beta} = \mu_{As_\gamma} - \mu_{V_\gamma}. \tag{28}$$

Recall that the Freiberg model restricts the Ga to the α sublattice, and for this reason μ_{Ga_α} does not appear here.

Finally there results an algebraic condition that characterizes that fact that vacancies exclusively appears in local equilibrium states. This is described by the condition

$$\mu_{V_\alpha} + \mu_{V_\beta} + \mu_{V_\gamma} = 0, \tag{29}$$

which also was derived in [1].

The chemical potentials contain linear terms as well as quadratic terms in the strain, which itself is a small quantity, so that we only need to consider linear strain contributions. In this case the chemical potential read

$$\begin{aligned} \mu_{a_\mathrm{S}} &= \mu^{\mathrm{chem}}_{a_\mathrm{S}} - K_\mathrm{S}\frac{a}{\bar{n}_\mathrm{G}} + K_\mathrm{S}\frac{4G_\mathrm{S}}{3K_\mathrm{S}+4G_\mathrm{S}}\frac{h^*(r)}{\bar{n}_\mathrm{G}} \\ &= \bar{\mu}^{\mathrm{chem}}_{a_\mathrm{S}} + RT\ln\left(\frac{Y_{a_\mathrm{S}}(r)}{\bar{Y}_{a_\mathrm{S}}}\right) + \frac{p_0-\bar{p}}{3\bar{n}_\mathrm{G}} + \frac{4\,G_\mathrm{S}\,K_\mathrm{S}}{3K_\mathrm{S}+4G_\mathrm{S}}\frac{h^*(r)-h^*(r_\mathrm{O})}{\bar{n}_\mathrm{G}}. \end{aligned} \tag{30}$$

From 28, 29 and 30 we obtain three algebraic equations which may serve to eliminate three further lattice occupancies, viz. Y_{As_β}, Y_{V_α}, Y_{V_β}. Inspection of the explicit representation of the chemical potentials reveals: (i) The mechanical parts drop out of (28), (ii) the chemical potentials of the vacancies do contain mechanical contributions, (iii) the reference values of the chemical potentials cancel each other in (28) and (29) by definition, (iv) the remaining contributions only depend on relative sublattice concentration, which are defined by $y_a = Y_a/\bar{Y}_a(T)$.

With the abbreviation $y = y_{As_\gamma}$ we obtain from (28) and (29)

$$\frac{y_{As_\alpha}}{y_{V_\alpha}} = \frac{y_{As_\beta}}{y_{V_\beta}} \qquad \frac{y}{y_{V_\gamma}} = \frac{y_{As_\beta}}{y_{V_\beta}} \qquad y_{V_\alpha}y_{V_\beta}y_{V_\gamma} = f_\mu(p_0, h^*, h^*_\mathrm{O}) \tag{31}$$

with

$$f_\mu(p_0, h^*, h^*_\mathrm{O}) = \exp\left(\frac{\bar{p} - p_0 + \frac{12G_S K_S}{3K_S+4G_S}(h^*_O - h^*)}{\bar{n}_\mathrm{G}RT}\right), \tag{32}$$

which implies

$$f_\mu(p_0, h^*_\mathrm{O}, h^*_\mathrm{O}) \;=\; \exp\left(\frac{\bar{p}-p_0}{\bar{n}_\mathrm{G}RT}\right) \quad \text{and} \quad f_\mu(\bar{p}, h^*_\mathrm{O}, h^*_\mathrm{O}) = 1. \tag{33}$$

Next we use (27) and (31) to express all lattice occupancies in terms of the remaining variable y, viz.

$$\begin{aligned}
Y_{\mathrm{As}_\gamma} &= y\bar{Y}_{\mathrm{As}_\gamma}, \\
Y_{\mathrm{V}_\gamma} &= 1 - \bar{Y}_{\mathrm{As}_\gamma}\, y, \\
Y_{\mathrm{V}_\beta} &= \frac{Y_{\mathrm{V}_\gamma}\bar{Y}_{\mathrm{V}_\beta}}{Y_{\mathrm{V}_\gamma}\bar{Y}_{\mathrm{V}_\beta} + y\bar{Y}_{\mathrm{As}_\beta}\bar{Y}_{\mathrm{V}_\gamma}} \\
Y_{\mathrm{As}_\beta} &= 1 - Y_{\mathrm{V}_\beta} \\
Y_{\mathrm{V}_\alpha} &= f_\mu(p_0, h^*, h^*_{\mathrm{O}}) \frac{\bar{Y}_{_{\mathrm{V}_\alpha}}\bar{Y}_{_{\mathrm{V}_\beta}}\ \bar{Y}_{_{\mathrm{V}_\gamma}}}{Y_{_{V_\beta}}\ Y_{_{V_\gamma}}}, \\
Y_{\mathrm{As}_\alpha} &= Y_{\mathrm{V}_\alpha} \frac{y\bar{Y}_{\mathrm{As}_\alpha}\, \bar{Y}_{_{\mathrm{V}_\gamma}}}{Y_{_{\mathrm{V}_\gamma}}}, \\
Y_{\mathrm{Ga}_\alpha} &= 1 - Y_{_{V_\alpha}} \left(1 + \frac{y\bar{Y}_{\mathrm{As}_\alpha}\, \bar{Y}_{_{\mathrm{V}_\gamma}}}{Y_{_{\mathrm{V}_\gamma}}}\right).
\end{aligned} \tag{34}$$

The quantities Y_{As_γ}, Y_{V_γ}, Y_{As_β}, Y_{V_β} can thus be expressed by y. Due to (33) this is likewise possible at $r = r_O$ for Y_{As_α}, Y_{V_α}, Y_{Ga_α}.

From (14) we obtain at $r = r_O$

$$h^*_{\mathrm{O}} = 1 - \sqrt[3]{\frac{M_{\mathrm{Ga}}\tilde{Y}_{\mathrm{Ga}_\alpha}(y_{\mathrm{O}}, p_0) + M_{\mathrm{As}}\Big(\tilde{Y}_{\mathrm{As}_\alpha}(y_{\mathrm{O}}, p_0) + \tilde{Y}_{\mathrm{As}_\beta}(y_{\mathrm{O}}) + \tilde{Y}_{\mathrm{As}_\gamma}(y_{\mathrm{O}})\Big)}{M_{\mathrm{Ga}}\bar{Y}_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(\bar{Y}_{\mathrm{AS}_\alpha} + \bar{Y}_{\mathrm{As}_\beta} + \bar{Y}_{\mathrm{As}_\gamma})}}. \tag{35}$$

For $r < r_O$, there is no such an explicit representation, because f_μ depends via h^* on Y_{Ga_α} and Y_{As_α}.

We now introduce

$$\tilde{f}_\mu(p_0, h^*, y_{\mathrm{O}}) = f_\mu(p_0, h^*, h^*_{\mathrm{O}}) \tag{36}$$

to write down in compact notation the dependence of Y_{V_α} on p_0, h^* and y_{O}, viz.

$$Y_{\mathrm{V}_\alpha} = \tilde{f}_\mu(p_0, h^*, y_{\mathrm{O}}) \frac{\bar{Y}_{_{\mathrm{V}_\beta}}\ \bar{Y}_{_{\mathrm{V}_\gamma}}}{\tilde{Y}_{_{V_\beta}}(y)\ \tilde{Y}_{_{V_\gamma}}(y)} \bar{Y}_{\mathrm{V}_\alpha}. \tag{37}$$

The remaining variables are determined by interface conditions, conditions at the outer boundary and the diffusion equation.

3.2 The diffusion problem

The diffusion equation relies on the local conservation laws of particle number and mass. In these conservation laws, the partial and the barycentric velocities of the corresponding constituents appear, and these will be introduced at first.

We denote by $v_{\mathrm{Ga_L}}$ and $v_{\mathrm{As_L}}$ the partial velocities of the liquid constituents, and we calculate the barycentric velocity of the liquid according to

$$\rho_L v_{\mathrm{L}}^k = M_{\mathrm{Ga}} n_{\mathrm{Ga_L}} v_{\mathrm{Ga_L}}^k + M_{\mathrm{As}} n_{\mathrm{As_L}} v_{\mathrm{As_L}}^k, \tag{38}$$

The quantities v_{Ga_α}, v_{As_α}, v_{As_β} and v_{As_γ} are the partial velocities of the material solid constituents. The barycentric velocity of the solid mixture is thus defined by

$$\rho_S v_{\mathrm{S}}^k = M_{\mathrm{Ga}} n_{\mathrm{Ga}_\alpha} v_{\mathrm{Ga}_\alpha}^k + M_{\mathrm{As}} (n_{\mathrm{As}_\alpha} v_{\mathrm{As}_\alpha}^k + n_{\mathrm{As}_\beta} v_{\mathrm{As}_\beta}^k + n_{\mathrm{As}_\gamma} v_{\mathrm{As}_\gamma}^k), \tag{39}$$

3.2.1 Equations of balance

In the liquid phase, the local conservation law of the arsenic mole density reads

$$\frac{\partial n_{\mathrm{As_L}}}{\partial t} + \frac{\partial (n_{\mathrm{As_L}} v_{\mathrm{As_L}}^k)}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{L}}. \tag{40}$$

The local conservation law of the total mass of the liquid phase is given by

$$\frac{\partial \varrho_{\mathrm{L}}}{\partial t} + \frac{\partial (\varrho_{\mathrm{L}} v_{\mathrm{L}}^k)}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{L}}. \tag{41}$$

The corresponding equations in the solid phase are

$$\frac{\partial n_{\mathrm{As_S}}}{\partial t} + \frac{\partial (n_{\mathrm{As_S}}\ v_{\mathrm{As_S}}^k)}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{S}}, \tag{42}$$

and

$$\frac{\partial \varrho_{\mathrm{S}}}{\partial t} + \frac{\partial (\varrho_{\mathrm{S}}\ v_{\mathrm{S}}^k)}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{S}}. \tag{43}$$

At the liquid-solid interface we have

$$n_{\mathrm{As_L}} (v_{\mathrm{As_L}}^\nu - w_{\mathrm{I}}^\nu) = n_{\mathrm{As_S}} (v_{\mathrm{As_S}}^\nu - w_{\mathrm{I}}^\nu) \quad \text{on} \quad I, \tag{44}$$

and

$$\varrho_{\mathrm{L}} (v_{\mathrm{L}}^\nu - w_{\mathrm{I}}^\nu) = \varrho_{\mathrm{S}} (v_{\mathrm{S}}^\nu - w_{\mathrm{I}}^\nu) \quad \text{on} \quad I. \tag{45}$$

3.2.2 Constitutive law for the solid phase

The total arsenic diffusion flux in the solid phase is defined by

$$j_{\mathrm{As_S}}^k = n_{\mathrm{As_S}} (v_{\mathrm{As_S}}^k - v_{\mathrm{S}}^k) \quad \text{in} \quad \Omega_{\mathrm{S}} \cup \partial\Omega_{\mathrm{S}}, \tag{46}$$

whereas the corresponding definition in the liquid phase is not needed here because the liquid only exists in equilibrium states.

In [1] the constitutive law for $j_{\mathrm{As_S}}^k$ was derived and reads

$$j_{\mathrm{As_S}}^k = -\frac{B}{RT} \frac{\partial \left((\mu_{\mathrm{As}_\gamma} - \mu_{\mathrm{V}_\gamma}) - \frac{M_{\mathrm{As}}}{M_{\mathrm{Ga}}} (\mu_{\mathrm{Ga}_\alpha} - \mu_{\mathrm{V}_\alpha}) \right)}{\partial x^k} \equiv -\frac{\partial f_{\mathrm{D}}}{\partial x^k} \quad \text{in} \quad \Omega_{\mathrm{S}}. \tag{47}$$

The mobility $B > 0$ depends only on temperature and R denotes the universal gas constant.

3.2.3 Evaluation of the homogeneity of the liquid phase

The assumption that the liquid phase is in equilibrium at any time $t > 0$ implies its homogeneity. We conclude

$$\frac{\partial n_{\mathrm{As_L}}}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{L}}. \tag{48}$$

Thus (40) reduces to

$$\dot{n}_{\mathrm{As_L}} + n_{\mathrm{As_L}} \frac{\partial v^k_{\mathrm{As_L}}}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{L}} \tag{49}$$

After integration we obtain

$$\dot{n}_{\mathrm{As_L}} V_{\mathrm{L}} + n_{\mathrm{As_L}} v^{\nu}_{\mathrm{As_L}} O_{\mathrm{L}} = 0 \quad \text{on} \quad \partial\Omega_{\mathrm{L}} \tag{50}$$

The homogeneity of the mass density implies

$$\frac{\partial \varrho_{\mathrm{L}}}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{L}}, \tag{51}$$

and likewise we obtain from (41)

$$\dot{\varrho}_{\mathrm{L}} + \varrho_{\mathrm{L}} \frac{\partial v^k_{\mathrm{L}}}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{L}}. \tag{52}$$

This gives after integration

$$\dot{\varrho}_{\mathrm{L}} V_{\mathrm{L}} + \varrho_{\mathrm{L}} v^{\nu}_{\mathrm{L}} O_{\mathrm{L}} = 0 \quad \text{on} \quad \partial\Omega_{\mathrm{L}}. \tag{53}$$

3.2.4 Evaluation of the spherical symmetry

Due to the assumed spherical symmetry, volume, surface and normal speed of the liquid phase are given by

$$V_{\mathrm{L}} = \frac{4\pi r_{\mathrm{I}}^3}{3}, \quad O_{\mathrm{L}} = 4\pi r_{\mathrm{I}}^2, \quad \text{and} \quad w^{\nu}_{\mathrm{I}} = \dot{r}_{\mathrm{I}}. \tag{54}$$

At the interface, the partial and barycentric velocities of the liquid are thus given by

$$v^{\nu}_{\mathrm{As_L}} = -\frac{\dot{n}_{\mathrm{As_L}}}{n_{\mathrm{As_L}}} \frac{r_{\mathrm{I}}}{3} \quad \text{and} \quad v^{\nu}_{\mathrm{L}} = -\frac{\dot{\varrho}_{\mathrm{L}}}{\varrho_{\mathrm{L}}} \frac{r_{\mathrm{I}}}{3} \quad \text{on} \quad I. \tag{55}$$

We insert $(55)_1$ and the definition (46) in (44) to obtain

$$-n_{\mathrm{As_L}} \left(\frac{\dot{n}_{\mathrm{As_L}}}{n_{\mathrm{As_L}}} \frac{r_{\mathrm{I}}}{3} + \dot{r}_{\mathrm{I}} \right) = n_{\mathrm{As_S}} (v^{\nu}_{\mathrm{S}} - \dot{r}_{\mathrm{I}}) + j^{\nu}_{\mathrm{As_S}} \quad \text{on} \quad I. \tag{56}$$

Insertion of $(55)_2$ in (45) yields

$$-\varrho_{\mathrm{L}} \left(\frac{\dot{\varrho}_{\mathrm{L}}}{\varrho_{\mathrm{L}}} \frac{r_{\mathrm{I}}}{3} + \dot{r}_{\mathrm{I}} \right) = \varrho_{\mathrm{S}} (v^{\nu}_{\mathrm{S}} - \dot{r}_{\mathrm{I}}) \quad \text{on} \quad I, \tag{57}$$

which can be combined with (56) to give

$$n_{\mathrm{As_S}}\left(\frac{\dot\varrho_{\mathrm{L}}}{\varrho_{\mathrm{S}}}\frac{r_{\mathrm{I}}}{3}+\frac{\varrho_{\mathrm{L}}}{\varrho_{\mathrm{S}}}\dot r_{\mathrm{I}}\right)-n_{\mathrm{As_L}}\left(\frac{\dot n_{\mathrm{As_L}}}{n_{\mathrm{As_L}}}\frac{r_{\mathrm{I}}}{3}+\dot r_{\mathrm{I}}\right)=j^{\nu}_{\mathrm{As_S}}\quad\text{on}\quad I. \tag{58}$$

The equation (58) serves as the basis for the so called STEFAN condition. If we were to ignore the time derivatives and moreover set the ratio $\varrho_{\mathrm{L}}/\varrho_{\mathrm{S}}=1$, then (58) assumes the form of a classical Stefan condition. However, here we meet a more subtle case and a long calculation, see Section 3.2.7, is necessary to end up with a Stefan type condition. We will observe that it is not possible to obtain a condition that exclusively relates the diffusion flux to the interfacial normal speed.

The evolution of $n_{\mathrm{As_L}}$, $n_{\mathrm{As_S}}$, ρ_{L} and ρ_{S} follows from the solution of the mechanical problem according to

$$n_{\mathrm{As_L}} = X_{\mathrm{L}}\bar n_{\mathrm{L}}\left(1-3(a_{\mathrm{L}}-h^*_{\mathrm{L}})\right)=\hat n_{\mathrm{As_L}}(X_{\mathrm{L}},r_{\mathrm{I}},y_{\mathrm{O}},p_0) \tag{59}$$

$$\begin{aligned}
\varrho_{\mathrm{L}} &= M(\bar X_{\mathrm{L}})\bar n_{\mathrm{L}}(1-3a_{\mathrm{L}})=\hat\varrho_{\mathrm{L}}(X_{\mathrm{L}},r_{\mathrm{I}},y_{\mathrm{O}},p_0), && (60)\\
n_{\mathrm{As_S}} &= Y_{\mathrm{As_S}}\bar n_{\mathrm{G}}\left(1-3\left(\frac{\bar p-p_0}{3k_S}+\frac{4G_{\mathrm{S}}}{3k_{\mathrm{S}}+4G_{\mathrm{S}}}(h^*_{\mathrm{O}}-h^*)\right)\right)\\
&= \hat n_{\mathrm{As_S}}(y,h^*,y_{\mathrm{O}},p_0), && (61)\\
\varrho_{\mathrm{S}} &= \bar\varrho_{\mathrm{S}}\left(1-3\left(\frac{\bar p-p_0}{3k_S}+h^*_{\mathrm{O}}+\frac{3k_{\mathrm{S}}}{3k_{\mathrm{S}}+4G_{\mathrm{S}}}(h^*-h^*_{\mathrm{O}})\right)\right)\\
&= \hat\varrho_{\mathrm{S}}(y,h^*,y_{\mathrm{O}},p_0). && (62)
\end{aligned}$$

3.2.5 Phase equilibrium on *I*

The assumption that the interface only exists in states of phase equilibrium was exploited in [1] and leads to two conditions, that we may write

$$f_{\mathrm{I}}:=\mu_{\mathrm{As}\gamma}-\mu_{\mathrm{V}\gamma}-\frac{M_{\mathrm{As}}}{\rho_{\mathrm{S}}}\sigma^{<ij>}\nu^i\nu^j-\mu_{\mathrm{AsL}}=0\quad\text{on}\quad I,\quad\text{and} \tag{63}$$

$$f_{\mathrm{L}}:=\mu_{\mathrm{G}\alpha}+\mu_{\mathrm{As}\beta}+\mu_{\mathrm{V}\gamma}-\frac{M_{\mathrm{As}}+M_{\mathrm{Ga}}}{\rho_{\mathrm{S}}}\sigma^{<ij>}\nu^i\nu^j-\mu_{\mathrm{AsL}}-\mu_{\mathrm{GaL}}=0\quad\text{on}\quad I. \tag{64}$$

The second condition (64) is often called equation of liquidus line. The right hand sides of (63) and (64) depend on six quantities, and we indicate this by the notation

$$f_{\mathrm{I}}=\hat f_{\mathrm{I}}(X_{\mathrm{L}},r_{\mathrm{I}},h^*_{\mathrm{I}},y_{\mathrm{I}},y_{\mathrm{O}},p_0)\quad\text{und}\quad f_{\mathrm{L}}=\hat f_{\mathrm{L}}(X_{\mathrm{L}},r_{\mathrm{I}},y_{\mathrm{I}},h^*_{\mathrm{I}},y_{\mathrm{O}},p_0). \tag{65}$$

Analogously we write (14) in the form

$$f_h(y_{\mathrm{I}},h^*_{\mathrm{I}},y_{\mathrm{O}},p_0)=0. \tag{66}$$

3.2.6 Boundary conditions on the outer boundary of the solid

In this study we exclusively consider the case that the liquid-solid sphere is immersed in an inert gas at constant pressure p_0. The mechanical boundary condition thus reads

$$p_S = p_0 \quad \text{with} \quad \dot{p}_0 = 0 \quad \text{on} \quad \partial\Omega_{\mathrm{S}} \setminus I. \tag{67}$$

The impermeability of the outer solid sphere implies

$$\dot{r}_O = v^{\nu}_{\mathrm{S}} \quad \text{and} \quad j^{\nu}_{\mathrm{As_S}} = 0 \quad \text{on} \quad \partial\Omega_{\mathrm{S}} \setminus I. \tag{68}$$

3.2.7 Exploitation of the Stefan condition

The Stefan condition (58) needs the evolution of $n_{\mathrm{As_L}}$ and ρ_{L}. In particular we need $\dot{n}_{\mathrm{As_L}}$ and $\dot{\rho}_{\mathrm{L}}$, which we calculate at first. Due to (67) we obtain from (59)

$$\dot{n}_{\mathrm{As_L}} = \frac{\partial n_{\mathrm{As_L}}}{\partial X_{\mathrm{L}}}\dot{X}_{\mathrm{L}} + \frac{\partial n_{\mathrm{As_L}}}{\partial r_{\mathrm{I}}}\dot{r}_{\mathrm{I}} + \frac{\partial n_{\mathrm{As_L}}}{\partial y_{\mathrm{O}}}\dot{y}_{\mathrm{O}} \tag{69}$$

and from (60)

$$\dot{\varrho}_{\mathrm{L}} = \frac{\partial \varrho_{\mathrm{L}}}{\partial X_{\mathrm{L}}}\dot{X}_{\mathrm{L}} + \frac{\partial \varrho_{\mathrm{L}}}{\partial r_{\mathrm{I}}}\dot{r}_{\mathrm{I}} + \frac{\partial \varrho_{\mathrm{L}}}{\partial y_{\mathrm{I}}}\dot{y}_{\mathrm{O}}. \tag{70}$$

In order to eliminate $\dot{X}_{\mathrm{L}}$ we form the derivatives of (63) and (64):

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \dot{f}_{\mathrm{I}} \\ \dot{f}_{\mathrm{L}} \end{pmatrix} = \begin{pmatrix} \frac{\partial f_{\mathrm{I}}}{\partial r_{\mathrm{I}}} \\ \frac{\partial f_{\mathrm{L}}}{\partial r_{\mathrm{I}}} \end{pmatrix} \dot{r}_{\mathrm{I}} + \begin{pmatrix} \frac{\partial f_{\mathrm{I}}}{\partial X_{\mathrm{L}}} & \frac{\partial f_{\mathrm{I}}}{\partial y_{\mathrm{I}}} \\ \frac{\partial f_{\mathrm{L}}}{\partial X_{\mathrm{L}}} & \frac{\partial f_{\mathrm{L}}}{\partial y_{\mathrm{I}}} \end{pmatrix} \begin{pmatrix} \dot{X}_{\mathrm{L}} \\ \dot{y}_{\mathrm{I}} \end{pmatrix} + \begin{pmatrix} \frac{\partial f_{\mathrm{I}}}{\partial y_{\mathrm{O}}} \\ \frac{\partial f_{\mathrm{L}}}{\partial y_{\mathrm{O}}} \end{pmatrix} \dot{y}_{\mathrm{O}} + \begin{pmatrix} \frac{\partial f_{\mathrm{I}}}{\partial h^*_{\mathrm{I}}} \\ \frac{\partial f_{\mathrm{L}}}{\partial h^*_{\mathrm{I}}} \end{pmatrix} \dot{h}^*_{\mathrm{I}}, \tag{71}$$

This system may serve to calculate $\dot{X}_{\mathrm{L}}$ and $\dot{y}_{\mathrm{I}}$. For this purpose we eliminate at first $\dot{h}^*_{\mathrm{I}}$ by means of the derivative of (14), which reads

$$\dot{h}^*_{\mathrm{I}} = -\frac{\frac{\left(M_{\mathrm{Ga}}\frac{\partial Y_{\mathrm{Ga}_\alpha \mathrm{I}}}{\partial h^*_{\mathrm{I}}} + M_{\mathrm{As}}\frac{\partial Y_{\mathrm{As}_\alpha \mathrm{I}}}{\partial h_{\mathrm{I}}}\right)}{M_{\mathrm{Ga}}\bar{Y}_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(\bar{Y}_{\mathrm{AS}_\alpha} + \bar{Y}_{\mathrm{As}_\beta} + \bar{Y}_{\mathrm{As}_\gamma})}}{3\left(\frac{M_{\mathrm{Ga}}Y_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(Y_{\mathrm{As}_\alpha} + Y_{\mathrm{As}_\beta} + Y_{\mathrm{As}_\gamma})}{M_{\mathrm{Ga}}\bar{Y}_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(\bar{Y}_{\mathrm{AS}_\alpha} + \bar{Y}_{\mathrm{As}_\beta} + \bar{Y}_{\mathrm{As}_\gamma})}\right)^{\frac{2}{3}}}\dot{h}^*_{\mathrm{I}} \\ - \frac{\frac{\left(M_{\mathrm{Ga}}\frac{\partial Y_{\mathrm{Ga}_\alpha \mathrm{I}}}{\partial y_{\mathrm{I}}} + M_{\mathrm{As}}\left(\frac{\partial Y_{\mathrm{As}_\alpha \mathrm{I}}}{\partial y_{\mathrm{I}}} + \frac{\partial Y_{\mathrm{As}_\beta \mathrm{I}}}{\partial y_{\mathrm{I}}} + \frac{\partial Y_{\mathrm{As}_\gamma \mathrm{I}}}{\partial y_{\mathrm{I}}}\right)\right)\dot{y}_{\mathrm{I}} + \left(M_{\mathrm{Ga}}\frac{\partial Y_{\mathrm{Ga}_\alpha \mathrm{I}}}{\partial y_{\mathrm{O}}} + M_{\mathrm{As}}\frac{\partial Y_{\mathrm{As}_\alpha \mathrm{I}}}{\partial y_{\mathrm{O}}}\right)\dot{y}_{\mathrm{O}}}{M_{\mathrm{Ga}}\bar{Y}_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(\bar{Y}_{\mathrm{AS}_\alpha} + \bar{Y}_{\mathrm{As}_\beta} + \bar{Y}_{\mathrm{As}_\gamma})}}{3\left(\frac{M_{\mathrm{Ga}}Y_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(Y_{\mathrm{As}_\alpha} + Y_{\mathrm{As}_\beta} + Y_{\mathrm{As}_\gamma})}{M_{\mathrm{Ga}}\bar{Y}_{\mathrm{Ga}_\alpha} + M_{\mathrm{As}}(\bar{Y}_{\mathrm{AS}_\alpha} + \bar{Y}_{\mathrm{As}_\beta} + \bar{Y}_{\mathrm{As}_\gamma})}\right)^{\frac{2}{3}}}. \tag{72}$$

For further use we introduce the abbreviation

$$\dot{h}^*_{\mathrm{I}} = f_{\mathrm{hII}}\ \dot{y}_{\mathrm{I}} + f_{\mathrm{hIO}}\ \dot{y}_{\mathrm{O}}. \tag{73}$$

Insertion into (71) elimination with respect to $\dot{X}_\mathrm{L}$ and $\dot{y}_\mathrm{I}$ yields

$$\begin{pmatrix} \dot{X}_\mathrm{L} \\ \dot{y}_\mathrm{I} \end{pmatrix} = - \begin{pmatrix} \frac{\partial f_\mathrm{I}}{\partial X_\mathrm{L}} & \frac{\partial f_\mathrm{I}}{\partial y_\mathrm{I}} + \frac{\partial f_\mathrm{I}}{\partial h_\mathrm{I}^*} f_\mathrm{hII} \\ \frac{\partial f_\mathrm{L}}{\partial X_\mathrm{L}} & \frac{\partial f_\mathrm{L}}{\partial y_\mathrm{I}} + \frac{\partial f_\mathrm{L}}{\partial h_\mathrm{I}^*} f_\mathrm{hII} \end{pmatrix}^{-1} \left(\begin{pmatrix} \frac{\partial f_\mathrm{I}}{\partial r_\mathrm{I}} \\ \frac{\partial f_\mathrm{L}}{\partial r_\mathrm{I}} \end{pmatrix} \dot{r}_\mathrm{I} + \begin{pmatrix} \frac{\partial f_\mathrm{I}}{\partial y_\mathrm{O}} + \frac{\partial f_\mathrm{I}}{\partial h_\mathrm{I}^*} f_\mathrm{hIO} \\ \frac{\partial f_\mathrm{L}}{\partial y_\mathrm{O}} + \frac{\partial f_\mathrm{L}}{\partial h_\mathrm{I}^*} f_\mathrm{hIO} \end{pmatrix} \dot{y}_\mathrm{O} \right). \tag{74}$$

Thus (69) and (70) reduce to

$$\begin{aligned} \begin{pmatrix} \dot{n}_\mathrm{AsL} \\ \dot{\varrho}_\mathrm{L} \end{pmatrix} &= \begin{pmatrix} \frac{\partial n_\mathrm{AsL}}{\partial r_\mathrm{I}} \\ \frac{\partial \varrho_\mathrm{L}}{\partial r_\mathrm{I}} \end{pmatrix} \dot{r}_\mathrm{I} \\ &\quad - \begin{pmatrix} \frac{\partial n_\mathrm{AsL}}{\partial X_\mathrm{L}} & \frac{\partial n_\mathrm{AsL}}{\partial y_\mathrm{I}} \\ \frac{\partial \varrho_\mathrm{L}}{\partial X_\mathrm{L}} & \frac{\partial \varrho_\mathrm{L}}{\partial y_\mathrm{I}} \end{pmatrix} \begin{pmatrix} \frac{\partial f_\mathrm{I}}{\partial X_\mathrm{L}} & \frac{\partial f_\mathrm{I}}{\partial y_\mathrm{I}} + \frac{\partial f_\mathrm{I}}{\partial h_\mathrm{I}^*} f_\mathrm{hII} \\ \frac{\partial f_\mathrm{L}}{\partial X_\mathrm{L}} & \frac{\partial f_\mathrm{L}}{\partial y_\mathrm{I}} + \frac{\partial f_\mathrm{L}}{\partial h_\mathrm{I}^*} f_\mathrm{hII} \end{pmatrix}^{-1} \begin{pmatrix} \frac{\partial f_\mathrm{I}}{\partial r_\mathrm{I}} \\ \frac{\partial f_\mathrm{L}}{\partial r_\mathrm{I}} \end{pmatrix} \dot{r}_\mathrm{I} \\ &\quad + \begin{pmatrix} \frac{\partial n_\mathrm{AsL}}{\partial y_\mathrm{O}} \\ \frac{\partial \varrho_\mathrm{L}}{\partial y_\mathrm{O}} \end{pmatrix} \dot{y}_\mathrm{O} \\ &\quad - \begin{pmatrix} \frac{\partial n_\mathrm{AsL}}{\partial X_\mathrm{L}} & \frac{\partial n_\mathrm{AsL}}{\partial y_\mathrm{I}} \\ \frac{\partial \varrho_\mathrm{L}}{\partial X_\mathrm{L}} & \frac{\partial \varrho_\mathrm{L}}{\partial y_\mathrm{I}} \end{pmatrix} \begin{pmatrix} \frac{\partial f_\mathrm{I}}{\partial X_\mathrm{L}} & \frac{\partial f_\mathrm{I}}{\partial y_\mathrm{I}} + \frac{\partial f_\mathrm{I}}{\partial h_\mathrm{I}^*} f_\mathrm{hII} \\ \frac{\partial f_\mathrm{L}}{\partial X_\mathrm{L}} & \frac{\partial f_\mathrm{L}}{\partial y_\mathrm{I}} + \frac{\partial f_\mathrm{L}}{\partial h_\mathrm{I}^*} f_\mathrm{hII} \end{pmatrix}^{-1} \begin{pmatrix} \frac{\partial f_\mathrm{I}}{\partial y_\mathrm{O}} + \frac{\partial f_\mathrm{I}}{\partial h_\mathrm{I}^*} f_\mathrm{hIO} \\ \frac{\partial f_\mathrm{L}}{\partial y_\mathrm{O}} + \frac{\partial f_\mathrm{L}}{\partial h_\mathrm{I}^*} f_\mathrm{hIO} \end{pmatrix} \dot{y}_\mathrm{O} \\ &:= \begin{pmatrix} n'_{AsLrI} \\ \varrho'_{LrI} \end{pmatrix} \dot{r}_\mathrm{I} + \begin{pmatrix} n'_{AsLyO} \\ \varrho'_{LryO} \end{pmatrix} \dot{y}_\mathrm{O} \end{aligned} \tag{75}$$

The explicit elimination of $\dot{y}_\mathrm{O}$ is not possible because the mechanical solution contains y_O as a parameter, that can first be calculated after the diffusion problem is solved. In other words: We have to take care for the coupling between diffusion and mechanics up to the end.

Next we insert (75) into (58) to obtain the final form of the Stefan condition, as it will be used in the diffusion problem:

$$\begin{aligned} &\left(n_\mathrm{AsS} \left(\frac{\varrho'_\mathrm{LrI}}{\varrho_\mathrm{S}} \frac{r_\mathrm{I}}{3} + \frac{\varrho_\mathrm{L}}{\varrho_\mathrm{S}} \right) - n_\mathrm{AsL} \left(\frac{n'_\mathrm{AsLrI}}{n_\mathrm{AsL}} \frac{r_\mathrm{I}}{3} + 1 \right) \right) \dot{r}_\mathrm{I} \\ &\qquad + \left(n_\mathrm{AsS} \frac{\varrho'_\mathrm{LyO}}{\varrho_\mathrm{S}} - n'_\mathrm{AsLyO} \right) \frac{r_\mathrm{I}}{3} \dot{y}_\mathrm{O} = j^\nu_\mathrm{AsS} \quad \text{on} \quad I. \end{aligned} \tag{76}$$

3.2.8 The barycentric solid velocity at the liquid-solid interface

In the same manner as in Section 3.2.7 we calculate the normal component of the barycentric velocity at the solid side of the interface. From (57) we obtain

$$v_{\mathrm{S}}^{\nu} = \frac{1 - \left(\frac{\varrho'_{\mathrm{LrI}}}{\varrho_{\mathrm{S}}} \frac{r_{\mathrm{I}}}{3} + \frac{\varrho_{\mathrm{L}}}{\varrho_{\mathrm{S}}} \right)}{n_{\mathrm{AsS}} \left(\frac{\varrho'_{\mathrm{LrI}}}{\varrho_{\mathrm{S}}} \frac{r_{\mathrm{I}}}{3} + \frac{\varrho_{\mathrm{L}}}{\varrho_{\mathrm{S}}} \right) - n_{\mathrm{As_L}} \left(\frac{n'_{\mathrm{AsLrI}}}{n_{\mathrm{As_L}}} \frac{r_{\mathrm{I}}}{3} + 1 \right)} j_{\mathrm{As_S}}^{\nu}$$
$$- \left(\frac{n_{\mathrm{As_S}} \frac{\varrho'_{\mathrm{LyO}}}{\varrho_{\mathrm{S}}} - n'_{\mathrm{AsLyO}}}{n_{\mathrm{As_S}} \left(\frac{\varrho'_{\mathrm{LrI}}}{\varrho_{\mathrm{S}}} \frac{r_{\mathrm{I}}}{3} + \frac{\varrho_{\mathrm{L}}}{\varrho_{\mathrm{S}}} \right) - n_{\mathrm{As_L}} \left(\frac{n'_{\mathrm{AsLrI}}}{n_{\mathrm{As_L}}} \frac{r_{\mathrm{I}}}{3} + 1 \right)} + \frac{\varrho'_{\mathrm{LyO}}}{\varrho_{\mathrm{S}}} \right) \frac{r_{\mathrm{I}}}{3} \dot{y}_{\mathrm{O}} \quad \text{on} \quad I. \tag{77}$$

3.2.9 Exploitation of conservation laws of arsenic particle number and total mass in the solid

The exploitation of the diffusion equation and the conservation law of total mass in the solid needs the evolution of $n_{\mathrm{As_S}}$ and ρ_{S}. Their time derivatives result from (61) with (67),

$$\dot{n}_{\mathrm{As_S}} = \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} \dot{h}^* + \frac{\partial n_{\mathrm{As_S}}}{\partial y} \dot{y} + \frac{\partial n_{\mathrm{As_S}}}{\partial y_{\mathrm{O}}} \dot{y}_{\mathrm{O}} \tag{78}$$

and accordingly from (62) with (67)

$$\dot{\varrho}_{\mathrm{S}} = \frac{\partial \varrho_{\mathrm{S}}}{\partial h^*} \dot{h}^* + \frac{\varrho_{\mathrm{S}}}{\partial y} \dot{y} + \frac{\varrho_{\mathrm{S}}}{\partial y_{\mathrm{O}}} \dot{y}_{\mathrm{O}}. \tag{79}$$

Next we define in the same manner as in (72) and (73)

$$\dot{h}^* = f_{\mathrm{hi}}\, \dot{y} + f_{\mathrm{hiO}}\, \dot{y}_{\mathrm{O}}, \tag{80}$$

where f_{hi} and f_{hiO} can be read off from (73), and eliminate $\dot{h}^*$ in (78) and (79):

$$\dot{n}_{\mathrm{AsS}} = \left(\frac{\partial n_{\mathrm{AsS}}}{\partial y} + \frac{\partial n_{\mathrm{AsS}}}{\partial h^*} f_{\mathrm{hi}} \right) \dot{y} + \left(\frac{\partial n_{\mathrm{AsS}}}{\partial y_{\mathrm{O}}} + \frac{\partial n_{\mathrm{AsS}}}{\partial h^*} f_{\mathrm{hiO}} \right) \dot{y}_{\mathrm{O}}, \tag{81}$$

$$\dot{\varrho}_{\mathrm{S}} = \left(\frac{\partial \varrho_{\mathrm{S}}}{\partial y} + \frac{\partial \varrho_{\mathrm{S}}}{\partial h^*} f_{\mathrm{hi}} \right) \dot{y} + \left(\frac{\partial \varrho_{\mathrm{S}}}{\partial y_{\mathrm{O}}} + \frac{\partial \varrho_{\mathrm{S}}}{\partial h^*} f_{\mathrm{hiO}} \right) \dot{y}_{\mathrm{O}}. \tag{82}$$

The diffusion equation (42) and the conservation law of mass (43) may now be written

$$\left(\frac{\partial n_{\mathrm{As_S}}}{\partial y} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{hi}} \right) \dot{y} + \frac{\partial j_{\mathrm{As_S}}^{k}}{\partial x^k} + n_{\mathrm{As_S}} \frac{\partial v_{\mathrm{S}}^{k}}{\partial x^k} + \left(\frac{\partial n_{\mathrm{As_S}}}{\partial y_{\mathrm{O}}} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{hiO}} \right) \dot{y}_{\mathrm{O}} = 0 \quad \text{in} \quad \Omega_{\mathrm{S}} \tag{83}$$

and

$$\left(\frac{\partial \varrho_{\mathrm{S}}}{\partial y} + \frac{\partial \varrho_{\mathrm{S}}}{\partial h^*} f_{\mathrm{hi}}\right) \dot{y} + \varrho_{\mathrm{S}} \frac{\partial v_{\mathrm{S}}^k}{\partial x^k} + \left(\frac{\partial \varrho_{\mathrm{S}}}{\partial y_{\mathrm{O}}} + \frac{\partial \varrho_{\mathrm{S}}}{\partial h^*} f_{\mathrm{hiO}}\right) \dot{y}_{\mathrm{O}} = 0 \quad \text{in} \quad \Omega_{\mathrm{S}}. \tag{84}$$

We multiply (83) with $\frac{\partial \varrho_{\mathrm{S}}}{\partial y} + \frac{\partial \varrho_{\mathrm{S}}}{\partial h^*} f_{\mathrm{hi}}$ and (84) with $\frac{\partial n_{\mathrm{As_S}}}{\partial y} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{hi}}$ and subtract both equations to obtain

$$\begin{aligned}
&-\frac{1}{M_{\mathrm{Ga}}} \left(\frac{\partial \varrho_{\mathrm{S}}}{\partial y} + \frac{\partial \varrho_{\mathrm{S}}}{\partial h^*} f_{\mathrm{hi}}\right) \frac{\partial j_{\mathrm{As_S}}^k}{\partial x^k} \\
&\qquad + \Bigg(\left(\frac{\partial n_{\mathrm{As_S}}}{\partial y} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{hi}}\right) \left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y_{\mathrm{O}}} + \frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*} f_{\mathrm{hiO}}\right) \\
&\qquad - \left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y} + \frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*} f_{\mathrm{hi}}\right) \left(\frac{\partial n_{\mathrm{As_S}}}{\partial y_{\mathrm{O}}} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{hiO}}\right) \Bigg) \dot{y}_{\mathrm{O}} \\
&+ \left(n_{\mathrm{Ga_S}} \left(\frac{\partial n_{\mathrm{As_S}}}{\partial y} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{hi}}\right) - n_{\mathrm{As_S}} \left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y} + \frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*} f_{\mathrm{hi}}\right) \right) \frac{\partial v_{\mathrm{S}}^k}{\partial x^k} = 0 \\
&\text{in} \quad \Omega_{\mathrm{S}}.
\end{aligned} \tag{85}$$

This equation will now be used to eliminate in (83) the divergence of the barycentric velocity, so that we finally have

$$\begin{aligned}
&\left(n_{\mathrm{AsS}} \left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y} + \frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*} f_{\mathrm{h}}\right) - n_{\mathrm{Ga_S}} \left(\frac{\partial n_{\mathrm{As_S}}}{\partial y} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{h}}\right) \right) \dot{y} \\
&\quad + \left(n_{\mathrm{As_S}} \left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y_{\mathrm{O}}} + \frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*} f_{\mathrm{hiO}}\right) - n_{\mathrm{Ga_S}} \left(\frac{\partial n_{\mathrm{As_S}}}{\partial y_{\mathrm{O}}} + \frac{\partial n_{\mathrm{As_S}}}{\partial h^*} f_{\mathrm{hiO}}\right) \right) \dot{y}_{\mathrm{O}} \\
&\qquad - \frac{\varrho_{\mathrm{S}}}{M_{\mathrm{Ga}}} \frac{\partial j_{\mathrm{As_S}}^k}{\partial x^k} = 0 \quad \text{in} \quad \Omega_{\mathrm{S}}
\end{aligned} \tag{86}$$

3.2.10 Exploitation of the diffusion flux condition at the outer solid boundary

In this section we draw conclusions from the condition $(68)_2$, i.e. $j_{\mathrm{As_S}}^{\nu} = 0$ for $r = r_{\mathrm{O}}$. According to (47) this yields

$$\frac{\partial y}{\partial r} = 0 \quad \text{on} \quad \partial\Omega_{\mathrm{S}} \setminus \mathrm{I}. \tag{87}$$

We conclude that the material and partial time derivatives of y coincides on $\partial\Omega_{\mathrm{S}} \setminus \mathrm{I}$:

$$\dot{y}_{\mathrm{O}} = \frac{\partial y(t, r)}{\partial t} \quad \text{on} \quad \partial\Omega_{\mathrm{S}} \setminus \mathrm{I}. \tag{88}$$

3.2.11 Conservation laws of total mass and arsenic particle number in the solid in spherical coordinates

The transformation from cartesian to spherical coordinates of the conservation laws (85) and (86) and the constitutive law for the diffusion flux (47) yields

$$\begin{aligned}
&\frac{1}{M_{\mathrm{Ga}}}\left(\frac{\partial\varrho_{\mathrm{S}}}{\partial y}+\frac{\partial\varrho_{\mathrm{S}}}{\partial h^*}f_{\mathrm{h}}\right)\left(\frac{\partial f_{\mathrm{D}}^2}{\partial r^2}+\frac{2}{r}\frac{\partial f_{\mathrm{D}}}{\partial r}\right)\\
&\qquad+\left(\left(\frac{\partial n_{\mathrm{As_S}}}{\partial y}+\frac{\partial n_{\mathrm{As_S}}}{\partial h^*}f_{\mathrm{hi}}\right)\left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y_{\mathrm{O}}}+\frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*}f_{\mathrm{hiO}}\right)\right.\\
&\qquad\left.-\left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y}+\frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*}f_{\mathrm{hi}}\right)\left(\frac{\partial n_{\mathrm{As_S}}}{\partial y_{\mathrm{O}}}+\frac{\partial n_{\mathrm{As_S}}}{\partial h^*}f_{\mathrm{hiO}}\right)\right)\dot{y}_{\mathrm{O}}\\
&\quad+\left(n_{\mathrm{Ga_S}}\left(\frac{\partial n_{\mathrm{As_S}}}{\partial y}+\frac{\partial n_{\mathrm{As_S}}}{\partial h^*}f_{\mathrm{hi}}\right)-n_{\mathrm{As_S}}\left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y}+\frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*}f_{\mathrm{hi}}\right)\right)\left(\frac{\partial v_{\mathrm{S}}}{\partial r}+\frac{2v_{\mathrm{S}}}{r}\right)\\
&\qquad\qquad=0\quad\text{in}\quad\Omega_{\mathrm{S}}.
\end{aligned}\tag{89}$$

and

$$\begin{aligned}
&\left(n_{\mathrm{As_S}}\left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y}+\frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*}f_{\mathrm{hi}}\right)-n_{\mathrm{Ga_S}}\left(\frac{\partial n_{\mathrm{As_S}}}{\partial y}+\frac{\partial n_{\mathrm{As_S}}}{\partial h^*}f_{\mathrm{hi}}\right)\right)\left(\frac{\partial y}{\partial t}+v_{\mathrm{S}}\frac{\partial y}{\partial r}\right)\\
&\quad+\left(n_{\mathrm{As_S}}\left(\frac{\partial n_{\mathrm{Ga_S}}}{\partial y_{\mathrm{O}}}+\frac{\partial n_{\mathrm{Ga_S}}}{\partial h^*}f_{\mathrm{hiO}}\right)-n_{\mathrm{Ga_S}}\left(\frac{\partial n_{\mathrm{As_S}}}{\partial y_{\mathrm{O}}}+\frac{\partial n_{\mathrm{As_S}}}{\partial h^*}f_{\mathrm{hiO}}\right)\right)\dot{y}_{\mathrm{O}}\\
&\quad+\frac{\varrho_{\mathrm{S}}}{M_{\mathrm{Ga}}}\left(\frac{\partial f_{\mathrm{D}}^2}{\partial r^2}+\frac{2}{r}\frac{\partial f_{\mathrm{D}}}{\partial r}\right)=0\\
&\qquad\qquad\text{in}\quad\Omega_{\mathrm{S}}.
\end{aligned}\tag{90}$$

Schließlich ist v_{O} über $v_{\mathrm{O}}=\dot{r}_{\mathrm{O}}=\dot{R}_{\mathrm{O}}+\dot{u}_{\mathrm{O}}$ mit (18) unter Beachtung von $r_{\mathrm{O}}\gg r_{\mathrm{I}}$ und

$$M(\bar{X})N_0=\frac{4\pi}{3}n_{\mathrm{G}}^{\mathrm{R}}(3-\bar{Y}_{\mathrm{V}})\Big(R_{\mathrm{I}}^3(t)M(\bar{X}_{\mathrm{L}})+(R_{\mathrm{O}}^3(t)-R_{\mathrm{I}}^3(t))M(\bar{X}_{\mathrm{S}})\Big)\tag{91}$$

$$0=R_{\mathrm{I}}^2(t)\dot{R}_{\mathrm{I}}^2(t)(M(\bar{X}_{\mathrm{L}})-M(\bar{X}_{\mathrm{S}}))+R_{\mathrm{O}}^2(t)\dot{R}_{\mathrm{O}}(t)M(\bar{X}_{\mathrm{S}})\tag{92}$$

$$\dot{R}_{\mathrm{O}}(t)=\frac{(r_{\mathrm{I}}(t)-u(t,r_{\mathrm{I}}(t)))^2(\dot{r}_{\mathrm{I}}(t)-\dot{u}(t,r_{\mathrm{I}}(t)))\left(1-\frac{M(\bar{X}_{\mathrm{L}})}{M(\bar{X}_{\mathrm{S}})}\right)}{\left(\frac{M(\bar{X})}{M(\bar{X}_{\mathrm{S}})}\frac{3N_0}{4\pi n_{\mathrm{G}}^{\mathrm{R}}(3-\bar{Y}_{\mathrm{V}})}-(r_{\mathrm{I}}(t)-u(t,r_{\mathrm{I}}(t)))^3\left(\frac{M(\bar{X}_{\mathrm{L}})}{M(\bar{X}_{\mathrm{S}})}-1\right)\right)^{\frac{2}{3}}}\tag{93}$$

$$\begin{aligned}
\dot{u}(t,r_{\mathrm{I}}(t))=&\left(\frac{u(t,r_{\mathrm{I}}(t))}{r_{\mathrm{I}}(t)}+\frac{3K_{\mathrm{L}}}{4G_{\mathrm{S}}+3K_{\mathrm{L}}}\kappa(r_{\mathrm{I}}(t))\right)\dot{r}_{\mathrm{I}}(t)\\
&+\frac{4G_{\mathrm{S}}}{3K_{\mathrm{L}}+4G_{\mathrm{S}}}\frac{\partial h_{\mathrm{O}}^*}{\partial y_{\mathrm{O}}}r_{\mathrm{I}}(t)\dot{y}_{\mathrm{O}}(t)+\frac{3K_{\mathrm{L}}}{4G_{\mathrm{S}}+3K_{\mathrm{L}}}\frac{\partial h_{\mathrm{L}}^*(X_{\mathrm{L}})}{\partial X_{\mathrm{L}}}r_{\mathrm{I}}(t)\dot{X}_{\mathrm{L}}(t)
\end{aligned}\tag{94}$$

festgelegt durch

$$v_{\mathrm{O}} = \left(1 + h^*_{\mathrm{O}} + \frac{\bar{p} - p_0}{3K_{\mathrm{S}}}\right)\left(\dot{R}_{\mathrm{O}} + \frac{\partial h^*_{\mathrm{O}}}{\partial y_{\mathrm{O}}} r_{\mathrm{O}} \dot{y}_{\mathrm{O}}\right). \tag{95}$$

4 Das vollständige Anfangs-Randwert-Problem des Zwei- Phasengebiets

Gegeben:

T, p_0, t_0, $\bar{X}$, N_0, $X_{\mathrm{L}0}$, $r_{\mathrm{I}0}$, $r_{\mathrm{O}0}$, $y_0(r)$ für $r_{\mathrm{I}0} \leq r \leq r_{\mathrm{O}0}$

Gesucht:

$X_{\mathrm{L}}(t)$, $r_{\mathrm{I}}(t)$, $r_{\mathrm{O}}(t)$, $y(t,r)$, $v(t,r)$ und $h^*(t,r)$ für $r_{\mathrm{I}}(t) \leq r \leq r_{\mathrm{O}}(t)$ und $t \geq t_0$

Anfangsbedingungen:

$t = t_0$, $X_{\mathrm{L}}(t_0) = X_{\mathrm{L}0}$, $r_{\mathrm{I}}(t_0) = r_{\mathrm{I}0}$, $r_{\mathrm{O}}(t_0) = r_{\mathrm{O}0}$, $y(t_0,r) = y_0(r)$ für $r_{\mathrm{I}}(t_0) \leq r \leq r_{\mathrm{O}}(t_0)$ mit

$$\frac{4\pi\hat{\varrho}_{\mathrm{L}}(X_{\mathrm{L}0}, r_{\mathrm{I}0}, y_0(r_{\mathrm{O}0}), p_0) r_{\mathrm{I}0}^3}{3} + 4\pi \int_{r_{\mathrm{I}0}}^{r_{\mathrm{O}0}} r^2 \hat{\varrho}_{\mathrm{S}}(y_0(r), h^*_0(r), y_0(r_{\mathrm{O}0}), p_0)\,dr = (M_{\mathrm{As}}\bar{X} + M_{\mathrm{Ga}}(1 - \bar{X}))N_0$$

und

$$\frac{4\pi\hat{n}_{\mathrm{AsL}}(p_0, r_{\mathrm{I}0}, X_{\mathrm{L}0}, y_0(r_{\mathrm{O}0})) r_{\mathrm{I}0}^3}{3} + 4\pi \int_{r_{\mathrm{I}0}}^{r_{\mathrm{O}0}} r^2 \hat{n}_{\mathrm{AsS}}(y_0(r), h^*_0(r), y_0(r_{\mathrm{O}0}), p_0)\,dr = \bar{X} N_0.$$

Berechnung der inelastischen Anfangsverzerrungen und konsistenter Anfangsgeschwindigkeiten aus den gegebenen Anfangsbedingungen:

- Bestimmung von $h^*_0(r) = h^*(t_0, r)$ für $r_{\mathrm{I}0} \leq r \leq r_{\mathrm{O}0}$ aus Gleichung (14) unter Verwendung von (34)
- Bestimmung von $v_{I0} = v(t_0, r_{\mathrm{I}0})$ aus Gleichung (77) unter Verwendung von (95).
- Bestimmung von $v_0(r) = v(t_0, r)$ für $r_{\mathrm{I}0} < r \leq r_{\mathrm{O}0}$ aus Gleichung (89) unter Verwendung von (95).

Gleichungen für $t > t_0$:

- Bestimmung von $r_{\mathrm{I}}(t)$ aus Gleichung (76)
- Bestimmung von $r_{\mathrm{O}}(t)$ aus Gleichung $(68)_1$ zur

- Bestimmung von $X_{\mathrm{L}}(t)$, $y(t, r_{\mathrm{I}}(t))$ und $h^*(t, r_I(t))$ aus Gleichung (63), (64) und (66).
- Bestimmung von $y(t, r)$ für $r_{\mathrm{I}}(t) < r < r_{\mathrm{O}}(t)$ aus Gleichung (90)
- Bestimmung von $y(t, r_{\mathrm{O}}(t))$ aus Gleichung (87).
- Bestimmung von $v(t, r_{\mathrm{I}}(t))$ aus Gleichung (77) unter Verwendung von (95).
- Bestimmung von $v(t, r)$ für $r_{\mathrm{I}}(t) < r \leq r_{\mathrm{O}}(t)$ aus Gleichung (89) und(95).

5 Zur Konstruktion des numerischen Verfahrens

5.1 Die Ausgangsgleichungen

Das numerische Verfahren soll anhand des Systems mit Inertgas am Außenrand der festen Kugel, welches zusammenfassend im Abschnitt 4 dargestellt ist, erläutert werden. Hier werden die Größen $X_{\mathrm{L}}(t)$, $r_{\mathrm{I}}(t)$, $r_{\mathrm{O}}(t)$, $y(t, r)$ und $v(t, r)$ für $r_{\mathrm{I}}(t) \leq r \leq r_{\mathrm{O}}(t)$ gesucht. Gegeben ist t_0, r_{I0}, r_{O0}, $y_0(r)$ für $r_{\mathrm{I0}} \leq r \leq r_{\mathrm{O0}}$ mit

$$r_{\mathrm{I}}(t_0) = r_{\mathrm{I0}}, \quad r_{\mathrm{O}}(t_0) = r_{\mathrm{O0}} \quad \text{und} \quad y(t_0, r) = y_0(r). \tag{96}$$

Zur Bestimmung der Anfangsgeschwindigkeiten bringen wir (77) durch Umformung unter Verwendung von (95) auf die Gestalt

$$v_{\mathrm{I0}} = g_{\mathrm{vI}}\Big(r_{\mathrm{I0}}, X_{\mathrm{L0}}, y_{\mathrm{I0}}, y'_{\mathrm{I0}}, h^*_{\mathrm{I0}}, r_{\mathrm{O0}}, v_{\mathrm{O0}}, y_{\mathrm{O0}}\Big), \tag{97}$$

wobei wir die Abkürzungen $v(t_0, r_{\mathrm{I0}}) = v_{\mathrm{I0}}$, $y(t_0, r_{\mathrm{I0}}) = y_{\mathrm{I0}}$, $v(t_0, r_{\mathrm{O0}}) = v_{\mathrm{O0}}$ und $y(t_0, r_{\mathrm{O0}}) = y_{\mathrm{O0}}$ verwenden. Aus (89) bekommen wir entsprechend

$$\begin{aligned} &\frac{\partial v_0(r)}{\partial r} + 2\frac{v_0(r)}{r} \\ &\qquad = g_{\mathrm{v}}\left(X_{\mathrm{L0}}, r_{\mathrm{I0}}, y_{\mathrm{I0}}, y'_{\mathrm{I0}}, h^*_{\mathrm{I0}}, r, y_0(r), \frac{\partial y_0(r)}{\partial r}, \frac{\partial^2 y_0(r)}{\partial r^2}, h^*_0(r), r_{\mathrm{O0}}, v_{\mathrm{O0}}, y_{\mathrm{O0}}\right) \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{für} \quad r_{\mathrm{I0}} < r \leq r_{\mathrm{O0}}. \end{aligned} \tag{98}$$

was für $r = r_{\mathrm{O0}}$ auf eine Gestalt

$$\begin{aligned} &v'_{\mathrm{O0}} + \frac{v_{\mathrm{O0}}}{r_{\mathrm{O0}}}\left(2 + g_{\mathrm{vrO}}\left(X_{\mathrm{L0}}, r_{\mathrm{I0}}, y_{\mathrm{I0}}, y_{\mathrm{O0}}, r_{\mathrm{O0}}\right)\right) \\ &\qquad\qquad\qquad = g_{\mathrm{vjO}}\left(X_{\mathrm{L0}}, r_{\mathrm{I0}}, y_{\mathrm{I0}}, y'_{\mathrm{I0}}, h^*_{\mathrm{I0}}, y_{\mathrm{O0}}, y''_{\mathrm{O0}}, r_{\mathrm{O0}}\right) \end{aligned} \tag{99}$$

bringen lässt.

Zur Bestimmung der gesuchten Größen für $t > t_0$ starten wir mit der Gleichung (76). Sie lässt sich unter Verwendung von (95) durch Umformung auf die Gestalt

$$\frac{dr_{\mathrm{I}}(t)}{dt} = g_{\mathrm{I}}\Big(X_{\mathrm{L}}(t), r_{\mathrm{I}}(t), y_{\mathrm{I}}(t), y'_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), r_{\mathrm{O}}(t), v_{\mathrm{O}}(t), y_{\mathrm{O}}(t)\Big) \tag{100}$$

bringen. Die Gleichungen (63), (64) und (66) lassen sich darstellen als

$$\begin{aligned} f_{\mathrm{I}}\Big(X_{\mathrm{L}}(t), r_{\mathrm{I}}(t), y_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), y_{\mathrm{O}}(t)\Big) &= 0, \\ f_{\mathrm{L}}\Big(X_{\mathrm{L}}(t), r_{\mathrm{I}}(t), y_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), y_{\mathrm{O}}(t)\Big) &= 0 \quad \text{und} \\ f_{\mathrm{h}}(y_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), y_{\mathrm{O}}(t)) &= 0. \end{aligned} \tag{101}$$

Die Gleichung (68) lautet

$$\frac{dr_{\mathrm{O}}(t)}{dt} = v_{\mathrm{O}}(t). \tag{102}$$

Gleichung (90) wird unter Verwendung von (95) auf die Form

$$\begin{aligned} &\frac{\partial y(t,r)}{\partial t} \\ &\quad = g_{\mathrm{S}}\left(X_{\mathrm{L}}(t), r_{\mathrm{I}}(t), y_{\mathrm{I}}(t), y'_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), r, v_{\mathrm{S}}(t,r), y(t,r), \frac{\partial y(t,r)}{\partial r}, \right. \\ &\qquad\qquad \left. \frac{\partial^2 y(t,r)}{\partial r^2}, h^*(t,r), r_{\mathrm{O}}(t), v_{\mathrm{O}}(t), y_{\mathrm{O}}(t)\right) \\ &\qquad\qquad\qquad \text{für} \quad r_{\mathrm{I}}(t) < r < r_{\mathrm{O}}(t) \end{aligned} \tag{103}$$

gebracht. Dabei gilt mit (66)

$$f_h(y(t,r), h^*(t,r), y_{\mathrm{O}}(t)) = 0. \tag{104}$$

Außerdem gilt gemäß (87)

$$y'_{\mathrm{O}}(t) = 0. \tag{105}$$

Die Gleichung (77) lässt sich unter Verwendung von (95) durch Umformung auf die Gestalt

$$v_{\mathrm{I}}(t) = g_{\mathrm{vI}}\Big(r_{\mathrm{I}}(t), X_{\mathrm{L}}(t), y_{\mathrm{I}}(t), y'_{\mathrm{I}}(t), h^*_{I}(t), r_{\mathrm{O}}(t), v_{\mathrm{O}}(t), y_{\mathrm{O}}(t)\Big) \tag{106}$$

bringen. Entsprechend schreiben wir statt (89)

$$\begin{aligned} &\frac{\partial v_{\mathrm{S}}(t,r)}{\partial r} + 2\frac{v_{\mathrm{S}}(t,r)}{r} \\ &\quad = g_{\mathrm{v}}\left(X_{\mathrm{L}}(t), r_{\mathrm{I}}(t), y_{\mathrm{I}}(t), y'_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), r, y(t,r), \frac{\partial y(t,r)}{\partial r}, \right. \\ &\qquad\qquad \left. \frac{\partial^2 y(t,r)}{\partial r^2}, h^*(t,r), r_{\mathrm{O}}(t), v_{\mathrm{O}}(t), y_{\mathrm{O}}(t)\right) \\ &\qquad\qquad\qquad \text{für} \quad r_{\mathrm{I}}(t) < r \leq r_{\mathrm{O}}(t), \end{aligned} \tag{107}$$

was für $r = r_{\mathrm{O}}(t)$ mit (93), (74) und (76) auch durch

$$v'_{\mathrm{O}}(t) + \frac{v_{\mathrm{O}}(t)}{r_{\mathrm{O}}(t)} \Big(2 + g_{\mathrm{vj}}\left(X_{\mathrm{L}}(t), r_{\mathrm{I}}(t), y_{\mathrm{I}}(t), y'_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), y_{\mathrm{O}}(t)\right)\Big)$$
$$= g_{\mathrm{vy}}\left(X_{\mathrm{L}}(t), r_{\mathrm{I}}(t), y_{\mathrm{I}}(t), h^*_{\mathrm{I}}(t), r_{\mathrm{O}}, y_{\mathrm{O}}(t), y''_{O}(t)\right) \quad (108)$$

darstellbar ist.

5.2 Zeitintegration und Ortsdiskretisierung

Wir bezeichnen die aktuelle Zeit mit t^{n+1} und die etwas früher liegende Zeit mit t^n und definieren $\Delta t^{n+1} := t^{n+1} - t^n$ und betrachten jetzt die fünf Gleichungen, welche Zeitableitungen enthalten, (100), (102), (103), (106) und (107), bei festem r zum Zeitpunkt t^n. Wenn wir die Zeitableitung durch Vorwärts-Differenzenquotienten ersetzen, erhalten wir als Euler-Rückwärts-Näherung

$$r_{\mathrm{I}}(t^{n+1}) - r_{\mathrm{I}}(t^n)$$
$$= \Delta t^{n+1} \hat{g}_{\mathrm{I}}\Big(X_{\mathrm{L}}(t^n), r_{\mathrm{I}}(t^n), y_{\mathrm{I}}(t^n), y'_{\mathrm{I}}(t^n), h^*_{\mathrm{I}}(t^n), r_{\mathrm{O}}(t^n), v_{\mathrm{O}}(t^n), y_{\mathrm{O}}(t^n)\Big)$$
$$+ o(\Delta t^{n+1}), \quad (109)$$

$$r_{\mathrm{O}}(t^{n+1}) - r_{\mathrm{O}}(t^n) = \Delta t^{n+1} v_{\mathrm{O}}(t^n) + o(\Delta t^{n+1}) \quad (110)$$

und

$$y(t^{n+1}, r) - y(t^n, r)$$
$$= \Delta t^{n+1} \hat{g}_{\mathrm{S}}\Bigg(X_{\mathrm{L}}(t^n), r_{\mathrm{I}}(t^n), y_{\mathrm{I}}(t^n), y'_{\mathrm{I}}(t^n), h^*_{\mathrm{I}}(t^n), r, v(t^n, r), y(t^n, r), \frac{\partial y(t^n, r)}{\partial r},$$
$$\frac{\partial^2 y(t^n, r)}{\partial r^2}, h^*(t^n, r), r_{\mathrm{O}}(t^n), v_{\mathrm{O}}(t^n), y_{\mathrm{O}}(t^n)\Bigg) + o(\Delta t^{n+1}). \quad (111)$$

Teilen wir jetzt den Abstand $r_{\mathrm{O}}(t^n) - r_{\mathrm{I}}(t^n)$ in N Ortsintervalle und definieren $r_0^n = r_I(t^n)$ und $\Delta r^n = (r_{\mathrm{O}}(t^n) - r_{\mathrm{I}}(t^n))/N$ gilt

$$r_i^n = r_0^n + i\Delta r^n \quad \text{für} \quad i = 0, .., N. \quad (112)$$

Außerdem definieren wir nun $y_i^n = y(t^n, r_i^n)$ und $v_i^n = v_{\mathrm{S}}(t^n, r_i^n)$. Als Ortsdiskretisierung wählen beim Euler-Rückwärts-Verfahren $r = r_i^n$. Mit ihr ergeben sich für die oben bereits zeitdiskretisierten Gleichungen

$$r_0^{n+1} - r_0^n = \Delta t^{n+1} \hat{g}_{\mathrm{I}}\Big(r_0^n, y_0^n, {y'_0}^n, h_0^{*n}, r_N^n, v_N^n, y_N^n\Big) + o(\Delta t^{n+1}) \quad (113)$$

$$r_N^{n+1} - r_N^n = \Delta t^{n+1} v_N^n + o(\Delta t^{n+1}) \quad (114)$$

$$
\begin{aligned}
y(t^{n+1}, r_i^n) - y_i^n = \Delta t^{n+1} \hat{g}_{\mathrm{S}} \big(& X_{\mathrm{L}}^n, r_0^n, y_0^n, {y'_0}^n, h_0^{*n}, r_i^n, v_i^n, y_i^n, {y'_i}^n, {y''_i}^n, h_i^{*n}, \\
& r_N^n, v_N^n, y_N^n \big) + o(\Delta t^{n+1}) \\
& \text{für} \quad i = 1, .., N-1,
\end{aligned}
\tag{115}
$$

mit

$$
{y'_i}^n = \left. \frac{\partial y(t^n, r)}{\partial r} \right|_{r = r_i^n} . \tag{116}
$$

Die Größe $y(t^{n+1}, r_i^n)$ ist weder mit y_i^{n+1} noch mit y_i^n identisch. Aus einer Taylor-Reihenentwicklung folgt

$$
\begin{aligned}
y(t^{n+1}, r_i^n) &= y(t^{n+1}, r_i^{n+1}) + \left. \frac{\partial y(t^{n+1}, r)}{\partial r} \right|_{r = r_i^{n+1}} (r_i^n - r_i^{n+1}) + o(|r_i^n - r_i^{n+1}|) \\
&= y_i^{n+1} + (r_i^n - r_i^{n+1}) {y'_i}^{n+1} + o\Big(|r_i^n - r_i^{n+1}| \Big)
\end{aligned}
\tag{117}
$$

und wir schreiben statt (115)

$$
\begin{aligned}
y_i^{n+1} + (r_i^n - r_i^{n+1}) {y'_i}^{n+1} - y_i^n = \Delta t^{n+1} \hat{g}_{\mathrm{S}} \big(& X_{\mathrm{L}}^n, r_0^n, y_0^n, {y'_0}^n, h_0^{*n}, r_i^n, v_i^n, y_i^n, {y'_i}^n, \\
& {y''_i}^n, h_i^{*n}, r_N^n, v_N^n, y_N^n \big) \\
& + o\Big(\Delta t^{n+1}, |r_i^n - r_i^{n+1}| \Big) \quad \text{für} \quad i = 1, .., N-1.
\end{aligned}
\tag{118}
$$

Statt (101) schreiben wir

$$
\begin{aligned}
& f_{\mathrm{I}}\Big(X_{\mathrm{L}}^{n+1}, r_0^{n+1}, y_0^{n+1}, h_0^{*n+1}, y_N^{n+1} \Big) = 0, \quad f_{\mathrm{L}}\Big(X_{\mathrm{L}}^{n+1}, r_0^{n+1}, y_0^{n+1}, y_N^{n+1} \Big) = 0 \\
& \qquad \text{und} \quad f_h(y_0^{n+1}, h_0^{*n+1}, y_N^{n+1}) = 0,
\end{aligned}
\tag{119}
$$

statt (105)

$$
{y'}_N^{n+1} = 0. \tag{120}
$$

Approximieren wir nun die Ortsableitungen durch Differenzenquotienten, kann jetzt das vollständig diskretisierte Schema angegeben werden.

5.3 Approximation der Ortsableitungen

Es gilt

$$
{y'_i}^n = D_{1-}({y_i}^n) + o(\Delta r^n) \quad \text{und} \quad {y'_i}^n = D_{1+}({y_i}^n) + o(\Delta r^n) \tag{121}
$$

mit

$$
D_{1-}({y_i}^n) := \frac{{y_i}^n - y_{i-1}^n}{\Delta r^n} \quad \text{und} \quad D_{1+}({y_i}^n) := \frac{y_{i+1}^n - y_i^n}{\Delta r^n} \tag{122}
$$

Weiterhin gilt

$$
{y''_i}^n = D_{20}({y_i}^n) + o((\Delta r^n)^2) \tag{123}
$$

mit

$$
D_{20}(y_i^n) := \frac{y_{i+1}^n - 2 y_i^n + y_{i-1}^n}{(\Delta r^n)^2}. \tag{124}
$$

Wir nehmen die folgenden Approximationen für die auftretenden Ableitungen vor:

- ${y'_0}^n$ mit $D_{1+}({y_0}^n)$,
- ${y'_i}^n$ für $i > 0$ mit $D_{1-}({y_i}^n)$,
- ${v'_i}^n$ für $i > 0$ mit $D_{1-}({v_i}^n)$,
- ${y''_i}^n$ für $0 < i < N$ mit $D_{20}({y_i}^n)$,
- ${y''_N}^n$ mit $D_{2-}({y_N}^n)$.

5.4 Algorithmus

Die explizite Verfahrenvorschrift lautet damit:

1. Anfangswerte bereitstellen: Setze $n = 0$ und $t = 0$, gib einen konsistenten Anfangsdatensatz an, d.h.
   $X_{\mathrm{L}}^n, r_0^n, y_0^n, y_1^n, ..., y_N^n, h_0^{*n}, h_1^{*n}, ..., h_N^{*n}, r_N^n$ mit Δr^n aus
   $$\Delta r^n = \frac{r_N^n - r_0^n}{N} \tag{125}$$
2. neuer Zeitschritt $n + 1$
   (a) Berechne v_0^n, $v_1^n, ..., v_{N-1}^n$,v_N^n zum alten Zeitschritt aus
   $$v_0^n = g_{\mathrm{vI}}\Big(X_{\mathrm{L}}^n, r_0^n, y_0^n, D_{1+}(y_0^n), h_0^{*n}, r_N^n, v_N^n, y_N^n\Big), \tag{126}$$
   $$\begin{aligned} D_{1-}(v_i^n) + 2\frac{v_i^n}{r_i^n} & \\ &= \hat{g}_{\mathrm{v}}\left(X_{\mathrm{L}}^n, r_0^n, y_0^n, D_{1+}(y_0^n), h_0^{*n},\right. \\ &\quad \left. r_i^n, y_i^n, D_{1-}(y_i^n), D_{20}(y_i^n), h_i^{*n}, r_N^n, v_N^n, y_N^n\right) \\ &\qquad \text{für} \quad i = 1, .., N-1. \end{aligned} \tag{127}$$
   und
   $$D_{1-}(v_N^n) + \frac{v_N^n}{r_N^n}\left(2 + g_{\mathrm{vO}}\Big(y_N^n, D_{2-}(y_N^n)\Big)\right) = 0 \tag{128}$$
   (b) Berechne r_0^{n+1} aus
   $$r_0^{n+1} = r_0^n + \Delta t^{n+1}\hat{g}_{\mathrm{I}}\Big(r_0^n, X_{\mathrm{L}}^n, y_0^n, D_{1+}(y_0^n), h_0^{*n}, r_N^n, v_N^n, y_N^n\Big) \tag{129}$$
   (c) Berechne r_N^{n+1} aus
   $$r_N^{n+1} = r_N^n + \Delta t^{n+1} v_N^n \tag{130}$$

(d) Berechne Δr^{n+1} aus

$$\Delta r^{n+1} = \frac{r_N^{n+1} - r_0^{n+1}}{N} \tag{131}$$

(e) Prediktorschritt: $j = 0$. Berechne $y_N^{n+1(j)}$ aus

$$y_N^{n+1(j)} - y_N^n = \Delta t^{n+1} g_{uO}(r_N^n, v_N^n, y_N^n). \tag{132}$$

(f) Berechne $X_\mathrm{L}^{n+1(j)}$, $y_0^{n+1(j)}$ und $h_0^{*n+1(j)}$ aus

$$\begin{aligned} f_\mathrm{I}\Big(X_\mathrm{L}^{n+1(j)}, r_0^{n+1}, y_0^{n+1(j)}, h_0^{n+1(j)}, y_N^{n+1(j)}\Big) &= 0, \\ f_\mathrm{L}\Big(X_\mathrm{L}^{n+1(j)}, r_0^{n+1}, y_0^{n+1(j)}, h_0^{n+1(j)}, y_N^{n+1(j)}\Big) &= 0 \\ \text{und} \quad f_\mathrm{h}\Big(y_0^{n+1(j)}, h_0^{n+1(j)}, y_N^{n+1(j)}\Big) &= 0. \end{aligned} \tag{133}$$

(g) Berechne $y_i^{n+1(j)}$ aus

$$\begin{aligned} & y_i^{n+1(j)} + (r_i^n - r_i^{n+1}) D_{1-}({y_i}^{n+1(j)}) - y_i^n \\ & \quad = \Delta t^{n+1} g_\mathrm{S}\Big(r_i^n, v_i^n, y_i^n, D_{1-}(y_i^n), D_{20}(y_i^n), h_i^{*n}, r_N^n, v_N^n, y_N^n)\Big) \\ & \qquad \text{für} \quad i = 1, 2, .., N-1. \end{aligned} \tag{134}$$

(h) Berechne $h_i^{n+1(j)}$ aus

$$f_h(y_i^{n+1(j)}, h_i^{n+1(j)}, y_N^{n+1(j)}) = 0 \quad \text{für} \quad i = 1, 2, .., N-1. \tag{135}$$

(i) Korrektorschritt: Berechne $y_N^{n+1(j+1)}$ aus

$$y_N^{n+1(j+1)} = y_{N-1}^{n+1(j)} \tag{136}$$

(j) Fehlerkontrolle: Ist $|y_N^{n+1(j+1)} - y_N^{n+1(j+1)}| < \varepsilon_y$ wahr, gehe zum nächsten Schritt. Anderenfalls setze $j := j + 1$ und gehe zurück zu (e).

3. Update: $X_\mathrm{L}^{n+1} = X_\mathrm{L}^{n+1(j)}$, $y_\mathrm{i}^{n+1} = y_\mathrm{i}^{n+1(j)}$, $h_\mathrm{i}^{*n+1} = h_\mathrm{i}^{*n+1(j)}$ für $i = 0, ..., N$ und $t := t + \Delta t^{n+1}$.

4. Ist $t < t_{end}$ setze $n := n+1$ und gehe zurück zu (2), anderenfalls Abruch, Ende der Berechnung.

Mit diesen Schritten sind alle Größen zum aktuellen Zeitschritt bekannt. Bis auf den Schritt (2f) sind die zu lösenden Gleichungen alle linear. Alle Größen lassen sich in der vorgeschlagenen Reihenfolge nacheinander berechnen.

Anmerkung

Das explizite Euler-Rückwärts-Verfahren erfolgte für die Ortsdiskretisierung um $r = r_i^{n+1}$.

Beim Euler-Vorwärts-Verfahren wird günstigerweise die Ortsdiskretisierung um $r = r_i^{n+1}$ gewählt [2]. Dort tritt das Problem von höheren Ortsableitungen bei einer Ortsdiskretisierung um $r = r_i^n$ auf. Die so resultierenden Verfahren sind implizit. Wegen der nichtlinearen Kopplungen müssen alle Schritte gleichzeitig berechnet werden. Bei einer Ortsdiskretisierung um $r = r_i^{n+1}$ ergibt sich z.B.

$$\begin{aligned} & y_i^{n+1} - y_i^n - D_{1-}(y_i^n)\Delta r^n (r_i^{n+1} - r_i^n) \\ & \qquad = g_{\mathrm{S}}\Big(r_0^{n+1}, X_{\mathrm{L}}^{n+1}, y_0^{n+1}, r_i^{n+1}, v_i^{n+1}, y_i^{n+1}, D_{1-}(y_i^{n+1}), D_{20}(y_i^{n+1})\Big) \\ & \qquad\qquad\qquad\qquad\qquad\qquad \text{für} \quad i = 1, .., N-1. \end{aligned} \tag{137}$$

Im Falle von As-Gas am Außenrand der festen Kugel ist ähnlich zu verfahren. Hier liegt jetzt 3 Phasengebiet vor. Es kommen jedoch hier noch weitere Gleichungen hinzu da jetzt der feste Außenrand eine Phasengrenze ist.

References

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