Macroscopic diffusion models for precipitation in crystalline gallium arsenide

– Modelling, analysis and simulation –

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"Die Mathematiker sind eine Art Franzosen:
redet man zu ihnen,
so übersetzen sie es in ihre Sprache,
und dann ist es alsobald ganz etwas anders."

Johann Wolfgang von Goethe

Abstract

Based on a thermodynamically consistent model for precipitation in gallium arsenide crystals including surface tension and bulk stresses by Dreyer and Duderstadt [DD08], we propose two different mathematical models to describe the size evolution of liquid droplets in a crystalline solid. The first model treats the diffusion-controlled regime of interface motion, while the second model is concerned with the interface-controlled regime of interface motion. Our models take care of conservation of mass and substance. These models generalise the well-known Mullins-Sekerka model [MS63] for Ostwald ripening. We concentrate on arsenic-rich liquid spherical droplets in a gallium arsenide crystal. Droplets can shrink or grow with time but the centres of droplets remain fixed. The liquid is assumed to be homogeneous in space.

Due to different scales for typical distances between droplets and typical radii of liquid droplets we can derive formally so-called mean field models. For a model in the diffusion-controlled regime we prove this limit by homogenisation techniques under plausible assumptions. These mean field models generalise the Lifshitz-Slyozov-Wagner model, see [LS61], [Wag61], which can be derived from the Mullins-Sekerka model rigorously, see [Nie99], [NO01], and is well-understood.

Mean field models capture the main properties of our system and are well adapted for numerics and further analysis. We determine possible equilibria and discuss their stability. Numerical evidence suggests in which case which one of the two regimes might be appropriate to the experimental situation.

Zusammenfassung

Ausgehend von einem thermodynamisch konsistenten Modell von Dreyer und Duderstadt [DD08] für Tropfenbildung in Galliumarsenid-Kristallen, das Oberflächenspannung und Spannungen im Kristall berücksichtigt, stellen wir zwei mathematische Modelle zur Evolution der Größe flüssiger Tropfen in Kristallen auf. Das erste Modell behandelt das Regime diffusionskontrollierter Interface-Bewegung, während das zweite Modell das Regime Interface-kontrollierter Bewegung des Interface behandelt. Unsere Modellierung berücksichtigt die Erhaltung von Masse und Substanz. Diese Modelle verallgemeinern das wohlbekannte Mullins-Sekerka-Modell [MS63] für die Ostwald-Reifung. Wir konzentrieren uns auf arsenreiche kugelförmige Tropfen in einem Galliumarsenid-Kristall. Tropfen können mit der Zeit schrumpfen bzw. wachsen, die Tropfenmittelpunkte sind jedoch fixiert. Die Flüssigkeit wird als homogen im Raum angenommen.

Aufgrund verschiedener Skalen für typische Distanzen zwischen Tropfen und typischen Radien der flüssigen Tropfen können wir formal so genannte Mean-Field-Modelle herleiten. Für ein Modell im diffusionskontrollierten Regime beweisen wir den Grenzübergang mit Homogenisierungstechniken unter plausiblen Annahmen. Diese Mean-Field-Modelle verallgemeinern das Lifshitz-Slyozov-Wagner-Modell, siehe [LS61], [Wag61], welches rigoros aus dem Mullins-Sekerka-Modell hergeleitet werden kann, siehe [Nie99], [NO01], und gut verstanden ist.

Mean-Field-Modelle beschreiben die wichtigsten Eigenschaften unseres Systems und sind gut für Numerik und für weitere Analysis geeignet. Wir bestimmen mögliche Gleichgewichte und diskutieren deren Stabilität. Numerische Resultate legen nahe, wann welches der beiden Regimes gut zur experimentellen Situation passen könnte.

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Chapter 1.

Introduction

1.1. A real world problem in the production of semi-insulators

Semi-insulating gallium arsenide has a broad range of applications in micro- and opto-electronic devices e.g. for mobile phones working on wave bands used for UMTS. The industrial production process of semi-insulating gallium arsenide (GaAs) as done by Freiberger Compound Materials requires at the end some additional final heat treatment at high temperatures ($\sim$ 1000 K – 1200 K) in order to improve the quality of the semi-insulator. During this treatment undesirable liquid droplets precipitate in the solid phase due to misfits and due to supersaturation. The precipitation process is accompanied by surface tension and mechanical bulk stresses. Droplets negatively influence mechanical and semi-insulating properties of the crystal. Their elimination, if possible, is a crucial point for the production of semi-insulators.

One of the challenges is the necessity to guarantee a mean mole fraction of As in the wafer of $X_0 = 0.500082$, which is specified to an accuracy of $\mathcal{O}(10^{-6})$, in order to have the desired semi-insulating behaviour. Since experiments have to be carried out at high temperatures and high pressure, mathematical modelling is important in this situation in order to understand well the evolution of a large number of precipitates. The goal of a mathematical model that describes the nucleation and evolution of the precipitates is to look for regimes, where for large times either only a few relatively big droplets survive or where a homogeneous spatial distribution of relatively small droplets results.

1.2. Classical models for phase transitions

For the modelling of phase transitions various types of models are suggested. Sharp-interface models and phase-field models capture the spatial structure of a phase transition, while Lifshitz-Slyozov-Wagner models and Becker-Döring models do not. The first three of these models are diffusion models. We describe the different models in the following briefly.

1.2.1. Phase-field models

In a phase-field model the interface between two phases is modelled by a differential equation for the evolution of an auxiliary field c, the phase field, or also called order parameter. Two distinct values of the phase field, e.g. c_S or c_L, correspond to the two phases. Between the two phases is a so-called "mushy" region with a smooth change between the two values c_S and c_L. The set of points, where $c = \frac{1}{2}|c_S - c_L|$, are interpreted as position of the interface. Let the width of the mushy region be represented by a small dimensionless parameter δ. Phase-field models are usually constructed in such a way that in the limit $\delta \to 0$ the interfacial dynamics of a sharp-interface model is recovered. The advantage of phase-field models is, that one has to solve one differential equation for the whole domain and one has not to deal with many free boundaries.

The nonlinear Cahn-Hilliard equation [Cah61] is one of the most important phase-field models for the process of spinodal decomposition of a miscible chemical mixture. We assume here Ω to be a given open domain, which is not depending on time. Let $c(x,t)$ now be the concentration of one species of the mixture and let $u(x,t)$ denote the chemical potential, both defined for all $x \in \Omega$. A free energy functional is then assumed to be of the form

$$\mathcal{A}_{CH}(c) = \int_\Omega F(c(x)) + \frac{\delta^2}{2}|\nabla c(x)|^2 dx$$

with a given non-convex bulk free energy density F. The chemical potential is assumed to be related to c by $u = \frac{\delta \mathcal{A}_{CH}}{\delta c} = F'(c) - \delta^2 \Delta c$. The Cahn-Hilliard equation

$$\partial_t c = \Delta(F'(c) - \delta^2 \Delta c) \tag{1.1}$$

is then derived from the diffusion equation $\partial_t c = \Delta u$ neglecting concentration dependence of the mobility and assuming e.g. homogeneous Neumann boundary conditions on the chemical potential, $\nabla u \cdot \nu = 0$ on $\partial\Omega$. It follows, that $\int_\Omega c\, dx$ is conserved.

We remark, that the Allen-Cahn equation,

$$\partial_t c = \delta^2 \Delta c - F'(c),$$

which is also often used in material science, differs from the Cahn-Hilliard equation in particular in the point, that the order parameter c is not conserved.

Different thermodynamically consistent generalisations of the Cahn-Hilliard equation have been proposed e.g. by Gurtin and Fried [FE96] or by Alt and Pawłow [AP96]. A generalisation derived from a microforce balance, relying on the second law of thermodynamics in the form of the entropy principle according to Müller and Liu, is given by Pawłow [Paw06]. In the van der Waals-Cahn-Hilliard equation, which is a thermodynamically consistent phase-field model, the density ρ plays the role of the order parameter c and the free energy functional is of the form

$$\mathcal{A}_{WCH}(\rho, \Omega) = \int_\Omega \rho(x)\psi(\rho(x)) + \frac{\delta^2}{2}|\nabla \rho(x)|^2 dx + p_0|\Omega|, \tag{1.2}$$

with the constraint $\int_\Omega \rho\, dx = const.$ The term $p_0|\Omega|$ enters, if one considers the case of fixed external pressure, while in case of fixed volume this term does not appear.

A similar ansatz including elasticity is the Cahn-Larché equation [CL82], which deals in case of a time-dependent domain with a free energy functional

$$\mathcal{A}_{CL}(\rho, U) = \int_\Omega \rho(x)\psi(\rho(x)) + \frac{\delta^2}{2}|\nabla \rho(x)|^2 + W_{el}(\rho(x), e(U(x)))\, dx + p_0|\Omega|, \tag{1.3}$$

where the elastic energy density is $W_{el} = \frac{1}{2}e(U) : K(\rho)e(U)$, K here the elasticity tensor. Alternatively, it would be interesting to consider a $\rho\psi(\rho, U)$ in the van der Waals-Cahn-Hilliard phase-field model, where $\psi = \psi^{chem}(\rho) + \psi^{mech}(U)$.

A good overview over further phase-field models, its derivation from thermodynamics and the analysis thereof, can be found in the book of Brokate and Sprekels [BS96], ch. 4, 6 & 7.

1.2.2. Sharp interface models

In a sharp-interface model we have differential equations in each of the phases and boundary conditions on the free boundaries between the phases, the interfaces. A well-known sharp-interface model for phase transition is the Mullins-Sekerka model, which has been introduced by Mullins and Sekerka in 1963 from a physical point of view [MS63]. Pego [Peg89] rigorously derived the Mullins-Sekerka model from the nonlinear Cahn-Hilliard equation (1.1) in the limit $\delta \to 0$.
Let again σ denote the surface tension. Then close to phase-equilibrium the system can be described by

$$\begin{aligned} \Delta u &= 0 && \text{in } \Omega \setminus \overline{\cup_{i\in N} I_i}, && (1.4)\\ u &= \kappa\sigma && \text{on } I_i \quad \forall i \in N, && (1.5)\\ \nabla u \cdot \nu &= 0 && \text{on } \partial\Omega, && (1.6)\\ \dot{r}_i &= [[\nabla u \cdot \nu]] && \forall i \in N, && (1.7) \end{aligned}$$

for all times. We refer to the mathematical description of the Mullins-Sekerka model (1.4) – (1.7) as model (MS). The model (MS) conserves the volume of droplets. This can be seen for spherical droplets by combining (1.7) and (1.4) to $\partial_t \sum_i r_i^3 = \sum_i r_i^2 \dot{r}_i = -\int_\Omega \Delta u = 0$.
The classical Mullins-Sekerka model [MS63] does not include mechanical deformations. Dreyer and Kraus [DK05] derive sharp interface limits of the van der Waals-Cahn-Hilliard equation for time-dependent domains. They show that, if $W(\rho) := \rho\psi(\rho)$ is given and has two minima, $\overline{\rho}_S$ and $\overline{\rho}_L$, then close to the limit $\delta \to 0$ of (1.2) the available free energy is of the form

$$\mathcal{A}^{lim}_{WCH}(\rho,\Omega) = \int_{\Omega_S} \overline{\rho}_S \psi(\overline{\rho}_S)\,dx + \int_{\Omega_L} \overline{\rho}_L \psi(\overline{\rho}_L)\,dx + \delta \sum_{i\in N} \int_{I_i} \sigma_{WCH}\,dx + p_0|\Omega| + o(\delta), \qquad (1.8)$$

where σ_{WCH} is a constant determined by W and the geometry of Ω_L. σ_{WCH} can be interpreted as surface tension.
For the Cahn-Larché equation we expect to find close to the limit $\delta \to 0$ of (1.3)

$$\begin{aligned} \mathcal{A}^{lim}_{CL}(\rho,\Omega) = &\int_{\Omega_S} \overline{\rho}_S \psi(\overline{\rho}_S) + W_{el}(\overline{\rho}_S, e(U(x)))\,dx + \int_{\Omega_L} \overline{\rho}_L \psi(\overline{\rho}_L) + W_{el}(\overline{\rho}_L, e(U(x)))\,dx \\ &+ \delta \sum_{i\in N} \int_{I_i} \sigma_{WCH}\,dx + p_0|\Omega| + o(\delta). \end{aligned} \qquad (1.9)$$

1.2.3. Models of Becker-Döring type

In Becker-Döring processes [BD35] the liquid droplets are considered as clusters of identical particles, which can coagulate or fragmentate by gaining or loosing an atom. The mathematical Becker-Döring model, see [Fre45], [BCP86], is an infinite system of ODEs for the total number $z_l(t)$ of clusters, consisting of $l \geq 1$ particles, at time t. The number of free atoms is denoted by $z_1(t)$. The condensation rate $\Gamma_l^C(t)$ and the evaporation rate $\Gamma_{l+1}^E(t)$ give the probability, that an l cluster gains or looses an atom. The Becker-Döring system reads

$$\begin{aligned} \partial_t z_l &= j_{l-1} - j_l && \forall l \geq 2, && (1.10)\\ \partial_t z_1 &= -\sum_{k\geq 1} j_k - j_1, && && (1.11) \end{aligned}$$

with the fluxes $j_l = \Gamma_l^C z_l - \Gamma_{l+1}^V z_{l+1}$. The system is closed by constitutive assumptions on the transition rates Γ_l^C and Γ_{l+1}^E. We refer to (1.10) – (1.11) as model (BD).

Note, that in the literature the quantities z_l are often considered as the volume densities of l-clusters, and not as numbers, which clearly yields to contradictions if the total volume is not conserved. A thermodynamically consistent Becker-Döring system for precipitation in crystalline gallium arsenide is derived by Dreyer and Duderstadt [DD06]. They derive a thermodynamically consistent choice of the rates Γ_l^C and Γ_l^V. For rigorous mathematical results in this case we refer to Herrmann *et al.* [HNN06].

1.2.4. Models of Lifshitz-Slyozov-Wagner type

By formal arguments for spherical droplets and small volume fraction, Lifshitz, Slyozov [LS61] and Wagner [Wag61] reduced the evolution law (1.7) of the (MS) model to an evolution of the radii distribution ν. The surface tension, which is assumed to be a constant, is usually put into the time scale. The classical Lifshitz-Slyozov-Wagner model states that

$$u = \overline{u} \qquad \text{in } \Omega \setminus \overline{\cup_{i \in N} \Sigma_i}, \tag{1.12}$$

$$\Delta u = 0 \qquad \text{in } \Sigma_i \quad \forall i \in N, \tag{1.13}$$

$$u = \frac{1}{r_i} \qquad \text{on } I_i \quad \forall i \in N, \tag{1.14}$$

$$\dot{r}_i = \frac{\overline{u} - \frac{1}{r_i}}{r_i} \qquad \forall i \in N, \tag{1.15}$$

where (1.12) reflects, that far away from droplets the chemical potential is governed by an only time-dependent mean field $\overline{u}(t)$, while (1.13) means that close to a droplet the chemical potential is the harmonic solution for this droplet and its neighbourhood Σ_i alone. The evolution equation for the radii (1.15) follows then from (1.7). The mean field is determined by conservation of volume of droplets by $\overline{u} = (\sum_i 1)/(\sum_i r_i)$. We refer to the model (1.12) – (1.15) as (LSW).

Niethammer proved the limit (MS) → (LSW) and the corresponding limit for a non-stationary version of (MS). The limit (BD) → (LSW) has been derived rigorously in case of small excess density by Niethammer [Nie03], [Nie04b]. A modification of the classical equations of (LSW), which conserves the total volume of all droplets s.t. the total mass is conserved, has been also analysed, see [NP01].

1.3. Outline of the thesis

We consider a sharp-interface model since for phase-field models the right scaling is not clear *a priori* and has to be determined by fitting the phase-field model to a sharp-interface model. The availability $\mathcal{A}$, which we use as starting point in our model, is deduced from first principles, see [DD08]. In particular our model takes care, that liquid droplets which become too small, do not behave as liquid phase anymore, and thus a droplet vanishes in our model at a positive radius $r_{min} > 0$. This thermodynamically consistent sharp interface model leads to a mathematical problem of a nonlinear diffusion equation with a convective term, coupled to a linear mechanical problem and to ODEs for the free boundaries.

A similar problem for a model, which is not derived from thermodynamics and without a convective term, is solved by Blesgen and Weikard [BW05]. They use as techniques a time-discretisation of the model and the minimisation of the free energy functional for fixed time. Furthermore in their study the influence of small scales is not considered.

This work is built up in the following way. In the next chapter we present the thermodynamical modelling for liquid inclusions in crystalline solids, focussing on GaAs. There we introduce the central quantities and show, how we can reduce them to a set of independent variables. These variables can be determined from coupled PDE and ODE systems, which we derive. Throughout the work we consider simultaneously two regimes of interface motion, a diffusion-controlled and an interface-controlled regime.

In Section 3.1 we introduce typical scales of the problem and identify a small scaling parameter ε. ε is related to the small volume fraction of the liquid droplets. There are two interesting scaling regimes, which we discuss in Subsection 3.1.3: the critical regime, where the droplets contribute directly to the limit equation for the chemical potential and the dilute regime, where we find in the limit a only time-dependent mean field of the chemical potential. In Sections 3.3 and 3.4 we formally derive a homogenisation limit in case of the dilute scaling as $\varepsilon \to 0$ for the regimes (DC) and (IC). From an ansatz with a so-called "mean field" we get by formal homogenisation a macroscopic "mean field problem", which will turn out to capture the effective behaviour of the system.

In Chapters 4 and 5 we concentrate on regime (DC) in the critical scaling regime.

In Chapter 4 we examine existence and uniqueness of a class of coupled differential equations, which are systems of elliptic and parabolic equations together with ODEs for the free boundaries, for which no standard results exist as far as known by the author. This general problem includes our critically scaled problem of Section 3.1, if the latter is slightly simplified. In our analysis we proceed similarly to Niethammer [Nie99], who considered quasi-stationary and instationary linear diffusion equations on time-dependent domains. After transformation of the problem on a fixed domain we derive *a priori* estimates, where we use results on nonlinear parabolic PDEs and results from linear elasticity. By combining these estimates we prove local existence and uniqueness by means of Banach's fixed point theorem. Then we derive bounds on the geometric evolution by constructing suitable subsolutions and supersolutions, which allows to prove global existence and uniqueness. This main result is stated in Th. 4.8.

In Chapter 5 we derive estimates, which are uniformly in the scaling parameter, by combining estimates of Chapter 4 and explicitly calculating the dependence on the scaling parameter of some constants of the estimates. These uniform estimates allow us to rigorously derive effective equations, see Th. 5.7, for our problem under suitable assumptions, see Assumption 5.1. For special initial data this leads to "mean field problems" as already derived by formal homogenisation in Section 3.3 for the dilute regime.

The analysis of equilibria and its stability for the mean field problems as well as numerical results for the model in the dilute regime are shown in Chapter 6. In this Chapter we consider the dilute scaling regime for both regimes (DC) and (IC).

A discussion of our results and open questions follows in Chapter 7. The extension from gallium arsenide to precipitation in other crystalline solids fulfilling certain analogous assumptions as in the case of GaAs is discussed in Subsection 7.3.1.

We check some assumptions of our model for typical experimental situations in case of GaAs in Appendices A.2 – A.6. Explicit solutions for the special case of a spherical symmetric single droplet problem are given in Appendix C. Finally we list some material data in Appendix D.

Chapter 2.

Thermodynamically consistent model for gallium arsenide

We consider the precipitation process under the assumption that the external pressure p_0, temperature T and the number of atoms N_a of each substance $a \in \{\mathrm{Ga}, \mathrm{As}\}$ are constant in space and time.

Gallium arsenide crystals have a fcc-lattice with zinc-blend structure, for details of the lattice structure see [Got07]. There are three sublattices

$$SL := \{\alpha, \beta, \gamma\}$$

with the same number of lattice sites. In a perfect GaAs crystal a sublattice α would be completely occupied by Ga, a second sublattice β would be occupied by As while the interstitial sublattice γ is empty. In order to obtain semi-insulating GaAs the crystal is doped with trace elements (e.g. oxygen, silicon, boron) and a small amount of further As atoms. We work with a reduction of the so-called *Freiberg model*[1], where we consider only Ga, As and V, which denotes here vacancies, as species and assume that Ga occurs only on the α sublattice, β is mainly occupied by As and by some V, while γ is predominantly empty i.e. filled up mostly with vacancies and a few As atoms.

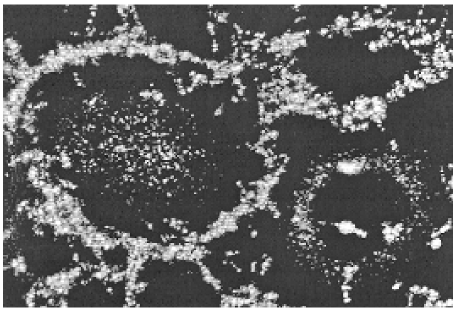

Figure 2.1.: “Sheep picture”, liquid droplets (light) in solid GaAs matrix (dark); droplets accumulate close to misfits of the crystal (From [Ste01], *Abb.* 3.7 i, for details see there).

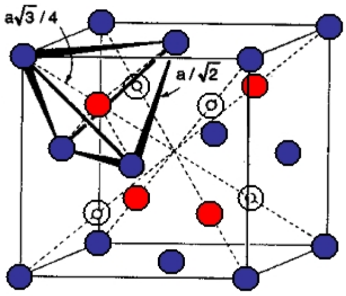

Figure 2.2.: Fcc-lattice, the crystal structure of the reduced Freiberg model, Ga (blue), As (red), vacancies (white) (From [DDHN04]).

We do not have to take quantum effects into account. Furthermore we neglect misfits of the crystal due to dislocations in the crystal structure and the resulting mechanical eigenstresses in this study.

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[1] For details of the full Freiberg model and its reduction see [DD08], [FJK$^+$99].

Now we give a short overview of the thermodynamically consistent model proposed by Dreyer and Duderstadt [DD08], which will be the starting point for our modelling and our analysis. They consider mainly the case of a single droplet. First we introduce some notation, which closely follows the notation of their paper.

2.1. Geometry

In our model droplets can vanish with time, but nucleation is not included in the model i.e. droplets are not created. We abbreviate the index set of all $\mathcal{N}(t)$ droplets existing at time t by $N(t)$. Initially we have given $\mathcal{N}(0) = \mathcal{N}^0 \in \mathbb{N}_0$ droplets and $N(0) = \{i \in \mathbb{N} | 1 \leq i \leq \mathcal{N}^0\}$.
We consider a body, represented by an open bounded domain

$$\Omega(t) = \Omega_S(t) \cup \Omega_L(t) \cup I(t) \subset \mathbb{R}^3,$$

where the simply connected open domain $\Omega_S(t)$ represents the solid phase, while

$$\Omega_L(t) = \cup_{i \in N(t)} \Omega_L^i(t)$$

is the union of disjoint $\Omega_L^i(t)$, which represent $\mathcal{N}(t) = |N(t)|$ liquid droplets. The union of all interfaces $I_i(t) := \partial\Omega_L^i(t)$, $i \in N(t)$ between the two phases is denoted by

$$I(t) = \cup_{i \in N(t)} I_i(t).$$

The droplets are assumed to be completely included in the solid i.e. $\partial\Omega(t) \cap I(t) = \emptyset$. The outer boundary $\partial\Omega$ and the interfaces I_i may move with velocity $w(x,t)$ in direction of the corresponding outer normal ν.
We consider our model for times $t \in (0, \mathcal{T}) =: \mathcal{J}_t \subset \mathbb{R}_+$. At first we choose $\mathcal{T} \in (0, \infty)$ sufficiently small s.t. no intersections between droplets with each other or with the outer boundary occur i.e.

$$\mathcal{T} < \inf_t \{\exists i, j \in N(t) : I_i(t) \cap I_j(t) \neq \emptyset \text{ or } \exists i \in N(t) : I_i(t) \cap \partial\Omega(t) \neq \emptyset\}. \tag{2.1}$$

The space variable is $x \in \Omega(t)$. The 3-dimensional measure of Ω will be denoted by $|\Omega|$ and analogously the 2-dimensional Hausdorff measure of I by $|I|$. Note that all geometric variables depend on time, that is due to the free boundaries $I_i(t)$ and to the fact that the external pressure is constant, so we cannot prescribe the total volume $\Omega(t)$. We define the parabolic cylinder

$$\Omega_{\mathcal{T}} = \{(x,t) \in \mathbb{R}^3 \times (0, \mathcal{T}) | x \in \Omega(t)\}. \tag{2.2}$$

Furthermore we may assume later that the droplets form spherical balls $\Omega_L^i = B_{r_i}(X_i)$ for all $i \in N$ and that $\Omega = B_{R_{bd}}(0)$. The motivation for these assumptions is given in Subsection 2.5.4. Thus the interface I_i can be parametrised by the radius $r_i(t)$ and the whole domain by $R_{bd}(t)$. The centres of the droplets $X_i \in \Omega(0), i \in N(0)$ are assumed to be fixed i.e. independent of time. In the case of GaAs it is quite reasonable to consider radial symmetry of droplets since the isotropic approximation of the cubic anisotropy of the crystal is good, see [DDEJ06]. Let us mention that this does not hold in general for semi-insulating crystals.
Droplets with too less atoms, i.e. smaller than a given minimal radius $r_{min} > 0$, do not behave like a liquid anymore and we have to take care of this, if we model the disappearance of a droplet. We come back to this point later in 2.6.7 in detail. We denote the times where the i-th droplet vanishes by

$$\tau_i := \inf_t \{|\Omega_L^i(t)| = \frac{4\pi}{3} r_{min}^3\} \quad i \in N(0). \tag{2.3}$$

In case of a spherical droplet we have $\tau_i = \inf_t\{r_i(t) = r_{min}\}$, $i \in N(0)$.

If we consider only a single droplet i.e. $\mathcal{N}(0) = 1$ we use analogous to [DD08] the following notations $I = I_1, r_I := r_1$ and w.l.o.g. we set $X_1 = 0$. The geometry for a single droplet problem with spherical $\Omega(t) = B_{R_{bd}(t)}(0)$ is illustrated in Fig. 2.3. We refer to this as spherically symmetric single droplet problem (SDP).

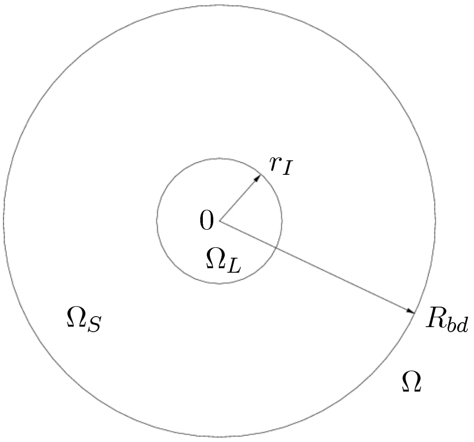

Figure 2.3.: Geometry of spherically symmetric single droplet problem.

For a many droplet problem with $\mathcal{N}(t) = 7$ the geometry is shown in Fig. 2.4. We refer to a many droplet problem with spherical Ω as (MDP).

Typically in the production process of GaAs the distances between droplets are of order $\mathcal{D}_0 := 1\mu$m, while typical radii are of order $\mathcal{R}_0 := 1$nm. This motivates later in Section 3.3.1 a monopole approximation, where we assume that the "influence" of a single droplet can be limited in good approximation to a spherical shell $\Sigma_i := B_{R^i_{ext}}(X_i)\backslash\overline{B_{r_i}(X_i)}$ with outer radius R^i_{ext}, $r_i < R^i_{ext} \ll \mathcal{D}_0$, while the mean field region (or far field region) $F := \Omega\backslash\overline{\cup_{i=1}^{\mathcal{N}} B_{R^i_{ext}}(X_i)}$ then represents the coupling between the $\mathcal{N}$ droplets and the mean field of the chemical potential $\overline{u}$, which turns out to depend only on time. Then the exact geometric relations between the X_i are neglected.

2.2. Some thermodynamics of mixtures

2.2.1. Basic variables for the solid and liquid phases of GaAs

We abbreviate the species of atoms on the various sublattices in the solid or liquid by the sets

$$\mathbf{a_S} := \{\mathrm{Ga}_\alpha, \mathrm{As}_\alpha, \mathrm{As}_\beta, \mathrm{As}_\gamma, \mathrm{V}_\alpha, \mathrm{V}_\beta, \mathrm{V}_\gamma\}, \quad \mathbf{a_L} := \{\mathrm{Ga}_L, \mathrm{As}_L\}.$$

The basic variables are the mole densities n_a for $a \in \mathbf{a_S} \cup \mathbf{a_L}$ and the mechanical displacement field $U : \mathcal{J}_t \times \Omega(t) \to \mathbb{R}^3$ as well as the free boundaries $\partial\Omega(t)$ and $I_i(t)$.

The restriction on Ω_S of a function f, defined on the whole Ω, is denoted by f_S or again by f, if mentioned so. f_L is the restriction on Ω_L. The restriction on Ω^i_L of a function g defined in the liquid is $g^i_L = g_L|_{\Omega^i_L}$. Due to these conventions we write e.g. $U^i_L := U|_{\Omega^i_L}$ and n^i_a for $a \in \mathbf{a_L}$, where $i \in N$. All variables in the whole study will be functions $\mathcal{J}_t \times \Omega_S(t) \to \mathbb{R}^+_0$ if they are defined in the solid part or $\mathcal{J}_t \times \Omega_L(t) \to \mathbb{R}^+_0$ for the liquid part, unless otherwise stated.

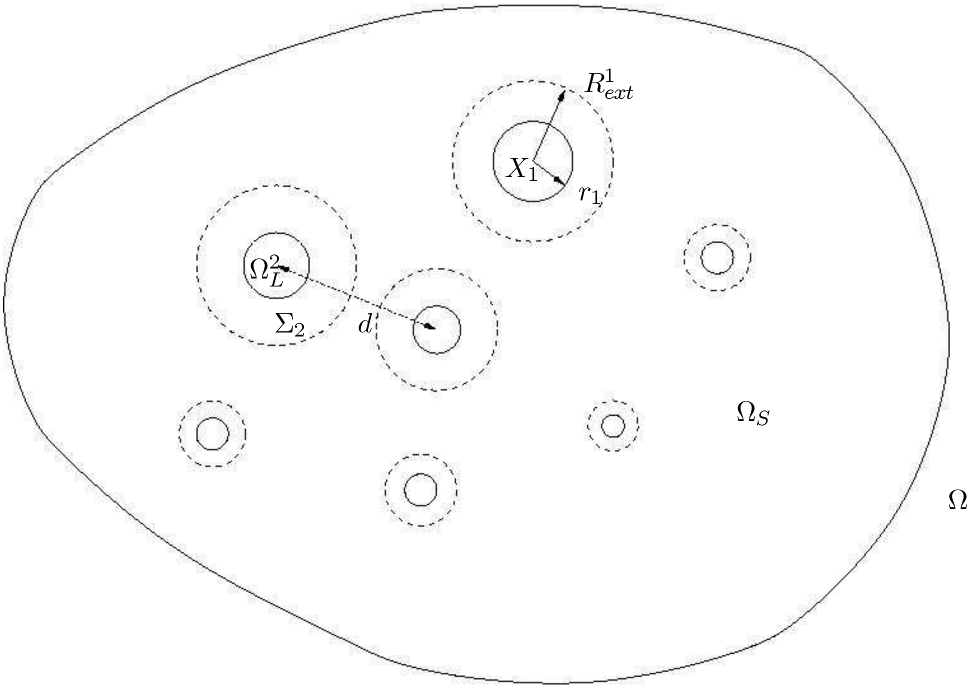

Figure 2.4.: Many droplet problem with arbitrary convex shape. Dashed radii R^i_{ext} model "influence" of a droplet in the monopole approximation, see Section 3.3.1.

2.2.2. Chemical constitution of GaAs in the solid and liquid phases

We define the mole density of atoms in the solid and in the liquid phase by

$$n := \begin{cases} n_S := n_{Ga_\alpha} + \sum_{b\in SL} n_{As_b}; & x \in \Omega_S(t), \\ n_L^i := n^i_{Ga_L} + n^i_{As_L} \qquad ; & x \in \Omega^i_L(t), \quad \forall i \in N. \end{cases}$$

The common mole density of sublattice sites is

$$n_G := \frac{1}{3} \sum_{a \in \mathbf{a_S}} n_a.$$

The factor 3 is chosen because we have three sublattices. In the Freiberg model we have equal number of lattice sites on each sublattice, i.e.

$$n_G = n_{Ga_\alpha} + n_{As_\alpha} + n_{V_\alpha} = n_{As_\beta} + n_{V_\beta} = n_{As_\gamma} + n_{V_\gamma}. \tag{2.4}$$

Note, that we have the following relation between the number density of atoms in the solid and the number density of sublattice sites:

$$n_S = n_G(3 - Y_V). \tag{2.5}$$

Further we define lattice occupancies by

$$Y_a := \frac{n_a}{n_G} \in [0,1], \quad a \in \mathbf{a_S}.$$

For keeping notation short we write

$$n_{Ga} := n_{Ga_\alpha}, \quad n_{As} := \sum_{b\in SL} n_{As_b}, \quad n_V := \sum_{b \in SL} n_{V_b},$$

and

$$Y_{Ga} := Y_{Ga_\alpha}, \quad Y_{As} := \sum_{b \in SL} Y_{As_b}, \quad Y_V := \sum_{b \in SL} Y_{V_b},$$

where we sum over the set of all sublattices SL.

The total mass density is

$$\rho := \begin{cases} \rho_S := \sum_{a \in \mathbf{a_S}} M_a n_a; & x \in \Omega_S(t), \\ \rho_L^i := \sum_{a \in \mathbf{a_L}} M_a n_a^i; & x \in \Omega_L^i(t), \quad \forall i \in N \end{cases} \tag{2.6}$$

where M_a denotes the molecular weight of the constituents $a \in \{\mathbf{a_S} \cup \mathbf{a_L}\}$. Note that $M_{Ga_\alpha} = M_{Ga}$, $M_{As_b} = M_{As}$ and $M_{V_b} = 0$ for all $b \in SL$. We abbreviate, since in many formulas only the relation between the relative atomic mass of arsenic and gallium enters,

$$\tilde{\mu} = \frac{M_{Ga}}{M_{As}} \approx \frac{69.723\,\mathrm{g\,mol^{-1}}}{74.922\,\mathrm{g\,mol^{-1}}} \approx 0.93061$$

where the data is taken from [SLBT01]. We only need, that $\frac{1}{3} < \tilde{\mu} < 1$ in this study.

The arsenic mole fraction is

$$X := \begin{cases} X_S := \frac{n_{As}}{n_S} = \frac{Y_{As}}{Y_{Ga}+Y_{As}}; & x \in \Omega_S(t), \\ X_L^i := \frac{n^i_{As_L}}{n^i_L} & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N \end{cases} \tag{2.7}$$

and the mean molecular weight is

$$M(X) := M_{Ga}(1-X) + M_{As}X = \frac{\rho}{n} = \begin{cases} M(X_S) = \frac{\rho_S}{n_S}; & x \in \Omega_S(t), \\ M(X_L^i) = \frac{\rho_L^i}{n_L^i}; & x \in \Omega_L^i(t), \quad \forall i \in N. \end{cases} \tag{2.8}$$

We introduce as abbreviation for the concentration of mass of As with respect to the total mass

$$P(X) := \frac{M_{As} n_{As}}{\rho} = \frac{M_{As} X}{M(X)}. \tag{2.9}$$

2.2.3. Motion and strain in the solid and liquid phases

We consider the GaAs as a material body, which is a continuum of material points, that are at time t at some point x. These coordinates are called Eulerian (or spatial) coordinates. The whole set of all points is the instantaneous configuration ("Momentankonfiguration") Ω. The state of deformation is described w.r.t. a reference configuration Ω^R. The material points of the reference configuration are given by Langragian (or material) coordinates $\mathbf{X}$. Every point $\mathbf{X}$ is related to a point x by the function $\chi(t,x) : (0,\mathcal{T}) \times \Omega^R \to \Omega$, which is called motion. We assume the motion

$$x = \chi(t, \mathbf{X})$$

to be bijective. The displacement field in material coordinates $\tilde{U} : \mathcal{J}_t \times \Omega^R \to \mathbb{R}^3$ or in spatial coordinates $U : \mathcal{J}_t \times \Omega \to \mathbb{R}^3$ is given by

$$\tilde{U}(t, \mathbf{X}) := \chi(t, \mathbf{X}) - \mathbf{X}, \quad U(t,x) := \tilde{U}(t, \chi^{-1}(t,x)) = x - \chi^{-1}(t,x). \tag{2.10}$$

All indices, like i, j, of the following mechanical quantities have values in the set $\{1, 2, 3\}$ unless otherwise stated. In general we write vectors without indices for coordinates, but write matrices in a notation with indices.

We describe the local state of deformation in a neighbourhood of a material point of the actual configuration w.r.t. its reference configuration by means of the displacement gradient H or the deformation gradient F, which are defined as

$$H^{ij}(t,\mathbf{X}) = \frac{\partial \tilde{U}^i(t,\mathbf{X})}{\partial \mathbf{X}^j}, \quad F^{ij}(t,\mathbf{X}) = \frac{\partial \chi^i(t,\mathbf{X})}{\partial \mathbf{X}^j} = \delta^{ij} + \frac{\partial \tilde{U}^i(t,\mathbf{X})}{\partial \mathbf{X}^j} = \delta^{ij} + H^{ij}(t,\mathbf{X}),$$

where δ^{ij} denotes the Kronecker delta. The change of the volume element is given by

$$J := \det F. \tag{2.11}$$

The motion can be inverted iff $J > 0$. If this holds we can equivalently work in Eulerian coordinates and define analogously

$$h^{ij}(t,x) = \partial_j U^i(t,x), \quad (F^{-1})^{ij}(t,x) = \partial_j(\chi^{-1})^i(t,x) = \delta^{ij} - \partial_j U^i(t,x) = \delta^{ij} - h^{ij}(t,x),$$

where $\partial_j := \partial_{x_j} := \frac{\partial}{\partial x_j}$ denotes the partial derivative w.r.t. x_j. Analogously we write $\partial_t := \frac{\partial}{\partial t}$.

By means of the motion we can define the barycentric velocity of the mixture in Lagrangian description $\tilde{v} : \mathcal{J}_t \times \Omega^R \to \mathbb{R}^3$ or in Eulerian description $v : \mathcal{J}_t \times \Omega \to \mathbb{R}^3$,

$$\begin{aligned} \tilde{v}(t,\mathbf{X}) &:= \partial_t \chi(t,\mathbf{X}) = \partial_t \tilde{U}(t,\mathbf{X}), \\ v(t,x) &:= \tilde{v}(t,\chi^{-1}(t,x)) = D_t U(t,x) = \partial_t U(t,x) + \nabla U(t,x) v(t,x), \end{aligned}$$

where $D_t := \partial_t + v \cdot \nabla$ denotes the material derivative. We refer to v in the following often just as "velocity". In Eulerian description we find the following formula for the velocity, see [Seg07],

$$v = (\mathbb{I}_3 - \nabla U)^{-1} \partial_t U = (\mathbb{I}_3 + \nabla U)\partial_t U + \mathcal{O}(\|\nabla U\|^2), \tag{2.12}$$

where $\mathbb{I}_3$ denotes the identity matrix in three dimensions.

We make the general assumption:

Assumption 2.1 (Small displacement gradients)**.** *We work in approximation of small displacement gradients* $\|\nabla U\|$ *i.e.* $\|\nabla U\| = \mathcal{O}(\tilde{h})$, *where* $\tilde{h}$ *is a dimensionless quantity given by data and* $\tilde{h} \ll 1$, *which is a special case of linear elasticity. In this approximation, also called "geometric linearisation", Eulerian* h *and Lagrangian* H *do not differ.*

Throughout this study, whenever it makes a difference at all, we use spatial i.e. Eulerian and not material i.e. Lagrangian coordinates.

For typical material data, as given in Appendix D, we find indeed $\tilde{h} \approx 10^{-3}$.

As long as we are in the regime of small displacement gradients we have $J \approx 1 + \operatorname{tr}(\nabla U) > 0$. This justifies $J > 0$ for all these times. Furthermore Assumption 2.1 allows us to work with

$$v = \partial_t U. \tag{2.13}$$

We emphasise that we have defined so far U (or $\tilde{U}$), h (or H) and v (or $\tilde{v}$) also on the liquid, which we underline by an additional subindex L e.g. U_L (or $\tilde{U}_L$), when we refer to the restriction of these variables in the liquid. In the liquid we get the explicit formulas $U_L = (a_L|x - X_i| + b_L)e_r$, where a_L and b_L are independent of x, or

$$h_L = a_L \mathbb{I}_3, \tag{2.14}$$

where $e_r = \frac{x - X_i}{|x - X_i|}$ is the unit vector in normal direction. Since we assume X_i to remain fixed, then $U_L|_{x=X_i} = 0$ and $b_L = 0$,

$$U_L = a_L |x - X_i| e_r. \tag{2.15}$$

This implies

$$v_L = \partial_t a_L |x - X_i| e_r.$$

Stresses are measured by the Cauchy stress tensor $\sigma_S \in \mathbb{R}^{3\times3}$ in the solid and the pressure $p_L^i : \mathcal{J}_t \times \Omega_L^i \to \mathbb{R}, i \in N$ in the liquid. As further mechanical variables we introduce the pressure in the solid $p_S : \mathcal{J}_t \times \Omega_S \to \mathbb{R}$ and the stress deviator tensor $\sigma_S^{<\cdot,\cdot>} : \mathcal{J}_t \times \Omega_S \to \mathbb{R}^{3\times3}$, which are related to σ_S, by

$$p_S := -\frac{1}{3}\mathrm{tr}(\sigma_S), \quad \sigma_S^{<ij>} := \sigma_S^{ij} + p_S\delta^{ij}. \tag{2.16}$$

where we introduce by $\mathrm{tr}(A) := \sum_i A^{ii}$ the trace of a tensor A^{ij}. $\sigma_S^{<\cdot,\cdot>}$ represents the stresses due to change of shape.

2.3. Side conditions

Besides the side condition (2.4) we have conditions on local conservation of particles and on mass and material mole fluxes across the free boundaries.

2.3.1. Balance of particle numbers

Let v_a be the velocity corresponding to constituent $a \in \mathbf{a_S} \cup \mathbf{a_L}$. The only chemical reactions in the Freiberg model are the transfer of constituents between the three sublattices SL. Hence as a natural assumption we have local conservation of substance (i.e. of As and Ga)

$$\partial_t n_{As_S} + \sum_{a\in SL} \nabla \cdot (v_{As_a} n_{As_a}) = 0 \quad \forall x \in \Omega_S(t)\, \forall t \in (0, \mathcal{T}), \tag{2.17}$$

$$\partial_t n_{Ga_\alpha} + \nabla \cdot (v_{Ga_\alpha} n_{Ga_\alpha}) = 0 \quad \forall x \in \Omega_S(t)\, \forall t \in (0, \mathcal{T}), \tag{2.18}$$

and in the liquid we have

$$\partial_t n_{a_L} + \nabla \cdot (v_{a_L} n_{a_L}) = 0 \qquad \forall x \in \Omega_L^i(t)\, \forall i \in N(t)\, \forall t \in (0, \mathcal{T}) \qquad \forall a \in \mathbf{a_L}. \tag{2.19}$$

Local conservation of the material species implies local conservation of mass

$$\partial_t \rho + \nabla \cdot (v\rho) = 0 \quad \forall x \in \Omega_S(t) \cup \Omega_L(t)\, \forall t \in (0, \mathcal{T}), \tag{2.20}$$

which is called the continuity equation.

We could try to link v_a to U_a, which are the displacements for species of type $a \in \mathbf{a_S} \cup \mathbf{a_L}$, but instead we eliminate the unknown v_a by the diffusion fluxes j_a. We introduce atomic diffusion fluxes for all constituents $a \in \mathbf{a_S} \cup \mathbf{a_L}$ defined by

$$j_a := n_a(v_a - v). \tag{2.21}$$

We introduce the total diffusion flux of As,

$$j_{(As)} := \begin{cases} j_{As_S} := \sum_{a\in SL} j_{As_a} = \sum_{a\in SL} n_{As_a}(v_{As_a} - v)\,; x \in \Omega_S(t) & \forall t \in (0, \mathcal{T}) \\ j_{As_L}^i := n_{As_L}^i(v_{As_L}^i - v_L^i) \qquad ; x \in \Omega_L^i(t)\, \forall i \in N & \forall t \in (0, \mathcal{T}). \end{cases} \tag{2.22}$$

Analogously we define the total diffusion flux of Ga

$$j_{Ga} := \begin{cases} j_{Ga_S} := j_{Ga_\alpha} = n_{Ga_\alpha}(v_{Ga_\alpha} - v)\,; x \in \Omega_S(t) & \forall t \in (0, \mathcal{T}) \\ j_{Ga_L}^i := n_{Ga_L}^i(v_{Ga_L}^i - v_L^i) \qquad ; x \in \Omega_L^i(t)\, \forall i \in N & \forall t \in (0, \mathcal{T}). \end{cases} \tag{2.23}$$

Notice, that the conservation law for Ga i.e. n_{Ga} is not independent of the conservation law for As:

$$\sum_{a\in\{\mathrm{As}_\alpha,\mathrm{As}_\beta,\mathrm{As}_\gamma,\mathrm{Ga}_\alpha\}} M_a j_a = 0 \iff j_{Ga_S} = -\frac{1}{\tilde{\mu}} j_{As_S}, \tag{2.24}$$

$$\sum_{a\in\mathbf{a_L}} M_a j_a = 0 \iff j_{Ga_L} = -\frac{1}{\tilde{\mu}} j_{As_L}. \tag{2.25}$$

For the sake of completeness we give the conservation law for vacancies

$$\partial_t n_V + \sum_{a\in SL} \nabla\cdot(v_{V_\alpha} n_{V_\alpha}) = 0 \quad \forall x\in\Omega_S(t) \quad \forall t\in(0,\mathcal{T}).$$

It is suitable to consider for vacancies the flux $j_V := j_{V_\gamma} + j_{As_\gamma}$. Analogously to (2.4) we require

$$j_{Ga_\alpha} + j_{As_\alpha} + j_{V_\alpha} = j_{As_\beta} + j_{V_\beta} = j_{As_\gamma} + j_{V_\gamma}. \tag{2.26}$$

Together with (2.24) this leaves four independent fluxes in the solid, $j_{As_a}, a\in SL$ and j_V, and by (2.25) only one independent flux in the liquid, j_{As_L}.

2.3.2. Side conditions on the free boundaries

We did not define variables on an interface so far. For some $x_0\in I$ we use the notation

$$[[f]](x_0,t) := f_+(x_0,t) - f_-(x_0,t) = \lim_{x\to x_0+} f(x,t) - \lim_{x\to x_0-} f(x,t) \tag{2.27}$$

where the subindex "+" stands for taking limits for sequences $\{x_n\}_{n\in\mathbb{N}}$ with $x_n\in\Omega_S(t)$ for all $n\in\mathbb{N}$ i.e. limits from the solid side and the subindex "−" stands for taking limits for sequences $\{x_n\}_{n\in\mathbb{N}}$ with $x_n\in\Omega_L^i(t)$ for all $n\in\mathbb{N}$. This is important, since not all variables will turn out to be continuous on I.
We abbreviate the component of v in normal direction by $v^\nu := v\cdot\nu$. Analogously we define w^ν, j^ν_{As}, j^ν_{Ga} and j^ν_V. We introduce the one-sided mole fluxes across the interface

$$\dot{\mathcal{N}}_a := n_a(v_a^\nu - w^\nu) \quad \forall a\in\mathbf{a_S}\cup\mathbf{a_L}. \tag{2.28}$$

We assume local conservation of the material mole flux across each interface i.e. $\dot{\mathcal{N}}_{Ga} = \dot{\mathcal{N}}_{Ga_L}$ and $\sum_{a\in SL}\dot{\mathcal{N}}_{As_a} = \dot{\mathcal{N}}_{As_L}$ or

$$[[j^\nu_{As}]] + [[n_{As}v^\nu]] = [[n_{As}]]w^\nu \qquad \forall x\in I_i(t)\,\forall i\in N(t)\,\forall t\in(0,\mathcal{T}), \tag{2.29}$$

$$[[j^\nu_{Ga}]] + [[n_{Ga}v^\nu]] = [[n_{Ga}]]w^\nu \qquad \forall x\in I_i(t)\,\forall i\in N(t)\,\forall t\in(0,\mathcal{T}), \tag{2.30}$$

which implies the conservation of the mass flux through the interface

$$[[\rho v^\nu]] = [[\rho]]w^\nu \qquad \forall x\in I_i(t)\,\forall i\in N(t)\,\forall t\in(0,\mathcal{T}). \tag{2.31}$$

Analogously we assume no net material mole fluxes at the outer boundary, $\sum_{a\in SL}\dot{\mathcal{N}}_{As_a} = 0$ and $\dot{\mathcal{N}}_{Ga} = 0$, which agrees to our experimental situation of a solid embedded in an inert gas. Hence the net mass flux over the outer boundary is also zero and we have

$$j^\nu_{As} + n_{As}v^\nu = n_{As}w^\nu \qquad \forall x\in\partial\Omega(t)\,\forall t\in(0,\mathcal{T}), \tag{2.32}$$

$$j^\nu_{Ga} + n_{Ga}v^\nu = n_{Ga}w^\nu \qquad \forall x\in\partial\Omega(t)\,\forall t\in(0,\mathcal{T}), \tag{2.33}$$

$$\rho_S v^\nu = \rho_S w^\nu \qquad \forall x\in\partial\Omega(t)\,\forall t\in(0,\mathcal{T}). \tag{2.34}$$

The conditions (2.32) – (2.34) can be stated as

$$j^{\nu}_{As} = 0 \qquad \forall x \in \partial\Omega(t)\, \forall t \in (0, \mathcal{T}), \tag{2.35}$$

$$j^{\nu}_{Ga} = 0 \qquad \forall x \in \partial\Omega(t)\, \forall t \in (0, \mathcal{T}), \tag{2.36}$$

$$w^{\nu} = v^{\nu} \qquad \forall x \in \partial\Omega(t)\, \forall t \in (0, \mathcal{T}). \tag{2.37}$$

Later in 2.6.5 we will exploit that we can determine $v_L \cdot \nu$ and $j_{As_L} \cdot \nu$ explicitly in a homogeneous liquid and j is linked to the gradient of the chemical potential ∇u by a constitutive law.

The equations (2.29) – (2.34) make sense since they imply global conservation laws for Ga, As and total mass.

2.3.3. Global conservation laws of mass and substance

We recall that we consider a system with given number of atoms N_0 and fixed As content $X_0 = \frac{N_{As}}{N_0}$. We exploit the global conservation laws for As and Ga

$$\int_{\Omega(t)} n_{As} = N_{As} = N_0 X_0, \tag{2.38}$$

$$\int_{\Omega(t)} n_{Ga} = N_{Ga} = N_0(1 - X_0), \tag{2.39}$$

which imply together the conservation of total mass

$$\int_{\Omega(t))} \rho = N_0 M(X_0) =: M_0. \tag{2.40}$$

We remark that there is no global conservation law for the density of sublattice sites n_G, since if crystal gets lost, the vacancies and their sublattice sites vanish.

There holds the following lemma, which we prove in Appendix A.1.

Lemma 2.1 (Global conservation laws and side conditions)**.** *The side conditions (2.29) – (2.31), (2.35) – (2.37) and the local conservation laws (2.17) – (2.20) imply the global conservation laws (2.38) – (2.40).*

2.4. Available free energy of the system and the approach of a thermodynamical system to equilibrium

Dreyer and Duderstadt start from first principles i.e. the first and second fundamental law of thermodynamics

$$\frac{d}{dt}E + p_0 \frac{d}{dt}|\Omega| = \dot{Q}, \quad \frac{d}{dt}S \geq \frac{1}{T_0}\dot{Q}, \tag{2.41}$$

which are the global balance laws for total energy E and entropy S for constant outer pressure p_0, constant outer temperature T_0 and conservation of mass and substance, where we assume that the temperature within Ω is constant i.e. $T = T_0$. $\dot{Q}$ denotes the heat power[2], which might enter or leave the system to ensure a constant temperature T_0. E is equivalent to the internal energy of the system, since we may neglect the contribution of the kinetic energy, because its contribution is very small compared to the internal energy, if we are close to equilibria. The availability $\mathcal{A}$ (or available free energy or also just "energy") is defined as (see the textbook of Müller [Mül01], p.149

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[2] Note that $\dot{Q}$ is the established notion in the literature, but does not mean the time derivative $\frac{d}{dt}Q$, since such a Q does not exist in general.

– 151)

$$\mathcal{A} := E - TS + p_0|\Omega|,$$

From (2.41) we have that the availability is decreasing in time

$$\frac{d}{dt}\mathcal{A} \leq 0. \tag{2.42}$$

Next we introduce the Helmholtz free energy $\Psi = E - TS$, which we decompose into a solid part, liquid and interfacial parts, which yields

$$\mathcal{A} := \Psi + p_0|\Omega| = \Psi_S + \sum_i \Psi_L^i + \sum_i \Psi_I^i + p_0|\Omega|.$$

Corresponding to Ψ we introduce the density ψ w.r.t. the mass density i.e. $\Psi_b = \rho_b \psi_b$, $b \in \{S, L\}$ and on the interface we introduce $\Psi_I = \int_I \sigma$, σ the surface tension. We find

$$\mathcal{A} := \int_{\Omega_S} (\rho_S \psi_S + p_0) + \sum_i \int_{\Omega_L^i} (\rho_L^i \psi_L^i + p_0) + \sum_i \int_{I_i} \sigma. \tag{2.43}$$

We assume here σ to be a constant depending only on temperature. Thereby for the evaluation of the Helmholtz energy density, $\rho_S \psi_S(T, \{n_a\}_{a \in \mathbf{a_S}}, J^{-2/3} F^T F)$ in the solid and $\rho_L \psi_L(T, n_{As_L}, n_{Ga_L})$ in the liquid, the Gibbs-Duhem equation

$$\psi_b \rho_b = \sum_{a \in \mathbf{a_b}} \mu_a n_a - p_b \quad \forall b \in \{S, L\} \tag{2.44}$$

is needed, where $\mu_a, a \in \mathbf{a_S} \cup \mathbf{a_L}$ are the chemical potentials, which will be determined later by constitutive laws. For a derivation of (2.44) we refer to [Mül01]. With (2.44) we obtain

$$\mathcal{A} := \int_{\Omega_S} (\sum_{a \in \mathbf{a_S}} \mu_a n_a + p_0 - p) + \sum_{i \in N} \int_{\Omega_L^i} (\sum_{a \in \mathbf{a_L}} \mu_a n_a + p_0 - p) + \sum_{i \in N} \int_{I_i} \sigma. \tag{2.45}$$

Stoth [Sto97] has proven that the standard two-phase Stefan problem, as usually treated in literature, can be reduced to a one-phase Stefan problem. Contrary in our situation quantities in the liquid, like the chemical potentials in the liquid, are only constant in space and not in time.

Assumption 2.2 (Homogeneous liquid droplets)**.** *We assume the liquid to be homogeneous in space, i.e. n_a and μ_a, $a \in \mathbf{a_L}$ are independent of x and hence can depend only on the free boundary $I_i(t)$ or on boundary values of the basic variables on $I_i(t)$.*

In [DD08] differential equations and boundary conditions are derived explicitly under our assumptions from (2.42) in case of a single droplet. This can be easily extended to the case of many droplets. For the result in [DD08] the transport theorem is used, what can be applied since we assume to have Lipschitz boundaries. The side conditions (2.29) – (2.31) and (2.35) – (2.37), which correspond to balance fluxes of substance/mass at free boundaries, are used as well for the derivation of the differential equations from (2.42). We give a short summary of their result.

We decompose the availability into a mechanical, chemical, interfacial and diffusive contribution

$$\mathcal{A} =: \mathcal{A}^{chem} + \mathcal{A}^{mech} + \mathcal{A}^I + \mathcal{A}^{diff}.$$

Since interfaces are disjoint we can decompose further

$$\mathcal{A}^I =: \sum_{i \in N} \mathcal{A}^i. \tag{2.46}$$

For the derivation of an explicit expression for $\frac{d}{dt}\mathcal{A}$ and explicit expressions for $\mathcal{A}^{chem}$, $\mathcal{A}^{mech}$, $\mathcal{A}^{I}$, $\mathcal{A}^{diff}$ and their time derivative respectively we refer to [DD08]. It is physically reasonable to assume that mechanical and chemical equilibria are achieved within short relaxation times, so we can assume

$$(A1) \qquad \frac{d}{dt}\mathcal{A}^{chem} = 0, \qquad\qquad (A2) \qquad \frac{d}{dt}\mathcal{A}^{mech} = 0$$

as necessary conditions for possible equilibria. Both processes are assumed to be in quasi-stationary equilibrium at all times.

It is not clear for us by now if we can assume that interfacial equilibrium is achieved faster or within same relaxation time as diffusive equilibrium. We consider two cases. In the regime of *diffusion controlled interface motion*, which we abbreviate by (DC), we have

$$(A3^*) \qquad \frac{d}{dt}\mathcal{A}^{I_i} = 0 \quad \forall i \in N \qquad \text{and} \qquad (A4) \qquad \frac{d}{dt}\mathcal{A}^{diff} \leq 0.$$

In the regime of *interface controlled interface motion*, which we refer to as (IC), we work with

$$(A3) \qquad \frac{d}{dt}\mathcal{A}^{I_i} \leq 0 \qquad \forall i \in N \qquad \text{and} \qquad (A4^*) \qquad \frac{d}{dt}\mathcal{A}^{diff} = 0.$$

We have strict equality in (A3) and (A4) if and only if an equilibrium of the total system, i.e. a minimum or maximum of the availability, is achieved. We emphasise that we do not want to consider the case (DC & IC), where both equilibria are achieved within almost equal relaxation times i.e. (A3) and (A4) hold.

Furthermore we have to guarantee that the availability is non-increasing if a droplet vanishes i.e.

$$\mathcal{A}(\tau_i+) - \mathcal{A}(\tau_i-) \leq 0. \tag{2.47}$$

We give the necessary conditions for an equilibrium explicitly: the necessary conditions for chemical equilibrium following from (A1) are

$$\mu_{V_\alpha} + \mu_{V_\beta} + \mu_{V_\gamma} = 0 \qquad \text{in } \Omega_S(t), \tag{2.48}$$

$$\mu_{As_\gamma} + \mu_{V_\beta} = \mu_{V_\gamma} + \mu_{As_\beta} \qquad \text{in } \Omega_S(t), \tag{2.49}$$

$$\mu_{As_\alpha} + \mu_{V_\beta} = \mu_{V_\alpha} + \mu_{As_\beta} \qquad \text{in } \Omega_S(t). \tag{2.50}$$

From (A2) it follows that the mechanical BVP is

$$(\text{div } \sigma_S)_i := \sum_{j=1}^{3} \partial_j \sigma_S^{i,j} = 0 \qquad \text{in } \Omega_S(t) \; \forall i \in \{1,2,3\}, \tag{2.51}$$

$$\nabla p_L^i = 0 \qquad \text{in } \Omega_L^i(t) \; \forall i \in N, \tag{2.52}$$

$$\nu \cdot \sigma_S \nu = -p_0 \qquad \text{on } \partial\Omega(t), \tag{2.53}$$

$$\tau_l \cdot \sigma_S \nu = 0 \qquad \text{on } \partial\Omega(t) \cup I_i(t) \; \forall l \in \{1,2\} \; \forall i \in N(t), \tag{2.54}$$

$$\nu \cdot \sigma_S \nu + p_L = -2\sigma k_M \qquad \text{on } I_i(t) \; \forall i \in N(t), \tag{2.55}$$

where τ_l are normalised tangential vectors to the outer normal ν. $k_M := -\text{div } \nu$ is the mean curvature. k_M is defined following the usual sign convention and we have $k_M|_{I_i} = -\frac{1}{r_i} \leq 0$ for our spherical droplets. We remark that we denote scalar products by $f \cdot g = \sum_{j=1}^{3} f_j g^j$ and products of a matrix A and a vector g by $(Ag)^j = \sum_{k=1}^{3} A^{jk} g_k$.

The following conditions at the interface follow from (A3)

$$j^\nu_{Ga} + n_{Ga}(v^\nu - w^\nu) = -\frac{B^i_{Ga}}{RT}(\mu_{Ga_\alpha} - \mu_{V_\alpha} - \mu_{Ga_L} - \frac{M_{Ga}}{\rho_S}\nu \cdot \sigma_S^{<\cdot,\cdot>}\nu) \quad \text{on } I_i(t)\ \forall i \in N(t), \tag{2.56}$$

$$j^\nu_{As} + n_{As}(v^\nu - w^\nu) = -\frac{B^i_{As}}{RT}(\mu_{As_\gamma} - \mu_{V_\gamma} - \mu_{As_L} - \frac{M_{As}}{\rho_S}\nu \cdot \sigma_S^{<\cdot,\cdot>}\nu) \quad \text{on } I_i(t)\ \forall i \in N(t), \tag{2.57}$$

$$j^\nu_{V} + n_{G}(v^\nu - w^\nu) = -\frac{B^i_{V}}{RT}(\mu_{V_\alpha} + \mu_{V_\beta} + \mu_{V_\gamma}) \quad \text{on } I_i(t)\ \forall i \in N(t), \tag{2.58}$$

where we use for the last line (2.4). (A4) yields the diffusion fluxes in the bulk

$$j_{As} = -\frac{B^D}{RT}\nabla(\mu_{As_\gamma} - \mu_{V_\gamma} - \frac{1}{\tilde{\mu}}(\mu_{Ga_\alpha} - \mu_{V_\alpha})) \quad \text{on } \Omega_S(t), \tag{2.59}$$

$$j_V = -\frac{B_V}{RT}\nabla(\mu_{V_\alpha} + \mu_{V_\beta} + \mu_{V_\gamma}) \quad \text{on } \Omega_S(t), \tag{2.60}$$

where $t \in (0, \mathcal{T})$. The factors B^i_{Ga}, B^i_{As}, B^i_V, B^D and B_V are non-negative and are called mobilities. More precisely, we have two types of mobilities, the interface mobilities B^i_{As}, B^i_{Ga} and B^i_V, where $i \in \mathcal{N}^0$, and the bulk mobilities B^D and B_V. $B^{(D)}$ is the diffusion mobility[3] of interstitial As, and B_V the diffusion mobility of vacancies.

We want to assume that vacancies have always by far the highest mobility, hence $B^i_V, B_V \to \infty$. Under these limits the equations (2.58) and (2.59) yield that (2.48) holds also on interfaces and we only have to consider (2.56) and (2.57) on interfaces and a single diffusion law (2.59).

The interface mobilities B^i_{As} and B^i_{Ga} are given as functions depending on X^i_L and r_i e.g. following the ansatz in [DD08], eqns. (4.39), by

$$B^i_{As} \overset{\text{assumpt.}}{=} n^i_{As_L}\sqrt{\frac{RT}{2\pi M(X^i_L)}}, \quad B^i_{Ga} \overset{\text{assumpt.}}{=} n_{Ga^i_L}\sqrt{\frac{RT}{2\pi M(X^i_L)}}. \tag{2.61}$$

We emphasise that the ansatz (2.61) is used as a guess for B^i_{As} and B^i_{Ga} and reliable experimental data for these quantities is not available. In particular we note that due to $X^i_L \in (0,1)$ these two mobilities are for arbitrary X^i_L finite. We introduce for ease of presentation a common interface mobility, which does not depend on the specific droplet,

$$B^I := \sqrt{\frac{RT}{2\pi M(\overline{X}_L)}}n^R_L = B^i_{As}\frac{n^R_L}{n^i_{As_L}}\sqrt{\frac{M(X^i_L)}{M(\overline{X}_L)}} = B^i_{Ga}\frac{n^R_L}{n^i_{Ga_L}}\sqrt{\frac{M(X^i_L)}{M(\overline{X}_L)}}. \tag{2.62}$$

The bulk mobility B of interstitial arsenic is assumed to be either a constant

$$B = B(T), \tag{2.63}$$

determined by experiments, or to be a function linked to the diffusion constant $D(T)$ of interstitial As, which may be determined by experiments, via

$$\frac{B}{RT}\frac{\partial}{\partial n_{As}}(\mu_{As_\gamma} - \mu_{V_\gamma} - \frac{1}{\tilde{\mu}}(\mu_{Ga_\alpha} - \mu_{V_\alpha})) = D. \tag{2.64}$$

We consider the two limiting cases. In the regime (DC) we assume

$$\frac{\max_{i\in N(t)}\{B^i_{As}, B^i_{Ga}\}}{B} \to \infty, \tag{2.65}$$

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[3] For ease of presentation we often write B instead of B^D in the following.

while for (IC) we consider the limit

$$\frac{\max_{i\in N(t)}\{B^i_{As}, B^i_{Ga}\}}{B} \to 0. \tag{2.66}$$

This yields for (A3*) from (2.56) and (2.57)

$$\mu_{Ga_\alpha} - \mu_{V_\alpha} - \mu_{Ga_L} - \frac{M_{Ga}}{\rho_S}\nu\cdot\sigma_S^{<\cdot,\cdot>}\nu = 0 \qquad \text{on } I_i(t)\;\forall i\in N(t), \tag{2.67}$$

$$\mu_{As_\gamma} - \mu_{V_\gamma} - \mu_{As_L} - \frac{M_{As}}{\rho_S}\nu\cdot\sigma_S^{<\cdot,\cdot>}\nu = 0 \qquad \text{on } I_i(t)\;\forall i\in N(t), \tag{2.68}$$

and for (A4*) from (2.58)

$$\mu_{As_\gamma} - \mu_{V_\gamma} - \frac{1}{\tilde{\mu}}(\mu_{Ga_\alpha} - \mu_{V_\alpha}) = const(t) \qquad \forall x\in\Omega_S(t), \tag{2.69}$$

where $t\in(0,\mathcal{T})$.

Unless otherwise mentioned we treat both regimes simultaneously, considering (DC) and then, if it makes a difference, the (IC) regime.

In Subsection 2.6 we will exploit the consequences of (A1), (A2), (A3*), (A4), (A3) and (A4*) in this order together with further constitutive laws and assumptions, which we state in the next subsection.

Instead of (2.56) we consider $\frac{B^I}{B^i_{As}}$ (2.57) $-\frac{1}{\tilde{\mu}}\frac{B^I}{B^i_{Ga}}$ (2.56), which we combine with (2.62), (2.22), (2.29) and (2.30), i.e.

$$\begin{aligned} &n_L^R\sqrt{\frac{M(X_L^i)}{M(\overline{X}_L)}}\Big(v^\nu_{As_L} - \frac{1}{\tilde{\mu}}v^\nu_{Ga_L} + (1-\frac{1}{\tilde{\mu}})(v^\nu_L - w^\nu)\Big) \\ &= -\frac{B^I}{RT}\Big(\mu_{As_\gamma} - \mu_{V_\gamma} - \mu_{As_L} - \frac{1}{\tilde{\mu}}(\mu_{Ga_\alpha} - \mu_{V_\alpha} - \mu_{Ga_L})\Big) \qquad \text{on } I_i(t)\;\forall i\in N(t) \end{aligned} \tag{2.70}$$

and hence we replace (2.67) by

$$\mu_{As_\gamma} - \mu_{V_\gamma} - \mu_{As_L} - \frac{1}{\tilde{\mu}}(\mu_{Ga_\alpha} - \mu_{V_\alpha} - \mu_{Ga_L}) = 0 \quad \text{on } I_i(t)\;\forall i\in N(t). \tag{2.71}$$

2.5. Constitutive model for GaAs and further assumptions

We relate our system to a reference system. Then we close our system by constitutive laws for n_L, n_G, σ_S, p_L and $\mu_a, a\in\mathbf{a_S}\cup\mathbf{a_L}$. For the general constitutive model and further details on the derivations of the constitutive laws we refer the reader to [DD08], Ch. 3(e), Ch. 5 and Ch. 6.

2.5.1. Reference system and reference configuration

If one neglects surface tension and bulk stresses the system is well understood, that can be experimentally realised by a solid cube of GaAs crystal in a liquid GaAs bath where the external pressure acts by means of an inert gas of Ga and As on the system (see [DD08], Fig.2, p.21) such that the crystal is under hydrostatic pressure in 3-phase equilibrium. Therefore we relate some of our variables to known experimental values of this so-called *reference standard system* and consider the actual values as small deviations from the values of 3-phase equilibrium. These experimental values are constants and will be usually denominated by an overline on the corresponding variable of our system: $\overline{p}(T), \overline{n}_G(T), \overline{n}_L(T), \overline{Y}_a(T), \overline{X}_L(T), \overline{\mu}_a(T) = \overline{\mu}_a^{chem}(T)$. They are determined as the unique global minimisers of the available free energy of the reference standard system. We will drop the temperature dependence in our notation from now on.

Accordingly we define relative lattice occupancies

$$y_a := \frac{Y_a}{\overline{Y}_a}, \quad a \in \mathbf{a_S}.$$

We define stress/strain relations w.r.t. a reference configuration. As a reference configuration we choose the reference standard system, where the liquid/solid body of GaAs is free of surface tension and strain i.e. we have $n_G = n_G^R = \overline{n}_G$ in the solid and $n_L = n_L^R = \overline{n}_L$ in the liquid, which is the case if the body is under uniform pressure $\overline{p}$ and in chemical composition $\overline{Y}_a, a \in \mathbf{a_S}$ in the solid and $\overline{X}_L$ in the liquid. We express ρ, n_G and n_L in terms of $\overline{\rho}$, $\overline{n}_G$, $\overline{n}_L$ and U in the following.

We rewrite the definition of the mass density (2.6) by (2.8)

$$\rho = \begin{cases} \rho_S = (3 - Y_V)M(X_S)n_G; & x \in \Omega_S(t), \\ \rho_L^i = M(X_L^i)n_L^i & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N. \end{cases} \tag{2.72}$$

Next we introduce two states of the density, which we need to describe deformations: The mass density of the reference configuration

$$\overline{\rho} := \begin{cases} \overline{\rho}_S := M(\overline{X}_S)(3 - \overline{Y}_V)n_G^R = M(X_S(y=1))n_G^R; & x \in \Omega_S(t), \\ \overline{\rho}_L := M(\overline{X}_L)n_L^R & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N \end{cases}$$

and the mass density of a solid, whose lattice coincides with the lattice of the reference configuration, but with a different distribution of atoms as in the reference configuration,

$$\rho^* := \begin{cases} \rho_S^* := M(X_S)(3 - Y_V)n_G^R; & x \in \Omega_S(t), \\ \rho_L^* := M(X_L)n_L^R & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N. \end{cases}$$

Deformations itself are expressed via F which decompose into inelastic deformations F^* due to redistribution of atoms over lattice sites, which are assumed to be given uniquely as constitutive law, and elastic deformations, which are reversible,

$$F_{el} := F F^{*-1}.$$

For a detailed discussion on this subtle point we refer to [BDDM07], [DDK08].

We check that we have for the Jacobian according to its definition (2.11)

$$J = \frac{\overline{\rho}}{\rho} = \begin{cases} J_{(S)} = \frac{\overline{\rho}_S}{\rho_S} = \det((\mathbb{I}_3 - h)^{-1}); & x \in \Omega_S(t), \\ J_L = \frac{\overline{\rho}_L}{\rho_L} = (1 - h_L)^{-3} & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N \end{cases} \tag{2.73}$$

which is used in the following as definition of ρ instead of (2.72).

We introduce the quantity

$$h^* := \begin{cases} h^*_{(S)} := 1 - \sqrt[3]{\frac{3 - Y_V}{3 - \overline{Y}_V} \frac{M(X_S)}{M(\overline{X}_S)}}; & x \in \Omega_S(t), \\ h^*_L := 1 - \sqrt[3]{\frac{M(X_L)}{M(\overline{X}_L)}} & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N \end{cases} \tag{2.74}$$

as the inelastic counterpart to h. We define

$$J^* := \det F^* = \begin{cases} J^*_{(S)} := \frac{(3-\overline{Y}_V)M(\overline{X}_S)}{(3-Y_V)M(X_S)} = (1-h^*(X_S))^{-3}; & x \in \Omega_S(t), \\ J^*_L := \frac{M(\overline{X}_L)}{M(X_L)} = (1-h^*_L(X_L))^{-3} \qquad ; & x \in \Omega^i_L(t), \quad \forall i \in N, \end{cases}$$

and the multiplication rule for determinants yields

$$J_{el} := \det F_{el} = JJ^{*-1} = \begin{cases} \frac{n^R_G}{n_G} = \det(\mathbb{I}_3 - h)^{-1}(1-h^*(X_S))^3; & x \in \Omega_S(t), \\ \frac{n^R_L}{n^i_L} = (1-h_L)^{-3}(1-h^*_L(X_L))^3 \quad ; & x \in \Omega^i_L(t), \quad \forall i \in N. \end{cases}$$

For the rest of this work we want to deal with small deviations h^* i.e. deformations due to change of the chemical composition of the reference standard system are only of $\mathcal{O}(\tilde{h})$. We remark that inelastic deformations due to thermal expansion are already included in the temperature dependent constants $\overline{p}$ and further in the constants k_S, G_S and k_L, which we will meet later in the constitutive laws (2.77), (2.78) and (2.79) for the Cauchy stress and the pressure in the liquid.

Hence we have the following constitutive laws for n_G and n_L,

$$n_G = \frac{n^R_G}{J_{el}} = n^R_G \frac{J^*}{J}, \quad n_L = \frac{n^R_L}{J_{el,L}} = n^R_L \frac{J^*_L}{J_L}. \tag{2.75}$$

Remark 2.1 (Alternative ansatz for the deformations)**.** *Another ansatz, which might be suggested to include deformations due to rearrangement of atoms, is to work with a* n^R_L*, which is not the constant* $\overline{n}_L$ *and which depends on the chemical composition i.e. on* X_L*:*

$$n^R_L(X_L) := \left(\frac{1-X_L}{n^P_{Ga_L}} + \frac{X_L}{n^P_{As_L}} \right)^{-1}$$

for given reference values $n^P_{Ga_L}$ *and* $n^P_{As_L}$*. In our formulas we then have to replace* h^* *and* h^*_L *by zero. But this ansatz for* n^R_L *leads to inconsistencies with the conservation of mass.*

2.5.2. Constitutive laws for GaAs: Cauchy stress and pressure

We close our system by linking the Cauchy stress σ_S to U and h^* and the pressure in the liquid p_L to U_L and h^*_L by constitutive laws. We abbreviate the strain i.e. the symmetrised displacement gradient by

$$e^{ij}(\nabla U) := \frac{1}{2}(h^{ij} + h^{ji}) = \frac{1}{2}(\partial_j U^i + \partial_i U^j). \tag{2.76}$$

As derived in [DD08] the constitutive law, which links the Cauchy stress σ_S to the displacement gradient ∇U and to h^* in the solid, is in geometric linearisation

$$\sigma^{ij}_S = -\overline{p}\delta^{ij} + \sum_{k,l=1}^{3} K^{ijkl}(e^{kl}(\nabla U) - h^* \delta^{kl}), \tag{2.77}$$

where the stiffness tensor $K = K(T) \in \mathbb{R}^{4\times4}$ of crystalline GaAs in isotropic approximation is

$$K^{ijkl} \equiv K^{ijkl}(T) = k_S(T)\delta^{ij}\delta^{kl} + G_S(T)(\delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk} - \frac{2}{3}\delta^{ij}\delta^{kl}). \tag{2.78}$$

Here $k_S \equiv k_S(T)$ and $G_S \equiv G_S(T)$ denote temperature dependent material constants i.e. the bulk modulus and the shear modulus of crystalline GaAs.

For the pressure in the liquid we assume that we deal with a compressible liquid, which is linear in $J_{el,L}^{-1}$, i.e.

$$p_L := \overline{p} - k_L(1 - \frac{n_L}{\overline{n}_L}) = \overline{p} - 3k_L(a_L - h_L^*) + \mathcal{O}(\|h\|^2), \tag{2.79}$$

where $k_L \equiv k_L(T)$ is the bulk modulus of GaAs in the liquid.

Remark 2.2 (Formal extension of the Cauchy stress into the liquid)**.** *For the liquid we could make an ansatz, which is similar to* (2.77) *and* (2.78)*, for* σ_L *as Cauchy stress in the liquid and with* K_L *as stiffness tensor in liquid GaAs. Due to the properties of a liquid the shear modulus in the liquid is* $G_L = 0$*. This yields*

$$\sigma_L^{ij} = -\overline{p}\delta^{ij} + \sum_{k,l=1}^{3} K_L^{ijkl}(e^{kl}(\nabla U_L) - h_L^*\delta^{kl}) = (-\overline{p} + k_L(tr(e(\nabla U_L)) - 3h_L^*))\delta^{ij}. \tag{2.80}$$

But since we have only identical diagonal components in (2.80) *the pressure in the liquid prescribes completely the strains and stresses in the liquid,*

$$p_L = -\frac{1}{3}tr(\sigma_L). \tag{2.81}$$

We use later in Section 5.2 the equation (2.80) to extend the stress tensor σ_S, formally on the whole domain Ω, which is for technical reasons needed for the homogenisation.

2.5.3. Constitutive laws for GaAs: Chemical potentials

The chemical potentials in the solid and in the liquid decompose into a chemical and a mechanical part

$$\mu_a = \mu_a^{chem} + \mu_a^{mech}, \quad a \in \mathbf{a_S} \cup \mathbf{a_L}.$$

We have in the solid

$$\mu_a^{chem} = \overline{\mu}_a + RT\ln(\frac{Y_a}{\overline{Y}_a}), \quad a \in \mathbf{a_S}, \tag{2.82}$$

$$\mu_a^{mech} := \begin{cases} (p_S - \overline{p})\frac{M_a}{\rho_S} + \mathcal{O}(\tilde{h}^2); & a \in \{\mathrm{Ga}_\alpha, \mathrm{As}_\alpha, \mathrm{As}_\beta, \mathrm{As}_\gamma\}, \\ 0 \qquad\qquad\qquad\qquad ; & a \in \{\mathrm{V}_\alpha, \mathrm{V}_\beta, \mathrm{V}_\gamma\} \end{cases} \tag{2.83}$$

and in the liquid

$$\begin{aligned} \mu_{Ga_L}^{chem} &= \overline{\mu}_{Ga_L} + RT\ln(\frac{1 - X_L}{1 - \overline{X}_L}) + (L_0 + L_1(3 - 4X_L)){X_L}^2 \\ &\quad - (L_0 + L_1(3 - 4\overline{X}_L)){\overline{X}_L}^2, \end{aligned} \tag{2.84}$$

$$\begin{aligned} \mu_{As_L}^{chem} &= \overline{\mu}_{As_L} + RT\ln(\frac{X_L}{\overline{X}_L}) + (L_0 + L_1(1 - 4X_L))(1 - X_L)^2 \\ &\quad - (L_0 + L_1(1 - 4\overline{X}_L))(1 - \overline{X}_L)^2, \end{aligned} \tag{2.85}$$

$$\mu_a^{mech} = \frac{k_L}{n_L^R}\ln(\frac{n_L}{\overline{n}_L}) = \frac{k_L}{n_L^R}3(h_L^* - h_L) + \mathcal{O}(\tilde{h}^2), \quad a \in \mathbf{a_L}. \tag{2.86}$$

R is here the gas constant and $L_0 \equiv L_0(T), L_1 \equiv L_1(T)$ are the given Redlich-Kister coefficients. The explicit formulas (2.82), (2.84) and (2.85) for chemical parts of chemical potentials in GaAs $\mu_a, a \in \mathbf{a_S} \cup \mathbf{a_L}$ go back to Mika, Oates, Wenzl *et al.* [WMH90], [WOM93], [OEW95], while the mechanical parts (2.83) and (2.86) of chemical potentials are derived for GaAs in [DD08].

Note that (2.56) – (2.60) have to hold for the reference configuration, which is under pure hydrostatic pressure i.e. $\sigma_S^{<\cdot,\cdot>} = 0$, too, and we get immediately

$$\overline{\mu}_{Ga_\alpha} - \overline{\mu}_{V_\alpha} - \overline{\mu}_{Ga_L} = 0, \quad \overline{\mu}_{As_\gamma} - \overline{\mu}_{V_\gamma} - \overline{\mu}_{As_L} = 0, \quad \sum_{a \in SL} \overline{\mu}_{V_a} = 0. \tag{2.87}$$

Notice, that due to (2.87) the reference values $\overline{\mu}_a, a \in \mathbf{a_S} \cup \mathbf{a_L}$ drop out completely in (2.56) – (2.60). W.l.o.g. we set

$$\overline{\mu}_a := 0, \quad a \in \mathbf{a_S} \cup \mathbf{a_L} \tag{2.88}$$

in the following calculations.

As abbreviation we introduce by using twice (2.82) and (2.83)

$$\mu_{Ga}^{chem} := \mu_{Ga_\alpha}^{chem} - \mu_{V_\alpha} = RT \ln(\frac{y_{Ga_\alpha}}{y_{V_\alpha}}), \tag{2.89}$$

$$\mu_{As}^{chem} := \mu_{As_\gamma}^{chem} - \mu_{V_\gamma} = RT \ln(\frac{y}{y_{V_\gamma}}), \tag{2.90}$$

and now we can introduce some suitable chemical potentials, μ_{Ga} for the gallium and μ_{As} for the arsenic part in the solid:

$$\mu_a = \mu_a^{chem} + \mu_{a_\alpha}^{mech} \quad \forall a \in \{\mathrm{As}, \mathrm{Ga}\}.$$

The terms μ_{As} and μ_{Ga} appear in the necessary conditions (2.56) and (2.57) on interfacial equilibrium. Since in (2.59), the necessary condition for diffusional equilibrium, the following linear combination of chemical potentials appears, we introduce the *total chemical potential* in the solid

$$u = u^{chem} := \mu_{As} - \frac{1}{\tilde{\mu}}\mu_{Ga} = \mu_{As_\gamma}^{chem} - \mu_{V_\gamma} - \frac{1}{\tilde{\mu}}(\mu_{Ga_\alpha}^{chem} - \mu_{V_\alpha}), \tag{2.91}$$

where mechanical parts of the chemical potential drop out. We define

$$S := \frac{y_{As_\gamma}}{y_{V_\gamma}}(\frac{y_{V_\alpha}}{y_{Ga_\alpha}})^{\frac{1}{\tilde{\mu}}}. \tag{2.92}$$

This yields with (2.88)

$$u = RT \ln(S). \tag{2.93}$$

For the liquid side we define the total chemical potential u_L similar as (2.91). With (2.84), (2.85), (2.88) and (2.14) we have

$$\begin{aligned} u_L &:= \mu_{As_L} - \frac{1}{\tilde{\mu}}\mu_{Ga_L} \\ &= RT(\ln(\frac{X_L}{\overline{X}_L}(\frac{1-\overline{X}_L}{1-X_L})^{\frac{1}{\tilde{\mu}}})) - 2(L_0 + 3L_1)(X_L - \overline{X}_L) \\ &\quad + (L_0 + 9L_1 - \frac{1}{\tilde{\mu}}(L_0 + 3L_1))(X_L^2 - \overline{X}_L^2) - 4L_1(1 - \frac{1}{\tilde{\mu}})(X_L^3 - \overline{X}_L^3) \\ &\quad + \frac{3k_L}{\overline{n}_L}(\frac{1}{\tilde{\mu}} - 1)(a_L - h_L^*). \end{aligned} \tag{2.94}$$

2.5.4. Sphericity of the system and the droplets

Assumption 2.3 (Sphericity of the free boundaries)**.** *As we have already mentioned at the beginning we want to consider only the case of liquid droplets, which are spheres and the case of a* *spherical* Ω. *In order to preserve* Ω *and* $\Omega_L^i, i \in N$ *to be spheres for all times, we have to adjust suitably the growth conditions of the free boundaries since* w^ν *depends on* x, *too. Hence we consider*

$$\dot{r}_i(t) := \fint_{I_i(t)} w(x,t) \cdot \nu(x) dA(x), \quad \dot{R}_{bd} := \fint_{\partial\Omega} w(x,t) \cdot \nu(x) dA(x).$$

If the deviation $\int_{I_i^*} ||x - X_i| - r_i| dA(x)$ of an arbitrary shaped closed surface I_i^* from a sphere is of order ε, it was derived rigorously in [AF99] and in [Vel00] that taking the average over I_i about w yields only an error of higher order in ε to the classical LSW dynamics. Furthermore a restriction to spheres makes sense since a closed convex surface tries to minimise its geometrical surface energy under volume-preserving mean curvature flow and converges exponentially fast to a sphere, see [Hui87].

Since we will see that our Stefan condition is up to a factor the Stefan condition of the classical LSW model this justifies the restriction to spherical droplets in our model.

The error, we make by taking $\dot{R}_{bd}$, the average over v on the free boundary, can be estimated and turns out for sufficiently small ε to be of higher order in ε than v, which we show in Lemma 3.1.

Consequently we approximate from now on the boundary conditions on the interfaces, (2.55) for U and (2.70) and (2.57) for u and X_L by its expressions, which we get for a spherical droplet, respectively.

From now on we exploit the radial symmetry of droplets and $\Omega = B_{R_{bd}}(0)$.

2.6. Exploitation of the availability inequality and the constitutive laws

2.6.1. Reduction of variables by chemical equilibrium

In order to guarantee that the relative lattice occupancies $y_a, a \in \mathbf{as}$ are well-defined we have to assume that the domain of the y_a's is $D_0 = (0, 1/\overline{Y}), 1/\overline{Y} \le 1$. This yields that (2.82) is well-defined, too.

From now on we use the abbreviations $Y := Y_{As_\gamma}$ and $y := y_{As_\gamma}$. We will reduce explicitly the number of variables of our system by relating $\{y_a\}_{a \in \mathbf{as}}$ uniquely to y. This is due to the following six relations. Three of them are due to the same mole density n_G of each sublattice, (2.4),

$$Y_{V_\gamma} = 1 - Y, \qquad Y_{V_\beta} = 1 - Y_{As_\beta}, \qquad Y_{V_\alpha} = 1 - Y_{As_\alpha} - Y_{Ga_\alpha} \tag{2.95}$$

and three relations follow from the chemical "reactions" between sublattices under the necessary conditions (2.48) – (2.50), that the following reactions are instantly in chemical equilibrium

$$\mathrm{V}_\alpha + \mathrm{V}_\beta + \mathrm{V}_\gamma \rightleftharpoons 0 \;:\quad \mu_{V_\alpha} + \mu_{V_\beta} + \mu_{V_\gamma} = 0 \quad\Longleftrightarrow\quad Y_{V_\alpha} Y_{V_\beta} Y_{V_\gamma} = C_1, \tag{2.96}$$

$$\mathrm{As}_\gamma + \mathrm{V}_\beta \rightleftharpoons \mathrm{V}_\gamma + \mathrm{As}_\beta \;:\quad \mu_{As_\gamma} + \mu_{V_\beta} = \mu_{V_\gamma} + \mu_{As_\beta} \quad\Longleftrightarrow\quad \frac{Y Y_{V_\beta}}{Y_{V_\gamma} Y_{As_\beta}} = C_2, \tag{2.97}$$

$$\mathrm{As}_\alpha + \mathrm{V}_\beta \rightleftharpoons \mathrm{V}_\alpha + \mathrm{As}_\beta \;:\quad \mu_{As_\alpha} + \mu_{V_\beta} = \mu_{V_\alpha} + \mu_{As_\beta} \quad\Longleftrightarrow\quad \frac{Y_{As_\alpha} Y_{V_\beta}}{Y_{V_\alpha} Y_{As_\beta}} = C_3, \tag{2.98}$$

with constants $C_1 \equiv C_1(T), C_2 \equiv C_2(T)$ and $C_3 \equiv C_3(T)$. Note that (2.95) – (2.98) hold for the reference standard system, too. In the reference standard system the constants $C_i, 1 \le i \le 3$ can be expressed in terms of $\overline{Y}_a$. It is sufficient to give either explicitly $\overline{Y}$ and $C_i, 1 \le i \le 3$ or four of the lattice occupancies w.l.o.g. $\overline{Y}$, $\overline{Y}_{V_\beta}$, $\overline{Y}_{As_\alpha}$ and $\overline{Y}_{V_\alpha}$ to be given, which can be read of from the diagrams in [DD08], p.22 (EMS).

We have the following lemma which we prove in Appendix A.2.

Lemma 2.2. *For $y \in \mathcal{J}_y := (0,\zeta)$, where $\zeta := \min\{(y \in (0,\frac{1}{\overline{\overline{Y}}})|(1-C_1)C_2^2 - (C_1(1+C_3-2C_2)+3C_2)C_2\overline{Y}y - (C_1(1-C_2)(C_3-C_2)-3C_2^2)(\overline{Y}y)^2 - C_2^2(\overline{Y}y)^3), \frac{1}{\overline{\overline{Y}}}\}$ we can uniquely express $y_a, a \in \mathbf{a_S}\setminus\{As_\gamma\}$ as rational functions in y which are well defined i.e. $y_a \in (0,\frac{1}{\overline{\overline{Y}}_a}), a \in \mathbf{a_S}\setminus\{As_\gamma\}$.*

For typical experimental data we have the estimate $\zeta \leq \frac{1}{3\overline{\overline{Y}}}$.

For u which is a function in y only, we find $\mathcal{J}_u := (u(0), u(\zeta)) = (-\infty, +\infty)$. As we calculate in the appendix in (A.9) u is strictly monotone and continuous in y.

We assume n_L as a function of X_L and U, which we show in (2.112). Due to $n_{Ga_L} = (1-X_L)n_L$ and $n_{As_L} = X_L n_L$ there results only $X_L \in (0,1)$ as independent concentration in the liquid.

We estimate roughly the deviation of our chemical variables from the reference values.

Remark 2.3 (Deviation of X_L and y from reference values)**.** *The smallness of h_L^* implies the smallness of*

$$X_L - \overline{X}_L = -3(h_L^* + \mathcal{O}(\tilde{h}^2))(\overline{X}_L + \frac{\tilde{\mu}}{1-\tilde{\mu}}) = \frac{3}{1-\tilde{\mu}}\mathcal{O}(\tilde{h}) \tag{2.99}$$

since there holds exactly

$$M(X_L) = M(\overline{X}_L) + M_{As}(1-\tilde{\mu})(X_L - \overline{X}_L).$$

Hence for typical data we have $X_L - \overline{X_L} = \mathcal{O}(10^{-1}) \approx \mathcal{O}(\tilde{h}^{1/2})$. But we can only hope if $h^* = \mathcal{O}(\tilde{h})$ and $y \in \mathcal{J}_y$ that

$$y - 1 \approx -3h^* \frac{(1-\tilde{\mu})\overline{Y}_{As} + \tilde{\mu}(3-\overline{Y}_V)}{(1-\tilde{\mu})Y'_{As}(1) - \tilde{\mu}Y'_V(1)} \approx (\frac{\overline{Y}_{As_\alpha}}{\overline{Y}} + \frac{\overline{Y}_{As_\beta}}{\overline{Y}} + 1 + \tilde{\mu}\frac{\overline{Y}_{Ga_\alpha}}{\overline{Y}})\mathcal{O}(\tilde{h}) \overset{typ.\ data}{\approx} \mathcal{O}(10).$$

The approximations for $y-1$ are made rigorously later by a maximum/minimum principle in Lemma 4.2.

We now examine further variables which can be considered now as functions depending on y or on X_L.

According to the definition of the arsenic mole fraction of the solid X_S in (2.7),

$$X_S : \mathcal{J}_y \to (0,1), \quad y \mapsto \frac{Y_{As_\alpha}(y) + Y_{As_\beta}(y) + Y_{As_\gamma}(y)}{Y_{As_\alpha}(y) + Y_{As_\beta}(y) + Y_{As_\gamma}(y) + Y_{Ga_\alpha}(y)}.$$

We look for X_S varying slightly from $X_0 = 0.500082$, where we recall that X_0 is the mean value of X over Ω i.e. over solid and liquid, which guarantees semi-insulating behaviour of GaAs. Note, that in genereal $X_S(1) \neq X_0$.

We verify by some calculations, which can be found in Appendix A.3, that

$$0 < X'_S(y) < \infty \qquad \forall y \in \mathcal{J}_y$$

i.e. X_S is strictly monotone in y and bounded. Since X_S is continuous, we could invert X_S w.r.t. y on $\mathcal{J}_y$ and work with X_S instead of y as variable.

$$P : (0,1) \mapsto (0,1), \quad X \mapsto \frac{M_{As}X}{M(X)} = \frac{1}{1+\tilde{\mu}(\frac{1}{X}-1)}$$

is strictly monotone in X i.e. for its derivative we have

$$P'(X) = \frac{\tilde{\mu}}{(X + \tilde{\mu}(1-X))^2}.$$

As long as mechanical deformations are of order $\mathcal{O}(\tilde{h})$ the densities n_L and n_G, which are considered as functions in ∇U or a_L are well-defined i.e. positive and finite, $n_L \in (\overline{n}_L(1-\mathcal{O}(\tilde{h})), \overline{n}_L(1+\mathcal{O}(\tilde{h})))$ and $n_G \in (\overline{n}_G(1-\mathcal{O}(\tilde{h})), \overline{n}_G(1+\mathcal{O}(\tilde{h})))$. Furthermore since $1 \leq 3 - Y_V \leq 3$ this holds for n_S analogously.

Next we consider the densities ρ_S and ρ_L, which are determined by the variables ∇U or a_L. We see that ρ_S has values in $\overline{\rho}_S(1 \pm \mathcal{O}(\tilde{h}))$ i.e. the densities are indeed positive. By derivation of ρ^* w.r.t. X we see in the solid together with $X_S'(y) > 0$ that ρ_S^* is strictly monotone in y and in the liquid that ρ_L^* is strictly monotone in X_L. Thus $\rho_S^* : (0,1) \ni y \mapsto \rho_S^*(y) \in (M_{Ga}(1-C_1)C_2^2\overline{n}_G, M_{As}Y_{As}(\zeta)\overline{n}_G))$ and $\rho_L^* : (0,1) \ni X_L \mapsto \rho_L^*(X_L) \in (M_{Ga}\overline{n}_L, M_{As}\overline{n}_L)$. Consequently $\rho_S^*(y)$ and $\rho_L^*(X_L)$ are strictly monotone and well-defined.

Due to the definition of J there follows from the continuity equation (2.20)

$$\partial_t J^{-1} + \nabla \cdot (vJ^{-1}) = 0 \tag{2.100}$$

since $\overline{\rho}$ is constant. We introduce the only on y or on X_L depending functions,

$$\hat{n}_{As}(y, X_L) := \begin{cases} \hat{n}_{As_{(S)}}(y) := X_S(3 - Y_V)n_G^R J^* = \frac{M(\overline{X}_S)}{M(X_S)} X_S(3 - \overline{Y}_V)n_G^R; & x \in \Omega_S(t), \\ \hat{n}_{As_L}(X_L) := X_L n_L^R J_L^* = \frac{M(\overline{X}_L)}{M(X_L)} X_L n_L^R & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N \end{cases}$$

and

$$\hat{n}_{Ga}(y, X_L) := \begin{cases} \hat{n}_{Ga_{(S)}}(y) := (1 - X_S)(3 - Y_V)n_G^R J^* = Y_{Ga} n_G^R J^*; & x \in \Omega_S(t), \\ \hat{n}_{Ga_L}(X_L) := (1 - X_L)n_L^R J_L^* & ; \quad x \in \Omega_L^i(t), \quad \forall i \in N \end{cases}$$

s.t. $n_b = \hat{n}_b J^{-1}$, for all $b \in \{\text{As}, \text{Ga}\}$. Note that in general not $\overline{n}_{As} = \hat{n}_{As}$ etc. We check that due to (2.100) conservation laws hold for this functions in our approximation,

$$\partial_t \hat{n}_a + \nabla \cdot (\hat{n}_a v) = -\nabla \cdot j_a \quad \forall x \in \Omega_S(t) \qquad \forall t \in (0, \mathcal{T}) \quad \forall a \in \{\text{As}, \text{Ga}\}, \tag{2.101}$$

$$\partial_t \hat{n}_{a_L} + \nabla \cdot (\hat{n}_{a_L} v_L) = -\nabla \cdot j_{a_L} \quad \forall x \in \Omega_L^i(t) \quad \forall i \in N(t) \quad \forall t \in (0, \mathcal{T}) \quad \forall a \in \{\text{As}, \text{Ga}\}. \tag{2.102}$$

Since the product of two strictly monotone positive functions is again strictly monotone (and also positive), we find that due to (2.9) that n_{As} and $\hat{n}_{As}$ are strictly monotone (increasing) in y. An analogous result holds for n_{As_L} and $\hat{n}_{As_L}$ w.r.t. X_L: $\partial_{X_L} n_{As_L} = n_L > 0$, respectively. We also found

$$0 < \mathcal{X}_0(u, U) := \begin{cases} \frac{1}{M_{As}} \rho_S(U) P'(X_S(u)) X_S'(u) & ; \quad x \in \Omega_S(t), \\ \frac{1}{M_{As}} \rho_L(U_L) P'(X_L(u_L)) X_L'(u_L); & x \in \Omega_L^i(t), \quad \forall i \in N. \end{cases} \tag{2.103}$$

Following the monotonicities we can understand the functions $Y_{As}, Y_{Ga}, Y_V, X_S, y, h^*$ and $\hat{n}_{As}$ as given functions of u, which can be inverted. Analogously we express the unknowns h_L^*, $\hat{n}_{As_L}$ as invertible functions of X_L.

We summarise dependencies of other quantities on the variables. In the solid ρ_S is a function of U and n_G, n_S, n_a, $a \in \{\text{As}, \text{Ga}\}$ are functions of u and U. In the liquid ρ_L is a function of U_L, while n_L, n_{As_L}, n_{Ga_L} and j_{As_L} are functions of U_L and X_L.

2.6.2. Mechanical boundary value problem

We recall that we treat the mechanics in approximation of small displacement gradients, as stated in Assumption 2.1, which is a stronger assumption than linear elasticity, since linear elasticity would not imply that $\|\nabla U\|$ is small.

Due to (A2) we have the equations (2.51) – (2.55) for given surface tension σ and outer pressure p_0. The displacement vector U is related to σ_S and p_L by the constitutive laws (2.77) and (2.79). Thus we can reformulate (2.51) – (2.55). The mechanical mechanical boundary value problem is to find the displacement vector U, such that for fixed time $t \in \mathcal{J}_t = (0, \mathcal{T})$ the equations

$$\begin{aligned}
\operatorname{div}\,(\lambda_S \operatorname{tr}(\nabla U) + 2\mu_S e(\nabla U)) &= 3k_S h^{*\prime}(u)\nabla u && \text{in } \Omega_S(t), && (2.104)\\
p_L^i &= \overline{p} - 3k_L(a_L^i - h_L^*(X_L^i)) && \text{in } \Omega_L^i(t)\ \forall i \in N(t), && (2.105)\\
\nu \cdot (\lambda_S \operatorname{tr}(\nabla U) + 2\mu_S e(\nabla U))\nu &= \overline{p} - p_0 + 3k_S h^*(u) && \text{on } \partial\Omega(t), && (2.106)\\
\tau_l \cdot (\lambda_S \operatorname{tr}(\nabla U) + 2\mu_S e(\nabla U))\nu &= 0 && \text{on } \partial\Omega(t) \cup I_i(t) && \\
& && \forall l \in \{1,2\}\ \forall i \in N(t), && (2.107)\\
\nu \cdot (\lambda_S \operatorname{tr}(\nabla U) + 2\mu_S e(\nabla U))\nu + p_L^i &= \overline{p} - 2\sigma k_M + 3k_S h^*(u) && \text{on } I_i(t)\ \forall i \in N(t) && (2.108)
\end{aligned}$$

are solved.

Note that the relation between Lamé constants λ_S, μ_S and K is

$$\lambda_S(T) = k_S(T) - \frac{2}{3}G_S(T), \quad \mu_S(T) = G_S(T).$$

In particular $G_S > 0$ and $k_S > 0$ ensures $\mu_S > 0$ and $\lambda_S > -\frac{2}{3}\mu_S$, that is needed for the existence and uniqueness proof for the mechanical BVP in Th. 4.1. Analogously we could define formally for the liquid Lamé constants λ_L and μ_L. Since there are no shear stresses in a liquid $\mu_L = 0$ and $\lambda_L = k_L - \frac{2}{3}\mu_L = k_L$.

We have to specify how to determine $h_L = a_L \mathbb{I}_3$ or a_L. This is done by an argument similar to the so-called Eshelby argument, i.e. taking the liquid spherical droplet out of the solid, then considering a phase transition and then fitting the solid droplet into the solid back (cf. [DD08], p. 5/6, [DDK08]). We assume that we have a misfit situation i.e.

$$\overline{n}_L \le \overline{n}_S, \tag{2.109}$$

which is the case for GaAs. Let $\overline{Y}_V^I$ the given reference value of the lattice occupancy of vacancies near interface. As in [DD08] we assume $\overline{Y}_V^I = \overline{Y}_V$. We introduce the misfit parameter

$$\delta^R := 1 - \sqrt[3]{\frac{\overline{n}_L}{(3 - \overline{Y}_V^I)\overline{n}_G}} \tag{2.110}$$

which is positive due to (2.109). We remark, that if $\overline{n}_L > \overline{n}_S$ there would come a gaseous phase into play, since the liquid cannot exert traction on the solid.

Note, that we work with a “reference configuration free of strains/stresses” i.e. with discontinuous U on I_i i.e $[[U]] \neq 0$ in general. Equivalently we could work with $[[U]] = 0$ and a “initial configuration” with initial strains/stresses, which yields the same formula for p_L. For this subtle point see [DDK08].

This yields in case of a strain/stress-free reference configuration

$$a_L^i(⨍_{I_i} U \cdot \nu) = \frac{⨍_{I_i} U \cdot \nu}{r_i} - \delta^R, \tag{2.111}$$

which is equivalent to a discontinuity condition on the displacement U on I_i, $[[U]] = \delta^R r_i$. Hence

$$n_L^i = (3 - \overline{Y}_V) n_G^R \left(\frac{1 - \fint_{I_i} \frac{U(|x - X_i| = r_i) \cdot \nu}{r_i}}{1 - h_L^*(X_L(r_i))} \right)^3 . \tag{2.112}$$

Since we want to ensure having no contradiction to our assumption of spherically symmetric liquid droplets, we had to modify (2.111) by taking the mean value over all directions.
The trace of a tensor, spherically symmetric on I_i, has always this symmetry, too. Therefore the resulting modification of (2.117) enforces not only the spherical symmetry of σ_S on I_i but also of p_S due to its definition (2.16) and hence of $\sigma_S^{<\cdot,\cdot>}$. The spherical symmetry of $\sigma_S^{<\cdot,\cdot>}$ implies the spherical symmetry on I_i of $e(\nabla U)$ and hence of J.
We want to reformulate problem (2.104) – (2.108) in order to get a formulation similar as in Ciarlet [Cia98]. We can decompose locally every vector z on a smooth manifold w.r.t. the orthonormal base ν, τ_1, τ_2 i.e.

$$z = (z, \nu)\nu + (z, \tau_1)\tau_1 + (z, \tau_2)\tau_2 \tag{2.113}$$

where $(\cdot, \cdot)$ denotes the standard scalar product in $\mathbb{R}^3$. This allows us to equivalently express (2.106) and (2.107), which are three equations on $\partial\Omega$ in terms of one equation (2.116) for three components each. Analogously we proceed with (2.108) and (2.107), the three equations on I_i, which are expressed by (2.117). This yields equivalent to (2.104) – (2.108)

$$\text{div } (\lambda_S \text{tr}(\nabla U) + 2\mu_S e(\nabla U)) = 3k_S h^{*\prime}(u)\nabla u \qquad \text{in } \Omega_S(t), \tag{2.114}$$

$$p_L^i(\fint_{I_i} U \cdot \nu) = \overline{p} - 3k_L(\frac{\fint_{I_i} U \cdot \nu}{r_i} - \delta^R - h_L^*(X_L^i)) \qquad \text{in } \Omega_L^i(t)\ \forall i \in N(t), \tag{2.115}$$

$$(\lambda_S \text{tr}(\nabla U) + 2\mu_S e(\nabla U))\nu = (\overline{p} - p_0 + 3k_S h^*(u))\nu \qquad \text{on } \partial\Omega(t), \tag{2.116}$$

$$\begin{aligned}(\lambda_S \text{tr}(\nabla U) &+ 2\mu_S e(\nabla U) \\ -3k_L \frac{\fint_{I_i} U \cdot \nu}{r_i})\nu &= (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h_L^*(X_L^i)) \\ &\quad + 3k_S h^*(u))\nu \qquad \text{on } I_i(t)\ \forall i \in N(t).\end{aligned} \tag{2.117}$$

In order to decompose the Cauchy stress into parts which depend on ∇U and which do depend on the chemical composition we introduce a "elastic part of the Cauchy stress"

$$\check{\sigma}_S^{ij} := (k_S - \frac{2}{3}G_S)\text{tr}(\nabla U)\delta^{ij} + 2G_S e(\nabla U)^{ij} \tag{2.118}$$

s.t.

$$\sigma_S^{ij} = -(\overline{p} + 3k_S h_S^*)\delta^{ij} + \check{\sigma}_S^{ij}.$$

This implies

$$\check{\sigma}_S = \lambda_S \text{tr}(\nabla U)\mathbb{I}_3 + 2\mu_S e(\nabla U). \tag{2.119}$$

Furthermore we have now $p_S = \overline{p} - (\lambda_S + \frac{2}{3}\mu_S)(\text{tr}(\nabla U) - 3h^*(u))$ and $p_L = \overline{p} - 3\lambda_L(a_L^i(\fint_{I_i} U \cdot \nu) - h_L^*(X_L^i))$. We rewrite (2.114) – (2.117) for $\check{\sigma}_S = \check{\sigma}_S(\nabla U)$,

$$\text{div } \check{\sigma}_S(\nabla U) = 3k_S h^{*\prime}(u)\nabla y \qquad \text{in } \Omega_S(t), \tag{2.120}$$

$$p_L^i(\fint_{I_i} U \cdot \nu) = \overline{p} - 3k_L(\frac{\fint_{I_i} U \cdot \nu}{r_i} - \delta^R - h_L^*(X_L^i)) \qquad \text{in } \Omega_L^i(t)\ \forall i \in N(t), \tag{2.121}$$

$$\check{\sigma}_S(\nabla U)\nu = (\overline{p} - p_0 + 3k_S h^*(u)\nu \qquad \text{on } \partial\Omega(t), \tag{2.122}$$

$$(\check{\sigma}_S(\nabla U) - 3k_L \frac{\fint_{I_i} U \cdot \nu}{r_i})\nu = (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h_L^*(X_L^i)) + 3k_S h^*(u)\nu \qquad \text{on } I_i(t)\ \forall i \in N(t). \tag{2.123}$$

We can expect uniqueness in the mechanical BVP only in the sense that we consider solutions in H^1/RD with class of equivalence RD.

Definition 2.1 (Infinitesimal rigid displacements)**.** *We define RD as the set of all infinitesimal rigid deformations $\{\Omega_S^\varepsilon(t) \to \Omega_S^\varepsilon(t), x \to \phi(x) := a + b \times x | a, b \in \mathbb{R}^3$, where a, b can depend on time. Equivalently $\phi(x)$ can be represented by $a + Wx$, where W is a skew symmetric tensor corresponding to rotation around axis b. The uniqueness w.r.t. RD represents uniqueness up to the Galilei invariance of our model.*

Remark 2.4 (Modelling dislocations in the crystal)**.** *As a possibility for modelling influences by mechanical misfits due to dislocations in the crystal it would be possible to additionally introduce a so-called source term $\tilde{f}$ on the r.h.s. of* (2.120)*, but we omit this in the following. We remark that, our theorems could be adapted to include an additional term $\tilde{f} \in L^{6/5}(\Omega)$.*

Without the term $-3k_L \frac{\fint_{I_i} U\cdot\nu}{r_i}\nu$ on the l.h.s. of the boundary condition on I_i the mechanical BVP is the standard problem of linear elasticity, which is treated in [Cia98], p. 296, Th. 6.3-6. We prove later Theorem 4.2 for the displacement U and Theorem 4.3 for the velocity $\partial_t U$. In both theorems we see that, if the data is of order $\tilde{h}$, which holds if

$$X_L^i \in \mathcal{J}_{X_L} := (\overline{X}_L(1-\tilde{h}), 1), \tag{2.124}$$

$$y \in \mathcal{J}_y := (1-\tilde{h}, 10) \text{ or } u \in \mathcal{J}_u := (u(1-\tilde{h}), u(10)), \tag{2.125}$$

where we redefine $\mathcal{J}_y$ and $\mathcal{J}_u$, and if

$$r_i > r_{min} > \frac{2\sigma}{\max\{k_S, k_L, G_S\}}, \tag{2.126}$$

then ∇U and $\nabla v \in \mathcal{O}(\tilde{h})$. This confirms that our approximation from Assumption 2.1, in particular to work with (2.13), is consistent. We have from the data, that

$$\tilde{h} = \max\{\frac{p_0 - \overline{p}}{3k_S}, \delta^R, h^*(u(\zeta)), h_L^*(1)\}. \tag{2.127}$$

For an explicit solution of the mechanical BVP for a spherically symmetric single droplet problem see Appendix C.1.1. We remark that our solution formulas in case of the radial symmetric single droplet problem depend smoothly on the time-dependent data r_I and R_{bd}. That this holds also for non spherically symmetric mechanical problems will be proved later, when we will have stated the diffusion problem, which yields the evolution of the radii.

2.6.3. Boundary conditions on the interface

We now exploit (A3). We modify (2.70) and (2.57) for our model to guarantee spherical droplets at all times and have with the definitions (2.74), (2.91), (2.94) and (2.29)

$$\begin{aligned} &n_L^R(1-h_L^*(X_L^i))^{3/2}(v_{As_L}^\nu - \frac{1}{\tilde{\mu}}v_{Ga_L}^\nu + (1-\frac{1}{\tilde{\mu}})(v_L^\nu - \dot{r}_i)) \\ &= -\frac{B^I}{RT}(u - u_L^{chem}(X_L^i) + \frac{1-\tilde{\mu}}{\tilde{\mu}}\frac{3k_L}{n_L^R}(h_L^*(X_L^i) - \frac{\fint_{I_i} U\cdot\nu}{r_i} + \delta^R)) \qquad \forall x, |x| = r_i(t)\, \forall i \in N(t), \end{aligned} \tag{2.128}$$

$$\begin{aligned} &n_L^R(1-h_L^*(X_L^i))^{3/2}(v_{As_L}^\nu - \dot{r}_i) \\ &= -\frac{B^I}{RT}((\mu_{As}(u) - \mu_{As_L}(X_L^i, \fint_{I_i} U\cdot\nu) - \frac{M_{As}}{\rho_S(\fint_{I_i}\operatorname{tr}(\nabla U))}\nu\cdot\sigma_S^{<\cdot,\cdot>}\nu)) \quad \forall x, |x| = r_i(t)\, \forall i \in N(t), \end{aligned} \tag{2.129}$$

where $t \in (0, \mathcal{T})$ is fixed. We look in regime (DC) for solutions $(u|_{I_i}, X_L^i) = (u_{int}, X_L) \in \mathbb{R} \times (0,1)$ of the equations (2.128) and (2.129), where u_{int} and X_L are functions of the given parameters, r_i and the function U, which is assumed to be known from the mechanical BVP. We show in this subsection, that only r_i and the boundary value $U_M^i := \fint_{I_i} U \cdot \nu$ enter into u_{int} and X_L.
According to our approximation from Assumption 2.1 we have

$$\frac{\nu \cdot \sigma_S^{<\cdot,\cdot>} \nu}{\rho_S(U)} = \frac{\nu \cdot \sigma_S^{<\cdot,\cdot>} \nu}{\overline{\rho}_S} + \mathcal{O}(\tilde{h}^2).$$

Analogously to (2.91) and (2.94) we define chemical potentials $\tilde{u}$ and $\tilde{u}_L$ weighted with

$$\tilde{m} := \frac{1 - \tilde{\mu}\frac{M_{As}\overline{n}_L}{\overline{\rho}_S}}{1 - \frac{M_{As}\overline{n}_L}{\overline{\rho}_S}} > \tilde{\mu} \tag{2.130}$$

instead of $\tilde{\mu}$. This definitions are suitable s.t. some terms from the mechanics cancel out later. We have

$$\tilde{u}(y) := \mu_{As}(y) - \frac{1}{\tilde{m}}\mu_{Ga}(y) = RT\ln(\tilde{S}(y)) + (1 - \frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\overline{\rho}_S}(p_S - \overline{p}),$$

with

$$\tilde{S}(y) := \frac{y}{y_{V_\gamma}(y)}(\frac{y_{V_\alpha}(y)}{y_{Ga_\alpha}(y)})^{\frac{1}{\tilde{m}}}$$

and

$$\begin{aligned}
\tilde{u}_L(X_L) = {} & RT(\ln(\frac{X_L}{\overline{X}_L}(\frac{1-\overline{X}_L}{1-X_L})^{\frac{1}{\tilde{m}}})) - 2(L_0 + 3L_1)(X_L - \overline{X}_L) \\
& + (L_0 + 9L_1 - \frac{1}{\tilde{m}}(L_0 + 3L_1))(X_L^2 - \overline{X}_L^2) - 4L_1(1 - \frac{1}{\tilde{m}})(X_L^3 - \overline{X}_L^3) \\
& + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{m}}{\tilde{m}}(\frac{\fint_{I_i} U \cdot \nu}{r_i} - \delta^R - h_L^*(X_L)).
\end{aligned}$$

We abbreviate the chemical part of this weighted chemical potential

$$\begin{aligned}
\tilde{u}_L^{chem}(X_L) := {} & RT(\ln(\frac{X_L}{\overline{X}_L}(\frac{1-\overline{X}_L}{1-X_L})^{\frac{1}{\tilde{m}}})) - 2(L_0 + 3L_1)(X_L - \overline{X}_L) \\
& + (L_0 + 9L_1 - \frac{1}{\tilde{m}}(L_0 + 3L_1))(X_L^2 - \overline{X}_L^2) - 4L_1(1 - \frac{1}{\tilde{m}})(X_L^3 - \overline{X}_L^3)
\end{aligned}$$

and analogously introduce $\tilde{u}^{mech}$.

Due to (2.130) we have $\frac{M_{As}}{\overline{\rho}_S}(1 - \frac{\tilde{\mu}}{\tilde{m}}) + \frac{1}{\overline{n}_L}(1 - \frac{1}{\tilde{m}}) = 0$. Now the boundary conditions (2.128) and (2.129) can be rewritten with using further the mechanical boundary condition (2.108)

$$\begin{aligned}
& u_{int} - u_L(X_L, r_i, U) = \\
& u_{int} - u_L^{chem}(X_L) + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h_L^*(X_L) - a_L(r_i, U)) = 0 \qquad \forall x, |x| = r_i, \qquad (2.131) \\
& \tilde{u}(u_{int}) - \tilde{u}_L(X_L, r_i, U) - (1 - \frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\overline{\rho}_S}\nu \fint_{I_i} \sigma_S^{<\cdot,\cdot>}\nu = \\
& \tilde{u}^{chem}(u_{int}) - \tilde{u}_L^{chem}(X_L) + (1 - \frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\overline{\rho}_S}(\frac{2\sigma}{r_i} + 3k_S h^*(u_{int})) = 0 \qquad \forall x, |x| = r_i, \qquad (2.132)
\end{aligned}$$

where we got the last equation by taking $\frac{1}{B^I}(2.128) + (\frac{1}{\tilde{\mu}} - \frac{1}{\tilde{m}})\frac{1}{B^I}(2.129)$ for regime (DC). (2.131) is just the continuity of the total chemical potential on I.

In order $\tilde{h}$ we get $(1-\frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\rho_S} = \frac{1}{\overline{Y}_{As}\overline{n}_G}$ with (2.110).

We solve the last two equations, where (2.132) serves to give first u_{int} in terms of X_L and the parameters, r_i and the function U, and (2.132) serves to determine X_L for given parameters. Unfortunately this can't be done explicitly since we have equations which are transcendant in X_L and u_{int}.

We abbreviate $U^i_M = ⨍_{I_i} U \cdot \nu$ and $\overline{n}_{As} = \overline{Y}_{As}\overline{n}_G$. If we can neglect h^* in the second equation and assume strict monotonicity of $\tilde{u}^{chem}$ in u_{int} then (2.132) translates into

$$u_{int}(r_i, U^i_M) := (\tilde{u}^{chem})^{-1}[\tilde{u}^{chem}_L(X_L(r_i, U^i_M)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_i}] \tag{2.133}$$

and (2.131) into

$$\begin{aligned}(\tilde{u}^{chem})^{-1}[\tilde{u}^{chem}_L(X_L(r_i, U^i_M)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_i}] - u^{chem}_L(X_L(r_i, U^i_M))&\\ + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h^*_L(X_L(r_i, U^i_M)) - \frac{U^i_M}{r_i} + \delta^R) = 0,&\end{aligned}$$

equivalently

$$\begin{aligned}&\tilde{u}^{chem}_L(X_L(r_i, U^i_M)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_i}\\ &- \tilde{u}^{chem}(u^{chem}_L(X_L(r_i, U^i_M)) + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h^*_L(X_L(r_i, U^i_M)) - \frac{U^i_M}{r_i} + \delta^R)) = 0\end{aligned} \tag{2.134}$$

and by the mean value theorem one can prove existence of a $X_L(r_i, U^i_M)$ solving the last equation, given r_i and U^i_M. Therefore we have to use Assumption 2.1. We motivate the following assumption in detail in Appendix A.5.

Assumption 2.4 (Well-posedness of boundary conditions on interfaces).

1) If $r_i > r_{min} \geq \frac{2\sigma}{4G_S+3k_L}$, $\overline{X}_L \geq \frac{1}{2}$, $1 > \tilde{\mu} > \frac{1}{3}$ and $\tilde{m} > 1$, then exists a unique solution to $(u_{int}, X_L) \in \mathcal{J}_u \times \mathcal{J}_{X_L}$, as defined in (2.125) *and* (2.124)*, of the interface conditions (2.128) and (2.129) for all parameters $r_i \in \mathcal{J}_r := (r_{min}, \infty)$ and solutions U of the mechanical BVP (where in particular the data of the mechanical BVP is assumed to be in our approximation of $\mathcal{O}(\tilde{h})$).*

2) u_{int} and X_L depend smoothly on r_i and on $⨍_{I_i} U \cdot \nu$ in our approximation from Assumption 2.1.

3) u_{int} and X_L depend smoothly on r_i and are strictly monotone decreasing in r_i, if we make a further approximation, where we assume that u_{int} and X_L can be determined from a single droplet problem. This approximation is exactly up to order $\mathcal{O}(\tilde{h})$.

Unfortunately we cannot prove this, but under suitable scaling assumptions of droplet radii and distances we can give formally an asymptotic expansion of the mechanical BVP in Chapter 3 of our study, which allows to reduce the problem, to the point, that the boundary conditions on the interfaces have to be solved for a single droplet problem. Under suitable assumptions we give a proof of our assumption in case of a single droplet problem in Appendix C.1.2.

As abbreviation we write sometimes $u^i_{int} = u_{int}(r_i, ⨍_{I_i} U \cdot \nu)$. From now on we consider functions of u^i_{int} and X^i_L, e.g. $h^*(u^i_{int})$ or $h^*_L(X^i_L)$, as functions of r_i and $⨍_{I_i} U \cdot \nu$, unless otherwise stated.

Remark 2.5 (Comparison of b. c. on the interfaces with the classical Gibbs-Thomson law). *If we neglected bulk stresses i.e. $U \approx 0$ and $h^*_L \approx 0$ and assume no misfit i.e. $\delta^R = 0$ we would find*

$$\begin{aligned} u_{int}(r_i) &= u_L^{chem}(X_L(r_i)), \\ X_L(r_i) &= [\tilde{u}_L^{chem} - \tilde{u}^{chem} \circ u_L^{chem}]^{-1}(\frac{1}{\overline{n}_{As}} \frac{2\sigma}{r_i}) \end{aligned}$$

and with linearising this yields the classical Gibbs-Thomson law.

2.6.4. Diffusion equation

In this subsection we derive the diffusion equation in the solid

$$\mathcal{X}(u)(\partial_t u + v \cdot \nabla u) + \nabla \cdot v \, \Xi(u) - \frac{B}{RT} \Delta u = 0 \quad \forall x \in \Omega_S(t) \quad \forall t \in (0, \mathcal{T}) \tag{2.135}$$

$$\text{where } \mathcal{X}(u) = \hat{n}'_{As}(u), \tag{2.136}$$

$$\Xi(u) = \hat{n}_{As}(u). \tag{2.137}$$

We see that (2.135) is indeed parabolic. Corresponding to (A4) the constitutive law (2.59) guarantees, when we bulk mobility is strictly positive, a positive entropy production. B could be either a given constant $B = B(T)$ which we refer to as (B1) or a function $\frac{B(n_{As})}{RT} \partial_{n_{As}} u(n_{As}, U) = D(T)$ still depending on u, which can be determined by the diffusion constant D of interstitial As once a solution u is known. The latter case is abbreviated by (B2).
We combine the local conservation of As (2.17) with (2.22),

$$\nabla \cdot j = -\partial_t n_{As_S} - \sum_{a \in SL} \nabla n_{As_a} v \tag{2.138}$$

and with (2.59) and (2.91) we get the diffusion equation written with n_{As} as unknown for (B1)

$$\partial_t n_{As} + \nabla \cdot (n_{As} v) = \frac{1}{RT} \nabla \cdot (B(n_{As}) \nabla u(n_{As}, U)) = D \Delta n_{As} \tag{2.139}$$

or for (B2)

$$\partial_t n_{As} + \nabla \cdot (n_{As} v) = \frac{B}{RT} \Delta u(n_{As}, U). \tag{2.140}$$

In principle we can treat both cases (B1) and (B2), i.e. (2.63) and (2.64), simultaneously since the structure of the PDE remains the same. We present our analysis in the rest of the study in the first case, the results in the second case can be similarly obtained. The mathematical analysis is more interesting in the case (2.63), because in this case the diffusion equation is nonlinear, while in the case (2.64) the diffusion equation is linear.
We use (2.101) instead of the law (2.17) and get a diffusion equation where the mechanics enters only by the velocity and its divergence

$$\partial_t \hat{n}_{As_S} + \nabla \cdot (\hat{n}_{As} v) - \frac{B}{RT} \Delta u(\hat{n}_{As}) = 0. \tag{2.141}$$

Since $\hat{n}_{As}(u)$ is a continuous and strictly monotone function in u it is invertible w.r.t. u and we find equivalently to (2.141) the diffusion equation (2.135).

Remark 2.6 (Alternative version of the diffusion equation). *If we considered the density ρ_S as function of u by assuming that $U = U(u)$ in Ω_S, then we could eliminate by means of the continuity equation* (2.20) *the $\nabla \cdot v$ term and rewrite* (2.135) *as*

$$\mathcal{X}_0(u)(\partial_t u + v \cdot \nabla u) - \frac{1}{RT} \nabla \cdot (B \nabla u) = 0 \quad \forall x \in \Omega_S(t) \quad \forall t \in (0, \mathcal{T}) \tag{2.142}$$

with $\mathcal{X}_0$ *defined as in* (2.103). *But since we want to have equivalence between* (2.140) *and* (2.135) *without further assumptions we do not use* (2.142).

Analogously to (2.138), in the liquid we have

$$\nabla \cdot j_{As_L} = -\partial_t n_{As_L} - \nabla \cdot (n_{As_L} v), \tag{2.143}$$

which we can rewrite if we extend (2.136) and (2.137) for n_{As_L}

$$\mathcal{X}(u_L)(\partial_t u_L + v \cdot \nabla u_L) + \nabla \cdot v\, \Xi(u_L) = -\nabla \cdot j_{As_L} \quad \forall x \in \Omega^i_L(t) \quad \forall t \in (0, \mathcal{T}). \tag{2.144}$$

Remark 2.7 (Diffusion in the liquid). *If we did not assume a homogeneous liquid droplet i.e. neglect diffusion in the liquid, we would have*

$$j_{As_L} = -\frac{B^L}{RT} \nabla u_L \tag{2.145}$$

with $B^L(T)$ *(analogous to (2.63)) or* $(RT)^{-1} B^L(n_{As_L}) u'_L(n_{As_L}) = D_L$ *analogous to* (2.64). *Then we would find, corresponding to* (2.139),

$$\partial_t n_{As_L} + \nabla \cdot (n_{As_L} v) - D_L \Delta u_L(n_{As_L}, U_L)) = 0 \quad \forall x \in \Omega^i_L(t) \quad \forall t \in (0, \mathcal{T})$$

or equivalently by using (2.136) *and* (2.137), *extended onto the liquid,*

$$\mathcal{X}(u_L)(\partial_t u_L + v \cdot \nabla u_L) + \nabla \cdot v\, \Xi(u_L) - \frac{B^L}{RT} \Delta u_L = 0 \quad \forall x \in \Omega^i_L(t) \quad \forall t \in (0, \mathcal{T}). \tag{2.146}$$

But we want to assume that diffusion in the liquid is much faster than in the solid and that we deal with homogeneous liquid droplets. Accordingly we have to let $B^L/B \to \infty$ *s.t. we find* $u_L = const$*, which still could depend on* $r_i(t)$ *and* t *and (2.145) cannot be used anymore. So we must work with (2.143) instead of (2.146) and* u_L *is determined by (2.94) where the constitutive laws (2.84) and (2.85) enter.*

The velocities v_L and v_a, $a \in \mathbf{a_L}$ are spherically symmetric due to Assumption 2.3. With Gauss' theorem we derive from (2.20) and (2.19)

$$v_L|_{I_i} \cdot \nu = -\frac{\int_{I_i} \partial_t \rho_L}{\int_{\Omega^i_L} \rho_L}, \qquad v_a|_{I_i} \cdot \nu = -\frac{\int_{I_i} \partial_t n_a}{\int_{\Omega^i_L} n_a} \quad \forall a \in \mathbf{a_L}, \qquad \forall i \in N(t)\, \forall t \in (0, \mathcal{T}).$$

This yields for j_{As_L}

$$j_{As_L}|_{I_i} \cdot \nu = n_{As_L} \left(\frac{\int_{I_i} \partial_t n_{As_L}}{\int_{\Omega^i_L} n_{As_L}} - \frac{\int_{I_i} \partial_t \rho_L}{\int_{\Omega^i_L} \rho_L} \right) \qquad \forall i \in N(t)\, \forall t \in (0, \mathcal{T}).$$

With Assumptions 2.2 and 2.3 the last three equations simplify by using Gauss' theorem to

$$v_L|_{I_i} \cdot \nu = -\frac{r_i}{3} \frac{\partial_t \rho^i_L}{\rho^i_L} \qquad \forall x \in I_i(t)\, \forall i \in N(t)\, \forall t \in (0, \mathcal{T}), \tag{2.147}$$

$$v_a|_{I_i} \cdot \nu = -\frac{r_i}{3} \frac{\partial_t n^i_a}{n^i_a} \qquad \forall x \in I_i(t)\, \forall i \in N(t)\, \forall t \in (0, \mathcal{T}) \quad \forall a \in \mathbf{a_L}, \tag{2.148}$$

$$j_{As_L}|_{I_i} \cdot \nu = \frac{r_i}{3} \left(\partial_t n_{As_L} - \frac{n_{As_L}}{\rho_L} \partial_t \rho_L \right) \qquad \forall x \in I_i(t)\, \forall i \in N(t)\, \forall t \in (0, \mathcal{T}). \tag{2.149}$$

Due to the monotonicities derived in Lemma A.3 or Lemma A.5 we could state the diffusion equation in the solid also in the variables y or X_S and in the liquid we could state the diffusion equation in the variable X_L.

One might ask which is a suitable unknown for which the diffusion problem should be stated in order to simplify the analysis? There are four candidates: y/X_L, X_S/X_L, $\hat{n}_{As}$ and the chemical potential u. We decide to work with u and with $\hat{n}_{As}$ as unknown. For applying standard results for nonlinear diffusion equations it is more practical to work with $\hat{n}_{As}$, while in order to find a formally homogenised solution of the diffusion problem, it is more convenient to use u, which is the variable in the corresponding classical LSW models.

2.6.5. Stefan conditions and outer boundary conditions

We ask what can be said about the speed of a free boundary? For a given PDE with a free interface, we can derive an explicit formula for the normal speed $\dot{r}_i$ of a spherically free interface in terms of the variables, u, U, R_{bd} and r_i, called the Stefan condition. In this subsection we will derive this formula for our model.

For spherically symmetric droplets the conditions (2.29) – (2.31) are rewritten as

$$(\fint_{I_i} j_{As} - j_{As_L} + n_{As} \fint_{I_i} v_+ - n_{As_L} v_-) \cdot \nu = [[n_{As}]]\dot{r}_i \quad \forall x \in I_i(t)\, \forall i \in N(t)\, \forall t \in (0,\mathcal{T}), \tag{2.150}$$

$$(\fint_{I_i} j_{Ga} - j_{Ga_L} + n_{Ga} \fint_{I_i} v_+ - n_{Ga_L} v_-) \cdot \nu = [[n_{Ga}]]\dot{r}_i \quad \forall x \in I_i(t)\, \forall i \in N(t)\, \forall t \in (0,\mathcal{T}), \tag{2.151}$$

$$(\rho_S \fint_{I_i} v_+ - \rho_L v_-) \cdot \nu = [[\rho]]\dot{r}_i \quad \forall x \in I_i(t)\, \forall i \in N(t)\, \forall t \in (0,\mathcal{T}). \tag{2.152}$$

We abbreviate in the following

$$U_M^i := \fint_{I_i} U \cdot \nu, \quad (\nabla U)_M^i := \fint_{I_i} (\nabla U \cdot \nu) \cdot \nu, \quad v_M^i := \fint_{I_i} v \cdot \nu.$$

Furthermore we write $\partial_\nu u = \nabla u \cdot \nu$.

Lemma 2.3 (Stefan conditions and outer boundary condition)**.**

1) With Fick's law (2.59) and inserting (2.147) and (2.149) the equations (2.150), (2.152), (2.35) and (2.37) imply

$$\dot{r}_i = \frac{B}{RT} \frac{\fint_{I_i} \nabla u \cdot \nu}{\mathbb{X}(r_i, U_M^i)} \qquad \forall x \in I_i(t)\, \forall i \in N(t)\, \forall t \in (0,\mathcal{T}), \tag{2.153}$$

$$\frac{B}{RT} \partial_\nu u = 0 \qquad \forall x \in \partial\Omega(t) \quad \forall t \in (0,\mathcal{T}), \tag{2.154}$$

$$\dot{R}_{bd} = \fint_{\partial\Omega} v \cdot \nu \qquad \forall x \in \partial\Omega(t) \quad \forall t \in (0,\mathcal{T}) \tag{2.155}$$

where we abbreviated

$$\mathbb{X} = -\frac{\rho_L}{\rho_S} n_{As} + n_{As_L} + (\partial_{r_i} n_{As_L} - \frac{n_{As}}{\rho_S} \partial_{r_i} \rho_L) \frac{r_i}{3}. \tag{2.156}$$

2) In our approximation this yields

$$\begin{aligned} &\mathbb{X}(r_i, U_M^i) \\ &= \overline{n}_G (3 - \overline{Y}_V)[(\overline{X}_S - X_S)\frac{\overline{\rho}_L}{\overline{\rho}_S} + (X_L - \overline{X}_L)(1 + \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}) - (X_L - \overline{X}_S)\frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}] \end{aligned} \tag{2.157}$$

with $\varrho := 1 - \frac{\overline{\rho}_L}{\rho_S}$.

3) $\mathbb{X}$ *is strictly positive and strictly monotone increasing in* r_i.

Proof. We only prove 1) and show 2) and 3) in Appendix A.6. We plug in Fick's law (2.59) into (2.35) and get (2.154). From (2.37) follows (2.155).

The following assumption is crucial for the statement of the Stefan condition (2.153). We assume we have given: u_{int} and X_L as function of r_i and U_M^i, while $v_+ = [\partial_t U]_{I_i}$. We get from (2.150)

$$\fint_{I_i} w \cdot \nu = -\frac{(\frac{B}{RT} \fint_{I_i} \nabla u + j_{As_L}) \cdot \nu}{[[n_{As}]]} + \frac{\fint_{I_i} [[n_{As} v]] \cdot \nu}{[[n_{As}]]} \quad \text{on } I_i(t) \quad \forall i \in N(t) \quad \text{for a.a. } t \in (0, \mathcal{T}). \tag{2.158}$$

In a homogeneous and spherical liquid droplet we can solve the continuity equation for v_L and v_{As_L} and get (2.147) and (2.148). For spherically symmetric droplets $\fint_{I_i(t)} w(x,t) \cdot \nu = \dot{r}_i(t)$ for all $i \in N(t)$.

Note that, due to (2.152),

$$v_M^i = \fint_{I_i} v_+ \cdot \nu = \dot{r}_i \frac{[[\rho]]}{\rho_S} + \frac{\rho_L}{\rho_S} v_- \cdot \nu = (1 - \frac{\rho_L}{\rho_S}) \dot{r}_i - \frac{\partial_t \rho_L}{\rho_S} \frac{r_i}{3}. \tag{2.159}$$

We plug (2.147), (2.148), (2.149) and (2.159) into (2.158) and get

$$\dot{r}_i = \frac{-\frac{B}{RT} \fint_{I_i} \nabla u \cdot \nu - (\partial_t \rho_L \frac{n_{As_L}}{\rho_L} - \partial_t n_{As_L}) \frac{r_i}{3} + n_{As}((1 - \frac{\rho_L}{\rho_S}) \dot{r}_i - \frac{\partial_t \rho_L}{\rho_S} \frac{r_i}{3}) + n_{As_L} \frac{\partial_t \rho_L}{\rho_L} \frac{r_i}{3}}{[[n_{As}]]}.$$

That can be rewritten as

$$\dot{r}_i = \frac{-\frac{B}{RT} \fint_{I_i} \nabla u \cdot \nu + (\partial_t n_{As_L} - \frac{n_{As}}{\rho_S} \partial_t \rho_L) \frac{r_i}{3}}{\frac{\rho_L}{\rho_S} n_{As} - n_{As_L}}, \tag{2.160}$$

which is the formula given by Dreyer and Duderstadt [DD08]. But on the r.h.s. of (2.160) $\partial_t \rho_L$ and $\partial_t n_{As_L}$ depend on $\dot{r}_i$ and we want to state an explicit formula for $\dot{r}_i$.

If we assume that, we can write $\partial_t \rho_L = \partial_{r_i} \rho_L \dot{r}_i$ and $\partial_t n_{As_L} = \partial_{r_i} n_{As_L} \dot{r}_i$, then by defining

$$\mathbb{X} = -\frac{\rho_L}{\rho_S} n_{As} + n_{As_L} + (\partial_{r_i} n_{As_L} - \frac{n_{As}}{\rho_S} \partial_{r_i} \rho_L) \frac{r_i}{3}$$

we find the Stefan condition (2.153). □

The boundary condition on the interface, the diffusion equation and the Stefan conditions are different for (IC).

2.6.6. Differences for the regime (IC) in Subsections 2.6.3 – 2.6.5

We recall that in the interface controlled regime of interface motion the relation of the mobilities is (2.66), while for regime (DC) we considered (2.65). The diffusion equation for (IC), (2.69), gives directly that the chemical potential depends only on time,

$$u = \overline{u}(t) = const(t) \qquad \forall x \in \Omega_S(t)\ \forall t \in (0, \mathcal{T}). \tag{2.161}$$

Note, that the Stefan condition (2.153) is in the (IC) limit (2.66) of the form "$\frac{0}{0}$". We have two equations to derive $\dot{r}_i$ and X_L^i, which follow from the necessary conditions (A3) i.e. the equations

(2.128) and (2.129),

$$\begin{aligned}
&n_L^R(1-h_L^*(X_L^i))^{3/2}(v^\nu_{As_L}-\frac{1}{\tilde{\mu}}v^\nu_{Ga_L}+(1-\frac{1}{\tilde{\mu}})(v^\nu_L-\dot{r}_i))\\
&=-\frac{B^I}{RT}(\overline{u}-u_L^{chem}(X_L^i)+\frac{1-\tilde{\mu}}{\tilde{\mu}}\frac{3k_L}{n_L^R}(h_L^*(X_L^i)-\frac{\fint_{I_i}U\cdot\nu}{r_i}+\delta^R)) \qquad \forall x, |x|=r_i(t)\;\forall i\in N(t),\\
&n_L^R(1-h_L^*(X_L^i))^{3/2}(v^i_{As_L}-\dot{r}_i)\\
&=-\frac{B^I}{RT}(\mu_{As}(\overline{u})-\mu_{As_L}(X_L^i,\fint_{I_i}U\cdot\nu)-\frac{M_{As}}{\overline{\rho}_S}\nu\cdot\sigma_S^{<\cdot,\cdot>}\nu) \qquad \forall x, |x|=r_i(t)\;\forall i\in N(t),
\end{aligned}$$

where $t\in(0,\mathcal{T})$ is fixed. In regime (IC) we look for solutions $(\dot{r}_i, X_L^i)=(\dot{r}_i, X_L)\in\mathbb{R}\times(0,1)$ of the last two equations, where $\dot{r}_i$ and X_L each are functions of the given parameters r_i and the function U, which is assumed to be known from the mechanical BVP. The equation for $\dot{r}_i$ serves as Stefan condition for regime (IC).

We abbreviate

$$\mathbb{G}(X_L):=n_L^R(1-h_L^*(X_L))^{3/2}.$$

We use that $\partial_t n^i_{As_L}$, $\partial_t n^i_{Ga_L}$ and $\partial_t\rho^i_L$ can be expressed as functions $n'_{As_L}\dot{r}_i$, $n'_{Ga_L}\dot{r}_i$ and $\rho'_L\dot{r}_i$ as demonstrated in the proof of Lemma 2.3, and define

$$\mathbb{H}_{\tilde{n}}(X_L,r_i,U_M^i):=(1-\frac{1}{\tilde{n}})-\frac{r_i}{3}(\frac{n'_{As_L}}{n_{As_L}}-\frac{1}{\tilde{n}}\frac{n'_{Ga_L}}{n_{Ga_L}}+(1-\frac{1}{\tilde{n}})\frac{\rho'_L}{\rho_L}), \quad \tilde{n}\in\{\tilde{\mu},\tilde{m}\}.$$

Similar as in Subsection 2.6.3 we rewrite the second equation by combining $\frac{RT}{B^I}(2.128)+(\frac{1}{\tilde{\mu}}-\frac{1}{\tilde{m}})\frac{RT}{B^I}(2.129)$. Furthermore by using (2.147) and (2.148) and the definitions of $\mathbb{G}$ and $\mathbb{H}$, we get

$$\begin{aligned}
\mathbb{G}(X_L)\mathbb{H}_{\tilde{\mu}}(X_L,r_i,U_M^i)\dot{r}_i&=\frac{B^I}{RT}(\overline{u}-u_L^{chem}(X_L)+\frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h_L^*(X_L)-a_L(r_i,U))),\\
\mathbb{G}(X_L)\mathbb{H}_{\tilde{m}}(X_L,r_i,U_M^i)\dot{r}_i&=\frac{B^I}{RT}(\tilde{u}^{chem}(\overline{u})-\tilde{u}_L^{chem}(X_L)+(1-\frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\overline{\rho}_S}(\frac{2\sigma}{r_i}+3k_Sh^*(\overline{u}))).
\end{aligned}$$

Eliminating $\dot{r}_i$ yields one equation for X_L

$$\begin{aligned}
&\frac{\mathbb{H}_{\tilde{\mu}}(X_L,r_i,U_M^i)}{\mathbb{H}_{\tilde{m}}(X_L,r_i,U_M^i)}(\tilde{u}^{chem}(\overline{u})-\tilde{u}_L^{chem}(X_L)+(1-\frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\overline{\rho}_S}(\frac{2\sigma}{r_i}+3k_Sh^*(\overline{u})))\\
&=\overline{u}-u_L^{chem}(X_L)+\frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h_L^*(X_L)-a_L(r_i,U)),
\end{aligned} \tag{2.162}$$

and one for $\dot{r}_i$

$$\dot{r}_i=\frac{B^I}{RT}\frac{\overline{u}-u_L(X_L^i,U_M^i)}{\mathbb{G}(X_L)\mathbb{H}_{\tilde{\mu}}(X_L,r_i,U_M^i)}, \tag{2.163}$$

where we rewrite by means of (2.94) in the last equation.

Assumption 2.5 (Boundary conditions on the interfaces for regime (IC))**.** *We assume that (2.162) has a unique solution $X_L^i\in\mathcal{J}_{X_L}$ for given $\overline{u}$, r_i and U_M^i for typical material data as given in Appendix D.*

Then $\dot{r}_i$ is uniquely determined by (2.163). We rewrite this Stefan condition for regime (IC) as

$$\dot{r}_i=\frac{B^I}{RT}\frac{\overline{u}-u_L(X_L(\overline{u},r_i,U_M^i),U_M^i)}{\mathbb{Z}(\overline{u},r_i,U_M^i)} \tag{2.164}$$

with

$$\mathbb{Z}(\overline{u}, r_i, U_M^i) := \mathbb{G}(X_L)\mathbb{H}_{\tilde{\mu}}(X_L(\overline{u}, r_i, U_M^i), r_i, U_M^i). \tag{2.165}$$

and $\mathbb{Z}$ *is strictly positive.*

We can confirm this assumption so far only numerically.

We state as approximation in $\mathcal{O}(\tilde{h})$

$$\begin{aligned}\mathbb{Z}(\overline{u}, r_i, U_M^i) = n_L^R(1 - \frac{3}{2}h_L^*(X_L))\Big(1 - \frac{1}{\tilde{\mu}} - \frac{r_i}{3}X_L'(\frac{1}{X_L} + \frac{1}{\tilde{\mu}}\frac{1}{1-X_L})\\ - (1 - \frac{1}{\tilde{\mu}})(1+3a_L)(1 + \frac{(3\frac{\overline{\rho}_L}{\rho_S} - 1)\frac{U_M^i}{r_i} - 3\frac{\overline{\rho}_L}{\rho_S}\delta^R}{1 - \frac{\overline{\rho}_L}{\rho_S}})\Big),\end{aligned}$$

which simplifies further to

$$\begin{aligned}\mathbb{Z}(\overline{u}, r_i, U_M^i) = n_L^R(1 - \frac{1}{\tilde{\mu}})\Big(1 - \frac{3}{2}h_L^*(X_L) - [(1 + 3a_L - \frac{5}{2}h_L^*(X_L))\frac{\tilde{\mu}}{\tilde{\mu}-1}\frac{M(X_L)(\overline{X}_L - X_L)}{M_{Ga}X_L(1-X_L)}\\ - (1 + 3a_L - \frac{3}{2}h_L^*(X_L))](1 + \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho})\Big)\end{aligned}$$

where we use (A.22) and (A.25) for the last approximation. We see that $\mathbb{Z} > 0$ holds.

A rough approximation in $\mathcal{O}(\tilde{h}^{1/2})$ but keeping the surface tension term and assuming $\overline{Y} \ll 1$ and $\mathbb{H}_{\tilde{\mu}}/\mathbb{H}_{\tilde{m}} \approx 1$ yields

$$X_L(\overline{u}, r_i, U_M^i) = 1/\left(1 + (\frac{1}{\overline{X}_L} - 1)\exp((\frac{1+\tilde{m}}{1+\tilde{\mu}} - 1)\frac{1}{RT}\overline{u} - \frac{\tilde{\mu}}{\tilde{m}}(1 - \frac{\tilde{\mu}}{\tilde{m}})\frac{2\sigma}{r_i})\right), \tag{2.166}$$

$$\mathbb{Z}(\overline{u}, r_i, U_M^i) = n_L^R(1 - \frac{1}{\tilde{\mu}})\Big(2 - (\frac{\tilde{\mu}}{\tilde{\mu}-1}\frac{M(X_L)(\overline{X}_L - X_L)}{M_{Ga}X_L(1-X_L)}(1 + \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}) - \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho})\Big).$$

If we further assume that the argument of the exponential in (2.166) is small, we find

$$X_L(\overline{u}, r_i, U_M^i) \approx \overline{X}_L(1 + (1 - \overline{X}_L)((\frac{1+\tilde{m}}{1+\tilde{\mu}} - 1)\frac{1}{RT}\overline{u} - \frac{\tilde{\mu}}{\tilde{m}}(1 - \frac{\tilde{\mu}}{\tilde{m}})\frac{2\sigma}{r_i})). \tag{2.167}$$

This corresponds in regime (IC) to the approximation, which is considered in Remark 2.5 in case of regime (DC).

2.6.7. Dissolution of a droplet and the minimal radius

Despite we deal in our model with continuum mechanics we have to notice that liquid droplets do not behave physically as a liquid if they are made arbitrarily small, which is modelled by the introduction of a minimal radius r_{min}. Below r_{min} we do not consider liquid droplets as liquid phase anymore.

Let

$$N_L(r_i, U_M^i) := \frac{4\pi}{3}r_i^3 n_L(r_i, U_M^i)$$

denote the total number of particles in a droplet. In particular a liquid droplet has to have at least two atoms, that allows to determine a lower bound r_{min} for a minimal radius. We calculate r_{min} in the case of a As-droplet with two atoms, i.e. $X_L = 1$, and maximal displacement i.e. $|U_M^i| = \tilde{h}r_{min}$

with $\tilde{h}$ as determined in (2.127):

$$r_i = \sqrt[3]{\frac{3}{4\pi}\frac{2}{n_L(r_{min}, U^i_M)}} = \sqrt[3]{\frac{3}{2\pi}\frac{(1-h^*_L(1))^3}{\overline{n}_L(1-a_L(r_{min}, U^i_M))^3}} \geq \frac{1-h^*_L(1)}{1+\tilde{h}_{\max}}\sqrt[3]{\frac{3}{2\pi}\frac{3-\overline{Y}_V}{\overline{n}_G}} =: r_{min}.$$

For typical material data we can estimate

$$r_{min} \overset{>}{\approx} 4.63 \cdot 10^{-10}\mathrm{m},$$

but we make use of this explicit value for the first time in Ch. 6.

Due to Assumption 2.1 we cannot solve the mechanical BVP in our approximation and due to to Assumption 2.1 or Assumption 2.4 we also cannot solve the interface conditions (2.67) and (2.68) as well as (2.56) and (2.57) below some radius, but this radius is smaller than r_{min}.

We model the vanishing of a droplet s.t. if $r_i = r_{min}$ for the first time i.e. at time τ_i (as defined in (2.3)) we restart with a new problem with initial time τ_i where we have $\mathcal{N} - 1$ droplets. Let f be an arbitrary function in time, then $f(\tau_i+) := \lim_{t\to\tau_i+} f(t)$ denotes a limit from the r.h.s. while $f(\tau_i-) := \lim_{t\to\tau_i-} f(t)$ denote limits from times smaller than τ_i. We abbreviate $[f]^+_- := f(\tau_i+) - f(\tau_i-)$.

We have $\Omega_S(\tau_i+) = \Omega(\tau_i+) \setminus \overline{\cup_{j\neq i\in N(\tau_i+)}\Omega^j_L(\tau_i+)} = \Omega_S(\tau_i-) \cup \overline{\Omega^i_L(\tau_i-)}$.

In principal at time τ_i we have a solid-solid phase transition on $\partial B_{r_{min^*}}(X_i)$, where $r^*_{min} < r_{min}$ is the radius corresponding to a non-misfit situation of a solid sphere in a solid crystal, i.e. we have to solve the boundary value problem for regime (DC) with (2.114) – (2.117), (2.140), (2.133), (2.153) – (2.155) with suitable initial conditions where we replace for the i-th droplet the equations (2.117), (2.133) and (2.153) by

$$\begin{aligned} (\lambda_S \mathrm{tr}(\nabla U) + 2\mu_S e(\nabla U) - 3k_L \frac{\fint_{I_i} U\cdot\nu}{r^*_{min}})\cdot\nu &= 0 \qquad \text{on } \partial B_{r_{min^*}}(X_i)\ \forall t\in(\tau_i+, \mathcal{T}),\\ \partial_\nu u &= 0 \qquad \text{on } \partial B_{r_{min^*}}(X_i)\ \forall t\in(\tau_i+, \mathcal{T}) \end{aligned}$$

and

$$\dot{r}_i(t) = 0 \quad \forall t\in(\tau_i+, \mathcal{T}).$$

Furthermore we have a diffusion equation and a mechanical BVP in the solid droplet $B_{r_{min^*}}(X_i)$, which we have to solve.

We calculate r^*_{min}

$$\sqrt[3]{\frac{3}{4\pi}\frac{2}{n_G(r_{min}, U^i_M)}} \approx \sqrt[3]{\frac{3}{2\pi}\frac{(1-h^*(1))^3}{\overline{n}_G(1-\mathrm{tr}((\nabla U)^i_M))}} \geq (1-h^*(1))\sqrt[3]{\frac{3}{2\pi}\frac{1}{\overline{n}_G}} =: r^*_{min}.$$

and estimate

$$r^*_{min} \overset{>}{\approx} r_{min}\cdot\frac{1-h^*(1)}{1-h^*_L(1)}\frac{1}{\sqrt[3]{3-\overline{Y}_V}} = 1.81\cdot 10^{-10}\mathrm{m}.$$

For a spherically symmetric single droplet problem (SDP) in regime (DC), where we replace the boundary condition (2.154) by $u = u_{BC}$, u_{BC} given, we can calculate explicitly a solution and find semi-cusps close to the interface at τ_i-, before a droplet vanishes. At τ_i+ we expect to have a cusp with a singularity only at X_i. Since u_L or $n_{As}|_{I_i}$ is bounded we have that u or n_{As} stays finite in each point. It is not clear how to extend this directly to a many droplet problem.

Instead we want to assume that the solid droplet is integrated into the crystal immediately. This is an mathematically motivated technical assumption. We see later that the error, which might be made by our following assumption, can be made sufficiently small. We remark that the vanishing of a droplet cannot be modelled by $r_i \to 0$ as e.g. in [Nie99] since for arbitrary small r_i the interface boundary conditions are not well-posed.

Assumption 2.6 (Modelling of a vanishing droplet).

We assume that the new initial value $n_{As}(\tau_i+, x)$ *is given s.t.*

1) *Arsenic is conserved i.e.* $\int_{\Omega(\tau_i-)} n_{As}(\tau_i-, \cdot) = \int_{\Omega(\tau_i+)} n_{As}(\tau_i+, \cdot)$,
2) $\|n_{As}(\tau_i+, \cdot)\|_{H^1(\Omega_S(\tau_i+))} < \infty$,
3) $0 \leq n_{As}(\tau_i+, x) \leq n_S$ *for all* $x \in \Omega_S(\tau_i+)$.

The three conditions guarantee that $n_{Ga}(\tau_i+, \cdot)$ *fulfils conservation of gallium, is a* H^1 *function on* $\Omega_S(\tau_i+)$ *and is in* $(0, n_S)$.

A n_{As}*, which fulfils 1) - 3), can be constructed by means of polynomial interpolation. For example*

$$n_{As}(\tau_i+, x) := \begin{cases} n_{As}(\tau_i-, x) & ; \quad x \in \Omega_S(\tau_i-) \\ n_{As}^{int}(r_{min}) + \frac{p+3}{p+1}((\frac{|x-X_i|}{r_{min}})^p - 1)[[n_{As}(\tau_i-, x)|_{I_i}]]_L^S; & x \in \Omega_L^i(\tau_i-) \end{cases} \tag{2.168}$$

for a $p \in \mathbb{N} \setminus \{1\}$ *and* p *sufficiently large that condition 3) is fulfilled, since*

$$\min_{\Omega_L(\tau_i-)} n_{As}(\tau_i+, \cdot) = n_{As}^{int}(r_{min}), \tag{2.169}$$

$$\max_{\Omega_L(\tau_i-)} n_{As}(\tau_i+, \cdot) = n_{As}(\tau_i+, 0) = -\frac{2}{p+1} n_{As}^{int}(r_{min}) + (1 + \frac{2}{p+1}) n_{As_L}(\tau_i-). \tag{2.170}$$

We choose to work with $p = 20$*, since for As rich liquid droplets we have* $n_{As_L} - \frac{2}{21}[[n_{As}]]_L^S < n_S = n_G^R(3 - \overline{Y}_V)(1 + \mathcal{O}(\tilde{h}))$ *since* $X_L \in (X_L^R, X_L(r_{min}))$*,* $X_L(r_{min}) \approx 0.95 < 1$ *and* $X_S \in (\frac{1}{2}, 1)$*, see Subsection 2.6.3, and* $[[n]] = \mathcal{O}(\tilde{h})$.

Since the displacement and the velocity problem are elliptic, there is no initial data at time τ_i- *to prescribe. The droplets in the index set* $N(\tau_i+) := N(\tau_i-) \setminus \{i\}$ *are left. The new initial value for the radii are* $r_j(\tau_i+) = r_j(\tau_i-), j \in N(\tau_i+)$.

The error we make by our assumption is bounded by $\frac{4\pi}{3} r_{min}^3 \max n_{As}$ *and since we see later, that* r_{min} *scales with* ε*, the error vanishes in the limit* $\varepsilon \to 0$.

The continuity of n_{As} implies that the new initial data for the chemical potential $u^0(\tau_i+)$ is continuous on I_i, too.

For the availability the vanishing of a droplet corresponds to a change of the model and of the formula for the availability. We model this by defining

$$\mathcal{A}(\tau_i+) = \mathcal{A}(\tau_i-) - \mathcal{A}_i^d \tag{2.171}$$

where the energy of the droplet i which has dissolved is modelled by

$$\mathcal{A}_i^d = [\mathcal{A}(\tau_i-) - \mathcal{A}(\tau_i+)]_{\Omega_L^i(\tau_i-)} \tag{2.172}$$

s.t. the availability is continuous in time.

Note, that in the case that a droplet does not disappear at all we have $\tau_i := +\infty$ by the definition (2.3).

Important is that a fixed minimal radius r_{min} exists s.t. our assumptions on interface conditions and small displacement gradients are fulfilled. We do not work with a concrete value for r_{min} in the following. We recall, that the interval of possible radii is abbreviated by

$$\mathcal{J}_r = (r_{min}, \infty) \subset \mathbb{R}.$$

2.7. Problem B and Problem BI – Many droplet problems

We summarise and state the full problem for the independent variables u, $U_{(S)}$, $\{r_i\}_{i\in N}$ and R_{bd} in case of arbitrary many spherical droplets. Herein we express the basic variables n_a by u and U, σ_S by U and eliminate by exploiting the assumption of a homogeneous spherical droplet all quantities from the liquid e.g we express p_L by u, U and r_i.

Problem B[4] consists for regime (DC) of the mechanical BVP (2.114) – (2.117), the diffusion equation (2.135) or (2.140) with boundary conditions (2.154) and (2.131) and an ODE for the evolution of radii (2.153) and condition (2.155) for the evolution of the outer boundary. Further we have to close our equations by imposing initial conditions on u, $\{r_i\}_{i\in N(0)}$ and R_{bd} at $t = 0$. We emphasise that initial conditions on U are not needed.

The mechanical BVP is the elliptic PDE wherein p_L was eliminated by (2.115)

$$\begin{aligned}
\text{div }(\lambda_S \text{tr}(\nabla U) + 2\mu_S e(\nabla U)) &= 3k_S h^{*\prime}(u)\nabla u && \text{in } \Omega_S(t), && (2.173)\\
(\lambda_S \text{tr}(\nabla U) + 2\mu_S e(\nabla U))\nu &= (\overline{p} - p_0 + 3k_S h^*(u))\nu && \text{on } \partial\Omega(t), && (2.174)\\
(\lambda_S \text{tr}(\nabla U) + 2\mu_S e(\nabla U) & \\
-3k_L \frac{\fint_{I_i} U\cdot\nu}{r_i})\nu &= (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h_L^*(X_L^i)) \\
&\quad + 3k_S h^*(u_{int}(r_i, \fint_{I_i} U\cdot\nu)))\nu && \text{on } I_i(t) \quad \forall i \in N(t) && (2.175)
\end{aligned}$$

for all $t \in (0, \mathcal{T})$. The diffusion problem is a nonlinear PDE for u,

$$\begin{aligned}
\partial_t \hat{n}_{As}(u) + \nabla\cdot(\hat{n}_{As}(u)v) & \\
-\frac{B}{RT}\Delta u &= 0 && \text{in } \Omega_S(t)\ \forall t \in (0,\mathcal{T}), && (2.176)\\
u &= u_{int}(r_i, \fint_{I_i} U\cdot\nu) && \text{on } I_i(t)\ \forall i \in N(t)\ \forall t \in (0,\mathcal{T}), && (2.177)\\
\partial_\nu u &= 0 && \text{on } \partial\Omega(t)\ \forall t \in (0,\mathcal{T}), && (2.178)\\
u(\cdot, t=0) &= u^0 && \text{in } \Omega(0), && (2.179)
\end{aligned}$$

with free boundaries $I_i(t)$ and $\partial\Omega(t)$. The motion of the free boundaries is determined by

$$\begin{aligned}
\dot{R}_{bd} &= \fint_{\partial\Omega} v\cdot\nu && \forall t \in (0,\mathcal{T}), && (2.180)\\
\dot{r}_i &= \frac{B}{RT}\frac{\fint_{I_i}\nabla u\cdot\nu}{\mathbb{X}(r_i, \fint_{I_i} U\cdot\nu)} && \forall i \in N(t)\ \forall t \in (0,\mathcal{T}), && (2.181)\\
R_{bd}(t=0) &= R_{bd}^0, && && (2.182)\\
r_i(t=0) &= r_i^0 && \forall i \in N(0). && (2.183)
\end{aligned}$$

The velocity v is determined from U by (2.13). The further unknowns $X_L^i = X_L(r_i, \fint_{I_i} U\cdot\nu)$ and a_L, which replaces the unknown U_L, are explicitly determined by the formulas (2.132) and (2.111).

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[4] Problem A is the rescaled Problem B in the special case of a spherically symmetric single droplet problem and is solved explicitly in Appendix C.1.

In the liquid we have p_L^i and u_L^i given for all $i \in N(t)$ by the formulas (2.121) and (2.94). The vanishing of a droplet is modelled as in Subsection 2.6.7.

We have that $\hat{n}_{As}$ depends nonlinearly but monotone and smooth on u, independent of U. The Stefan condition exhibits a smooth nonlinearity in r_i and $\fint_{I_i} U \cdot \nu$.

We assume that at time $t = 0$ all droplets have radii $r_i^0 > r_{min}$. We recall that we denote the time when the i-th droplet vanishes with τ_i as defined in (2.3). We solve Problem B (2.173) – (2.183) up to times $t = \min_{i \in N(0)} \tau_i$, w.l.o.g. $\tau_{\mathcal{N}(0)} = \min_{i \in N(0)} \tau_i$, when the first droplet vanishes. We start again solving a problem of the type as Problem B, now with initial conditions at $\mathcal{T}$ and $\mathcal{N} - 1$ droplets, which are determined as described in Subsection 2.6.7. We solve up to time $\min_{i \in N(t)} \tau_i = \min_{1 \le i \le \mathcal{N}(0)-1}$. We want to bear the criteria on $\mathcal{T}$, stated in (2.1), in mind.

For the regime (IC) we consider **Problem BI**: find $U, \overline{u}, \{r_i\}_{i \in N}, R_{bd}$ s.t.

$$\begin{aligned} \operatorname{div}\,(\lambda_S \operatorname{tr}(\nabla U) + 2\mu_S e(\nabla U)) &= 0 && \text{in } \Omega_S(t), && (2.184)\\ (\lambda_S \operatorname{tr}(\nabla U) + 2\mu_S e(\nabla U))\nu &= (\overline{p} - p_0 + 3k_S h^*(\overline{u}))\nu && \text{on } \partial\Omega(t), && (2.185)\\ (\lambda_S \operatorname{tr}(\nabla U) + 2\mu_S e(\nabla U) & && && \\ -3k_L \frac{\fint_{I_i} U \cdot \nu}{r_i})\nu &= (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h_L^*(X_L^i)) && && \\ &\quad + 3k_S h^*(\overline{u}))\nu && \text{on } I_i(t) \quad \forall i \in N(t), && (2.186) \end{aligned}$$

for all $t \in (0, \mathcal{T})$,

$$\overline{u} = const(\{r_i\}_{i \in N}, R_{bd}, U) \qquad \forall t \in (0, \mathcal{T}), \qquad (2.187)$$

where $\overline{u}$ has to be determined s.t. mass and substance are conserved, and

$$\begin{aligned} \dot{r}_i &= B^I \frac{\overline{u} - u_L(\overline{u}, r_i, \fint_{I_i} U \cdot \nu)}{\mathbb{Z}(\overline{u}, r_i, \fint_{I_i} U \cdot \nu)} && \forall i \in N(t)\, \forall t \in (0, \mathcal{T}), && (2.188)\\ r_i(t = 0) &= r_i^0 && \forall i \in N(0), && (2.189)\\ \dot{R}_{bd} &= \fint_{\partial\Omega} \partial_t U \cdot \nu && \forall t \in (0, \mathcal{T}), && (2.190)\\ R_{bd}(t = 0) &= R_{bd}^0. && && (2.191) \end{aligned}$$

The unknowns X_L^i and a_L, which replaces the unknown U_L, are explicitly determined by the formulas (2.162) and (2.111).

In the liquid we have p_L^i and u_L^i given for all $i \in N(t)$ by the formulas (2.121) and (2.94). The vanishing of a droplet is modelled as in Subsection 2.6.7.

Note, that all parts of Problem B are coupled with each other. The diffusion problem depends on the free boundaries by the geometry and the radii enter as parameters in the boundary condition on I_i. And the diffusion problem depends on the mechanics by the velocity v and by the boundary condition on I_i. The Stefan condition (2.181) is coupled to the diffusion problem via $\fint_{I_i} \partial_\nu u$ and to the mechanics by $\mathbb{X}$. The mechanical BVP depends on free boundaries by the geometry and the data, the contribution from surface tension depends on $\frac{1}{r_i}$ and h_L^* depends on r_i by means of $X_L^i = X_L(r_i, U_M^i)$. The mechanics are coupled to the diffusion by the data h^*. We met a similar coupling in Problem BI.

Note, that we do not have a total spherical symmetry in Ω_S, which can be assumed in case of a single droplet centred in a spherical solid surrounding. For a single droplet in total spherical symmetry we can calculate explicitly U in terms of r_I, R_{bd} and u, see Appendix C.1.1), and then only have to solve the diffusion equation, which is then only coupled to the Stefan condition. This approach is followed in Appendix C where all explicit calculations are given.

We emphasise that the boundary conditions on the free boundaries ensure that we have spherical droplets and a spherical Ω at all times.

Lemma 2.4 (Equivalent diffusion problem for variable $\hat{n}_{As}$)**.** *Let $\hat{n}_{As}$ be a smooth, strictly monotone and convex function of u. Then the diffusion problem (2.176) – (2.179) is equivalent to*

$$\begin{aligned}
&\partial_t \hat{n}_{As} + \nabla\cdot(\hat{n}_{As} v) \\
&\quad - \frac{B}{RT}\Delta u(\hat{n}_{As}) = 0 && \text{in } \Omega_S(t)\ \forall t\in(0,\mathcal{T}), \qquad (2.192)\\
&\qquad\qquad \hat{n}_{As} = \hat{n}_{As}^{int}\Big(r_i, \fint_{I_i} U\cdot\nu\Big) && \text{on } I_i(t)\ \forall i\in N(t)\ \forall t\in(0,\mathcal{T}), \qquad (2.193)
\end{aligned}$$

and

$$\begin{aligned}
\partial_\nu \hat{n}_{As} &= 0 && \text{on } \partial\Omega(t)\ \forall t\in(0,\mathcal{T}), \qquad (2.194)\\
\hat{n}_{As}(\cdot, t=0) &= \hat{n}_{As}^0 := \hat{n}_{As}(u^0) && \text{in } \Omega(0). \qquad (2.195)
\end{aligned}$$

Proof. Since $\hat{n}_{As}$ is smooth, strictly monotone and convex in u we have the following relation between arbitrary norms $\|\cdot\|$ of u and norms of $\hat{n}_{As}$. By the mean value theorem there exists a $\xi\in\mathcal{J}_u$ s.t.

$$\|\hat{n}_{As}(u)\| = \|\hat{n}_{As}(u=0) + \hat{n}'_{As}(u=\xi)u\| \leq \overline{Y}_{As} n_G^R \|1\| + \hat{n}'_{As}(u=0)\|u\| \qquad (2.196)$$

and hence arbitrary norms of $\hat{n}_{As}$ can be estimated by norms of u, if $\|1\|$ is finite. By considering $u(\hat{n}_{As})$ norms of $\hat{n}_{As}$ can be estimated by u.

On the other hand u is smooth, strictly monotone and concave in $\hat{n}_{As}$ and we can estimate u by $\hat{n}_{As}(u)$ norms. ☐

From now on we use $\hat{n}_{As} = Y_{As} n_G^R$ instead of $n_{As} = Y_{As} n_G$, which does not appear anymore. Abusing notation, we again write n_{As}.

Remark 2.8 (Discussion of approximations in the diffusion equation)**.** *If we would neglect the drift-terms in the diffusion equation i.e. if we would set $v = 0$ this would violate the conservation laws for substance and mass.*

The case of a quasi-stationary approximation with completely neglecting the l.h.s. of the diffusion equation (2.176) *corresponds to the case $B^D \to \infty$ and hence to the diffusion problem in the (IC) regime.*

2.8. Available free energy – A Lyapunov function

In this chapter we have given so far a short derivation of Problem B for regime (DC) or Problem BI for (IC) from thermodynamics. The detailed derivation in [DD08] shows that the PDEs and ODEs are equivalent to (2.42).

Since we use in the rest of the study only that $\mathcal{A}$ is a Lyapunov function, we check in Appendix A.7 by direct calculations that solutions of Problem B or Problem BI fulfil indeed (2.42).

We remark, that the following calculations are *a priori* i.e. in the sense that we assume that all functions are smooth enough for differentiation and integration. These are justified, when we show existence of classical solutions of the PDEs and ODEs of our problems under further assumptions and that the energy, which turns out to be $\mathcal{A} = -\int_0^{\mathcal{T}}\int_{\Omega_S(t)} |\nabla u|^2\,dx\,dt$, is indeed finite.

Theorem 2.1 (Lyapunov function)**.** *Assume Problem B or Problem BI has a smooth solution and assume in particular that* $\partial\Omega$ *and* I_i *for all* $i \in N$ *are spheres and assume* $w|_{\partial\Omega} \approx \dot{R}_{bd}$ *in good approximation. We assume the Helmholtz energy density* $\rho\psi$ *to fulfil the relations (A.28) and (A.29), we use local conservation of substance and assume all assumptions which we made so far on material parameters to hold.*

Then the availability is decreasing in time i.e. there holds

$$\frac{d}{dt}\mathcal{A} \leq 0 \quad \forall t \neq \tau_i, i \in N(0) \tag{2.197}$$

where the availability is modelled at τ_i *as in* (2.171)*. The therin appearing "availability of two single atoms"* $\mathcal{A}_i^d$ *as defined by* (2.172) *is well-defined.*

The availability is bounded from below and by adding up a suitable constant we can achieve that

$$\mathcal{A} = 0$$

for an equilibrium. Hence $\mathcal{A}$ *is a Lyapunov function in sense of [Wal00] w.r.t. this equilibrium.*

For a proof we refer to Appendix A.7.

Chapter 3.

Relevant scales and formal homogenisation

We want to consider the case of small volume fraction of liquid droplets. In general for given $\mathcal{T}$ we can only solve Problem B and Problem BI for sufficiently small droplets, which we specify later in Section 4.4. In the next section we determine typical scales of the diffusion problem as well as of the mechanical BVP and rescale in order to formulate our Problems B and BI in dimensionless variables and with a dimensionless scaling parameter ε. We proceed in Section 3.1 as outlined in Eck et al. [EGK08], *Kap.* 1.4.

We find different scaling regimes. The corresponding problems are stated in Section 3.2.

Furthermore we are more interested in typical properties of our problem for a large number of droplets than in solving the problem exactly for a certain number of droplets. Letting the scaling parameter $\varepsilon \to 0$, our final goal is to derive effective equations, which describe the macroscopic behaviour with an error which vanishes as $\varepsilon \to 0$. The formal homogenisation of Problem B and Problem BI is considered in Section 3.3.

3.1. Dimensional analysis and scaling

3.1.1. Dedimensionalisation

Our independent dimensions are length **L**, time **T**, mass **M** and number **N**; e.g. the dimension of number of atoms is usually measured in units of 1mol. In order to state this clearly, we make the following definition.

Definition 3.1 (Scaling)**.** *We say that a quantity f scales with $\mathbf{F}$, denoted by $f \sim \mathbf{F}$, if $f = \mathbf{F}\hat{f}$ and the rescaled quantity $\hat{f}$ is dimensionless. Here and in the following we denote quantities without dimensions by hats* $\hat{\ }$ *.* $\mathbf{F}$ *is a product of a dimension multiplied with a power of a scaling parameter.*

We want to divide in Problem B and Problem BI all quantities by its dimension e.g. we divide x by typical length $\mathbf{L}$, t by typical time $\mathbf{T}$, n_{As} by typical atom number per volume $\mathbf{N}\mathbf{L}^{-3}$ and σ_S by typical pressure $\frac{\mathbf{M}}{\mathbf{L}^2\mathbf{T}}$. Already dimensionless are by definition e.g. $\frac{1}{RT}u, y, \overline{Y}, X_L$ and P. In this section we consider thus our Problems B and BI **without dimensions**.

As important length scales for radii we define

$$\mathcal{R}_0 := \frac{1}{\mathcal{N}^0} \sum_{i=1}^{\mathcal{N}^0} r_i^0. \tag{3.1}$$

Since we assume that distances $d_{ij} = |X_i - X_j|$, $i, j \in N(0)$ between neighbouring droplets and distances $d_{i0} = \operatorname{dist}(X_i, \partial\Omega(0))$, $i \in N(0)$ between droplets and the outer boundary are of same order, we define as relevant length scale for distances

$$\mathcal{D}_0 := \frac{1}{\mathcal{N}^0(\mathcal{N}^0+1)} \sum_{i=1}^{\mathcal{N}^0} \sum_{j=0}^{\mathcal{N}^0} d_{ij}. \tag{3.2}$$

Further we define

$$d_i := \min_{j \in N(t) \cup \{0\}} d_{ij}. \tag{3.3}$$

If we can guarantee

$$r_i < \frac{d_i}{2}, \quad \operatorname{dist}(X_i, \partial\Omega(0)) < \frac{d_i}{2} \quad \forall i \in N(0) \tag{3.4}$$

for all times t, this replaces (2.1).

As typical data of Problem B, which corresponds to the experimental situation, we have $n^0_{As} = \overline{Y}_{As} n^R_G \approx n^R_G = 3.7 \cdot 10^4 \mathrm{mol\,m^{-3}}$, $r^0_i \approx \mathcal{R}_0 = 10^{-9}\mathrm{m}$ and $G_S \approx 3.5364 \cdot 10^{10} \mathrm{N\,m^{-2}}$. For regime (DC) we consider $B = 10^{-17} \mathrm{mol\,m^{-1}\,s^{-1}}$, while for regime (IC) $B^I = 7.3 \cdot 10^6 \mathrm{mol\,m^{-2}\,s^{-1}}$. Furthermore we assume $\mathcal{L}_0 = R^0_{bd} \approx 10^{-9/2}\mathrm{m} - -10^{-5}\mathrm{m}$ and $\mathcal{D}_0 = 10^{-6}\mathrm{m}$. For a sphere Ω follows

$$\mathcal{N}^0 \approx \frac{|\Omega(0)|}{\mathcal{D}_0^3} = \frac{4\pi}{3} 10^9. \tag{3.5}$$

We continue with our dedimensionalisation. We emphasise that we still have the choice to scale parameters like $\overline{Y}$ or data of the problems like σ. At first we consider regime (DC) and determine possible scaling parameters. Applying the Pi-theorem of Buckingham [Buc14] we want to determine all representations Π s.t.

$$\Pi = (n^0_{As})^\alpha (\mathcal{R}_0)^\beta (G_S)^\gamma B^\delta (\mathcal{L}_0)^\zeta (\mathcal{D}_0)^\eta \overline{Y}^\theta \sigma^\iota,$$

which are dimensionless. There holds for the dimensions

$$[\Pi] = (\frac{\mathbf{N}}{\mathbf{L}^3})^\alpha \mathbf{L}^\beta (\frac{\mathbf{M}}{\mathbf{L}\mathbf{T}^2})^\gamma (\frac{\mathbf{N}}{\mathbf{L}\mathbf{T}})^\delta \mathbf{L}^\zeta \mathbf{L}^\eta (\frac{\mathbf{M}}{\mathbf{T}^2})^\iota = \mathbf{N}^{\alpha+\delta} \mathbf{L}^{-3\alpha+\beta-\gamma-\delta+\zeta+\eta} \mathbf{M}^{\gamma+\iota} \mathbf{T}^{-2\gamma-\delta-2\iota}.$$

Since all exponents have to vanish in a dimensionless representation we find $\alpha + \delta = 0$, $-3\alpha + \beta - \gamma - \delta + \zeta + \eta = 0$, $\gamma + \iota = 0$ and $-2\gamma - \delta - 2\iota = 0$. Finally this implies $\alpha = 0$, $\beta = -\zeta - \eta - \iota$, $\gamma = -\iota$, $\delta = 0$ and hence

$$\Pi = (\frac{\mathcal{D}_0}{\mathcal{L}_0})^{-\zeta} (\frac{\mathcal{R}_0}{\mathcal{D}_0})^{-\zeta-\eta} \overline{Y}^\theta (\frac{\sigma}{G_S \mathcal{R}_0})^\iota.$$

We introduce as dimensionless scaling parameter

$$\varepsilon := \frac{\mathcal{D}_0}{\mathcal{L}_0}$$

and assume

$$\frac{\mathcal{R}_0}{\mathcal{D}_0} = \varepsilon^{r-1}, \quad \overline{Y} = \overline{Y}_R \varepsilon^p, \quad \frac{\sigma}{G_S \mathcal{R}_0} = \varepsilon^{o-r},$$

where $r > 1$, $p > 0$, $o \geq r$ and $\overline{Y}_R$ is dimensionless. We determine r, p and o in the next Subsection 3.1.2.

The scaling of the mass is chosen s.t. stresses, strains and pressure are scale invariant i.e. $\frac{\mathbf{M}}{\mathbf{L}\mathbf{T}^2} \sim \varepsilon^0$. For the scale of mole $\mathbf{N} = \varepsilon^l$ we recall that we have defined the minimal radius r_{min} by $N_L = 2$ and $r_{min} \sim r_i \sim \mathcal{R}$, which motivates $l = 3r$. This implies e.g. $\overline{n}_L, \overline{n}_G \sim 1$. That $\overline{n}_L$ and $\overline{n}_G$ have to have the same scaling follows from (2.112). W.l.o.g. we choose as typical length scale, time scale, mass scale and number scale

$$\mathbf{L} = \varepsilon^r \mathcal{L}_0,\ \mathbf{T} = \varepsilon^q \ 1\text{s},\ \mathbf{M} = \varepsilon^{r+2q}\ M_{As}\ 1\text{mol},\ \mathbf{N} = \varepsilon^{3r}\ 1\text{mol}.$$

For regime (IC) we have

$$[\Pi] = \mathbf{N}^{\alpha+\delta}\mathbf{L}^{-3\alpha+\beta-\gamma-2\delta+\zeta+\eta}\mathbf{M}^{\gamma+\iota}\mathbf{T}^{-2\gamma-\delta-2\iota} \tag{3.6}$$

and as in regime (DC) $\alpha = 0$, $\beta = -\zeta - \eta - \iota$, $\gamma = -\iota$, $\delta = 0$ and the same scaling parameter ε. The typical scales are

$$\mathbf{L} = \varepsilon^r \mathcal{L}_0,\ \mathbf{T} = \varepsilon^{q_I} \ 1\text{s},\ \mathbf{M} = \varepsilon^{r+2q_I}\ M_{As}\ 1\text{mol},\ \mathbf{N} = \varepsilon^{3r}\ 1\text{mol},$$

where time and mass are scaled different as for (DC).

Since it is for technical reasons easier to work on finite domain we scale R^0_{bd} with ε^{-3}. This implies with (3.5) that $\mathcal{N}^0 \sim \varepsilon^3$.

We emphasise that the relation between the microscopic length scale $\mathcal{R}_0$ and the macroscopic length scale 1 corresponds to a single droplet problem where we scale $r_i \sim \mathcal{R}_0$ and $R^i_{bd} \sim \mathcal{L}_0$ and that the relation between mesoscopic and macroscopic length scale is only relevant for the relation between the number of liquid droplets and their distances d_{ij} to each other and distances to the outer boundary $d_{i0} = \operatorname{dist}(X_i, \partial\Omega^\varepsilon)$. The scaling of $d_{ij}, d_{i0} \sim \mathcal{D}_0$ is important in order to avoid encounters.

From now on we consider everything without dimensions, unless otherwise stated. We introduce the abbreviations $\mathcal{R} = \varepsilon^r$ and $\mathcal{D} = \varepsilon$, which correspond to the dimensionful quantities $\mathcal{R}_0$ and $\mathcal{D}_0$.

3.1.2. Problem C and Problem CI

In order not to deal with fractions of droplets we require ε^{-1} to be a natural number. We could get rid of this constraint by replacing everywhere ε by $([\varepsilon^{-1}])^{-1}$ where $[\cdot]$ denotes Gauss' brackets and requiring $\varepsilon \leq 1$.

In order not to have to many indices we drop the hats $\hat{}$ on dedimensionalised quantities and write only f^ε instead of $\hat{f}$ if the quantity or function depends on ε.

The scaling of $\overline{Y}$ with ε^p represents that we deal with the last stage of phase separation and that the deviation from the equilibrium concentration of the system is expected to be small. This effect is called small "undercooling" in models of Ostwald ripening, where temperature instead of concentration is varying, see [Nie99]. Our scaling implies that, $X_S, X_L \sim \varepsilon^0 = 1$, while $\overline{Y} \sim \varepsilon^p$. This implies that $\mathcal{X}, h^* \sim \varepsilon^p$.

We assume $\Xi\, \nabla \cdot v \sim \varepsilon^p$, too. This can be motivated by considering a monopole approximation for the displacement $U^{(A)}$ and the velocity $v^{(A)}$, which we derive in the following. Inserting $U^{(A)}$ into the density yields in this approximation $\rho_S^{(A)'}(u) \propto h^*$. By $\rho_S^{(A)} = \Xi + \tilde{\mu}(n_S^{(A)}(\Xi) - \Xi)$ the continuity equation $\rho_S^{(A)} \nabla \cdot v^{(A)} = \rho_S^{(A)'}(u)(\partial_t u - v^{(A)} \cdot \nabla u)$ yields the scaling of this term.

According to the last subsection we scale space variables s.t. $x \sim \varepsilon^{-r}$ i.e. $x \to x^\varepsilon = \varepsilon^r x$ and hence gradients scale as $\nabla_x \sim \varepsilon^r$ by the chain rule. Analogously $X \sim \varepsilon^{-r}$ and due to its definition (2.10) we find $U \sim \varepsilon^{-r}$.

The elastic part of the Cauchy stress reads now $\check{\sigma}_S(\nabla_{x^\varepsilon} U^\varepsilon) = \lambda_S \operatorname{tr}(\nabla_{x^\varepsilon} U^\varepsilon) + 2\mu_S e(\nabla_{x^\varepsilon} U^\varepsilon)$.

Incorporating all scalings our Problem B translates into **Problem C**:

$$
\begin{aligned}
\operatorname{div} \check{\sigma}_S(\nabla_{x^\varepsilon} U^\varepsilon) &= 3k_S \varepsilon^p h^{*\prime}(u^\varepsilon)\nabla_{x^\varepsilon} u^\varepsilon && \text{in } \Omega_S^\varepsilon(t^\varepsilon), && (3.7)\\
\check{\sigma}_S(\nabla_{x^\varepsilon} U^\varepsilon)\nu &= (\overline{p} - p_0 + 3k_S\varepsilon^p h^*(u^\varepsilon))\nu && \text{on } \partial\Omega^\varepsilon(t^\varepsilon), && (3.8)\\
(\check{\sigma}_S(\nabla_{x^\varepsilon} U^\varepsilon) - 3k_L \frac{\fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu}{\varepsilon^r r_i^\varepsilon})\nu &= (\varepsilon^{o-r}\frac{2\sigma}{r_i^\varepsilon} - 3k_L(\delta^R + h_L^*(X_L^i)) && &&\\
&\quad + 3k_S\varepsilon^p h^*(u_{int}^i))\nu && \text{on } I_i^\varepsilon(t^\varepsilon)\ \forall i \in N^\varepsilon(t^\varepsilon) && (3.9)
\end{aligned}
$$

for all $t^\varepsilon \in (0, \varepsilon^q \mathcal{T})$, and

$$
\begin{aligned}
&\varepsilon^{p+q}(\mathcal{X}^\varepsilon(u^\varepsilon)(\partial_{t^\varepsilon} u^\varepsilon + \nabla_{x^\varepsilon} u^\varepsilon\ v^\varepsilon) && &&\\
&\quad + \Xi^\varepsilon(u^\varepsilon)\nabla_{x^\varepsilon}\cdot v^\varepsilon) - \varepsilon^{2r}\Delta_{x^\varepsilon} u^\varepsilon = 0 && \text{in } \Omega_S^\varepsilon(t^\varepsilon)\ \forall t^\varepsilon \in (0,\varepsilon^q\mathcal{T}), && (3.10)\\
&u^\varepsilon = u_{int}(r_i^\varepsilon, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu) && \text{on } I_i^\varepsilon(t^\varepsilon)\ \forall i \in N^\varepsilon(t^\varepsilon)\ \forall t^\varepsilon \in (0,\varepsilon^q\mathcal{T}), && (3.11)\\
&\nabla_{x^\varepsilon} u^\varepsilon \cdot \nu = 0 && \text{on } \partial\Omega^\varepsilon(t^\varepsilon)\ \forall t^\varepsilon \in (0,\varepsilon^q\mathcal{T}), && (3.12)\\
&u^\varepsilon(t^\varepsilon = 0) = u^{0,\varepsilon} && \text{in } \Omega^\varepsilon(0), && (3.13)
\end{aligned}
$$

with

$$
\begin{aligned}
\dot{r}_i^\varepsilon &= \varepsilon^{r-q}\frac{\fint_{I_i^\varepsilon} \nabla_{x^\varepsilon} u^\varepsilon \cdot \nu}{\mathbb{X}(r_i^\varepsilon, \varepsilon^3 \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} && \forall i \in N^\varepsilon(t^\varepsilon)\ \forall t^\varepsilon \in (0,\varepsilon^q\mathcal{T}), && (3.14)\\
\dot{R}_{bd} &= \fint_{\partial\Omega^\varepsilon} v^\varepsilon \cdot \nu && \forall t^\varepsilon \in (0,\varepsilon^q\mathcal{T}), && (3.15)\\
r_i^\varepsilon(t^\varepsilon = 0) &= r_i^0 && \forall i \in N^\varepsilon(0), && (3.16)\\
R_{bd}(t = 0) &= R_{bd}^0. && && (3.17)
\end{aligned}
$$

In the liquid we have that, p_L^i and u_L^i are scale-invariant, for all $i \in N^\varepsilon(t^\varepsilon)$ by the formulas (2.121) and (2.94). The vanishing of a droplet is modelled as in Subsection 2.6.7.
(3.9) implies to choose $o = r$, in order to work in linear elasticity. Since only the term $(r_i^\varepsilon)^{-1}\fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu$ enters into u_{int} and $\frac{\sigma}{r_i^\varepsilon} \sim 1$, this implies that u_{int} is scale-invariant. The scaling $\sigma \sim \varepsilon^3$ fits to given material data and to (1.8) or (1.9), if we assume that our sharp-interface model can be derived as the limit of a phase-field model similar to the Van der Waals-Cahn-Hilliard or Cahn-Larché equations.

The scaled version of Problem BI is **Problem CI**: we have (3.7) – (3.9), (2.187), (3.15) – (3.17) and instead of (3.14) holds

$$
\dot{r}_i^\varepsilon = \varepsilon^{-q_I}\frac{[[u^\varepsilon]]}{\mathbb{Z}(\overline{u}, r_i^\varepsilon, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} \quad \forall i \in N^\varepsilon(t^\varepsilon)\ \forall t^\varepsilon \in (0, \varepsilon^{q_I}\mathcal{T}). \tag{3.18}
$$

Though the dimensionless droplets have radii $\varepsilon^r r_i^\varepsilon$ we want to characterise the radii just by r_i^ε which are of order 1. Note that now $w^\varepsilon = \varepsilon^r \dot{r}_i^\varepsilon$. Furthermore we have $|I_i^\varepsilon| = \varepsilon^{2r}|I_i|$ and $|\Omega_L^{i,\varepsilon}| = \varepsilon^{3r}|\Omega_L^i|$. Our scaling of parameters $r_i \sim \mathcal{R}$ leaves r_i invariant under application of both scalings.

If we want to consider the homogenised system up to non-vanishing and finite times $\mathcal{T}^\varepsilon = \frac{\mathcal{T}}{\varepsilon^q}$ we have to scale $\mathcal{T} \sim \varepsilon^q = 1$ for (DC) or $\mathcal{T} \sim \varepsilon^{q_I} = 1$ for (IC) i.e. $q = q_I = 0$. For notation purposes we introduce an average sum

$$
\mathop{\sum\!\!\!\!\!\!-\;}_{i \in N^\varepsilon} := \varepsilon^3 \sum_{i \in N^\varepsilon} = \frac{1}{\mathcal{N}^0}\sum_{i \in N^\varepsilon}, \tag{3.19}
$$

which is scale invariant. We skip the ε on t and x from now on.

3.1.3. Determination of the scaling exponents

For the scaling of radii we recall the following results of Cioranescu and Murat [CM82, CM97] or Niethammer [Nie99]. Cioranescu and Murat consider for a similar geometry and fixed $\Omega \subset \mathbb{R}^3$ the Laplace equation with homogeneous Dirichlet boundary conditions. In this case $u^\varepsilon \rightharpoonup u^\infty$ weakly in $H^1_0(\Omega)$ and u^∞ solves uniquely the Helmholtz equation $\Delta u^\infty - \lambda^{-2} u^\infty = 0$, where $\lambda = \lim_{\varepsilon \to 0} \lambda^\varepsilon$ and $\lambda^\varepsilon = (\frac{4\pi\mathcal{R}}{\mathcal{D}^3})^{-1/2}$ is the so-called screening length in three dimensions. The screening length λ^ε is related to the capacity of all balls $\Omega^{i,\varepsilon}_L$, $i \in N^\varepsilon$ in Ω, which is proportional to ε^{r-3}. The fundamental solution of this equation is $u^\infty = \frac{1}{|x|}\exp(-\frac{|x|}{\lambda})$. Hence effective interactions take place over the length scale λ, which should be of order of the length of the domain Ω i.e. $\lambda^\varepsilon \sim 1$. Thus the result of Cioranescu and Murat is that the critical case is, if radii of droplets scale as $r_i \sim \mathcal{R} = \varepsilon^r$, $r = 3$, compared to their distance $\mathcal{D} = \varepsilon$.

For Laplace's equation with Dirichlet or periodic boundary conditions this shows that, if the radii scale with ε^r, $1 \leq r < 3$, the radii dominate the solution u^∞ as $\varepsilon \to 0$, while for $r > 3$ they have no influence on the equation, which is $\Delta u^\infty = 0$. The scaling $r = 3$ is considered for the Mullins-Sekerka model in [Nie00].

In case of the heat equation and Dirichlet boundary conditions on I_i, $i \in N^\varepsilon$ and homogeneous Neumann boundary conditions on $\partial\Omega$ Niethammer [Nie99] showed that if one scales radii with $r = 4$ and $p = 3r - 3 = 9$, i.e. p like the volume fraction, then one finds in the limit an ODE for an only time-dependent u^∞.

We consider our situation. We plug our scaling into the time-derivative of the conservation of arsenic law (2.38), which is nothing else than to test the diffusion equation (3.10) with 1, and get in case of (DC) by means of the Reynolds' transport theorem (see [EGK08], *S.* 205, *Satz* 5.4)

$$\begin{aligned}
0 &= \varepsilon^q \partial_{t^\varepsilon} \int_{\Omega^\varepsilon} n^\varepsilon_{As} \\
&= \int_{\Omega^\varepsilon_S} \varepsilon^p \mathcal{X}^\varepsilon(u^\varepsilon)\partial_t u^\varepsilon + \varepsilon^{3(r-1)} \sum_{i \in N^\varepsilon} \int_{\Omega^{i,\varepsilon}_L} \partial_t n^{i,\varepsilon}_{As_L} + \int_{\partial\Omega^\varepsilon} n^\varepsilon_{As} v^\varepsilon + \int_{\partial\Omega^\varepsilon} n^\varepsilon_{As}(\dot{R}_{bd} - v^\varepsilon \cdot \nu) \\
&\quad - \varepsilon^{3r-3} \sum_{i \in N^\varepsilon} \int_{I^\varepsilon_i} [[n^\varepsilon_{As}]] \dot{r}^\varepsilon_i .
\end{aligned} \tag{3.20}$$

By exploiting the diffusion equation (3.10) in the solid and the conservation law (2.19) in the liquid and Gauss' theorem we find

$$\begin{aligned}
0 &= \int_{\Omega^\varepsilon_S} \varepsilon^{2r} \Delta u^\varepsilon + \int_{\partial\Omega^\varepsilon} n^\varepsilon_{As}(\dot{R}_{bd} - v^\varepsilon \cdot \nu) - \varepsilon^{2r-3} \sum_{i \in N^\varepsilon} \int_{I^\varepsilon_i} ([[n^\varepsilon_{As}]]\varepsilon^r \dot{r}^\varepsilon_i - [[n^\varepsilon_{As} v^\varepsilon \cdot \nu]] + j^{i,\varepsilon}_{As_L} \cdot \nu) \\
&= \int_{\Omega^\varepsilon_S} \varepsilon^{2r} \Delta u^\varepsilon + \int_{\partial\Omega^\varepsilon} n^\varepsilon_{As}(\dot{R}_{bd} - v^\varepsilon \cdot \nu) - \varepsilon^{3r-3} \sum_{i \in N^\varepsilon} \int_{I^\varepsilon_i} \nabla u^\varepsilon \cdot \nu,
\end{aligned} \tag{3.21}$$

where we use the jump condition (2.29) on the interfaces for the last step.

We have $\int_{\partial\Omega^\varepsilon} n^\varepsilon_{As}(\dot{R}_{bd} - v^\varepsilon \cdot \nu) = \varepsilon^p \int_{\partial\Omega^\varepsilon} \Xi^\varepsilon(u^\varepsilon)(\dot{R}_{bd} - v^\varepsilon) + o(\varepsilon^p)$ by a Taylor expansion. We use this and multiply with ε^{-2r}

$$0 = \int_{\Omega^\varepsilon_S} \Delta u^\varepsilon + \varepsilon^{p-2r} \int_{\partial\Omega^\varepsilon} \Xi^\varepsilon(u^\varepsilon)(\dot{R}_{bd} - v^\varepsilon \cdot \nu) + o(\varepsilon^{p-2r}) - \varepsilon^{r-3} \sum_{i \in N^\varepsilon} \int_{I^\varepsilon_i} \nabla u^\varepsilon \cdot \nu .$$

The factor in front of the last term is just the capacity of all balls in Ω up to a constant. In order not to loose the last term, which contains the contribution of the droplets, as $\varepsilon \to 0$, we have to set $r = 3$. We call this the "critical regime". The second term is of order $p - 2r$ and does not contribute, if $p > 2r$ or if $v^\varepsilon \cdot \nu \approx \dot{R}_{bd}$ in higher order in ε.

By comparing (3.20) and (3.21) we see that the $\mathcal{X}^\varepsilon(u^\varepsilon)\partial_t u^\varepsilon$ term enters into the homogenised equation if $p = 3r - 3$ i.e. the "undercooling" equals the volume fraction. W.l.o.g. we consider here $p = 9$.

If we want to consider the "dilute regime", that the third term vanishes in the limit, then we have to work with $r > 3$. W.l.o.g. we set $r = 4$. In order to end up in the homogenisation procedure with an ODE for the mean field u^∞, which is the limit of u^ε as $\varepsilon \to 0$ in an appropriate sense, we have to choose $p = 3r - 3 = 9$. This choice is justified in the formal homogenisation in (3.78).

Another interesting scaling regime, which we do not consider, would be a critical regime where we end up with a parabolic equation and a "radii term", which follows for $r = 3$ and $p = 6$.

We consider the (IC) regime only in the dilute case

$$\dot{r}_i^\varepsilon = \frac{[[u^\varepsilon]]}{\mathbb{Z}(\overline{u}, r_i^\varepsilon, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} \quad \forall i \in N^\varepsilon(t^\varepsilon)\, \forall t^\varepsilon \in (0, \mathcal{T}). \tag{3.22}$$

In order to compare our homogenisation result for (IC) with (DC) we choose $p = 9$.

Remark 3.1 (Dilute and critical scaling)**.** *We consider in the formal homogenisation, Sections 3.3 and 3.4, and for the simulations in Ch. 6, the dilute (or also called supercritical) scaling regime with* $r = 4$ *and* $p = 9$*. The dilute scaling, with only time-dependent mean field, seems to fit better to experiments.*

In the existence and uniqueness result, Ch. 4 and the mathematical homogenisation, Ch. 5, we consider the critical scaling, since this case is from a mathematical point of view more interesting. In the critical scaling an additional term appears in the PDE for the mean field in the homogenisation limit and the resulting mean field will be depending on time and slowly varying in space. At the end of Ch. 5 we state the expected result for the dilute scaling.

We work now in the dilute scaling with $r = 4$, $p = 9$ for (DC) and (IC) in the rest of this chapter, unless otherwise stated.

As a consequence of scaling $\overline{Y} \sim \varepsilon^9$, the quantities $\overline{Y}_a, a \in \mathbf{a_S}$ of the reference standard system in the solid depend on ε, too. As we see from Appendix A.2 we get formally, if u or y is bounded, that $\overline{Y}_a \to 1$ for $a \in \{\mathrm{Ga}_\alpha, \mathrm{As}_\beta, \mathrm{V}_\gamma\}$ and $\overline{Y}_b \to 0$, $b \in \mathbf{a_S} \setminus \{\mathrm{Ga}_\alpha, \mathrm{As}_\beta, \mathrm{V}_\gamma\}$ (that corresponds to scale $C_1, C_2 \sim \varepsilon^{18}$ and $C_3 \sim \varepsilon^9$). This implies $3 - \overline{Y}_V \to 2$ as $\varepsilon \to 0$. Furthermore $\overline{Y} \sim \varepsilon^9$ implies that ζ, as defined in Lemma A.2, converges to ∞ as $\varepsilon \to 0$. Hence $\mathcal{J}_y$ depends on ε and $\lim_{\varepsilon\to 0} \mathcal{J}_y = \mathbb{R}^+$.

Remark 3.2 (An alternative scaling for the mechanics)**.** *We recall that we consider the mechanical BVP in approximation of small displacement gradients, where we assume* $\nabla U = \mathcal{O}(\tilde{h})$ *for some small* $\tilde{h} \approx 10^{-3}$*. Our dimensional analysis shows that* $\tilde{h}$ *is independent of* ε *and fixed for our homogenisation. Hence the limit* $\tilde{h} \to 0$ *would have to be performed separately.*

3.2. The Problems D, DI and DCR for the different scaling regimes

In this section we solve formally for sufficiently small ε the following **Problem D**, which follows from Problem C by inserting all scaling exponents, i.e. o, p and r, which have been determined in the last subsections. It only makes sense to consider the Problem D for sufficiently small ε, because then one can ensure that our problem is well-defined i.e. (3.4) is fulfilled.

3.2.1. Rescaled differential equations in the dilute regime (Problems D and DI)

In rescaled variables we look for solutions $U^\varepsilon, u^\varepsilon, \{r_i\}_{i\in N^\varepsilon}, R^\varepsilon_{bd}$ of the following coupled differential equations for regime (DC) of the following **Problem D**.

$$
\begin{aligned}
\operatorname{div}\, \check{\sigma}_S(\nabla U^\varepsilon) &= \varepsilon^9 3k_S h^{*\prime}(u^\varepsilon)\nabla u^\varepsilon && \text{in } \Omega^\varepsilon_S(t), && (3.23)\\
\check{\sigma}_S(\nabla U^\varepsilon)\nu &= (\overline{p} - p_0 + \varepsilon^9 3k_S h^*(u^\varepsilon))\nu && \text{on } \partial\Omega^\varepsilon(t), && (3.24)\\
(\check{\sigma}_S(\nabla U^\varepsilon) - \frac{3k_L}{\varepsilon^4 r_i}\fint_{I_i^\varepsilon}(U^\varepsilon\cdot\nu))\nu &= (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h^*_L(X^i_L)) \\
&\quad + \varepsilon^9 3k_S h^*(u_{int}(r_i, \fint_{I_i} U^\varepsilon\cdot\nu)))\nu && \text{on } I_i^\varepsilon(t)\ \forall i\in N^\varepsilon(t), && (3.25)
\end{aligned}
$$

and

$$
\begin{aligned}
\varepsilon(\mathcal{X}^\varepsilon(u^\varepsilon)(\partial_t u^\varepsilon + v^\varepsilon\cdot\nabla u^\varepsilon) + \nabla\cdot v^\varepsilon\ \Xi(u^\varepsilon)) - \Delta u^\varepsilon &= 0 && \text{in } \Omega^\varepsilon_S(t) && (3.26)\\
\nabla u^\varepsilon\cdot\nu &= 0 && \text{on } \partial\Omega^\varepsilon(t), && (3.27)\\
u^\varepsilon &= u_{int}(r_i, \fint_{I_i} U^\varepsilon\cdot\nu) && \text{on } I_i^\varepsilon(t)\forall i\in N^\varepsilon(t), && (3.28)\\
u^\varepsilon(\cdot, t=0) &= u^{0,\varepsilon} && \text{in } \Omega^\varepsilon_S(0), && (3.29)
\end{aligned}
$$

for all $t\in(0,\mathcal{T})$ with ODEs for the radii (Stefan conditions and ODE for external boundary)

$$
\begin{aligned}
\dot{r}_i &= \varepsilon^4\frac{\fint_{I_i^\varepsilon}\nabla u^\varepsilon\cdot\nu}{\mathbb{X}(r_i, \varepsilon^4\fint_{I_i^\varepsilon} U^\varepsilon\cdot\nu)} && \forall i\in N^\varepsilon(t)\ \forall t\in(0,\mathcal{T}), && (3.30)\\
r_i(t=0) &= r_i^0 && \forall i\in N^\varepsilon(0), && (3.31)\\
\dot{R}_{bd} &= \fint_{\partial\Omega^\varepsilon} v^\varepsilon\cdot\nu && \forall t\in(0,\mathcal{T}), && (3.32)\\
R^\varepsilon_{bd}(t=0) &= R^0_{bd}. && && (3.33)
\end{aligned}
$$

The velocity v^ε is linked to U^ε by (2.13). In the liquid we have p^i_L and u^i_L given for all $i\in N^\varepsilon(t)$ by the formulas (2.121) and (2.94) and the vanishing of a droplet is modelled as in Subsection 2.6.7.

For the regime (IC) we consider the **Problem DI**: find $U^\varepsilon, \overline{u}^\varepsilon, \{r_i\}_{i\in N^\varepsilon}, R^\varepsilon_{bd}$ s.t.

$$
\begin{aligned}
\operatorname{div}\, \check{\sigma}_S(\nabla U^\varepsilon) &= 0 && \text{in } \Omega^\varepsilon_S(t), && (3.34)\\
\check{\sigma}_S(\nabla U^\varepsilon)\nu &= (\overline{p} - p_0 + 3k_S h^*(\overline{u}^\varepsilon))\nu && \text{on } \partial\Omega^\varepsilon(t), && (3.35)\\
(\check{\sigma}_S(\nabla U^\varepsilon) - \frac{3k_L}{\varepsilon^4 r_i}\fint_{I_i^\varepsilon}(U^\varepsilon\cdot\nu))\nu &= (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h^*_L(X^i_L)) \\
&\quad + 3k_S h^*(\overline{u}))\nu && \text{on } I_i^\varepsilon(t)\ \forall i\in N^\varepsilon(t), && (3.36)
\end{aligned}
$$

for all $t\in(0,\mathcal{T})$, and, supposed $u^0\in\mathbb{R}$ is given,

$$
\begin{aligned}
\partial_t\overline{u}^\varepsilon &= -\frac{4\pi\sum_{i\in N^\varepsilon} r_i^2\frac{\overline{\mathbb{X}}(r_i, \overline{u}^\varepsilon, r_i, \fint_{I_i^\varepsilon} U^\varepsilon\cdot\nu)}{\mathbb{Z}(\overline{u}^\varepsilon, r_i, \fint_{I_i^\varepsilon} U^\varepsilon\cdot\nu)}(\overline{u}^\varepsilon - u_L(\overline{u}^\varepsilon, r_i, \fint_{I_i} U^\varepsilon\cdot\nu))}{|\Omega^\varepsilon_S(t)|\mathcal{X}^\varepsilon(u^\varepsilon)} && \forall t\in(0,\mathcal{T}), && (3.37)\\
\overline{u}^\varepsilon(t=0) &= u^0, && && (3.38)
\end{aligned}
$$

and

$$\begin{aligned} \dot r_i &= \frac{\overline{u}^\varepsilon - u_L(\overline{u}^\varepsilon, r_i, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)}{\mathbb{Z}(\overline{u}^\varepsilon, r_i^\varepsilon, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} && \forall i \in N^\varepsilon(t)\ \forall t \in (0, \mathcal{T}), && (3.39)\\ r_i(t=0) &= r_i^0 && \forall i \in N^\varepsilon(0), && (3.40)\\ \dot R_{bd} &= \fint_{\partial\Omega^\varepsilon} v^\varepsilon \cdot \nu && \forall t \in (0, \mathcal{T}), && (3.41)\\ R_{bd}^\varepsilon(t=0) &= R_{bd}^0. && && (3.42) \end{aligned}$$

In the liquid we have p_L^i and u_L^i given for all $i \in N^\varepsilon(t)$ by the formulas (2.121) and (2.94) and the vanishing of a droplet is modelled as in Subsection 2.6.7.

The equation (3.37) replaces (2.187) and will be derived later in (3.85), but is already stated here in order to give a better overview over the full Problem DI.

3.2.2. Rescaled differential equations in the critical regime (Problem DCR)

In this subsection we state the corresponding problem to Problem D in the critical scaling regime, **Problem DCR**. In rescaled variables we look for solutions $U^\varepsilon, u^\varepsilon, \{r_i\}_{i \in N^\varepsilon}, R_{bd}^\varepsilon$ of the following coupled differential equations for regime (DC):

$$\begin{aligned} \operatorname{div} \check\sigma_S(\nabla U^\varepsilon) &= \varepsilon^9 3k_S h^{*\prime}(u^\varepsilon) \nabla u^\varepsilon && \text{in } \Omega_S^\varepsilon(t), && (3.43)\\ \check\sigma_S(\nabla U^\varepsilon)\nu &= (\overline{p} - p_0 + \varepsilon^9 3k_S h^*(u^\varepsilon))\nu && \text{on } \partial\Omega^\varepsilon(t), && (3.44)\\ (\check\sigma_S(\nabla U^\varepsilon) - \frac{3k_L}{\varepsilon^3 r_i} \fint_{I_i^\varepsilon} (U^\varepsilon \cdot \nu))\nu &= (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h_L^*(X_L^i)) && && \\ &\quad + \varepsilon^9 3k_S h^*(u_{int}(r_i, \fint_{I_i} U^\varepsilon \cdot \nu)))\nu && \text{on } I_i^\varepsilon(t)\ \forall i \in N^\varepsilon(t), && (3.45) \end{aligned}$$

and

$$\begin{aligned} \varepsilon^3 \mathcal{X}^\varepsilon(u^\varepsilon)(\partial_t u^\varepsilon + v^\varepsilon \cdot \nabla u^\varepsilon + \nabla \cdot v^\varepsilon\, \Xi(u^\varepsilon)) - \Delta u^\varepsilon &= 0 && \text{in } \Omega_S^\varepsilon(t) && (3.46)\\ \nabla u^\varepsilon \cdot \nu &= 0 && \text{on } \partial\Omega^\varepsilon(t), && (3.47)\\ u^\varepsilon &= u_{int}(r_i, \fint_{I_i} U^\varepsilon \cdot \nu) && \text{on } I_i^\varepsilon(t)\ \forall i \in N^\varepsilon(t), && (3.48)\\ u^\varepsilon(\cdot, t=0) &= u^{0,\varepsilon} && \text{in } \Omega_S^\varepsilon(0), && (3.49) \end{aligned}$$

with ODEs for the radii

$$\begin{aligned} \dot r_i &= \varepsilon^3 \frac{\fint_{I_i^\varepsilon} \nabla u^\varepsilon \cdot \nu}{\mathbb{X}(r_i, \varepsilon^3 \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} && \forall i \in N^\varepsilon(t)\ \forall t \in (0, \mathcal{T}), && (3.50)\\ r_i(t=0) &= r_i^0 && \forall i \in N^\varepsilon(0), && (3.51)\\ \dot R_{bd} &= \fint_{\partial\Omega^\varepsilon} v^\varepsilon \cdot \nu && \forall t \in (0, \mathcal{T}), && (3.52)\\ R_{bd}^\varepsilon(t=0) &= R_{bd}^0. && && (3.53) \end{aligned}$$

The velocity v^ε is linked to U^ε by (2.13). In the liquid we have p_L^i and u_L^i given for all $i \in N^\varepsilon(t)$ by the formulas (2.121) and (2.94) and the vanishing of a droplet is modelled as in Subsection 2.6.7.

In regime (IC) we do not consider the critical scaling regime. We return now to the dilute regime.

3.3. Formal homogenisation for regime (DC) in the dilute scaling

In order to solve Problem D or Problem DI formally we have a look at the following approximations of our differential equations by superposition of solutions of the respective single droplet problems for small ε. This allows us further to check if the scaling regime is appropriate to the experimental situation.

We consider a fixed ε and drop the indices ε for the rest of this section.

3.3.1. Monopole approximation of the mechanical BVP

The solutions of the single droplet problems are called "monopoles". We make a so-called mean field ansatz. We assume that outside of shells $\Sigma_i = B_{\varepsilon R^i_{bd}}(X_i) \setminus \overline{B_{\varepsilon^4 r_i}(X_i)}$ around liquid droplets i.e. in $F := \Omega_S \setminus \overline{\cup_{i\in N}\Sigma_i}$ these single droplet problems are coupled by an only time-dependent mean field of the chemical potential $\overline{u}(t)$ and a only time-dependent mean pressure field, which is the outer pressure p_0.

In this *mean field approximation* the chemical potential is denoted by u_A, the displacement by W and the radii are again denoted by r_i and R_{bd}.

First we give an approximation by monopoles of the mechanical BVP and then use this approximation for stating an approximation of the diffusion problem.

Since the mechanical BVP, the diffusion problem and the ODEs for the free boundaries are all coupled with each other, we have to put some assumptions in, which will be justified later. So we assume that $u_A = \overline{u}$ up to terms of $\mathcal{O}(\varepsilon)$ far away from droplets i.e. for x s.t. $|x - X_i| > \varepsilon\mathcal{D}$ for all $i \in N$. Furthermore X^i_L and u^i_{int} depend again on U, but we assume these terms as given for the moment. u^i_{int} will drop out by taking only leading order terms in ε with us and X^i_L can be determined later.

Let U be the exact solution of the following problem for $\mathcal{N}$ droplets, which is the problem (3.43) – (3.45) and the rescaled equation (2.121): Find $U \in C^2(\Omega(t))$ for all $t \in (0, \mathcal{T})$ and given radii evolution $r_i^{(A)}$, given chemical potential $u_{(A)}$ and data s.t.

$$\operatorname{div} \check{\sigma}_S(\nabla U) = \varepsilon^9 3k_S h^{*\prime}(u_A)\nabla u_A \qquad \text{in } \Omega_S(t), \tag{3.54}$$

$$\check{\sigma}_S(\nabla U)\nu = (\overline{p} - p_0 + \varepsilon^9 3k_S h^*(u_A))\nu \qquad \text{on } \partial\Omega(t), \tag{3.55}$$

$$(\check{\sigma}_S(\nabla U) - \tag{3.56}$$

$$-\frac{3k_L}{\varepsilon^4 r_i}(\fint_{I_i} U\cdot\nu))\nu = (\frac{2\sigma}{r_i} - 3k_L(\delta^R + h^*_L(X^i_L)) + \varepsilon^9 3k_S h^*(u^i_{int}))\nu \qquad \text{on } I_i(t)\,\forall i \in N, \tag{3.57}$$

$$p^i_L(U) = \overline{p} - 3k_L(\frac{1}{\varepsilon^4 r_i}\fint_{I_i}(U\cdot\nu) - \delta^R - h^*_L(X^i_L)) \qquad \text{in } \Omega^i_L(t)\,\forall i \in N. \tag{3.58}$$

The idea of a so-called monopole approximation is that W is a good approximation to U, if W is given by superposition of the solutions of totally radial symmetric single droplet problems in a spherical shell Σ_i around the centres.

We introduce the normalised vectors $e_{r_i} = \frac{x - X_i}{|x - X_i|}$ for all $i \in N$. The solutions W_i for problems, where we consider each Σ_i separately, with possibly modified data, are the "monopoles":

$$W_i(x) := (a|x - X_i| + \varepsilon^{-3} b_i \frac{\varepsilon^{12} r_i^3}{|x - X_i|^2} + c_i|x - X_i|)e_{r_i}.$$

That we scale the term with b_i additionally with a factor ε^{-3} is due to our expectation that locally only one b_i term contributes in $\mathcal{O}(\varepsilon^0)$. The coefficients are from the solution of our mechanical part of the cell problem as given in Appendix C.1.1.

$$
\begin{aligned}
a_i = a &= \frac{\overline{p} - p_0}{3k_S} + \varepsilon^9 \frac{4G_S}{4G_S + 3k_S} h^*(\overline{u}),\\
b_i &= \frac{(1 - \frac{k_L}{k_S})(\overline{p} - p_0) - \frac{2\sigma}{r_i} + 3k_L(\delta^R + h_L^*(X_L^i) - \varepsilon^9 h^*(\overline{u}))}{4G_S + 3k_L} + \varepsilon^9 \frac{3k_S(h^*(\overline{u}) - h^*(u_{int}^i))}{4G_S + 3k_S},\\
c_i = c(|x - X_i|) &= \varepsilon^9 \frac{3k_S}{4G_S + 3k_S}(h^*(u(|x - X_i|)) - \frac{1}{|x - X_i|^3} \int_{r_i}^{|x-X_i|} z^3 h^{*\prime}(u(z))u'(z)dz).
\end{aligned}
$$

Our ansatz is now

$$
W(x) = \sum_{i \in N} W_i(x) = \sum_{i \in N} ((a + c_i)(x - X_i) + b_i \varepsilon^9 r_i^3 \frac{x - X_i}{|x - X_i|^3}). \tag{3.59}
$$

We compute

$$
\nabla W = (a + \sum_{i \in N} c_i)\mathbb{I}_3 + \sum_{i \in N} c_i' \frac{(x - X_i) \otimes (x - X_i)}{|x - X_i|}) + \sum_{i \in N} b_i \frac{\varepsilon^9 r_i^3}{|x - X_i|^3}(\mathbb{I}_3 - 3\frac{(x - X_i) \otimes (x - X_i)}{|x - X_i|^2}).
$$

∇W is symmetric, i.e. $e(\nabla W) = \nabla W$, where $e(\nabla W)$ is defined as in (2.76).

Since the following terms appear in the boundary conditions on the interfaces we give explicitly

$$
\begin{aligned}
W|_{I_j} \cdot e_{r_j} &= (a + b_j + \varepsilon^3 c_j))\varepsilon^4 r_j + \sum_{i \neq j}(b_i \frac{\varepsilon^6 r_i^9}{|x - X_i|^3} + c_i)\frac{(x - X_i) \cdot (x - X_j)}{\varepsilon^4 r_j},\\
[\nabla W]_{I_j} \cdot e_{r_j} &= (a + -2b_j + \varepsilon^3(c_j + c_j' r_j))e_{r_j} + \sum_{i \neq j} b_i \frac{\varepsilon^9 r_i^3}{|x - X_i|^3}(\mathbb{I}_3 - 3\frac{(x - X_i) \otimes (x - X_i)}{|x - X_i|^2})e_{r_j}\\
&\quad + \sum_{i \neq j}(c_i + c_i' \frac{(x - X_i) \otimes (x - X_i)}{|x - X_i|})e_{r_j}.
\end{aligned}
$$

Note that

$$
\fint_{I_j} (x - X_i) \cdot (x - X_j) = \varepsilon^8 r_j^2 - \varepsilon^4 \fint_{\partial B_{r_j}(0)} X_i \cdot x = \varepsilon^8 r_j^2
$$

and hence

$$
\fint_{I_j} (W \cdot e_{r_j}) = (a + b_j + \varepsilon^3 c_j)\varepsilon^4 r_j + \sum_{i \neq j} \fint_{I_j} b_i (\frac{\varepsilon^9 r_i^3}{|x - X_i|^3} \frac{(x - X_i) \cdot (x - X_j)}{\varepsilon^4 r_j}) + \sum_{i \neq j} (\fint_{I_j} c_i)\varepsilon^4 r_j.
$$

For the trace of $e(\nabla W)$, which enters into the diffusion problem, holds

$$
tr(e(\nabla W)) = \sum_{i \in N}(3(a + c_i) + c_i'|x - X_i|).
$$

Since we have an explicit formula for W we can give directly a monopole approximation $v_A = \partial_t W$ of $v = \partial_t U$,

$$
\partial_t W(x) = \sum_{i \in N} \partial_t W_i(x) = \sum_{i \in N} (\partial_t(a + c_i)|x - X_i| + \varepsilon^9(\partial_t b_i r_i + 3b_i \dot{r}_i)\frac{r_i^2}{|x - X_i|^2})e_{r_i}. \tag{3.60}
$$

For the part of the Cauchy stress tensor which depends only in U we get from our monopole approximation

$$\begin{aligned}\check{\sigma}_S(\nabla W) = 3k_S\sum_{i\in N}(a + c_i + \frac{c_i'}{3}|x-X_i|)\mathbb{I}_3 \\ + 2G_S\sum_{i\in N}(b_i\frac{\varepsilon^9 r_i^3}{|x-X_i|^3} - \frac{c_i'}{3}|x-X_i|)(\mathbb{I}_3 - 3\frac{(x-X_i)\otimes(x-X_i)}{|x-X_i|^2}).\end{aligned}$$

By construction we have div $\sigma_S(\nabla W) = \varepsilon^9 3k_S\nabla h^{*\prime}(u)$ in Ω_S, but the boundary conditions are not fulfilled by W:

$$\begin{aligned}\check{\sigma}_S(\nabla W)\nu = (3k_S\sum_{i\in N}(a + c_i + \frac{c_i'}{3}|x-X_i|)\mathbb{I}_3 \\ + 2G_S\sum_{i\in N}(b_i\frac{\varepsilon^9 r_i^3}{|x-X_i|^3} - \frac{c_i'}{3}|x-X_i|)(\mathbb{I}_3 - 3\frac{(x-X_i)\otimes(x-X_i)}{|x-X_i|^2}))\nu \quad \text{on } \partial\Omega(t),\end{aligned}$$

and

$$\begin{aligned}(\check{\sigma}_S(\nabla W) - \frac{3k_L}{\varepsilon^4 r_j}\fint_{I_j}(W\cdot e_{r_j}))e_{r_j} = {} & (3k_S\sum_{i\in N}(a + c_i)\mathbb{I}_3 + 2G_S\sum_{i\in N} b_i\frac{\varepsilon^9 r_i^3}{|x-X_i|^3}\times \\ & \times(\mathbb{I}_3 - 3\frac{(x-X_i)\otimes(x-X_i)}{|x-X_i|^2}) \\ & - 3k_L((a + b_j + \varepsilon^3 c_j) + \sum_{i\neq j}\fint_{I_j} b_i\frac{\varepsilon^9 r_i^3}{|x-X_i|^3}\times \\ & \times\frac{(x-X_i)\cdot(x-X_j)}{\varepsilon^4 r_j^2} + \sum_{i\neq j}\fint_{I_j} c_i))e_{r_j} \qquad \text{on } I_j(t)\,\forall j\in N\end{aligned}$$

where we use $c(\varepsilon^4 r_i)' = 0$. By plugging in a, b_i, $c(R_{bd}) = \varepsilon^9(\frac{3k_S}{4G_S+3k_S}h^*(\overline{u}) + \mathcal{O}(\varepsilon^4))$ and $c(\varepsilon^4 r_i) = \varepsilon^9\frac{3k_S}{4G_S+3k_S}h^*(u^i_{int}))$ and, since we assume (3.4) for the scaling of the geometry, we see that the boundary conditions (3.55) and (3.56) only hold within an error of $\mathcal{O}(\varepsilon^3)$:

$$\begin{aligned}\check{\sigma}_S(\nabla W)\nu = (\overline{p} - p_0 + \varepsilon^9 3k_S h^*(\overline{u}) + \mathcal{O}(\varepsilon^6))\nu \qquad & \text{on } \partial\Omega(t), \\ (\check{\sigma}_S(\nabla W) - \\ -\frac{3k_L}{\varepsilon^4 r_j}\fint_{I_j}(W\cdot e_{r_j}))e_{r_j} = (3k_S(a + \varepsilon^9\frac{3k_S}{4G_S+3k_S}h^*(u^i_{int})) - 4G_S b_j \\ - 3k_L((a + b_j + \varepsilon^9\frac{3k_S}{4G_S+3k_S}h^*(u^i_{int}))))e_{r_j} + \mathcal{O}(\varepsilon^6) \quad & \text{on } I_j(t)\,\forall j\in N.\end{aligned}$$

We have taken so far all terms in ε in the mechanical BVP in the monopole approximation with us. Let $\mathbb{I}_{\Omega^{(\varepsilon)}} \to \mathbb{I}^\dagger_\Omega$ as $\varepsilon \to 0$, where $\mathbb{I}_S$ denotes the characteristic function of a set S. Now we let formally $W^{(\varepsilon)} \to W^\dagger$ and get

$$W^\dagger(x) = a^\dagger\sum_{i\in N}(x - X_i) \quad \forall x\in\Omega^\dagger\setminus\{X_i\}_{i\in N^\dagger},$$

with

$$a^\dagger = \frac{\overline{p} - p_0}{3k_S} \tag{3.61}$$

and

$$(\nabla W^\dagger(x)) = a^\dagger\mathbb{I}_3 \quad \forall x\in\Omega^\dagger\setminus\{X_i\}_{i\in N^\dagger}.$$

Furthermore

$$\frac{W^\dagger(X_i)\cdot\nu}{\varepsilon^4 r_j} = a^\dagger + b^\dagger(r_i) \quad \forall x \in \{X_i\}_{i\in N^\dagger}, \tag{3.62}$$

where

$$b^\dagger(r_i) := \frac{(1-\frac{k_L}{k_S})(\overline{p}-p_0) - \frac{2\sigma}{r_i} + 3k_L(\delta^R + h_L^*(X_L^A(r_i)))}{4G_S + 3k_L}. \tag{3.63}$$

The complete formally homogenised mechanical BVP is stated in Subsection 3.3.5.

We define by inserting the solution of the monopole approximation of the mechanical BVP in leading order in ε

$$\begin{aligned}\overline{u_{int}}(r_i) &= u_{int}(r_i, a^\dagger + b^\dagger(r_i)) + \mathcal{O}(\varepsilon^6),\\ \overline{\mathbb{X}}(r_i) &= \mathbb{X}(r_i, a^\dagger + b^\dagger(r_i)) + \mathcal{O}(\varepsilon^6).\end{aligned}$$

Since $b^\dagger$ depends again on X_L^A we make a further approximation and take

$$X_L^A(r_i) = X_L(r_i, a^\dagger + \frac{(1-\frac{k_L}{k_S})(\overline{p}-p_0) - \frac{2\sigma}{r_i} + 3k_L(\delta^R + h_L^*(\overline{X}_L))}{4G_S + 3k_L}) + \mathcal{O}(\varepsilon^6).$$

In functions which are defined in the solid Ω_S we cannot neglect terms of order ε, if we want to calculate $\overline{u}$, when we insert the solution of the mechanical BVP:

$$\rho^A(\overline{u}) = \overline{\rho}(1 - 3a^\dagger - 3\varepsilon^9 k_S h^*(\overline{u})), \tag{3.64}$$

$$\overline{\mathcal{X}}(\overline{u}) = \mathcal{X}^R(\overline{u})(1 - 3a^\dagger - 3\varepsilon^9 \frac{4G_S}{4G_S + 3k_S} h^*(\overline{u})) \tag{3.65}$$

where we consider $\mathcal{X}$ now as $\mathcal{X}_0$ (see (2.142)) and split $\mathcal{X}_0(u, U) = \mathcal{X}^R(u)(1 - \mathrm{tr}(\nabla U))$. Abusing notation we write again u_{int} instead of $\overline{u_{int}}$ as well as ρ instead of ρ^A till the end of this chapter.

3.3.2. Monopole approximation of the diffusion problem and Stefan condition

We remark, that the following formal monopole approximation is just for illustration and is not needed for the mathematical analysis in the Chapters 4 and 5.

On the left-hand side of the dimensionless diffusion equation we have a factor ε. This allows us for an approximation to ignore at first the l.h.s. of the diffusion equation and we work on time-dependent domain with $\Delta u = 0$. We assume $u \approx \overline{u}$ far away from droplets, where we determine the only time dependent mean field $\overline{u}(t)$ by conservation of mass and substance. Close to droplets we approximate u by “monopoles” u_i

$$u_A(x,t) = \overline{u}(t) + \sum_{i\in N} u_i(x,t), \quad u_i(x,t) := -\frac{\overline{u}(t) - u_{int}(r_i(t))}{|x - X_i|}\varepsilon^4 r_i(t). \tag{3.66}$$

This ansatz is motivated by $u_A \to \overline{u}$ as $\varepsilon \to 0$, $x \notin I_i, i \in N$ and by the assumption that small droplets do interact with each other only via a space-independent mean field $\overline{u}$ between them.

This corresponds to the classical LSW theory, see Subsection 1.2.4, if one considers the ansatz (3.66) only in a neighbourhood of a droplet Σ_i and truncates the terms with $u_{int}(r_j)$, $j \neq i$. Furthermore an LSW-ansatz for our situation would suggest

$$\overline{u} = \frac{\sum_{i\in N} u_{int}(r_i) r_i}{\sum_{i\in N} r_i}. \tag{3.67}$$

However, we do not truncate (3.66) and continue with a monopole approximation for the diffusion problem. One checks that u_A has then the following properties

$$\begin{aligned}
\nabla u_A &= \sum_{i\in N} \frac{\overline{u} - u_{int}(r_i)}{|x - X_i|^3} \varepsilon^4 r_i (x - X_i) && \text{in } \Omega_S^\varepsilon,\\
\Delta u_A &= 0 && \text{in } \Omega_S^\varepsilon,\\
\partial_\nu u_A &= \sum_{i\in N} \frac{\overline{u} - u_{int}(r_i)}{|x - X_i|^3} \varepsilon^4 r_i (x - X_i)\cdot \nu = \mathcal{O}(\varepsilon) && \text{on } \partial\Omega,
\end{aligned}$$

where the last equation holds, since the number of droplet centres, which is within distance of ε of a point on $\partial\Omega$, is of order 1, due to our assumption on typical particle distances. For the generalised Gibbs-Thomson condition we find

$$u_A = u_{int}(r_j) + \sum_{i\neq j} \frac{\overline{u} - u_{int}(r_i)}{|x - X_i|} \varepsilon^4 r_i = u_{int}(r_j) + \mathcal{O}(\varepsilon) \qquad \text{on } I_j^\varepsilon \ \forall j \in N.$$

We make a different ansatz than (3.67), see Section 3.3.3, in order to determine $\overline{u}$ since we have no volume conservation, but conservation of mass and substance. We will see later in Remark 6.4 that (3.67) approximately holds, if we are close to equilibria of the system.

For the time derivative of u_A the monopole approximation yields

$$\partial_t u_A = \dot{\overline{u}} - \sum_{i\in N} \Big(\frac{\dot{\overline{u}} + (-\partial_{r_i} u_{int}(r_i) + \frac{\overline{u} - u_{int}(r_i)}{r_i}) \dot{r}_i}{|x - X_i|} \varepsilon^4 r_i \Big) \tag{3.68}$$

which is of order 1 in ε if $\dot{\overline{u}} = \mathcal{O}(\varepsilon^0)$. For the Stefan condition we find

$$\overline{\mathbb{X}}(r_j)\dot{r}_j = \varepsilon^4 \fint_{I_j} \partial_\nu u_A = \frac{\overline{u} - u_{int}(r_j)}{r_j} - \varepsilon^5 \sum_{i\neq j} (\overline{u} - u_{int}(r_i)) r_i \fint_{I_j} \frac{1}{|x - X_i|^3} (x - X_i)\cdot \nu. \tag{3.69}$$

The second summand scales for droplets j which are within distance of ε of X_i with ε^3. Hence in leading order in ε we have as Stefan condition for (DC)

$$\dot{r}_j = \frac{\overline{u} - u_{int}(r_j)}{r_j \overline{\mathbb{X}}(r_j)}. \tag{3.70}$$

3.3.3. Mean field formula and outer boundary radius

We still have to determine $\overline{u}$. We derive now an explicit formula for the mean field $\overline{u}$ and a formula for the outer boundary R_{bd}. We could derive the outer boundary by (3.60) but the determination of $\overline{u}$ yields another approach to determine $\dot{R}_{bd}$. Calculating in leading order in ε we can neglect the dependence of U and v on $\dot{\overline{u}}$.

We rewrite the global conservation laws for As and for total mass, (2.38) and (2.40), for our mean field ansatz,

$$N_{As_0} = (N_0 - \frac{4\pi}{3}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3(t) n_L(r_i(t))) X_S(\overline{u}(t)) + \frac{4\pi}{3}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3(t) n_{As_L}(r_i(t)), \tag{3.71}$$

$$M_0 = (|\Omega(t)| - \frac{4\pi}{3}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3(t)) \rho(\overline{u}(t)) + \frac{4\pi}{3}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3(t) \rho_L(r_i(t)). \tag{3.72}$$

Note, that in our scaling the number of atoms N_0 is of order 1 in ε. (3.71) allows to compute uniquely $\overline{u}$, if we neglect, according to our mechanical monopole approximation, that n_L does depend on $\overline{u}$ via a_L,

$$\overline{u} = X_S^{-1}\Big(\frac{X_0 - \frac{4\pi}{3N_0}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3(t) X_L^A(r_i(t)) n_L(r_i(t))}{1 - \frac{4\pi}{3N_0}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3(t) n_L(r_i(t))}\Big) \tag{3.73}$$

since X_S is strictly monotone, see Appendix A.3. We refer to (3.73) as *mean field formula.*

(3.72) yields for the volume the formula

$$|\Omega(t)| = \frac{1}{\rho(\overline{u}(t))}\left[M_0 - \frac{4\pi}{3}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3 \rho_L^i\right] + \frac{4\pi}{3}\varepsilon^9 \sum_{i=1}^{\mathcal{N}} r_i^3, \tag{3.74}$$

which yields also a formula for R_{bd}.

Once we have determined $\overline{u}$ and r_i we can reconstruct $|\Omega(t)|$ for given $|\Omega(0)| > 0$ or M_0 via (3.74) for all $t \in (0, \mathcal{T})$. Notice that we would not have needed any assumptions on the shape of $\partial\Omega(t)$ here.

3.3.4. ODEs for mean field and for outer boundary

By means of the system of ODEs, which consists in regime (DC) of (3.70) for the radii together with the explicit formulas (3.73) for the mean field $\overline{u}$ and (3.74) for the external boundary R_{bd}, we could completely solve the formal asymptotics problem for a fixed ε. But X_S still depends on ε and for $\varepsilon \to 0$, we find formally $X_S \to 1/2$. Thus we derive from (3.73) and (3.74) ODEs for $\overline{u}$ and R_{bd} and then solve the system of ODEs for $\{r_i\}_{i\in N}$, $\overline{u}$ and R_{bd}. This is also interesting for some other purposes e.g. for stability analysis, see Section 6.3.

We recall that the sums are taken over all $\mathcal{N} = \mathcal{N}(t)$ droplets, which still exist, i.e. with $r_i(t) > r_{min}$, at time t. The following considerations hold for all $t \in (0, \mathcal{T})$ except of times τ_i, when the i-th droplet vanishes.

We determine an ODE for $\overline{u}$ by global conservation laws. We exploit the conservation law for As,

$$0 = \frac{d}{dt}\int_\Omega n_{As} = \varepsilon^9 \int_\Omega \partial_t n_{As} + \varepsilon^9 \sum_{i\in N} \int_{\Omega_L^i} \partial_t n_{As_L} + \int_{\partial\Omega} n_{As} v - \varepsilon^9 \sum_{i\in N} \int_{I_i} [[n_{As}]]\dot{r}_i$$

where we apply Reynolds' transport theorem, where we use, that we consider domains with Lipschitz boundaries. In the time derivative of u we neglect according to (3.68) terms of order ε^{12}. This yields for our mean field ansatz, where we use in particular that $n_{As}(\overline{u})$ is constant on $\partial\Omega$,

$$0 = \varepsilon^9 |\Omega_S(t)| n'_{As}(\overline{u})\dot{\overline{u}} + \varepsilon^9 \sum_{i\in N} |\Omega_L^i| \partial_t n_{As_L} + |\partial\Omega| n_{As}(\overline{u})\dot{R}_{bd} - \varepsilon^9 \sum_{i\in N} |I_i|(n_{As}(\overline{u}) - n^i_{As_L})\dot{r}_i. \tag{3.75}$$

We recall, that in the mean field ansatz we assume that, the dependence of ρ_S or $\mathcal{X}_0$ on the mechanics is eliminated by inserting the monopole approximation and hence $\rho_S^{(A)}$ or $\overline{\mathcal{X}}$ are in this ansatz considered as functions of $\overline{u}$. Analogously as (3.75) by global conservation of mass we get

$$0 = \frac{d}{dt}\int_\Omega \rho(\overline{u}) = \varepsilon^9 \int_\Omega \partial_t \rho(\overline{u}) + \varepsilon^9 \sum_{i\in N} \int_{\Omega_L^i} \partial_t \rho_L + |\partial\Omega| \rho(\overline{u})\dot{R}_{bd} - \varepsilon^9 \sum_{i\in N} \int_{I_i} [[\rho]]\dot{r}_i$$

and with the mean field ansatz

$$0 = \varepsilon^9 |\Omega_S(t)| \rho'(\overline{u})\dot{\overline{u}} + \varepsilon^9 \sum_{i\in N} |\Omega_L^i| \partial_t \rho_L + \rho(\overline{u}) \int_{\partial\Omega} v - \varepsilon^9 \sum_{i\in N} |I_i|(\rho(\overline{u}) - \rho_L^i)\dot{r}_i.$$

This allows to eliminate

$$\dot{R}_{bd} = \frac{1}{|\partial\Omega|\rho(\overline{u})}[-|\Omega_S(t)|\varepsilon^9\rho'(\overline{u})\dot{\overline{u}} - \varepsilon^9\sum_{i\in N}|\Omega_L^i|\partial_t\rho_L + \varepsilon^9\sum_{i\in N}|I_i|(\rho(\overline{u}) - \rho_L^i)\dot{r}_i] \tag{3.76}$$

in (3.75)

$$\begin{aligned} 0 = {} & \varepsilon^9|\Omega_S(t)|(n'_{As}(\overline{u}) - \frac{n_{As}(\overline{u})}{\rho(\overline{u})}\rho'(\overline{u}))\dot{\overline{u}} + \varepsilon^9\sum_{i\in N}|\Omega_L^i|(\partial_t n_{As_L} + \frac{n_{As}(\overline{u})}{\rho(\overline{u})}\partial_t\rho_L^i) \\ & - \varepsilon^9\sum_{i\in N}\int_{I_i}((n_{As}(\overline{u}) - n^i_{As_L}) - \frac{n_{As}(\overline{u})}{\rho(\overline{u})}(\rho(\overline{u}) - \rho_L^i))\dot{r}_i. \end{aligned}$$

This can be rewritten by multiplying with ε^{-9}

$$0 = |\Omega_S(t)|\overline{\mathcal{X}}(\overline{u})\dot{\overline{u}} + \sum_{i\in N}|\Omega_L^i|(\partial_t n_{As_L} - P(\overline{u})\partial_t\rho_L^i) + \sum_{i\in N}\int_{I_i}(n^i_{As_L} - P(\overline{u})\rho_L^i))\dot{r}_i.$$

With the homogeneity of the liquid we find

$$0 = (|\Omega(t)| - \varepsilon^9\sum_{i\in N}r_i^3)\overline{\mathcal{X}}(\overline{u})\dot{\overline{u}} + \sum_{i\in N}|I_i|(\frac{r_i}{3}(\partial_t n_{As_L} - P(\overline{u})\partial_t\rho_L^i) + (n^i_{As_L} - P(\overline{u})\rho_L^i)\dot{r}_i) \tag{3.77}$$

and now with (2.160) and (3.70), which we both combine with the scaling in (3.70) for (DC),

$$0 = (|\Omega(t)| - \varepsilon^9\sum_{i\in N}r_i^3)\overline{\mathcal{X}}(\overline{u})\dot{\overline{u}} + 4\pi\sum_{i\in N}(\overline{u} - u_{int}(r_i))r_i.$$

This yields finally the ODE for the mean field, our so-called *mean field equation*

$$\dot{\overline{u}} = -4\pi\frac{\sum_i r_i(\overline{u} - u_{int}(r_i))}{\overline{\mathcal{X}}(\overline{u})|\Omega(t)|}, \tag{3.78}$$

where we finally neglect terms of order ε^9. By plugging in $\dot{\overline{u}}$ in (3.76) we get an explicit formula for $\dot{R}_{bd}$ for given $\overline{u}$

$$\dot{R}_{bd} = \frac{1}{|\partial\Omega|\rho(\overline{u})}[\varepsilon^9\rho'(\overline{u})\frac{4\pi\sum_{i\in N}(\overline{u} - u_{int}(r_i))r_i}{\overline{\mathcal{X}}(\overline{u})} + \varepsilon^9\sum_{i\in N}|I_i|(-\frac{r_i}{3}\partial_t\rho_L + (\rho(\overline{u}) - \rho_L^i)\dot{r}_i)]. \tag{3.79}$$

Plugging in the formula (2.159) into (3.79)

$$\dot{R}_{bd} = \varepsilon^9\frac{\rho'(\overline{u})}{\rho(\overline{u})}\frac{4\pi\sum_{i\in N}(\overline{u} - u_{int}(r_i))r_i}{|\partial\Omega|\overline{\mathcal{X}}(\overline{u})} + \varepsilon^9\frac{4\pi\sum_{i\in N}r_i^2 v_+^i\cdot\nu}{|\partial\Omega|}.$$

We compare $\dot{R}_{bd}$ with $v|_{\partial\Omega}$, where we do not take the mean value over $\partial\Omega$.

Lemma 3.1 (Approximation of the evolution equation for the outer boundary)**.** *We assume that* (3.4) *holds and that the velocity v_A derived from our formally homogenised solution of Problem D, see* (3.60)*, is a good approximation to v. Let Ω^* be a convex set of $\mathbb{R}^3$. If the deviation of sphericity of $\partial\Omega^*$ is of order $\tilde{\varepsilon}$, i.e.*

$$\int_{\partial\Omega^*}(|x^*| - R_{bd})dA(x^*) = \mathcal{O}(\tilde{\varepsilon}) \tag{3.80}$$

and $|\Omega^*| - |\Omega| = \mathcal{O}(\tilde{\varepsilon})$, then we have

$$\dot{R}_{bd}(t) - \fint_{\partial\Omega^*}v(x^*,t)dA(x^*) = \mathcal{O}(\tilde{\varepsilon}). \tag{3.81}$$

This justifies the approximation of $v(x,t)|_{\partial\Omega}$ *by* $\dot{R}_{bd}$*, since the error is of higher order in* $\tilde{\varepsilon}$*.*

W.l.o.g. we could take $\tilde{\varepsilon} = \varepsilon$.

Proof. We have $|\Omega^*| = |\Omega|$ in $\mathcal{O}(\tilde{\varepsilon})$ due to our assumption (3.81). This implies that we can assume to have in both cases the same $\overline{u}$ in approximation of highest order terms in $\tilde{\varepsilon}$ and hence from (3.70) the same radii r_i in this approximation.

In distances bigger than $\mathcal{O}(\varepsilon)$ from droplets we find from our formal homogenisation (3.60), i.e.

$$v_A(x) := \partial_t W(x) = \partial_{\overline{u}} a\, \dot{\overline{u}} \sum_{j\in N} (x - X_j) + \sum_{j\in N} (\partial_{r_j} b_j r_j + 3b_j)\dot{r}_j \varepsilon^9 \frac{r_j^2 (x - X_j)}{|x - X_j|^3}, \tag{3.82}$$

that $|v_A| = \mathcal{O}(\varepsilon)$. We evaluate (3.82) in direction of the outer normal on $\partial\Omega$ and get

$$v_A(x) \cdot \nu|_{\partial\Omega} = \partial_{\overline{u}} a\, \dot{\overline{u}} \sum_{j\in N} (x - X_j) \cdot \frac{x}{R_{bd}} + \sum_{j\in N} (\partial_{r_j} b_j r_j + 3b_j)\dot{r}_j \varepsilon^9 \frac{r_j^2 (x - X_j)}{|x - X_j|^3} \cdot \frac{x}{R_{bd}} + o(\varepsilon^6),$$

while on $\partial\Omega^*$ we have

$$v_A(x^*) \cdot \nu|_{\partial\Omega^*} = \partial_{\overline{u}} a\, \dot{\overline{u}} \sum_{j\in N} (x^* - X_j) \cdot \frac{x^*}{|x^*|} + \sum_{j\in N} (\partial_{r_j} b_j r_j + 3b_j)\dot{r}_j \varepsilon^9 \frac{r_j^2 (x^* - X_j)}{|x^* - X_j|^3} \cdot \frac{x^*}{|x^*|} + o(\varepsilon^6).$$

Equivalently to (3.80) we have

$$\fint_{\partial\Omega^*} |x^*| dA(x^*) = R_{bd} + \mathcal{O}(\tilde{\varepsilon}) = \fint_{\partial\Omega} |x| dA(x) + \mathcal{O}(\tilde{\varepsilon}).$$

Therewith we estimate in $o(\varepsilon)$

$$\begin{aligned}
&|\dot{R}_{bd}(t) - \fint_{\partial\Omega^*} v(x^*,t)\, dA(x^*)| \\
&\leq \sum_{j\in N} |\partial_{\overline{u}} a \dot{\overline{u}}| \left| \fint_{\partial\Omega} (x - X_j) \cdot \frac{x}{R_{bd}}\, dA(x) - \fint_{\partial\Omega^*} (x^* - X_j) \cdot \frac{x^*}{|x^*|}\, dA(x^*) \right| \\
&\quad + \varepsilon^9 |\partial_{r_j} b_j r_j + 3b_j|\, |\dot{r}_j|\, r_j^2 \left| \fint_{\partial\Omega} \frac{(x - X_j)}{|x - X_j|^3} \frac{x}{R_{bd}}\, dA(x) - \fint_{\partial\Omega^*} \frac{(x^* - X_j)}{|x^* - X_j|^3} \frac{x^*}{|x^*|}\, dA(x^*) \right| \\
&\leq \sum_{j\in N} |\partial_{\overline{u}} a \dot{\overline{u}}| \left| R_{bd} - \fint_{\partial\Omega} X_j \cdot \frac{x}{R_{bd}}\, dA(x) - \fint_{\partial\Omega^*} |x^*| - X_j \cdot \frac{x^*}{|x^*|}\, dA(x^*) \right| \\
&\quad + \varepsilon^9 |\partial_{r_j} b_j r_j + 3b_j|\, |\dot{r}_j|\, r_j^2 \left| \fint_{\partial\Omega} \frac{R_{bd} - X_j \cdot \frac{x}{R_{bd}}}{|x - X_j|^3}\, dA(x) - \fint_{\partial\Omega^*} \frac{|x^*| - X_j \cdot \frac{x^*}{|x^*|}}{|x^* - X_j|^3}\, dA(x^*) \right| \\
&\leq (\sum_{j\in N} |\partial_{\overline{u}} a \dot{\overline{u}}| + \varepsilon^9 |\partial_{r_j} b_j r_j + 3b_j|\, |\dot{r}_j| r_j^2) \mathcal{O}(\tilde{\varepsilon})
\end{aligned}$$

and (3.81) follows by (3.78), (3.70) and (3.80). □

We justify rigorously under suitable assumptions our mechanical monopole approximation later in Lemma 5.4. Instead of using the monopole approximation for the diffusion problem, we differently proceed later in Th. 5.7 in order to homogenise the diffusion problem.

3.3.5. Formally homogenised problem for (DC)

Since $\dot{R}_{bd} \to 0$ as $\varepsilon \to 0$ we have $\Omega^\dagger = \Omega(0)$. Let formally $p_L \to p_L^\dagger$. The formally homogenised mechanical BVP is the problem for $W^\dagger$

$$\begin{aligned} \operatorname{div} \breve{\sigma}_S(\nabla W^\dagger) &= 0 && \text{in } \Omega(0) \setminus \{X_i\}_{i\in N}, \\ \breve{\sigma}_S(\nabla W^\dagger)\nu &= (\overline{p} - p_0)\nu && \text{on } \partial\Omega(0), \\ p_L^\dagger(r_i) &= \overline{p} - 3k_L(a^\dagger + b^\dagger(r_i) - \delta^R - h_L^*(X_L^A(r_i))) && \forall i \in N. \end{aligned}$$

We give now $\overline{\mathbb{X}}(r_i)$ and $\overline{\mathcal{X}}$ explicitly in formal homogenisation i.e. we let formally $\overline{\mathbb{X}} \to \mathbb{X}^\dagger$ as $\varepsilon \to 0$ and introduce analogously $\overline{\mathcal{X}}^\dagger$. (2.157) yields, where we use that formally $X_S \to \frac{1}{2}$, $\overline{X}_S \to \frac{1}{2}$ and $\overline{Y}_V \to 1$ as $\varepsilon \to 0$,

$$\overline{\mathbb{X}}^\dagger = 2\overline{n}_G((X_L^\dagger(r_i) - \overline{X}_L) + \frac{1}{2} + (\frac{1}{2} - \overline{X}_L)\frac{a^\dagger + b^\dagger(r_i) - \delta^R}{\varrho}) \tag{3.83}$$

where $X_L^\dagger$ is the formally homogenised solution of the interface b.c. for (DC). From (A.19) we find formally, where have to assume that u or y is uniformly bounded in ε,

$$\overline{\mathcal{X}}^\dagger = M_{Ga}\overline{n}_G \frac{1 - 3a^\dagger}{1 + \tilde{\mu}}\overline{Y}.$$

For the diffusion problem and the interface radii, we then have (3.78) and (3.70)

$$\begin{aligned} \dot{\overline{u}} &= -4\pi \frac{\sum_i r_i(\overline{u} - u_{int}(r_i))}{\overline{\mathcal{X}}|\Omega(t)|} && \forall t \in (0, \mathcal{T}), \\ \dot{r}_j &= \frac{\overline{u} - u_{int}(r_j)}{r_j \overline{\mathbb{X}}(r_j)} && \forall j \in N \, \forall t \in (0, \mathcal{T}), \end{aligned}$$

together with initial conditions and $R_{bd} = R_{bd}^0$.

3.4. Formal homogenisation for regime (IC)

The formal homogenisation for regime (IC) is easier than for (DC) since, we already know that $\overline{u}$ is constant in Ω_S, that is a good approximation once we have determined $\overline{u}$ by (3.73) or a mean field ODE for regime (IC), which is similar to (3.78). The mechanical BVP has now no U_M^i on the r.h.s. since we have $u_{int}^i = \overline{u}$. We have for the displacement

$$W_i(x) := ((a + c_i)|x - X_i| + b_i \frac{\varepsilon^9 r_i^3}{|x - X_i|^2})e_{r_i},$$

where the coefficients are as described in Appendix C.2:

$$\begin{aligned} a &= \frac{\overline{p} - p_0}{3k_S} + \varepsilon^9 \frac{4G_S}{4G_S + 3k_S} h^*(\overline{u}), \\ b_i &= \frac{(1 - \frac{k_L}{k_S})(\overline{p} - p_0) - \frac{2\sigma}{r_i} + 3k_L(\delta^R + h_L^*(X_L^A(r_i)) - \varepsilon^9 h^*(\overline{u}))}{4G_S + 3k_L}, \\ c_i &= c(|x - X_i|) = \varepsilon^9 \frac{3k_S}{4G_S + 3k_S} h^*(\overline{u}). \end{aligned}$$

We put a and c_i together to

$$a_{\#} = a + c_i = \frac{\overline{p} - p_0}{3k_S} + \varepsilon^9 h^*(\overline{u})$$

and get

$$W_i(x) := (a_{\#}|x - X_i| + b_i \frac{\varepsilon^6 r_i^3}{|x - X_i|^2}) e_{r_i}.$$

The formally homogenised mechanical boundary value problem for regime (IC) has the same form as for regime (DC), see Subsection 3.3.1. We define by inserting the solution of the monopole approximation of the mechanical BVP in leading order in ε:

$$\begin{aligned}
\overline{u_L}(\overline{u}, r_i) &= u_L(\overline{u}, r_i, a^\dagger + b^\dagger(r_i)) + \mathcal{O}(\varepsilon^6),\\
\overline{\mathbb{Z}}(\overline{u}, r_i) &= \mathbb{Z}(\overline{u}, r_i, a^\dagger + b^\dagger(r_i)) + \mathcal{O}(\varepsilon^6),\\
\overline{\mathbb{X}}(\overline{u}, r_i) &= \mathbb{X}(\overline{u}, r_i, a^\dagger + b^\dagger(r_i)) + \mathcal{O}(\varepsilon^6),\\
X_L^A(\overline{u}, r_i) &= X_L(r_i, a^\dagger + \frac{(1 - \frac{k_L}{k_S})(\overline{p} - p_0) - \frac{2\sigma}{r_i} + 3k_L(\delta^R + h_L^*(\overline{X}_L))}{4G_S + 3k_L}) + \mathcal{O}(\varepsilon^6),
\end{aligned}$$

where we note that, X_L^A and $\mathbb{X}$ are defined different as for regime (DC). As in (3.64) and (3.65) we define $\rho^{(A)}$ and $\overline{\mathcal{X}}$.

For the (IC) regime (without any mean field ansatz for $\overline{u}$) we can proceed as in Subsection 3.3.4 until (3.77). We substitute $\dot{r}_i$ by the Stefan condition of the (IC) regime, (2.164), where we inserted consequently $\overline{\mathbb{Z}}$ for $\mathbb{Z}$ and $\overline{u_L}$ for u_L, and get

$$0 = \varepsilon^9(|\Omega(t)| - \varepsilon^9 \sum_{i \in N} r_i^3)\overline{\mathcal{X}}(\overline{u})\dot{\overline{u}} + \varepsilon^9 \sum_{i \in N} |I_i| \frac{\overline{\mathbb{X}}(r_i, \overline{u})}{\overline{\mathbb{Z}}(\overline{u}, r_i)}(\overline{u} - \overline{u_L}(\overline{u}, r_i)) \tag{3.84}$$

or

$$\dot{\overline{u}} = -4\pi \frac{\sum_{i \in N} r_i^2 \frac{\overline{\mathbb{X}}(r_i, \overline{u})}{\overline{\mathbb{Z}}(\overline{u}, r_i)}(\overline{u} - \overline{u_L}(\overline{u}, r_i))}{|\Omega|\overline{\mathcal{X}}(\overline{u})}. \tag{3.85}$$

The formula for $\dot{R}_{bd}$ for regime (IC) reads:

$$\dot{R}_{bd} = \varepsilon^9 \frac{\rho'(\overline{u})}{\rho(\overline{u})} \frac{4\pi \sum_{i \in N} r_i^2 (\overline{u} - \overline{u_L}(\overline{u}, r_i)) \frac{\overline{\mathbb{X}}(r_i, \overline{u})}{\overline{\mathbb{Z}}(\overline{u}, r_i)}}{|\partial\Omega|\overline{\mathcal{X}}(\overline{u})} + \varepsilon^9 \frac{4\pi \sum_{i \in N} r_i^2 v_+^i \cdot \nu}{|\partial\Omega|}. \tag{3.86}$$

We give now for regime (IC) the formally homogenised functions $\overline{u_L}(\overline{u}, r_i)$, $\overline{\mathbb{X}}(r_i, \overline{u})$ and $\overline{\mathbb{Z}}(\overline{u}, r_i)$ explicitly, by abuse of notation without an additional index "†" as above for (DC). Let $X_L^A(r_i, \overline{u})$ be the solution of (2.162), in the approximation of the formal homogenisation,

$$\begin{aligned}
&\frac{\overline{\mathbb{H}}_{\tilde{\mu}}(X_L^A, r_i)}{\overline{\mathbb{H}}_{\tilde{m}}(X_L^A, r_i)}(\tilde{u}^{chem}(\overline{u}) - \tilde{u}_L^{chem}(X_L^A) + (1 - \frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\overline{\rho}_S}\frac{2\sigma}{r_i})\\
&= \overline{u} - u_L^{chem}(X_L^A) + \frac{3k_L}{\overline{n}_L}\frac{1 - \tilde{\mu}}{\tilde{\mu}}(h_L^*(X_L^A) - a_L(r_i))
\end{aligned} \tag{3.87}$$

where

$$\begin{aligned}
\overline{\mathbb{H}}_{\tilde{n}}(X_L^A, r_i) = (1 - \frac{1}{\tilde{n}})(1 - [(1 + 3a_L(r_i) - h_L^*(X_L^A))\frac{\tilde{n}}{\tilde{n} - 1}\frac{M(X_L^A)(\overline{X}_L - X_L^A)}{M_{Ga}X_L^A(1 - X_L^A)}\\
- (1 + 3a_L(r_i))](1 + \frac{2(a^\dagger + b^\dagger(r_i)) - 3\delta^R}{\varrho})).
\end{aligned}$$

A rough approximation for X_L^A is given by (2.167). Then we get

$$\begin{aligned}
\overline{u_L}(\overline{u}, r_i) &= \overline{u} - \frac{\mathbb{H}_{\tilde{\mu}}(X_L^A, r_i)}{\mathbb{H}_{\tilde{m}}(X_L^A, r_i)}(\tilde{u}^{chem}(\overline{u}) - \tilde{u}_L^{chem}(X_L^A) + (1 - \frac{\tilde{\mu}}{\tilde{m}})\frac{M_{As}}{\overline{\rho}_S}\frac{2\sigma}{r_i}), && (3.88)\\
\overline{\mathbb{X}}(r_i, \overline{u}) &= 2\overline{n}_G((X_L^A - \overline{X}_L) + \frac{1}{2} + (\frac{1}{2} - \overline{X}_L)\frac{a^\dagger + b^\dagger(r_i) - \delta^R}{\varrho}), && (3.89)\\
\overline{\mathbb{Z}}(\overline{u}, r_i) &= n_L^R(1 - \frac{1}{\tilde{\mu}})(2 - (\frac{\tilde{\mu}}{\tilde{\mu} - 1}\frac{M(X_L^A)(\overline{X}_L - X_L^A)}{M_{Ga}X_L^A(1 - X_L^A)}(1 + \frac{2(a^\dagger + b^\dagger(r_i)) - 3\delta^R}{\varrho}) - 1)\times \\
&\quad \times \frac{2(a^\dagger + b^\dagger(r_i)) - 3\delta^R}{\varrho}). && (3.90)
\end{aligned}$$

We see that we found in both cases, (DC) and (IC), for the formal homogenisation an ODE to determine the mean field $\overline{u}$, where we have to add the initial condition

$$\overline{u}(t = 0) = \overline{u}^0.$$

For existence and uniqueness results of the so far formally derived mean field model we refer to Lemma 6.1, for numerical simulations we refer to Section 6.6.

3.5. The relation of an experimental situation to the scaling

In this section we compare the dimensionless Problems D, DI and DCR including the scaling parameter ε with the unscaled Problems B and BI. We establish that the experimental situation i.e. our original problem corresponds to the case of $\varepsilon = \varepsilon_0 := 10^{-3/2} \approx 0.031623$ for the critical scaling regime and to $\varepsilon = \varepsilon_0 \approx 0.1$ for the dilute scaling regime. We compare with typical values for our original system.

Critical radii are about 1 nm and the minimal radius is about 0.2 nm. Thus our typical radii are $\mathcal{R}_0 = 10^{-9}\text{m} = \varepsilon_0^3\mathcal{L}_0$ and typical particle distances are $\mathcal{D}_0 = 10^{-6}\text{m} = \varepsilon_0\mathcal{L}_0$, which implies that $\mathcal{L}_0 \approx R_{bd}$ should be $10^{-9/2}\text{m} \approx 31.6\mu\text{m}$ for the critical case and $\mathcal{L}_0$ should be 10^{-5}m for the dilute case. The typical length scale of a wafer in height is about 0.2mm and about 20mm in diameter, while from experiments it is known that the diameter of the region in a GaAs crystal in the interior of a dislocation ring, in which we have homogeneous nucleation is about $10^{-4}\text{m} = 100\mu\text{m}$ (see [DDN06]). But in the last case we would have to consider different boundary conditions. We emphasise that a $\mathcal{L}_0$ could be chosen arbitrarily by the experimenter.

It is confirmed by Fig. 6.2 and Fig. 6.4 later, that our choice of the length scales $\mathcal{R}_0$ and $\mathcal{D}_0$ yields critical and stable radii in agreement with experiments.

Since in our critical case $\mathcal{R}_0$ and $\mathcal{D}_0$ are well-known we have that $\mathcal{L}_0 > 10^{-9/2}\text{m}$ corresponds to $r < 3$ and $\mathcal{L}_0 < 10^{-9/2}\text{m}$ to $r > 3$, that leads to our choice of $\mathcal{L}_0$ in the critical case. In our analysis we treat however the case $r = 3$ and also the case $r = 4$ where $u \to \overline{u} = const$ as $\varepsilon \to 0$ and conjecture, if $r < 3$ then $u - \lim_{r \to \infty} u_{int} \to 0$ as $\varepsilon \to 0$.

Summarised our scaling corresponds to the case of an area, in which homogeneous nucleation takes place and which is cut out of the wafer and undergoes a heat treatment separately. We consider the critical case and the dilute case, which are mathematically most interesting, i.e. we assume a length scale $\mathcal{L}_0$ of the wafer under heat treatment, which corresponds to the critical or the dilute case. From the real length of the wafer we can then decide, which case applies.

We continue with the dilute regime and $\mathcal{L}_0 = 10^{-5}\text{m}$.

Remark 3.3 (Number of precipitates and atoms in an experimental system)**.** *Our original system deals hence with about* $\mathcal{N}_0^0 \varepsilon_0^{-3} = \mathcal{N}_0^0 \cdot 10^3$ *precipitates. In order to determine* $\mathcal{N}_0^0$ *we compare with the data from experiments, see [Ste01], p. 92 f. and p. 112, where as density of precipitates* $N_{DP} = 10^8 cm^{-3}$ *is given, which was determined by laser scattering experiments. This yields approximately* $\frac{4\pi}{3}\mathcal{L}_0^3 N_{DP} \approx 0.42$ *precipitates in our original system.*

Further by comparison with the density $\overline{n}_G$*,* $\overline{n}_L$ *and the value for* N_{As} *given in [Ste01], p.112, which is in this study the number of As atoms in all precipitates, we see that the value of* N_{DP} *from scattering experiments is too small. This claim is enforced by the diagrams in [Ste01], p. 93, where* N_{DP} *grows with time, where we in general expect the number of precipitates to decrease with time. This is explained, if we assume that in scattering experiments only large enough droplets can be seen, while we expect droplets to increase in size with time. We will work with* $N_{DP} = 10^{14} cm^{-3}$ *instead, which fits to our values for the densities* $\overline{n}_G$ *and* $\overline{n}_L$*. This yields approximately* 4200 *precipitates in our original system. This holds for both regimes (DC) and (IC).*

The typical time scale τ_0 for regime (DC) is derived from the diffusion constant resp. the bulk mobility. For the diffusion constant Steinegger ([Ste01], *S.* 106) gives in a corresponding experimental situation, but at $T = 1373K$,

$$D = \frac{10^{-12}\ \text{m}^2}{1\ \text{s}} = 1\frac{\text{nm}^2}{10^{-6}\text{s}}. \tag{3.91}$$

With $\mathcal{R} = 10^{-9}$m this implies as typical time scale in our original problem in regime (DC) that $\tau_0 = 10^{-6}$s. This yields times τ_j for vanishing of droplets, which correspond to the study of Steinegger [Ste01] as we see later in Chapter 6. The typical time scale τ_0 is the same for the case of constant mobility (2.63) and for the case of constant diffusion coefficient (2.64).

For regime (DC) the bulk mobility is calculated from the Stefan condition to

$$B = n_G^R D = \frac{n_G^R \mathcal{R}_0^2}{\tau_0} = \frac{37000\ \text{mol}}{\text{m}^3}\frac{(10^{-9}\text{m})^2}{10^{-6}\text{s}} = 3.7 \cdot 10^{-8}\frac{\text{mol}}{\text{m s}} = 3.7 \cdot 10^{-23}\frac{\text{mol}}{\text{nm}\ \mu\text{s}} \approx 2.2 \cdot 10\frac{1}{\text{nm}\ \mu\text{s}}. \tag{3.92}$$

In case of interface controlled interface motion we have the interface mobility by the formula (2.62)

$$B^I = \sqrt{\frac{8.314 \cdot 1100}{2\pi \cdot 74.56 \cdot 10^{-3}}\frac{\text{J}}{\text{kg}}} \cdot 70000\frac{\text{mol}}{\text{m}^3} \approx 9.8 \cdot 10^6\frac{\text{mol}}{\text{m}^2\text{s}} = 9.8 \cdot 10^{-12}\frac{\text{mol}}{\text{nm}^2\text{s}} \approx 5.9 \cdot 10^{12}\frac{1}{\text{nm}^2\text{s}}. \tag{3.93}$$

Then for (IC) the typical time scale is determined by $\tau_0^I = \frac{n_G^R \mathcal{R}}{B^I} \approx 3.8 \cdot 10^{-12}$s.

Remark 3.4 (Uncertain data)**.** *Since the data for* B*,* D *and* B^I *is still uncertain, we cannot decide from the data for mobilities and considering the relations* (2.65) *or* (2.66)*, whether the (DC) regime whether the (IC) regime corresponds to the experimental situation.*

For comparison to (3.91)*, measurements by Uematsu et al. [UWS⁺95] in a slightly different experimental situation suggest by extrapolation as diffusion constant for interstitial As in GaAs values between* 10^{-16} $cm^2\ s^{-1}$ *and* 10^{-18} $cm^2\ s^{-1}$ *at* $T = 1100\ K$ *and under* $p_0 = 10^5\ N\ m^{-2}$*.*

The equation (2.62) *is used as a guess, since there are no data from measurements available.*

This implies that the time scales τ_0 *or* τ_0^I *relying on* D *or* B^I *cannot be determined accurately.*

We work with $\tau_0 = 10^{-6}$s and $\tau_0^I = 10^{-12}$s and return to this question in Section 6.5.

Due to the experimental data we expect $\mathcal{L}_0$ between 10^{-5}m and $3.16 \cdot 10^{-5}$m. Numerics yield the guess, that the dilute regime might fit to our original problem. We give now an overview of most of the used unscaled quantities and their scaling behaviour in Problem D or DI and Problem B or BI, see Table 3.1.

Quantity	**Value without scaling**	**Scaling (cf. Def. 3.1)**	**Value in Pb. D/DI**	**Value in Pb. B/BI**
Quantity	f	$\mathbf{F}$	$\hat{f}$	$\hat{f}$ with dim.
Scaling parameter	1	ε	$\varepsilon^0 = 10^{-1}$	ε^0
Length of wafer $\mathcal{L}_0 = R_{bd}^0$	10^{-5}m	R_{bd}^0	1	10^{-5}m
Typ. droplet dist. $\mathcal{D}_0$	10^{-5}m	$\varepsilon^1 R_{bd}^0$	1	10^{-6}m
Typ. initial radii $\mathcal{R}_0$	10^{-5}m	$\mathbf{L} = \varepsilon^4 R_{bd}^0$	1	10^{-9}m
Typical times (DC) τ_0	10^{-6}s	$\mathbf{T} = \tau^0$	1	10^{-6}s
Typical times (IC) τ_0^I	10^{-12}s	$\mathbf{T} = \tau_0^I$	1	10^{-12}s
Typical masses $\mathcal{M}$	$7.492 \cdot 10^3$kg	$\mathbf{M} = \varepsilon^4 M_{As}\ 1\text{mol}$	1	$M_{As}\ 1\text{mol}$ $= 7.492 \cdot 10^{-1}$kg
# of droplets $\mathcal{N}^0$	$\mathcal{N}_0^0 = \frac{4\pi}{3} \approx 4$	$(\frac{\mathcal{L}_0}{\mathcal{D}_0})^3 = \varepsilon^{-3}$	$\frac{4\pi}{3} \cdot 10^3$ $\approx 4.2 \cdot 10^3$	$\frac{4\pi}{3} \cdot 10^3$ $\approx 4.2 \cdot 10^3$
Typ. # of atoms N_0	$1.01 \cdot 10^2$mol	$\mathbf{N} = \varepsilon^{12}\ 1\text{mol}$	$1.01 \cdot 10^{-10}$	$1.01 \cdot 10^{-10}$mol $\approx (3 - \overline{Y}_V) n_G^R R_{bd}^3$
$N_0^R = \frac{N_0}{\mathcal{N}^0}$	$2.4 \cdot 10^1$mol	$\mathbf{N} = \varepsilon^{15}\ 1\text{mol}$	$2.4 \cdot 10^{-14}$	$2.4 \cdot 10^{-14}$mol
Concentr. As$_\gamma$ $\overline{Y}$	$(10^{19/2})$	ε^9	10^{-4}	10^{-4}
Mobility (DC) B	$3.7 \cdot 10^{-6} \frac{\text{mol}}{\text{m s}}$	$\frac{\mathbf{N}}{\mathbf{LT}} \propto \varepsilon^8$	$3.7 \cdot 10^{-23}$	$3.7 \cdot 10^{-23} \frac{\text{mol}}{\text{nm s}}$ by (3.92)
Mobility (IC) B^I	$9.8 \cdot 10^{10} \frac{\text{mol}}{\text{m}^2\text{ s}}$	$\frac{\mathbf{N}}{\mathbf{L}^2\mathbf{T}} \propto \varepsilon^4$	$9.8 \cdot 10^{-24}$	$9.8 \cdot 10^{-12} \frac{\text{mol}}{\text{nm}^2\text{ s}}$ by (3.93) $= 9.8 \cdot 10^{-24} \frac{\text{mol}}{\text{nm}^2\ 10^{-12}\text{s}}$
Diff. const. (DC) D	$10^{-4} \frac{\text{m}^2}{\text{s}}$	$\frac{\mathbf{L}^2}{\mathbf{T}} \propto \varepsilon^8$	1	$1 \frac{\text{nm}^2}{\mu\text{s}}$ by (3.91)
Typ. stresses	$10^{10} \frac{\text{N}}{\text{m}^2}$	$\frac{\mathbf{M}}{\mathbf{LT}^2} \propto \varepsilon^0$	1	$10^{10} \frac{\text{N}}{\text{m}^2}$
Typ. forces	1N	$\frac{\mathbf{ML}}{\mathbf{T}^2} \propto \varepsilon^8$	10^{-8}	10^{-8}N
Surface tension	$7.5 \cdot 10^3 \frac{\text{N}}{\text{m}}$	$\frac{\mathbf{M}}{\mathbf{T}^2} \propto \varepsilon^4$	0.0075	0.075N m^{-1}
Typ. energy	$n_G^R RT \mathcal{L}_0^3$	$\frac{\mathbf{ML}^2}{\mathbf{NT}^2} \propto 1$	$6.76 \cdot 10^{-6}$	$6.76 \cdot 10^{-7}$J
Typ chem. pot.	RT	$\frac{\mathbf{ML}^2}{\mathbf{NT}^2} \propto 1$	$9.14 \cdot 10^3$	$RT = 9.14 \cdot 10^3\text{J mol}^{-1}$

Table 3.1.: Overview of typical quantities for a fictive unscaled problem i.e. $\varepsilon = 1$, the scaling, the scaled Problems D or DI and the original Problems B or BI.

From the value of $\overline{Y}$ for $\varepsilon = 1$ we see that the maximal possible value for our scaling parameter in order to ensure $\overline{Y} < 1$ is $\varepsilon < 10^{-19/18} \approx 8.7992 \cdot 10^{-2}$, which is fulfilled for ε_0.

In particular we expect as typical displacements

$$\tilde{U} = 10^{-21/2}\text{m} \approx 3.16 \cdot 10^{-11}\text{m} = \mathcal{O}(\tilde{h})\mathcal{R}_0.$$

We remark that the displacements are small compared to distances between droplets, $U \ll \mathcal{D}_0 \sim \varepsilon$, that motivates again that the mechanical BVP is more or less a superposition of pairwise independent mechanical BVPs for single droplets.

From now on we drop the upper index ε on all scaled quantities.

Chapter 4.

Existence and uniqueness for a class of models

In this chapter we prove for sufficiently small but fixed ε existence and uniqueness of the following Problem E. Contrary to Problem DCR (3.43) – (3.53) we neglect the h^* term on the r.h.s of the mechanical BVP (3.43) – (3.45). Furthermore we modify (3.52) of Problem DCR and make stronger assumptions on the dependences of u_{int} and $\mathbb{X}$ on the variables, see Assumptions 4.3 and 4.4. Because ε is fixed we could transfer all results of this chapter to a modification of Problem D.

4.1. The abstract problem E

In rescaled variables we look for solutions $U^\varepsilon, u^\varepsilon, \{r_i\}_{i\in N}, R_{bd}$ of the following coupled differential equations for regime (DC):

$$\operatorname{div}\check\sigma_S(\nabla U^\varepsilon) = f_0^\varepsilon \qquad \text{in } \Omega_S^\varepsilon(t), \tag{4.1}$$

$$\check\sigma_S(\nabla U^\varepsilon)\nu = g_0^\varepsilon\nu \qquad \text{on } \partial\Omega(t), \tag{4.2}$$

$$(\check\sigma_S(\nabla U^\varepsilon) - \frac{3k_L}{\varepsilon^3 r_i}\fint_{I_i^\varepsilon}(U^\varepsilon\cdot\nu))\nu = g_i^\varepsilon\nu \qquad \text{on } I_i^\varepsilon(t)\,\forall i\in N^\varepsilon(t), \tag{4.3}$$

for all $t\in(0,\mathcal{T})$, where f_0^ε, g_i^ε, $i\in N^\varepsilon\cup\{0\}$ can depend on all r_i, $i\in N^\varepsilon$ but not on other variables,

$$\varepsilon^3(\mathcal{X}(u^\varepsilon)(\partial_t u^\varepsilon + v^\varepsilon\cdot\nabla u^\varepsilon) + \nabla\cdot v^\varepsilon\,\Xi(u^\varepsilon)) - \Delta u^\varepsilon = 0 \qquad \text{in } \Omega_S^\varepsilon(t) \tag{4.4}$$

$$\nabla u^\varepsilon\cdot\nu = 0 \qquad \text{on } \partial\Omega(t), \tag{4.5}$$

$$u^\varepsilon = u_{int}(r_i) \qquad \text{on } I_i^\varepsilon(t)\,\forall i\in N^\varepsilon(t), \tag{4.6}$$

$$u^\varepsilon(\cdot, t=0) = u^{0,\varepsilon} \qquad \text{in } \Omega_S^\varepsilon(0), \tag{4.7}$$

for all $t\in(0,\mathcal{T})$, and with ODEs for the radii

$$\dot r_i = \varepsilon^3\frac{\fint_{I_i^\varepsilon}\nabla u^\varepsilon\cdot\nu}{\mathbb{X}(r_i, \fint_{I_i}U^\varepsilon\cdot\nu)\cdot\nu)} \qquad \forall i\in N^\varepsilon(t)\,\forall t\in(0,\mathcal{T}), \tag{4.8}$$

$$r_i(t=0) = r_i^0 \qquad \forall i\in N^\varepsilon(0), \tag{4.9}$$

$$\dot R_{bd} = (\mathbb{I} - \fint_{\partial\Omega}\nabla U\,\partial_{R_{bd}}\Phi(\Phi^{-1}))^{-1}\times\fint_{\partial\Omega}v^\varepsilon\cdot\nu \qquad \forall t\in(0,\mathcal{T}), \tag{4.10}$$

$$R_{bd}(t=0) = R_{bd}^0. \tag{4.11}$$

The velocity is $v^\varepsilon = U^\varepsilon$ as defined in (2.13). In the liquid we have p_L^i and u_L^i given for all $i \in N^\varepsilon(t)$ by the formulas (2.121) and (2.94) and the vanishing of a droplet is modelled as in Subsection 2.6.7.

We have modified in (4.10) the original evolution equation for R_{bd},

$$\dot{R}_{bd} = \fint_{\partial\Omega} v^\varepsilon \cdot \nu$$

in order to avoid technical difficulties after transformation of Problem E on fixed domain $\Omega(0)$, which is carried out in Section 4.2. The corresponding transformation Φ, which enters in (4.10), is constructed in Appendix B and is assumed to be a given smooth invertible function, which depends on R_{bd} and r_i, $i \in N$. The norm of the matrix term $\fint_{\partial\Omega} \nabla U \, \partial_{R_{bd}} \Phi(\Phi^{-1})$ is of order $\mathcal{O}(\tilde{h})$ and hence our modification is small in our approximation of small displacement gradients, see Assumption 2.1.

In (4.1) – (4.3) the r.h.s. f_0^ε, g_i^ε, $i \in \{0\} \cup N^\varepsilon$ would correspond to Problem DCR if we set

$$f_0^\varepsilon = \varepsilon^9 k_S h^{*\prime}(u^\varepsilon) \nabla u^\varepsilon, \tag{4.12}$$

$$g_0^\varepsilon = \overline{p} - p_0 + \varepsilon^9 3 k_S h^*(u^\varepsilon), \tag{4.13}$$

$$g_i^\varepsilon = \frac{2\sigma}{r_i} - 3k_L(\delta^R + h_L^*(r_i)) + 3k_S \varepsilon^9 h^*(u_{int}(r_i, \fint_{I_i} U^\varepsilon \cdot \nu)) \quad \forall i \in N^\varepsilon, \tag{4.14}$$

but since we neglect h^* and the dependence of u_{int} on U^ε, compared to our original situation, we set in Problem E

$$f_0^\varepsilon = 0, \tag{4.15}$$

$$g_0^\varepsilon = \overline{p} - p_0, \tag{4.16}$$

$$g_i^\varepsilon = \frac{2\sigma}{r_i} - 3k_L(\delta^R + h_L^*(r_i)) \quad \forall i \in N^\varepsilon. \tag{4.17}$$

We consider Problem E under the following assumptions, which we summarise here.

Assumption 4.1 (Assumptions on the mechanics). *The constants k_S, G_S and k_L are strictly positive and h_L^* is considered as given function of r_i.*

The data of the mechanical BVP is small i.e.

$$\frac{\overline{p} - p_0}{3k_S}, \; \frac{2\sigma}{3k_L r_{min}}, \; \delta^R, \; h_L^* \leq \tilde{h}, \tag{4.18}$$

where $\tilde{h} \ll 1$, confer Assumption 2.1.

Assumption 4.2 (Assumptions on the diffusion problem). *We assume:*

1) *$\Xi(u^\varepsilon) := n_{As}^\varepsilon(u^\varepsilon)$ is bounded and strictly positive, uniformly for all ε.*
2) *The function $\mathcal{X}(u^\varepsilon) = {n_{As}^\varepsilon}'(u^\varepsilon)$ depends continuously on u^ε and is bounded, strictly positive and strictly monotone (increasing). Vice versa this holds for $u^\varepsilon(n_{As}^\varepsilon)$, if we consider n_{As}^ε instead of u^ε as variable. This implies, that $n_{As}^\varepsilon(u^\varepsilon)$ is convex or $u^\varepsilon(n_{As}^\varepsilon)$ is concave.*
3) *As assumptions on initial data we make $u^0(x) \in \mathcal{J}_u$ (or equivalently $n_{As}^0(x) \in \mathcal{J}_n := n_{As}^\varepsilon(\mathcal{J}_u)$) for all $x \in \Omega_S(0)$ and $u^0 \in H^1(\Omega_S(0))$ (or $n_{As}^0 \in H^1(\Omega_S(0))$) and we make assumptions on new initial data after vanishing of a droplet as in Assumption 2.6.*

The last assumptions allow to consider equivalently to (4.4) – (4.11) the diffusion problem for the regime (DC), written for the variable n^ε_{As},

$$\begin{aligned} \varepsilon^3(\partial_t n^\varepsilon_{As} + \nabla\cdot(n^\varepsilon_{As} v^\varepsilon)) - \Delta u^\varepsilon(n^\varepsilon_{As}) &= 0 && \text{in } \Omega^\varepsilon_S(t) && (4.19)\\ \nabla n^\varepsilon_{As}\cdot\nu &= 0 && \text{on } \partial\Omega(t), && (4.20)\\ n^\varepsilon_{As} &= n^{int}_{As}(r_i) && \text{on } I_i(t)\ \forall i\in N^\varepsilon(t), && (4.21)\\ n^\varepsilon_{As}(\cdot,t=0) &= n^{0,\varepsilon}_{As} && \text{in } \Omega^\varepsilon_S(0), && (4.22) \end{aligned}$$

which is sometimes more suitable for our analysis than the formulation (4.4) – (4.7) with u^ε.

Assumption 4.3 (Generalised Gibbs-Thomson law)**.** *We assume that the boundary value for the chemical potential in the solid u_{int} depends only on the radius i.e. $u_{int}(r_i, ⨍_{I_i} U^\varepsilon\cdot\nu) = u_{int}(r_i) = u^i_{int}$, that is expected from the formal homogenisation of Chapter 3 to be a good approximation for sufficiently small $\varepsilon\to 0$. Furthermore let u_{int} be monotone decreasing and*

$$0 < u_{int}(r_i) \le u_{int}(r_{min}) \quad \forall r_i \in \mathcal{J}_r.$$

Assumption 4.4 (Assumptions on the radii evolution)**.** *The denominator $\mathbb{X}$ of the Stefan condition depends continuously on r_i and on the trace of U on the interface I_i. $\mathbb{X}$ is strictly positive*

$$\mathbb{X}(r_i, ⨍_{I_i} U\cdot\nu) > 0 \quad \forall r_i\in\mathcal{J}_r\ \forall U \text{ with } \|\nabla U\| = \mathcal{O}(\tilde h).$$

and bounded.

Neglecting the possible dependence of $\mathbb{X}$ on ∇U might be motivated by replacing ∇U by the explictly known solution for the displacement problem for a single droplet problem (SDP) with $h^* = 0$, $W = W(r_i)$, which is sensible for sufficiently small ε.

Assumption 4.5 (Assumptions on geometry and scaling)**.** *We assume initial data r^0_i, R^0_{bd} and X_i s.t. the droplets are disjoint and do not intersect the outer boundary for $t = 0$:*

$$r^0_i < \varepsilon^{-2}\frac{d_i}{2}, \quad dist(X_i, \partial\Omega(0)) < \varepsilon\frac{d_i}{2} \quad \forall i\in N^\varepsilon, \tag{4.23}$$

i.e. (3.4) *is fulfilled for all ε for $t = 0$.*

One can check that Assumptions 4.1, 4.2 1), 4.2 2) and 4.4 are fulfilled for typical material data and experimental values, as given in Appendix D.

We always assume in the Chapters 4 and 5 that the Assumptions 4.1 – 4.5 hold – without further reference on these assumptions.

Since solutions of Problem E depend on time and space we need the following function spaces.

Definition 4.1 (Bochner spaces)**.** *Let here Ω an open, bounded, possibly time-dependent domain in $\mathbb{R}^3$. Let $L^q(\Omega(t))$, $1\le q\le\infty$ the space of functions $f:\Omega(t)\to\mathbb{R}^k$, $k\in\mathbb{N}$, with $|f|^p$ integrable and f measurable in the sense of Lebesgue.*

1) *The space $L^p(0,\mathcal{T};L^q(\Omega(t)))$ are all strongly measurable functions $f:[0,\mathcal{T}]\to L^q(\Omega(t))$, defined by $[f(t)](x) := f(x,t)$, with*

$$\|f\|_{L^p(0,\mathcal{T};L^q(\Omega(t)))} = (\int_0^{\mathcal{T}} \|f(t)\|^p_{L^q(\Omega(t))}dt)^{1/p} < \infty$$

for $1\le p<\infty$. We abbreviate $L^pL^q := L^p(0,\mathcal{T};L^q(\Omega_S))$.

2) We define $C^0(0,\mathcal{T};L^q(\Omega(t)))$ as the set of all continuous functions $f : [0,\mathcal{T}] \to L^q(\Omega(t))$, defined by $[f(t)](x) := f(x,t)$, with

$$\|f\|_{C^0(0,\mathcal{T};L^q(\Omega(t)))} := \max_{0\leq t\leq \mathcal{T}} \|f(t)\|_{L^q(\Omega)} < \infty$$

which is abbreviated by C^0L^q.

3) Analogously we define spaces like H^kL^q, $W^{k,p}L^q$, $L^\infty L^q$, C^kL^q and $W^{k,p}C^k$.

For this definition, further definitions regarding Bochner spaces, definitions of Banach spaces and definitions of Sobolev spaces we refer to [Eva02], §5.9.2, p. 285f.

Definition 4.2 (Generalised solution of Problem E). *Let us define a generalised solution of Problem E as functions $(u^\varepsilon, U^\varepsilon, \{r_i\}, R_{bd})$ in $L^\infty H^1 \cap H^1L^2 \times L^\infty C^2 \cap H^1C^1 \times [H^1]^{\mathcal{N}^0} \times H^1$ which fulfil the usual weak formulations of Problem E.*

In order to guarantee the validity of our model i.e. that Problem E makes sense we have to show that u is in a suitable interval e.g. $u \in \mathcal{J}_u$ which includes our reference value $u = 0$ for all times $t \in (0,\mathcal{T})$. For our approach to work in linear elasticity, we have to show $\|\nabla U^\varepsilon\|_{L^2(\Omega_S(t))}$, $\|\nabla v^\varepsilon\|_{L^2(\Omega_S(t))} = \mathcal{O}(\tilde{h})$ for all times t.

This definition of a generalised solution turns out to be adequate for our problem, see Th. 4.7.

Definition 4.3 (Classical solution of Problem E). *By a classical solution we mean that all partial derivatives up to the partial derivatives of highest order, which appear in the statement of the PDE, exist and are continuous and bounded. Precisely, we introduce for the diffusion problem the space*

$$C_1^2(0,\mathcal{T};\Omega_S(t)) := C^1((0,\mathcal{T}];C^1(\overline{\Omega_S(t)})) \cap C^0([0,\mathcal{T}];C^2(\overline{\Omega_S(t)})).$$

The space $C_1^2(0,\mathcal{T};\Omega_S(t))$ will turn out to be the right space in the light of the regularity result in Th. 4.5, 3).

We expect to find generalised solutions $U^\varepsilon \in L^\infty C^2 \cap H^1C^1$, $u^\varepsilon \in H^1L^2 \cap L^\infty H^1$ and $r_i, R_{bd} \in H^1$ for small times. By exploiting further regularity of geometry and data we expect then to find classical solutions $U^\varepsilon \in C^1C^2$, $u^\varepsilon \in C_1^2(0,\mathcal{T};\Omega_S(t))$ and $r_i, R_{bd} \in C^1$ as long as no encounters or the disappearance of a droplet occurs.

4.2. Transformation of the problem on a fixed domain

We want to prove existence and uniqueness of solutions to Problem E. We follow the idea of proof given in [Nie99] or given with more details in [Nie96] and transform Problem E on a fixed domain, where we can apply standard results.

To keep notation short we introduce vectors, in which we list the radii of the free boundaries.

Definition 4.4 (Vector of free boundaries). *The vector of all interface radii is $R(t) := (r_i(t))_i \in [\mathcal{J}_r]^{\mathcal{N}^0}$ and the vector of all radii, including the outer free boundary, is $\tilde{R}(t) := (R_{bd}, R(t)) \in [\mathcal{J}_r]^{\mathcal{N}^0+1}$ where $\tilde{R}_0 = R_{bd}, \tilde{R}_i = R_i = r_i$, for all $i \in N$.*

Furthermore we write $R_i^{-1} := (R_i)^{-1}, i \in N$ and analogously we understand $\tilde{R}_i^{-1}$.

We consider the transformation

$$\phi(\cdot,\tilde{R}(t)) : \overline{\Omega_S^\varepsilon(0)} \to \overline{\Omega_S^\varepsilon(t)},$$

with the additional property that particle centres X_i remain fixed.

Since the time dependence enters into the transformation only by free boundaries we consider instead

$$\Phi(\cdot,t) : \overline{\Omega_S^\varepsilon(0)} \to \overline{\Omega_S^\varepsilon(t)}, \quad \Phi(z,t) := \phi(z, R(t), R_{bd}(t)).$$

We write

$$\partial_t \Phi = \nabla_{\tilde{R}} \phi \cdot \partial_t \tilde{R} := \sum_{i \in N^\varepsilon} \partial_{\tilde{R}_i} \phi \, \partial_t \tilde{R}_i = \sum_{i \in N^\varepsilon} \partial_{r_i} \phi \, \dot{r}_i + \partial_{R_{bd}} \phi \, \dot{R}_{bd}.$$

We consider $\overline{\Omega_S^\varepsilon(t)}$, the closure of the domain $\Omega_S^\varepsilon(t)$, in Cartesian coordinates $x := \Phi(z,t)$, in which our PDEs are stated. Now we change coordinates to the coordinates $z = \Phi^{-1}(x,t)$ of the closure of the initial domain, $\overline{\Omega_S^\varepsilon(0)}$, which will be equipped with a new time-dependent metric $g(z,t) := D\Phi^T(z,t) D\Phi(z,t)$. Accordingly the PDEs transform to PDEs in this new coordinates z. By definition there holds $g(\cdot, t=0) = \mathbb{I}_3$ and g is positive definite and symmetric.

Our notation and our treatment of the coordinate transformation follows the textbook of Ciarlet [Cia00]. For the rest of this chapter indices take their values in $\{1,2,3\}$ unless otherwise mentioned and we use the Einstein summation convention. Here we have to distinguish in our notation between contravariant indices, which are upper indices, and covariant indices, which are lower indices, because only for Cartesian coordinates co- and contravariant coincide.

Consequently, we write for covariant components of the metric g_{ij} and for contravariant components g^{ij}, which furthermore fulfil $g^{ij} = (g_{ij})^{-1}$. Furthermore we introduce three vectors g_q by $[g_q(z)]^i := \partial_{z_q} \Phi^i(z)$ and analogously we define g^q by $[g^q(z)]_i := \partial_{x_i} (\Phi^{-1})^q (x(z))$.

Remark 4.1 (New coordinates and Lagrangian coordinates)**.** *The coordinates z are in general not the Lagrangian coordinates $\boldsymbol{X}$. Only in the special case that $\dot{r}_i = v_+ = v_-$ on all interfaces or $N = \emptyset$ the coordinates z and $\boldsymbol{X}$ could be chosen s.t. $z \equiv \boldsymbol{X}$.*

We give explicitly a transformation $\Phi \in C^\infty(\overline{\Omega_S^\varepsilon(0)})$ from the fixed domain onto the time-dependent domain $\overline{\Omega_S^\varepsilon(t)}$ in Appendix B.1. In particular the transformation Φ is a regular matrix and smooth i.e. $\det D\Phi \neq 0$ and $\Phi \in C^\infty$, if for all droplets the Assumption 4.5 holds.

We repeat a definition and a result from differential geometry, which we need in the following.

Definition 4.5 (Christoffel symbols of the second kind)**.** *We introduce Christoffel symbols of the second kind as functions $\Gamma^q_{lk} : \overline{\Omega_S(0)} \to \mathbb{R}$ defined by $\Gamma^q_{lk}(z) := [g^q(z)]_i \partial_{z_l} [g_k(z)]^i$ as defined in [Cia00], pp. 27-32 or [Arf85], pp. 160-167. By this definition $\Gamma^q_{lk} = \Gamma^q_{kl}$.*

We note that one should keep attention, that another definition of Christoffel symbols of the second kind, which is not symmetric in l and k, is sometimes used in literature, e.g. [MTW73], p. 209 and the remarks in [RSW08].

Since Φ is smooth in space and as regular in time as $\tilde{R}$, we see that the Christoffel symbols have the same regularity.

Lemma 4.1 (Covariant derivatives)**.** *Let $v_i [g^i]_k$ a vector field with covariant components $v_i \in C^1(\overline{\Omega_S(0)})$ and let $A^{ij} [g_i]^k [g_j]^l$ a tensor field with contravariant components $A^{ij} \in C^1(\overline{\Omega_S(0)})$.*

1) *The covariant derivative $v_{i||j} : \overline{\Omega_S(0)} \to \mathbb{R}$ of a vector field with covariant components $v_i : \overline{\Omega_S(0)} \to \mathbb{R}^3$ is $v_{i||j} := \partial_{z_j} v_i - \Gamma^p_{ij} v_p$.*
2) *The covariant derivative $A^{ij}||_k : \overline{\Omega_S(0)} \to \mathbb{R}^3$ of the contravariant components of a tensor field $A^{ij} : \overline{\Omega_S(0)} \to \mathbb{R}^{3\times 3}$ is $A^{ij}||_k := \partial_{z_k} A^{ij} + \Gamma^i_{pk} A^{pj} + \Gamma^j_{kq} A^{iq}$.*

For a proof we refer to [Cia00], Th. 1.4-1 and Th. 1.6-1.

We denote the transformed function of a function f by $\tilde{f}$, unless otherwise stated. We give now how the important quantities of Problem E are transformed. Due to our choice of $\Omega_S^\varepsilon(0)$ or $\Omega_S^\varepsilon(t)$, which have both spherical interfaces and spherical outer boundary, we have on all boundaries $\tilde{\nu} = \nu$ and in particular $\partial_t \tilde{\nu} = \partial_t \nu = 0$.

Furthermore the volume element transforms accordingly to

$$dx = \sqrt{\det g(z)}\, dz,$$

and the surface area element transforms as

$$dA(x) = \sqrt{\det g(z)} \sqrt{\nu(z) g(z) \nu(z)}\, d\tilde{A}(z).$$

Note that scalar products are invariant under change of coordinates of this type.

We define the transformed functions

$$\tilde{u}^\varepsilon(z,t) := u^\varepsilon(\Phi(z,t),t), \quad \tilde{U}^\varepsilon(z,t) := U^\varepsilon(\Phi(z,t),t).$$

In particular

$$\begin{aligned} \nabla u^\varepsilon &= D\Phi^{-T} \nabla \tilde{u}^\varepsilon, \\ \partial_t u^\varepsilon &= \partial_t \tilde{u}^\varepsilon - D\Phi^{-T} \nabla \tilde{u}^\varepsilon \cdot \partial_t \Phi, \\ \frac{1}{|I_i^\varepsilon(t)|} \int_{I_i^\varepsilon(t)} \nabla u^\varepsilon \cdot \nu &= \frac{1}{|I_i^\varepsilon(0)|} \int_{I_i^\varepsilon(0)} D\Phi^{-T} \nabla \tilde{u}^\varepsilon \cdot \nu, \\ \nabla U^\varepsilon &= D\Phi^{-T} \tilde{U}^\varepsilon_{\cdot||\cdot} D\Phi^{-1}, \end{aligned}$$

where, since the displacement has covariant components,

$$\tilde{U}^\varepsilon_{i||j} := \partial_j \tilde{U}^\varepsilon_i - \Gamma^q_{ij} \tilde{U}^\varepsilon_q = (\nabla \tilde{U}^\varepsilon)_{ij} - \Gamma^q_{ij} \tilde{U}^\varepsilon_q. \tag{4.24}$$

Analogously for the symmetrisation of the displacement gradient

$$e_{i||j}(\nabla \tilde{U}^\varepsilon) := e_{ij}(\nabla \tilde{U}^\varepsilon) - \Gamma^q_{ij} \tilde{U}^\varepsilon_q.$$

For brevity of notation we state in $e_{i||j}(\nabla \tilde{U}^\varepsilon)$ only the dependence on the function $\nabla \tilde{U}^\varepsilon$ and not on $\tilde{U}^\varepsilon$ and $\nabla \tilde{U}^\varepsilon$.

The part of the Cauchy stress $\check{\sigma}_S$ has contravariant components and transforms, written in components, to

$$\tilde{\sigma}_S(\nabla \tilde{U}^\varepsilon)^{ij} = \tilde{K}^{ijkl} e_{k||l}(\nabla \tilde{U}^\varepsilon) = \tilde{K}^{ijkl}(e_{kl}(\nabla \tilde{U}^\varepsilon) - \Gamma^q_{kl} \tilde{U}^\varepsilon_q) \tag{4.25}$$

with the transformed stiffness tensor

$$\tilde{K}^{ijkl} = \lambda_S g^{ij} g^{kl} + \mu_S (g^{ik} g^{jl} + g^{il} g^{jk}).$$

In principle we would have to write $\tilde{\sigma}_S(\nabla \tilde{U}^\varepsilon, \tilde{U}^\varepsilon)^{ij}$ in order to state the dependence of $\tilde{\sigma}_S$ on the gradient of the displacement and the displacement itself, but for keeping notation short we write $\tilde{\sigma}_S(\nabla \tilde{U}^\varepsilon)^{ij}$ instead. The formula (4.25) is derived in [Cia00], too.

Summarising after transformation on fixed domain the mechanical BVP (4.1) – (4.3) reads

$$\tilde{\sigma}_S^{\cdot j}||_j(\nabla \tilde{U}^\varepsilon) = \tilde{f}_0^\varepsilon \qquad \text{in } \Omega_S^\varepsilon(0), \tag{4.26}$$

$$\tilde{\sigma}_S(\nabla \tilde{U}^\varepsilon)\nu = \tilde{g}_0^\varepsilon \nu \qquad \text{on } \partial\Omega(0), \tag{4.27}$$

$$\Big(\tilde{\sigma}_S(\nabla \tilde{U}^\varepsilon) - \frac{3k_L}{\varepsilon^3 r_i} \fint_{I_i^\varepsilon(0)} (\tilde{U}^\varepsilon \cdot \nu)\Big)\nu = \tilde{g}_i^\varepsilon \nu \qquad \text{on } I_i^\varepsilon(0)\ \forall i \in N, \tag{4.28}$$

where the transformed divergence of the reduced Cauchy stress is according to Lemma 4.1, 2)

$$\begin{aligned}\tilde{\sigma}^{i\cdot}_S||_{\cdot}(\nabla\tilde{U}^\varepsilon) &:= \tilde{\sigma}^{ij}_S||_j(\nabla\tilde{U}^\varepsilon) := \operatorname{div}\tilde{\sigma}^{i\cdot}_S(\nabla\tilde{U}^\varepsilon) + \Gamma^i_{pj}\tilde{\sigma}^{pj}_S(\nabla\tilde{U}^\varepsilon) + \Gamma^j_{jp}\tilde{\sigma}^{ip}_S(\nabla\tilde{U}^\varepsilon)\\ &= \tilde{K}^{ijkl}(\partial_{z_j}e_{kl}(\nabla\tilde{U}^\varepsilon) - \Gamma^q_{kl}(\nabla\tilde{U}^\varepsilon)_{qj}) - (\Gamma^k_{pj}\tilde{K}^{plij} + \Gamma^l_{pj}\tilde{K}^{pkij})e_{kl}(\nabla\tilde{U}^\varepsilon)\\ &\quad + (\Gamma^k_{pj}\tilde{K}^{plij} + \Gamma^l_{pj}\tilde{K}^{pkij})\Gamma^q_{kl}\tilde{U}^\varepsilon_q.\end{aligned}$$

We examine the dependence of the mechanical BVP in time in order to state a problem for the transformed velocity field

$$\tilde{v}^\varepsilon = \partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_t\Phi. \tag{4.29}$$

By transformation on fixed domain of the problem (4.26) – (4.28) for the displacement $\tilde{U}^\varepsilon$ and derivation w.r.t. time we find the following problem for $\eta := \partial_t\tilde{U}^\varepsilon$.

$$\begin{aligned}\tilde{\sigma}^{\cdot j}_S||_j(\nabla\eta) &= -(\operatorname{div}(\partial_t\tilde{\sigma}_S)(\nabla\tilde{U}^\varepsilon)\\ &\quad + \partial_t\Gamma^{\cdot}_{pj}\tilde{\sigma}^{pj}_S(\nabla\tilde{U}^\varepsilon) + \partial_t\Gamma^j_{jp}\tilde{\sigma}^{\cdot p}_S(\nabla\tilde{U}^\varepsilon)\\ &\quad + \partial_t f^\varepsilon_0 && \text{in } \Omega^\varepsilon_S(0), \quad (4.30)\\ \tilde{\sigma}_S(\nabla\eta)\nu &= (-(\partial_t\tilde{\sigma}_S)(\nabla\tilde{U}^\varepsilon) + \partial_t g^\varepsilon_0)\nu && \text{on } \partial\Omega(0), \quad (4.31)\\ (\tilde{\sigma}_S(\nabla\eta) - \frac{3k_L}{\varepsilon^3 r_i}\fint_{I^\varepsilon_i(0)}(\eta\cdot\nu))\nu &= (-(\partial_t\tilde{\sigma}_S)(\nabla\tilde{U}^\varepsilon)\\ &\quad + [-\frac{3k_L}{\varepsilon^3 r_i^2}\fint_{I^\varepsilon_i(0)}(\tilde{U}^\varepsilon\cdot\nu) + \partial_{r_i}g^\varepsilon_i]\dot{r}_i)\nu && \text{on } I^\varepsilon_i(0)\ \forall i\in N^\varepsilon, \quad (4.32)\end{aligned}$$

$$\begin{aligned}\text{where } (\partial_t\tilde{\sigma}_S)(\nabla\tilde{U}^\varepsilon)^{ij} &:= \lambda_S[\partial_t g^{ij}e_{k||l}(\nabla\tilde{U}^\varepsilon)g^{kl} + g^{ij}(\partial_t e)_{k||l}(\nabla\tilde{U}^\varepsilon)g^{kl} + g^{ij}e(\nabla\tilde{U}^\varepsilon)_{k||l}\partial_t g^{kl}]\\ &\quad + \mu_S[\partial_t g^{ik}e_{k||l}(\nabla\tilde{U}^\varepsilon)g^{jl} + g^{ik}(\partial_t e)_{k||l}(\nabla\tilde{U}^\varepsilon)g^{jl} + g^{ik}e_{k||l}(\nabla\tilde{U}^\varepsilon)\partial_t g^{jl}\\ &\quad + \partial_t g^{il}e_{l||k}(\nabla\tilde{U}^\varepsilon)g^{jk} + g^{il}(\partial_t e)_{l||k}(\nabla\tilde{U}^\varepsilon)g^{jk} + g^{il}e_{l||k}(\nabla\tilde{U}^\varepsilon)\partial_t g^{jk}]\\ \text{and } (\partial_t e)_{i||j}(\nabla\tilde{U}^\varepsilon) &:= -\partial_t\Gamma^q_{ji}\tilde{U}^\varepsilon_q.\end{aligned}$$

For details of the derivation of the velocity problem we refer to Appendix B.3.

The transformed diffusion problem in the regime (DC) is

$$\begin{aligned}&\varepsilon^3\sqrt{\det g}\mathcal{X}(\tilde{u}^\varepsilon)(\partial_t\tilde{u}^\varepsilon - D\Phi^{-T}\nabla\tilde{u}^\varepsilon(\partial_t\Phi - \partial_t\tilde{U}^\varepsilon +\\ &\quad + D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_t\Phi)) - \nabla\cdot(\sqrt{\det g}g^{-1}\nabla\tilde{u}^\varepsilon)\\ &+\varepsilon^3\nabla\cdot(\sqrt{\det g}D\Phi^{-1}(\partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}))\Xi(\tilde{u}^\varepsilon) = 0 && \text{in } \Omega^\varepsilon_S(0) \quad (4.33)\\ &\nabla\tilde{u}^\varepsilon\cdot\nu = 0 && \text{on } \partial\Omega(0), \quad (4.34)\\ &\tilde{u}^\varepsilon = \tilde{u}_{int}(r_i) && \text{on } I^\varepsilon_i(0)\ \forall i\in N^\varepsilon, \quad (4.35)\\ &\tilde{u}^\varepsilon(\cdot, t=0) = u^0 && \text{in } \Omega^\varepsilon_S(0), \quad (4.36)\end{aligned}$$

and the transformed ODEs are

$$\begin{aligned}\dot{r}_i &= \varepsilon^3\frac{\fint_{I^\varepsilon_i(0)} D\Phi^{-T}\nabla\tilde{u}^\varepsilon\cdot\nu}{\mathbb{X}(\tilde{R}, \fint_{I^\varepsilon_i(0)}\tilde{U}^\varepsilon\cdot\nu)} && \forall i\in N^\varepsilon, \quad (4.37)\\ r_i(t=0) &= r^0_i && \forall i\in N^\varepsilon, \quad (4.38)\\ \dot{R}_{bd} &= \fint_{\partial\Omega(0)}(\partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_R\Phi\cdot\partial_t R)\cdot\nu, && (4.39)\\ R_{bd}(t=0) &= R^0_{bd}. && (4.40)\end{aligned}$$

We remark, that the modification of (4.10) yields that, $\dot{R}_{bd}$ does not appear on the r.h.s. in (4.39). We also give the transformed diffusion problem in the formulation with $\tilde{n}^\varepsilon_{As}$ as unknown

$$\begin{aligned}
&\varepsilon^3(\partial_t\tilde{n}^\varepsilon_{As} - D\Phi^{-1}\partial_t\Phi\cdot\nabla\tilde{n}^\varepsilon_{As}) + \varepsilon^3\frac{1}{\sqrt{\det g}}\times\\
&\times\nabla\cdot(\sqrt{\det g}D\Phi^{-1}\tilde{n}^\varepsilon_{As}(\partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_t\Phi))\\
&\qquad -\frac{1}{\sqrt{\det g}}\nabla\cdot(\sqrt{\det g}g^{-1}\nabla u^\varepsilon(\tilde{n}^\varepsilon_{As})) = 0 \qquad \text{in } \Omega^\varepsilon_S(0), && (4.41)\\
&\nabla\tilde{n}^\varepsilon_{As}\cdot\nu = 0 \qquad \text{on } \partial\Omega(0), && (4.42)\\
&\tilde{n}^\varepsilon_{As} = \tilde{n}^{int}_{As}(r_i) \qquad \text{on } I^\varepsilon_i(0)\,\forall i\in N^\varepsilon, && (4.43)\\
&\tilde{n}^\varepsilon_{As}(\cdot, t=0) = n^{0,\varepsilon}_{As} \qquad \text{in } \Omega^\varepsilon_S(0), && (4.44)
\end{aligned}$$

and in the transformed ODEs we replace (4.37) by

$$\dot{r}_i = \varepsilon^3\frac{u'(\tilde{n}^{int}_{As})\,⨍_{I^\varepsilon_i(0)} D\Phi^{-T}\nabla\tilde{n}^\varepsilon_{As}\cdot\nu}{\mathbb{X}(\tilde{R}, ⨍_{I^\varepsilon_i(0)}\tilde{U}^\varepsilon\cdot\nu)} \qquad \forall i\in N^\varepsilon. \tag{4.45}$$

With the formulas $\partial_{z_i}\sqrt{\det g} = \sqrt{\det g}\Gamma^q_{qi}$ (for a proof we refer to [Cia00], proof of Th. 1.6-1, step (i)) we can rewrite (4.41) as

$$\begin{aligned}
\partial_t\tilde{n}^\varepsilon_{As} + \frac{1}{\sqrt{\det g}}&\nabla\cdot(\sqrt{\det g}D\Phi^{-1}(\partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_t\Phi))\tilde{n}^\varepsilon_{As}\\
&-D\Phi^{-1}(\partial_t\Phi - (\partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_t\Phi))\cdot\nabla\tilde{n}^\varepsilon_{As}\\
&-\Gamma^q_{qi}g^{i,\cdot}\varepsilon^{-3}\tilde{u}^{\varepsilon\prime}(\tilde{n}^\varepsilon_{As})\nabla\tilde{n}^\varepsilon_{As} - \nabla\cdot(g^{-1}\varepsilon^{-3}\tilde{u}^{\varepsilon\prime}(\tilde{n}^\varepsilon_{As})\nabla\tilde{n}^\varepsilon_{As}) = 0.
\end{aligned}$$

We introduce

$$\alpha := D\Phi^{-1}(\partial_t\tilde{U}^\varepsilon - (\mathbb{I} + D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1})\partial_t\Phi) - \Gamma^q_{qi}g^{i,\cdot}\varepsilon^{-3}\tilde{u}^{\varepsilon\prime}(\tilde{n}^\varepsilon_{As}), \tag{4.46}$$

$$\beta := D\Phi^{-1}\nabla\cdot(\partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_t\Phi), \qquad \gamma := \varepsilon^{-3}g^{-1}\tilde{u}^{\varepsilon\prime}(\tilde{n}^\varepsilon_{As}). \tag{4.47}$$

For our following analysis it turns out to be useful to treat the more general case of a transformed diffusion problem with a source term $\tilde{f}$ on the r.h.s. Instead of (4.41) we look at the diffusion equation, written in divergence form,

$$\begin{aligned}
&\partial_t\tilde{n}^\varepsilon_{As} - \nabla\cdot(\gamma(x,t,\tilde{n}^\varepsilon_{As})\nabla\tilde{n}^\varepsilon_{As}) + \alpha(x,t,\tilde{n}^\varepsilon_{As},\partial_t\tilde{U}^\varepsilon,\tilde{U}^\varepsilon,\nabla\tilde{U}^\varepsilon,\partial_t\tilde{R},\tilde{R})\cdot\nabla\tilde{n}^\varepsilon_{As}\\
&+\beta(x,t,\nabla\cdot\partial_t\tilde{U}^\varepsilon,\tilde{U}^\varepsilon,\nabla\tilde{U}^\varepsilon,\Delta\tilde{U}^\varepsilon,\partial_t\tilde{R},\tilde{R})\tilde{n}^\varepsilon_{As} = \tilde{f}.
\end{aligned} \tag{4.48}$$

Sometimes it is more useful to work with the PDE in nondivergence form

$$\partial_t\tilde{n}^\varepsilon_{As} - a(x,t,\tilde{n}^\varepsilon_{As},\tilde{R})\Delta\tilde{n}^\varepsilon_{As} + b(x,t,\tilde{n}^\varepsilon_{As},\nabla\tilde{n}^\varepsilon_{As},\nabla\cdot\partial_t\tilde{U}^\varepsilon,\tilde{U}^\varepsilon,\nabla\tilde{U}^\varepsilon,\Delta\tilde{U}^\varepsilon,\partial_t\tilde{R},\tilde{R}) = \tilde{f}, \tag{4.49}$$

where we abbreviated

$$\begin{aligned}
b &= [\alpha - \nabla_x\gamma]\cdot\nabla\tilde{n}^\varepsilon_{As} + \beta\tilde{n}^\varepsilon_{As} - \partial_{\tilde{n}^\varepsilon_{As}}\gamma\,|\nabla\tilde{n}^\varepsilon_{As}|^2\\
&= [D\Phi^{-1}(\partial_t\tilde{U}^\varepsilon - (\mathbb{I} + D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1})\partial_t\Phi) - \Gamma^q_{qi}g^{i,\cdot}\varepsilon^{-3}\tilde{u}^{\varepsilon\prime}(\tilde{n}^\varepsilon_{As}) - \nabla g^{-1}\varepsilon^{-3}\tilde{u}^{\varepsilon\prime}(\tilde{n}^\varepsilon_{As})]\cdot\nabla\tilde{n}^\varepsilon_{As}\\
&\quad + (D\Phi^{-1}\nabla\cdot(\partial_t\tilde{U}^\varepsilon - D\Phi^{-T}\tilde{U}^\varepsilon_{\cdot||\cdot}D\Phi^{-1}\partial_t\Phi)))\tilde{n}^\varepsilon_{As} - g^{-1}\varepsilon^{-3}u''(\tilde{n}^\varepsilon_{As}))|\nabla\tilde{n}^\varepsilon_{As}|^2\\
a &= \gamma = g^{-1}\varepsilon^{-3}u'(\tilde{n}^\varepsilon_{As})).
\end{aligned}$$

In the case that we assume $\tilde{U}$ and $\tilde{R}$ to be given we write in the following just

$$\alpha(x,t,\tilde{n}^{\varepsilon}_{As}), \quad \beta(x,t), \quad \gamma(x,t,\tilde{n}^{\varepsilon}_{As}) \quad \text{or} \quad a(x,t,\tilde{n}^{\varepsilon}_{As}), \quad b(x,t,\tilde{n}^{\varepsilon}_{As},\nabla\tilde{n}^{\varepsilon}_{As}).$$

We refer to the mechanical BVP (4.26) – (4.28) with the velocity problem (4.30) – (4.32) and the diffusion problem (4.48), (4.42) – (4.44) and the radii evolutions, (4.45), (4.38) – (4.40), as **transformed Problem E**.

4.3. Local existence and uniqueness

First we solve independently a general version of both the mechanical problem (4.26) – (4.28) and the velocity problem (4.30) – (4.32), then the diffusion problem (4.48), (4.41) – (4.44) and then the ODEs (4.45), (4.38) – (4.40) for interfaces on fixed domain, where we assume that the data in each of the problems is already known. This serves as a building block for proving local existence and uniqueness of a generalised solution to the transformed Problem E by a fixed point argument in this section.

We emphasise that ε is fixed and our local existence and uniqueness result holds for any allowed choice of ε. Later it turns out, that ε has to be sufficiently small in order to avoid collisions of droplets with each other or with the outer boundary, that is needed for the global existence and uniqueness result, which follows in Section 4.4.

We skip in the following the indices ε on scaled functions and domains, since we consider only scaled functions and scaled domains from now on.

4.3.1. Mechanical boundary value problems

Instead of the problem (4.26) – (4.28) and (4.30) – (4.32) we analyse in the following the more general type of mechanical boundary value problem. We recall that Φ and g depend on x, t and $\tilde{R}$. Find a function $\eta \in H^1(\Omega_S(0);\mathbb{R}^3)$ s.t.

$$\tilde{S}^{jk}||_k(\nabla\eta,\tilde{R}) = -F_0^j(\nabla\tilde{U}^{\varepsilon},\tilde{R},\partial_t\tilde{R}) + F_1^{jk}||_k(\tilde{u}^{\varepsilon},\tilde{R}) \qquad \text{in } \Omega_S^{\varepsilon}(0), \tag{4.50}$$

$$\tilde{S}^{jk}(\nabla\eta,\tilde{R})\nu_k = (G_0(\nabla\tilde{U}^{\varepsilon},\tilde{R},\partial_t\tilde{R}) + F_1^{jk}(\tilde{u}^{\varepsilon},\partial_t u^{\varepsilon}))\nu_k \qquad \text{on } \partial\Omega(0), \tag{4.51}$$

$$(\tilde{S}^{jk}(\nabla\eta,\tilde{R}) \tag{4.52}$$

$$-C(r_i)\fint_{I_i^{\varepsilon}(0)}\eta^l\nu_l)\nu_k = (G_i(\nabla\tilde{U}^{\varepsilon},\tilde{R},\partial_t\tilde{R}) + F_1^{jk}(\tilde{u}^{\varepsilon},\partial_t u^{\varepsilon}))\nu_k \qquad \text{on } I_i^{\varepsilon}(0)\ \forall i\in N^{\varepsilon}, \tag{4.53}$$

where the equations hold for all components $j \in \{1,2,3\}$ and the tensor field $\tilde{S}$ fulfils

$$\tilde{S}^{jk}(\nabla\eta,\tilde{R}) = \tilde{K}^{jklm}(\tilde{R})e_{l||m}(\nabla\eta,\tilde{R})$$

with $\tilde{K}^{jklm}(\tilde{R}) = \tilde{K}^{jkml}(\tilde{R})$ and $e_{l||m} = e_{m||l}$ as defined in (4.2). If we assume $\tilde{R}$ to be given explicitly then we write only $\tilde{S}^{jk}(\nabla\eta)$ and $\tilde{e}(\nabla\eta)$. Furthermore we do not denote the dependency on x explicitly.

The abstract problem (4.50) – (4.52) can be applied to the displacement problem and the velocity problem as well. For the problem for $\tilde{U}$ i.e. (4.26) – (4.28) we set $\eta = \tilde{U}$ and for the data

$$F_0^j = 0, \quad F_1{}^{jk} = 0 \quad G_0^{jk} = (\overline{p}-p_0)\delta^{jk}, \quad G_i^{jk} = (\frac{2\sigma}{r_i} - 3k_L(\delta^R(r_i) + h_L^*(r_i)))\delta^{jk} \quad \forall i \in N,$$

or for the problem for $\partial_t \tilde{U}$ i.e. (4.30) – (4.32) we set $\eta = \partial_t \tilde{U}$ and

$$\begin{aligned}
&F_0^j = 0, \quad F_1 = -(\partial_t \tilde{\sigma}_S)(\tilde{U}^{\varepsilon})^{jk}, \quad G_0^{jk} = 0, \\
&G_i^{jk} = -[\frac{3k_L}{\varepsilon^3 r_i^2} \fint_{I_i^{\varepsilon}(0)} ((\tilde{U}^{\varepsilon})^l \nu_l) + 3k_L {h_L^*}'(r_i) - 3k_S h^{*\prime} + \frac{2\sigma}{r_i^2}]\dot{r}_i \delta^{jk} \quad \forall i \in N,
\end{aligned}$$

where the time-derivatives of the Christoffel symbols, of g and of $D\Phi$ depend on the given evolution of $\tilde{R}$. In both cases $C(r_i) = \frac{3k_L}{\varepsilon^3 r_i}$. We formulate the consequences of the following theorem for the transformed Problem E in Th. 4.2 and Th. 4.3.

Theorem 4.1 (Abstract mechanical BVP)**.** *Assume for all* $t \in (0, \mathcal{T})$ *that* $\Omega_S(t) \in \mathbb{R}^3$ *is given and that* Φ *is a* C^2 *diffeomorphism of* $\overline{\Omega_S(0)}$ *onto* $\overline{\Omega_S(t)}$*, s.t. the three vectors* g_q *are linearly independent at all points* $z \in \overline{\Omega_S(0)}$*.*

Let $\lambda_S \geq 0, \mu_S > 0, k_L > 0$*.*

We assume that our data fulfils the compatibility condition

$$\int_{\Omega_S(0)} F_0^k \phi_k \, dz + \int_{\partial\Omega_S(0)} G_0^{jk} \phi_k \nu_j \, d\tilde{A} - \sum_{i \in N} \int_{I_i} G_i^{jk} \phi_k \nu_j \, d\tilde{A} = 0 \tag{4.54}$$

for all $\phi \in RD$*.*

1) (Existence of a weak solution)

If $F_0^j, F_1^{jk} \in L^{6/5}(\Omega_S(0))$*,* $G_0^{jk}\nu_k \in L^{4/3}(\partial\Omega(0))$ *and* $G_i^{jk}\nu_k \in L^{4/3}(I_i(0))$ *for all* $i \in N$*, then there exists a weak solution* $\eta \in H^1(\Omega_S(0); \mathbb{R}^3)$ *of (4.50)-(4.52), i.e.*

$$\begin{aligned}
&\int_{\Omega_S(0)} \tilde{K}^{jklm} e_{l||m}(\nabla\eta) e_{j||k}(\nabla\phi) \sqrt{\det g} \, dz + \sum_{i \in N} C(r_i) (\fint_{I_i} \eta^k \nu_k) \int_{I_i} \phi^k \nu^k \sqrt{\det g} \, d\tilde{A} \\
&= \int_{\Omega(0)} (F_0^j \phi_j - F_1^{jk} \partial_k \phi_j) \sqrt{\det g} \, dz + \int_{\partial\Omega_S(0)} G_0 \delta^{jk} \phi_k \nu_j \sqrt{\det g} \, d\tilde{A} - \sum_{i \in N} \int_{I_i} G_i \delta^{jk} \nu_j \phi_j \sqrt{\det g} \, d\tilde{A}
\end{aligned}$$

for all $\phi \in H^1(\Omega_S(0); \mathbb{R}^3)$*. Furthermore* $|\frac{\fint_{I_i} \eta^k \nu_k}{r_i}| \leq Const(F_0, F_1, \{G_i, r_i\}_{i \in \{0\} \cup N})$*.*

2) (Uniqueness)

η *is unique only up to functions in the class of equivalence RD as defined in Def. 2.1, i.e.* η *is non unique up to translations and rotations (that corresponds to Galilei invariance of the PDE) and only* $\nabla\eta$ *can be determined uniquely.*

3) (Regularity result)

If the boundary is smooth i.e. $\partial\Omega_S(0) \in C^{m+2}$*,* $m \in \mathbb{N} \setminus \{0\}$ *and* $F_0^j \in W^{m,p}(\Omega_S(0))$ *for* $p \geq \frac{6}{5}$ *and* $F_1^{jk} \in W^{m+1,6/5}(\Omega_S(0))$*,* $G_0^{jk}\nu_k \in H^{1-1/p,p}(\partial\Omega(0))$*,* $G_i^{jk}\nu_k \in H^{1-1/p,p}(I_i(0))$ *then* $\eta \in W^{m,p}$*.*

Hence for $m = 2$ *and* $p = 2$ *there exists a classical solution* $\eta \in C^2$*.*

4) (Consistence with approximation of small displacement gradients)

If $\|F_0\|_{L^{6/5}(\Omega_S(0))}$*,* $\|F_1\|_{L^{6/5}(\Omega_S(0))}$*,* $\|G_0\|_{L^{4/3}(\partial\Omega_S(0))}$*,* $\{\|G_i\|_{L^{4/3}(I_i(0))}\}_{i \in N} \leq \max\{\lambda_S, \mu_S, k_L\} \mathcal{O}(\tilde{h})$*, then we have*

$$\|\nabla\eta\|_{L^2(\Omega_S(0))}, \; \|\frac{\fint_{I_i} \eta^k \nu_k}{r_i}\|_{L^2(I_i(0))} \leq Const_2(\lambda_S, \mu_S, k_L, \Omega_S(0), \Phi) \, \mathcal{O}(\tilde{h}),$$

where $Const_2$ *is independent of* $\tilde{h}$ *for sufficiently small but fixed* ε*. This justifies our approximation of small displacement gradients of Assumption 2.1 for* $\tilde{h} \ll 1$*.*

5) (Dependence on time)

In this problem time enters as a parameter. Assume the time evolution given by $\tilde{R} \in L^2(0, \mathcal{T})$ *and the data to be* L^2 *in time. Then we have* $\eta \in L^2H^1$*. For smooth enough boundaries and data we get* $\eta \in L^2C^2$*.*

6) (Results for time-dependent domain)

If $\mathcal{T} < \min_{i\in N} \tau_i$*, then the transformation* Φ *is smooth and then all results 1) - 5) carry over to the problem on* $\Omega_S(t)$*.*

We remark, that for the proof it is not important that we consider $\fint_{I_i} \eta^k\nu_k$ instead of $\eta^k\nu_k$ on the l.h.s. of (4.52), if each G_i is constant on I_i.

Proof. We want to follow the classical results like in [Cia98], p. 296, Th. 6.3-6 for cartesian coordinates and its generalisation to curvilinear coordinates [Cia00], p. 52+53, Th. 1.8-2. Note, that up to the term $-C(r_i) \fint_{I_i^\varepsilon(0)} \eta^p\nu_p$ on the l.h.s. of (4.52) our problem is a standard so-called pure-traction problem, which is treated in literature for Cartesian coordinates and curvilinear coordinates as well. The assumptions on the mapping Φ ensure that Γ^i_{jk} and g_{ij} are continuous on $\overline{\Omega_S(0)}$.

$\lambda_S \geq 0, \mu_S > 0$ guarantee that the tensor $\tilde{K}$ is uniformly positive definite i.e. there exists a constant $c(\Omega_S, \Phi, \mu_S)$, where $c \propto \frac{1}{2\mu_S}$, s.t.

$$\sum_{i,j} |t_{ij}|^2 \leq c\tilde{K}^{ijkl}(z) t_{kl} t_{ij} \tag{4.55}$$

for all $z \in \Omega_S(0)$ and for all symmetric matrices t_{ij}. For details we refer to [Cia00], Th. 1.8-1. $k_L > 0$ implies $C > 0$.

1) (Existence of a weak solution)

We consider first a fixed time $t \in (0, \mathcal{T})$ s.t. the data is well-defined at t. Due to definition of the covariant derivative and since $\tilde{S}$ is symmetric there holds

$$\begin{aligned}
&\int_{\Omega_S(0)} \tilde{S}^{jk}(\nabla\eta) e_{j||k}(\phi)\sqrt{\det g}\, dz \\
&= -\int_{\Omega_S(0)} \tilde{S}^{jk||k}(\nabla\eta)\phi_j \sqrt{\det g} dz + \int_{\partial\Omega_S(0)} \tilde{S}^{jk}(\nabla\eta)\phi_j\nu_k \sqrt{\det g}\, d\tilde{A}
\end{aligned}$$

for all $\phi \in H^1(\Omega_S; \mathbb{R}^3)$.

We test (4.50) with $\eta \in H^1(\Omega_S(0); \mathbb{R}^3)$ and get with the definition of $\tilde{S}$ and the boundary conditions

$$\begin{aligned}
&\int_{\Omega_S(0)} \tilde{K}^{jklm} e_{l||m}(\nabla\eta) e_{j||k}(\nabla\eta)\sqrt{\det g}\, dz + \sum_{i\in N} C(r_i)|I_i|[\fint_{I_i} \eta^k\nu_k\sqrt{\det g}\, d\tilde{A}]^2 \\
&= \int_{\Omega_S(0)} (F_0^j\eta_j - F_1^{jk}\partial_k\eta_j)\sqrt{\det g}\, dz + \int_{\partial\Omega(0)} G_0\delta^{jk}\eta_j\nu_k\sqrt{\det g}\, d\tilde{A} - \sum_{i\in N}\int_{I_i} G_i\delta^{jk}\eta_j\nu_k\sqrt{\det g}\, d\tilde{A}.
\end{aligned}$$

By exploiting (4.55) together with $C > 0$ we can estimate

$$\begin{aligned}
&\frac{1}{c}\int_{\Omega_S(0)} |e_{j||k}(\nabla\eta)|^2\sqrt{\det g}\, dz \\
&\leq \int_{\Omega_S(0)} (F_0^j\eta_j - F_1^{jk}\partial_k\eta_j)\sqrt{\det g}\, dz + \int_{\partial\Omega(0)} G_0\delta^{jk}\eta_j\nu_k\sqrt{\det g}\, d\tilde{A} - \sum_{i\in N}\int_{I_i} G_i\delta^{jk}\eta_j\nu_k\sqrt{\det g}\, d\tilde{A}.
\end{aligned}$$

By using again our assumptions on Φ we can apply Korn's inequality for curvilinear coordinates (see [Cia98], [Cia00], Th. 1.7-4) on the space H^1/RD, since $\|e_{j||k}\|_{L^2(\Omega_S(0))}$ is not only a semi-norm as on $H^1(\Omega_S(0))$ but a norm on the quotient space $H^1(\Omega_S(0))/RD$ ([Cia98]; [DL76], p. 119),

$$\sum_{j,k}\int_{\Omega_S(0)} |\partial_j\eta^k|^2\sqrt{\det g}\,dz \le K\int_{\Omega_S(0)} |e_{j||k}(\nabla\eta)|^2\sqrt{\det g}\,dz,$$

where $K = K(\Omega_S(0),\Phi) > 0$ is Korn's constant. Now we can estimate together with the Sobolev embedding theorem $H^1(G) \subset L^6(G)$ ([Cia98], Th. 6.1-3 1.) and the trace theorem $H^1(G) \subset L^4(\partial G)$ ([Cia98], Th. 6.1-7 (a) 1.) since $n = 3$, that

$$\|\nabla\eta\|_{L^2(\Omega_S(0))} \le \frac{c}{K}(\|F_0\|_{L^{6/5}(\Omega_S(0))} + \|F_1\|_{L^{6/5}(\Omega_S(0))} + \|G_0\|_{L^{4/3}(\partial\Omega(0))} + \sum_{i\in N}\|G_i\|_{L^{4/3}(I_i(0))}). \tag{4.56}$$

This shows existence of an $\eta \in H^1/RD$ fulfilling the given integral identity for data $F_j \in L^{6/5}$, $0 \le j \le 2$, $G_i \in L^{4/3}, i \in \{0\} \cup N$. Furthermore we can estimate

$$|\int_{I_i}\eta^k\nu_k\sqrt{\det g}\,d\tilde{A}| \le \frac{c}{K}\frac{\sqrt{4\pi}}{\sqrt{3k_L}}\varepsilon^{9/2}r_i^{3/2}(\sum_{j=0}^{1}\|F_j\|_{L^{6/5}(\Omega_S(0))} + \|G_0\|_{L^{4/3}(\partial\Omega(0))} + \sum_{i\in N}\|G_i\|_{L^{4/3}(I_i(0))}). \tag{4.57}$$

2) (Uniqueness)

If we assume that there exist two solutions $\eta^{(1)}$ and $\eta^{(2)}$, then the difference $\eta = \eta^{(1)} - \eta^{(2)}$ solves the problem with zero data. The space of infinitesimal rigid displacements RD, which is defined in Def. 2.1, is the kernel of $\tilde{S}(\nabla\eta)$, see [Cia00], Th. 1.7-3 a). In our estimate (4.57), where the norms of the data on the l.h.s. are now zero, also the square of $\fint_{\Gamma_i}\eta\cdot\nu$ has to vanish for a function $a + b \times z$ in RD. We compute $\fint_{\Gamma_i}(a + b \times z)\cdot\nu = 0$ by exploiting local spherical coordinates i.e. $\fint_{\Gamma_i}(a+b\times z)\cdot\nu = \fint_{\Gamma_i}(a^r e_r + b\times r_i e_r)\cdot e_r r_i^2 dA(r)$ and then that the parallelepipedal product $(b\times x)\cdot\nu$ is cyclic. Hence we have uniqueness if and only if $\eta \in H^1/RD$.

3) (Regularity result)

We refer to the remark following Th. 6.3-6 in the first volume of the book of Ciarlet [Cia98], the third volume [Cia00] and the references there in: There hold regularity results for problems with pure Dirichlet boundary conditions, also called pure-displacement problems, or problems with pure Neumann boundary conditions, also called pure-traction problems, or for problems with Neumann b.c. and Dirichlet b.c., so-called displacement-traction problems. For the proof of these regularity results it is to verify in particular that $\tilde{S}$ is uniformly elliptic and the supplementary and complementing conditions of Agmon, Douglis, Nirenberg [ADN64], [RR04] for the space H_0^1 in the first case and for the quotient space H^1/RD in the last two cases are satisfied. Important is for the displacement-traction problem, that there is no point of the boundary, where the type of boundary condition changes.

In order to transfer this to our situation — we have Neumann b.c. on $\partial\Omega$ or mixed b.c. on I_i — we split up our mechanical problem into a problem for U_1, where we modify the b.c. on I_i s.t. we have only Neumann b.c. $\tilde{S}^{jk}(\nabla\eta,\tilde{R})\nu_k = 0$ on I_i, and into a problem for U_2 s.t. we have only Dirichlet b.c. $C(r_i)\fint_{I_i^\varepsilon(0)}\eta^l\nu_l\nu_k = 0$ on $I_i^\varepsilon(0)$, $\tilde{S}^{jk}(\nabla\eta,\tilde{R}) = 0$ on $\partial\Omega$ and $\mathrm{div}\tilde{S}^{jk} = 0$ in Ω_S. For U_1 we can apply the regularity result of the pure-traction problem and $U_2 \equiv 0$ is a solution, which is unique according to 2). Then $U = U_1 + U_2$ solves our full problem and the regularity results transfer from the pure-traction problem to the U in our situation.

The condition that the boundary is of class C^{m+2} is fulfilled for all m due to our restriction on spherical boundaries. Then from $\eta \in H^{m+2,2}(\Omega_S(0))$, for $m \geq 3/2$ the Sobolev to Hölder embedding theorem yields the C^2 result. Hence η is a classical solution for all times t.

4) (Consistence with approximation of small displacement gradients)

From the estimates (4.56) and (4.57) proved in 1) follows that, if the norms are bounded by $\mathcal{O}(\tilde{h})$ times a constant, that this holds for $\|\nabla\eta\|_{L^2(\Omega_S(0))}$ and $\fint_{I_i} \eta^k \nu_k$, where

$$Const_2 = \max(\lambda_S, \mu_S, k_L)\frac{c(\Omega_S(0), \Phi, \mu_S)}{K(\Omega_S(0), \Phi)}.$$

Since $c \propto \frac{1}{2\mu_S}$ and $\lambda_S, k_L = \mathcal{O}(\mu_S)$ and we can expect for sufficiently small but fixed ε that the influence of the geometry and the transformation is limited on the constants and $\|\nabla\eta\|_{L^2(\Omega_S(0))}$, $|\fint_{I_i} \eta^k \nu_k| = \mathcal{O}(\tilde{h})$.

5) (Dependence on time)

Now we let t vary in $(0, \mathcal{T})$. For the regularity in time of η we consider a sequence of corresponding BVP's on fixed domain $\Omega_S(0)$ with solution $\eta(t)$, where t is a parameter. Since our problem is a linear PDE the norms of $\eta(t)$ depend linearly on the data, whose regularity in time is given: the statement about the integrability in time follows for $\Omega_S(0)$ by integrating (4.56) and (4.57) on both sides w.r.t. time.

6) (Results for time-dependent domain)

If $\mathcal{T} < \min_{i \in N} \tau_i$ we can assume the existence of a smooth transformation Φ and all estimates carry over to the problem on time-dependent domain Ω_S. ☐

We formulate the consequences of Th. 4.1 for our transformed Problem E. We note that it can also be applied to the mechanical displacement problem as considered in Problem DCR if $\tilde{u}^\varepsilon \in H^2(\Omega_S^\varepsilon(0))$ or to the velocity problem corresponding to Problem DCR if $\partial_t \tilde{u}^\varepsilon \in H^1(\Omega_S^\varepsilon(0))$.

Theorem 4.2 (Displacement problem on fixed domain)**.**
Assume for all $t \in (0, \mathcal{T})$ that $\Omega_S(t) \in \mathbb{R}^3$ is given and that Φ is a C^2 diffeomorphism of $\overline{\Omega_S(0)}$ onto $\overline{\Omega_S(t)}$, s.t. the three vectors g_q are linearly independent at all points $z \in \overline{\Omega_S(0)}$. Let $\partial\Omega_S(0)$ be smooth.

Let $\lambda_S \geq 0, \mu_S > 0, k_L > 0$, let $r_i \geq r_{min}$, let $\sigma > 0$, $\overline{p}$, p_0, δ^R be given constants and let h^*, h_L^* be given smooth functions.

1) (Existence of a weak solution)

If $\tilde{n}_{As} \in L^{6/5}(\Omega_S(0))$, then there exists a weak solution $\tilde{U} \in H^1(\Omega_S(0); \mathbb{R}^3)$ of (4.26) – (4.28). Furthermore $|\frac{\fint_{I_i} \tilde{U}^k \nu_k}{r_i}| \leq Const(\tilde{n}_{As})$.

2) (Uniqueness)

$\tilde{U}$ is unique only up to functions in the class of equivalence RD, as defined in Def. 2.1, i.e. $\tilde{U}$ is non unique up to translations and rotations (that corresponds to Galilei invariance of the PDE), only $\nabla\tilde{U}$ can be determined uniquely.

3) (Regularity result)

If $\tilde{n}_{As} \in W^{m,p}(\Omega_S(0))$ for $p \geq \frac{6}{5}$, then $\tilde{U} \in W^{m,p}$. Hence for $m = 2$ and $p = 2$ i.e. if $\tilde{n}_{As} \in H^2(\Omega_S(0))$ there exists a classical solution $\tilde{U} \in C^2$.

4) (Consistence with approximation of small displacement gradients)

Let $\frac{\overline{p}-p_0}{3k_S}, h^*, \frac{2\sigma}{3k_L r_{min}}, \delta^R$ be of order $\mathcal{O}(\tilde{h})$ and let $\|\tilde{n}_{As}\|_{L^{6/5}(\Omega_S(0))} \leq \kappa$, $\kappa \in \mathcal{O}(\tilde{h}^0)$.

Then we have

$$\|\nabla\tilde{U}\|_{L^2(\Omega_S(0))},\ \|\frac{\fint_{I_i}\tilde{U}^k\nu_k}{r_i}\|_{L^2(I_i(0))} \leq Const_1(\lambda_S,\mu_S,k_L,\Omega_S(0),\Phi)\mathcal{O}(\tilde{h}),$$

where $Const_1 = \mathcal{O}(\tilde{h}^0)$ *for sufficiently small but fixed* ε*. This justifies our approximation of small displacement gradients of Assumption 2.1, if* $\tilde{h} \ll 1$*.*

5) (Dependence on time)

Assume the free boundaries $\tilde{R} = (R, R_{bd})$ *to be given and at least in* $[L^2(0,\mathcal{T})]^{\mathcal{N}^0+1}$ *and the data of the displacement problem to be* L^2 *in time, then we have* $\tilde{U} \in L^2H^1$*.*

For the time derivative of the displacement we have the following result.

Theorem 4.3 (Velocity problem on fixed domain)**.** *We make the same assumptions as in the last theorem 4.2. Furthermore we assume now the evolutions of free boundaries to be given,* $\tilde{R} \in [H^1(0,\mathcal{T})]^{\mathcal{N}^0+1}$ *with* $\sup_{i\in N}\tilde{R}_i \leq k$*.*

1) (Existence of a weak solution)

If $\tilde{n}_{As} \in H^1W^{1,6/5}(\Omega_S(0))$*,* $\tilde{U} \in L^2H^1$ *then there exists a weak solution* $\partial_t\tilde{U} \in H^1(\Omega_S(0);\mathbb{R}^3)$ *of (4.30) – (4.32). Furthermore* $|\frac{\fint_{I_i}\partial_t\tilde{U}^k\nu_k}{r_i}| \leq Const(\tilde{n}_{As},\Phi)$*.*

2) (Uniqueness)

$\partial_t\tilde{U}$ *is unique only up to functions in the class of equivalence RD. If* $\tilde{U}$ *is unique up to* $a + b \times z$ *then* $\partial_t\tilde{U}$ *is unique up to* $\partial_t a + \partial_t b \times z$*.*

3) (Regularity result)

If $\tilde{n}_{As} \in H^1W^{m,p}(\Omega_S(0))$ *for* $p \geq \frac{6}{5}$*, then* $\partial_t\tilde{U} \in W^{m,p}$*. Note, that* $\tilde{U} \in L^2H^2(\Omega_S(0))$*, needed here, follows from Th. 4.2 3) by the regularity assumptions on* $\tilde{n}_{As}$*. Hence for* $m = 2$ *and* $p = 2$*, i.e. if* $\tilde{n}_{As} \in H^1H^2(\Omega_S(0))$*, there exists a classical solution* $\partial_t\tilde{U} \in C^2$*.*

4) (Consistence with approximation of small displacement gradients)

If $\frac{2\sigma}{3k_L r_{min}}$ *are of order* $\mathcal{O}(\tilde{h})$ *and if* $\|\tilde{n}_{As}\|_{H^1W^{1,6/5}(\Omega_S(0))} \leq \kappa$*,* $\kappa \in \mathcal{O}(\tilde{h}^0)$*, then we have*

$$\|\nabla\partial_t\tilde{U}\|_{L^2(\Omega_S(0))},\ \|\frac{\fint_{I_i}\partial_t\tilde{U}^k\nu_k}{r_i}\|_{L^2(I_i(0))} \leq \frac{k}{r_{min}}Const_1'(\lambda_S,\mu_S,k_L,\Omega_S(0),\Phi)\mathcal{O}(\tilde{h}),$$

where $Const_1' = \mathcal{O}(\tilde{h}^0)$ *for sufficiently small but fixed* ε*. This justifies our approximation of small displacement gradients of Assumption 2.1, if* $\tilde{h} \ll 1$*.*

5) (Dependence on time)

Under the assumptions of 1) the data of the velocity problem is L^2 *in time. Then we have together with Th. 4.2 5) that* $\tilde{U} \in H^1H^1$*. For smooth enough boundaries and data, i.e. we get* $\tilde{U} \in H^1C^2 \subset C^0C^2$*.*

6) (Velocity)

For the velocity $\tilde{v}$ *as defined in 4.29 we get together with Th. 4.2 the same results as in 1) – 5) for* $\partial_t\tilde{U}$*.*

We check that the assumptions on the data in the Th. 4.1 are fulfilled by the assumptions in Th. 4.2 and in Th. 4.3. The compatibility condition (4.54) is fulfilled for the displacement problem and the velocity problem, since

$$\int_S \phi_j\nu_k\delta^{jk} = \int_S A_{kl}b_l\nu_k + \int_S c_k\nu_k = 0 \tag{4.58}$$

for A a skew-symmetric matrix, c a constant vector and S an arbitrary smooth closed surface.

Hence Th. 4.2 and Th. 4.3 follow.

Remark 4.2. *The assumptions on the constants $\lambda_S, \mu_S, k_L, \sigma, r_{min}, \overline{p}, p_0, \delta^R$ in Theorem 4.2 and Theorem 4.3 are fulfilled for typical experimental values.*

Theorem 4.4 (Displacement and velocity problem on time-dependent domain)**.**
If $\mathcal{T} < \min_{i \in N(0)} \tau_i$ and further the transformation Φ on fixed domain is smooth, then all statements from Theorem 4.2 and Theorem 4.3 hold also for the problem on $\Omega_S(t)$ instead on $\Omega_S(0)$, too.

The statement from 4.2 4) justifies our approximation of (2.12) by (2.13) i.e. $v = \partial_t U$.

4.3.2. Diffusion problem

In order to prove local existence of a solution of the transformed diffusion problem we need a maximum and minimum principle while for global existence we will even need a comparison principle. We prove a comparison principle which implies a maximum and minimum principle for n_{As} and, since the chemical potential u depends strictly monotone on n_{As}, the As particle density in the solid, we get a comparison, maximum and minimum principle on u as well. Analogously we could replace n_{As} (or u) by the relative lattice occupancy $y = y_{As_\gamma}$ of As on the γ sublattice in the following lemmata and theorems of this subsection. We chose to work in the remaining part of this subsection with n_{As} as variable, since this allows to compare with standard results for quasilinear parabolic PDE more directly.

Since our transformation Φ is smooth we can equivalently deal with the equation on time-dependent domain as long as we assume that an evolution of free boundaries is given. But before we have to introduce some general definitions.

Definition 4.6 (Sub- and supersolution)**.** *We say that $\underline{\eta}$ is a subsolution to the diffusion problem in the regime (DC)* (4.19) – (4.22) *if*

$$\partial_t \underline{\eta} + \nabla \cdot (\underline{\eta} v) - \varepsilon^{-3} \Delta u(\underline{\eta}) \leq 0 \qquad \text{in } \Omega_S(t) \tag{4.59}$$

$$\nabla \underline{\eta} \cdot \nu \leq 0 \qquad \text{on } \partial\Omega(t), \tag{4.60}$$

$$\underline{\eta} \leq n_{As}^{int}(r_i) \qquad \text{on } I_i(t)\, \forall i \in N, \tag{4.61}$$

$$\underline{\eta}(\cdot, t = 0) \leq n_{As}^0 \qquad \text{in } \Omega_S(0). \tag{4.62}$$

Analogously, we say that $\hat{\eta}$ is a supersolution to (4.19) – (4.22) *if*

$$\partial_t \hat{\eta} + \nabla \cdot (\hat{\eta} v) - \varepsilon^{-3} \Delta u(\hat{\eta}) \geq 0 \qquad \text{in } \Omega_S(t) \tag{4.63}$$

$$\nabla \hat{\eta} \cdot \nu \geq 0 \qquad \text{on } \partial\Omega(t), \tag{4.64}$$

$$\hat{\eta} \geq n_{As}^{int}(r_i) \qquad \text{on } I_i(t)\, \forall i \in N, \tag{4.65}$$

$$\hat{\eta}(\cdot, t = 0) \geq n_{As}^0 \qquad \text{in } \Omega_S(0). \tag{4.66}$$

We emphasise that we assume that a solution U of the mechanical BVP and a radii evolution $\tilde{R}$ is given and fixed for all solutions, sub- and supersolutions.

Remark 4.3 (Equality and inequalities in Sobolev spaces)**.** *In the preceding definition we understand "$\geq$" for the weak formulation in the sense of $H^1(\Omega)$, which is defined as in [KS00], p. 35, Def. 5.1. This means that we expect $\Delta u(\eta) \in L^2$.*

This definition says: Let Ω be a bounded connected domain of $\mathbb{R}^N$, $E \subset \overline{\Omega}$ and $f \in H^1(\Omega)$. $u \geq 0$ on E in $H^1(\Omega)$, iff there exists a sequence $f_n \in H^{1,\infty}$ s.t. $f_n(x) \geq 0$ for $x \in E$, $f_n \to f \in H^1(\Omega)$.

Analogously we define "$\leq$" in sense of H^1 and "$=$" in sense of H^1 if "$\geq$" and "$\leq$" hold in sense of H^1.

We remind that this definition is equivalent to the notion $f \geq 0$ on Ω a.e., but this equivalence does not hold e.g. for sets E of measure zero, see [KS00], p. 35, prop. 5.2 and the following remark therein.

Lemma 4.2 (Comparison principle for the diffusion problem)**.** *We assume the evolution of free boundaries $\tilde{R} \in H^1(0, \mathcal{T})$ to be given and that $v \in L^\infty(0, \mathcal{T}; W^{1,\infty}(\Omega_S(t)))$.*

Let u be a strictly monotone and smooth function in n_{As} and let for two functions $\underline{n}_{As}, \hat{n}_{As}$

$$\begin{aligned}
\partial_t(\underline{n}_{As} - \hat{n}_{As}) + \nabla \cdot (v(\underline{n}_{As} - \hat{n}_{As})) - \varepsilon^{-3}\Delta(u(\underline{n}_{As}) - u(\hat{n}_{As})) &\leq 0 && \text{in } \Omega_S(t) && (4.67)\\
\partial_\nu(\underline{n}_{As} - \hat{n}_{As}) &\leq 0 && \text{on } \partial\Omega(t), && (4.68)\\
\underline{n}_{As} - \hat{n}_{As} &\leq 0 && \text{on } I_i(t)\ \forall i \in N, && (4.69)\\
(\underline{n}_{As} - \hat{n}_{As})(\cdot, t = 0) &\leq 0 && \text{in } \Omega_S(0). && (4.70)
\end{aligned}$$

1) If $\underline{n}_{As}, \hat{n}_{As} \in C_1^2(0, \mathcal{T}; \Omega_S(t))$ then

$$\underline{n}_{As} \leq \hat{n}_{As} \quad \forall (x,t) \in \{(t, \Omega_S^\varepsilon(t)) | 0 \leq t < \mathcal{T}\}.$$

2) If $\underline{n}_{As}, \hat{n}_{As} \in L^\infty(0, \mathcal{T}, W^{1,\infty}(\Omega_S(t)))$ and $u'(n_{As})$ is bijective in $\mathcal{J}_n := n_{As}(\mathcal{J}_y)$, then

$$\underline{n}_{As} \leq \hat{n}_{As} \quad \text{for a. a. } (x,t) \in \{(t, \Omega_S^\varepsilon(t)) | 0 \leq t < \mathcal{T}\}.$$

The bijectivity of u w.r.t. n_{As} follows from Assumption 4.2.

We remark, that a maximum and minimum principle holds under assumptions, which are weaker than $\underline{n}_{As} \in L^\infty L^2 \cap L^2 H^1$ or $\hat{n}_{As} \in L^\infty L^2 \cap L^2 H^1$.

Proof of 2). Let $\phi := \max(\underline{n}_{As} - \hat{n}_{As}, 0) \in L^\infty W^{1,\infty}$. We prove the statement of the lemma by contradiction. We assume that there exists a set $M := \{(x,t) \in \Omega_T | \phi(x,t) > 0\}$, w.l.o.g. let $M = \{(t, G(t)) | t \in (0, \mathcal{T})\}$.

We test the problem (4.19) – (4.22) with ϕ in space and get after an integration by parts

$$\begin{aligned}
&\int_{G(\tau)} (\partial_t(\underline{n}_{As} - \hat{n}_{As}) + \nabla \cdot (v(\underline{n}_{As} - \hat{n}_{As})))(\underline{n}_{As} - \hat{n}_{As}) + \varepsilon^{-3}\nabla(u(\underline{n}_{As}) - u(\hat{n}_{As}))\cdot \\
&\cdot \nabla(\underline{n}_{As} - \hat{n}_{As}) - \int_{\partial G(\tau)\cap\partial\Omega(\tau)} \partial_\nu(\underline{n}_{As} - \hat{n}_{As})(\underline{n}_{As} - \hat{n}_{As}) \leq 0,
\end{aligned} \tag{4.71}$$

where we emphasise that $\partial G \cap I_i = \emptyset$ at any time and that we omit the last term in the following since it is nonnegative due to (4.68).

If we only wanted to prove a maximum or minimum principle we would set

$$\hat{n}_{As} = \max\{\max_{i\in N} n_{As}^{int,i}, \sup_{\Omega(0)} n_{As}^0\},$$

which is constant in space, and get

$$\int_{G(\tau)} (\partial_t(\underline{n}_{As} - \hat{n}_{As}) + \nabla \cdot (v(\underline{n}_{As} - \hat{n}_{As})))(\underline{n}_{As} - \hat{n}_{As}) + \int_{G(\tau)} \varepsilon^{-3} u'(\underline{n}_{As}) |\nabla \underline{n}_{As}|^2 \leq 0$$

which could be led to a contradiction as in the following without further regularity assumptions on $\underline{n}_{As}$.

For a minimum principle we would set $\underline{n}_{As} = \min\{\min_{i \in N} n_{As}^{int,i}, \inf_{\Omega(0)} n_{As}^0\}$, multiply with -1 and would get an inequality with inverse sign and proceed analogously.

But for a comparison principle we have to exploit the additional assumption $\underline{n}_{As}, \hat{n}_{As} \in L^\infty W^{1,\infty}$ and exploit that u' is bijective, which holds e.g. for $u \geq 0$ (i.e. $y \geq 1$).

The mean value theorem of differential calculus gives the existence of a function ξ, $\underline{n}_{As} < \xi < \hat{n}_{As}$ s.t.

$$u(\underline{n}_{As}) - u(\hat{n}_{As}) = u'(\xi)(\underline{n}_{As} - \hat{n}_{As}),$$

where ξ is as smooth as u, $\underline{n}_{As}$ and $\hat{n}_{As}$ if $u'(\xi)$ is bijective, since

$$\xi = (u')^{-1}(\frac{u(\underline{n}_{As}) - u(\hat{n}_{As})}{\underline{n}_{As} - \hat{n}_{As}}).$$

This allows us to rewrite the second integral in (4.71) as

$$\begin{aligned}
&\int_{G(\tau)} |\nabla(\underline{n}_{As} - \hat{n}_{As})|^2 u'(\xi) + \varepsilon^{-3} u''(\xi) \nabla\xi (\underline{n}_{As} - \hat{n}_{As}) \cdot \nabla(\underline{n}_{As} - \hat{n}_{As}) \\
\geq &\int_{G(\tau)} |\nabla(\underline{n}_{As} - \hat{n}_{As})|^2 u'(\xi) - \varepsilon^{-3} \|u''(\xi)\|_{L^\infty(G(\tau))} \|\nabla\xi\|_{L^\infty(G(\tau))} \times \\
&\times (\frac{1}{2\delta} \|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))} + \frac{\delta}{2} \|\nabla(\underline{n}_{As} - \hat{n}_{As})\|^2_{L^2(G(\tau))}) \\
\geq &\frac{\min_{\xi \in \mathcal{J}_n} u'(\xi)}{2} \int_{G(\tau)} |\nabla(\underline{n}_{As} - \hat{n}_{As})|^2 - \frac{\varepsilon^{-3}}{2\delta} \|u''(\xi)\|_{L^\infty(G(\tau))} \|\nabla\xi\|_{L^\infty(G(\tau))} \|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))},
\end{aligned}$$

where we have chosen $\delta < \frac{\varepsilon^3 \min_{\xi \in \mathcal{J}_n} u'(\xi)}{\|u''(\xi)\|_{L^\infty(G(\tau))} \|\nabla\xi\|_{L^\infty(G(\tau))}}$ small enough. Since the first term in the last inequality is nonnegative we have to consider only

$$\begin{aligned}
\int_{G(\tau)} \frac{1}{2}(\partial_t |\underline{n}_{As} - \hat{n}_{As}|^2 + \nabla \cdot (v |\underline{n}_{As} - \hat{n}_{As}|^2)) + \frac{1}{2}(\nabla \cdot v) |\underline{n}_{As} - \hat{n}_{As}|^2 \\
- \frac{1}{2\delta\varepsilon^3} \|u''(\xi)\|_{L^\infty(G(\tau))} \|\nabla\xi\|_{L^\infty(G(\tau))} \|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))} \leq 0.
\end{aligned}$$

We apply Reynolds transport theorem and Lemma 3.1 and estimate downwards

$$\partial_\tau \|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))} - (\|\nabla \cdot v\|_{L^\infty(M)} + \frac{1}{\delta\varepsilon^3} \|u''(\xi)\|_{L^\infty(M)} \|\nabla\xi\|_{L^\infty(M)}) \|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))} \leq 0$$

and integrate now in time

$$\|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))} - \tilde{c} \int_0^t \|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))} d\tau \leq 0,$$

where we introduced the positive constant $\tilde{c} = \|\nabla \cdot v\|_{L^\infty(M)} + \frac{1}{\delta\varepsilon^3} \|u''(\xi)\|_{L^\infty(M)} \|\nabla\xi\|_{L^\infty(M)}$ and exploited $\partial M \cap \Omega_S(0) = \emptyset$. We apply the lemma of Gronwall and get since we had no additive constant on the r.h.s. of the last inequality that

$$\|\underline{n}_{As} - \hat{n}_{As}\|^2_{L^2(G(\tau))} \leq 0,$$

which is a contradiction, unless $G(t) = \emptyset$ where $0 < t < \mathcal{T}$ is arbitrary. $\square$

We remark that if an inequality holds in sense of H^1 in time this implies that the inequality holds pointwise in time due to the embedding $H^1 \hookrightarrow C^0$ in one dimension.

Proof of 1). For comparison principles it is appropriate to work with the differential operator in nondivergence form. We follow the proof of ([Fri64], Th. 16, p.52), but we have to include a homogeneous Neumann boundary condition on $\partial\Omega$ additionally and we deal with inequalities in some statements, where our reference works with strict inequalities, and vice versa. We introduce $p_i := \partial_i \eta$, $P_{i,j} := \partial_{i,j}\eta$, $1 \le i,j \le 3$ and check preliminarily that

$$F(x,t,\eta,p,P) := -\nabla\cdot v(x,t)\eta - v(x,t)\cdot p + \varepsilon^{-3}u''(\eta)|p|^2 + \varepsilon^{-3}u'(\eta)\sum_{i=1}^{3} P_{i,i}$$

is continuous together with its first derivative w.r.t. $P_{i,j}$, $1 \le i,j \le 3$ and $\partial_{P_{i,j}}F$ is a positive definite matrix, since due to the strict monotonicity of u

$$\partial_{P_{i,j}}F(x,t,\eta,p,P) = \varepsilon^{-3}u'(\eta)\delta_{i,j} > 0. \tag{4.72}$$

First we examine the case, when we have strict inequality in (4.67).

We consider the maximal time $\tau := \sup_{t\in[0,\mathcal{T})}\{\hat{n}_{As} \ge \underline{n}_{As} \quad \forall x \in \overline{\Omega_S(t)}\}$. If we prove that $\tau = \mathcal{T}$, then our lemma is demonstrated.

Due to (4.70) we have $\tau > 0$. If we assume $\tau < \mathcal{T}$ then $\hat{n}_{As} - \underline{n}_{As}$ is nonnegative in $Z_\tau := \{(x,t)|x \in \overline{\Omega_S(t)}, 0 \le t \le \tau\}$ and there exists a point $(x_0,t_0) \in Z_{t_0}$ for some space point $x_0 \in \Omega_S(t_0) \cap \partial\Omega(t_0)$ ($x_0 \notin I_i$ due to (4.69)) and some time t_0, $\tau < t_0 < \mathcal{T}$ s.t. $\hat{n}_{As} < \underline{n}_{As}$. If the only such space point $x_0 \in \partial\Omega(t_0)$, this is a contradiction to $\partial_\nu(\hat{n}_{As} - \underline{n}_{As}) \ge 0$. Hence there exists a minimum point (x_0,t_0) in $\Omega_S(t_0)$ and necessarily, $\nabla(\hat{n}_{As} - \underline{n}_{As})(x_0,t_0) = 0$.

Consider now the infimum of all t_0, i.e. $t_0 = \tau$ with corresponding x_0. Then $\hat{n}_{As}(x_0,t_0) = \underline{n}_{As}(x_0,t_0)$. Since (x_0,t_0) is a minimum in $\Omega_S(t_0)$, the Hessian is positive semidefinite:

$$\partial_{i,j}(\hat{n}_{As} - \underline{n}_{As})(x_0,t_0) \ge 0.$$

W.l.o.g. by a change of coordinate system, where we exploit that $\partial_{P_{i,j}}F$ is symmetric and uniformly elliptic, see (4.72), we can assume

$$\sum_{i,j=1}^{3} \partial_{P_{i,j}}F(\xi)\partial_{i,j}(\hat{n}_{As} - \underline{n}_{As})(x_0,t_0) \ge 0, \tag{4.73}$$

for any $\xi \in \Omega_{\mathcal{T}} \times \mathbb{R}^3 \times \mathbb{R}^{3\times 3}$. Indeed by a linear transformation $x \to y = Cx$, $\Omega_S(t) \to \Omega_S^*(t)$ with C s.t. $C\partial_{P_{i,j}}F(\xi)C^T = \mathbb{I}_3$, $(\hat{\eta} - \underline{\eta})(y,t) = (\hat{n}_{As} - \underline{n}_{As})(x,t)$ and then $y_0 = Cx_0$ is the new minimum in $\Omega_S^*(t)$. Then (4.73) follows, where we replaced w.l.o.g. y_0 by x_0 and $\hat{\eta} - \underline{\eta}$ by $\hat{n}_{As} - \underline{n}_{As}$.

The mean value theorem applied to $F(\cdot,P)$ in the minimum (x_0,t_0) yields with (4.73)

$$F(x_0,t_0,\hat{n}_{As},\nabla\hat{n}_{As},D^2\hat{n}_{As}) - F(x_0,t_0,\hat{n}_{As},\nabla\hat{n}_{As},D^2\underline{n}_{As}) \ge 0$$

and hence $\partial_t(\hat{n}_{As} - \underline{n}_{As})(x_0,t_0) > 0$ due to (4.67), but $(\hat{n}_{As} - \underline{n}_{As})(x_0,t_0) \le (\hat{n}_{As} - \underline{n}_{As})(x,t)$ for all $(x,t) \in Z_\tau$, a contradiction unless $\tau = \mathcal{T}$.

In order to enlarge our result to the case of non strict inequality in (4.67), we perturb $\hat{n}_{As} - \underline{n}_{As}$ and work with $z^\delta := (\hat{n}_{As} - \underline{n}_{As}) + \delta t$, $\delta > 0$ and replace F by $F^\delta := F + \delta t\,\eta(x,t)\nabla\cdot v(x,t)$. There exists $\mathcal{T}^\delta < \min\{\frac{\delta}{\max_{(0,\mathcal{T}^\delta)}\max_{\Omega_S(t)}|(\hat{n}_{As} - \underline{n}_{As})\nabla\cdot v|}, \mathcal{T}\}$ s.t. the strict inequality holds for t up to $\mathcal{T}^\delta$ and we can apply our previous result to z^δ and hence $z^\delta \ge 0$ or $\hat{n}_{As} - \underline{n}_{As} \ge -\delta t$. If we let $\delta \to 0$, where we remind that F^δ depends smoothly on δ, we find the statement of the lemma, since we can start again with $\mathcal{T}^\delta$ as new initial time. □

Remark: we allowed the non-strict inequality in (4.59), (4.63) and (4.67) only for the following corollary, for other applications of the comparison principle the strict inequality would be enough.

Remark: the last lemma does not apply for a subsolution $\underline{n}_{As}$ and a supersolution $\hat{n}_{As}$ but for any $\underline{n}_{As}$ and any $\hat{n}_{As}$ that fulfil the partial differential inequality (4.67) – (4.70).

We abbreviate

$$n_{As}^{int,min} := \lim_{r\to\infty} n_{As}^{int}(r), \quad n_{As}^{int,max} := n_{As}^{int}(r_{min})$$

or analogously

$$u_{int}^{min} := \lim_{r\to\infty} u_{int}(r), \quad u_{int}^{max} := u_{int}(r_{min}).$$

Furthermore we introduce

$$\hat{F} := \max\{n_{As}^{int,max}, sup_{\Omega_S(0)} n_{As}^0\}, \qquad \underline{F} := \min\{n_{As}^{int,min}, \inf_{\Omega_S(0)} n_{As}^0\} \tag{4.74}$$

$$\text{or } \hat{F} := \max\{u_{int}^{max}, sup_{\Omega_S(0)} u^0\}, \qquad \underline{F} := \min\{u_{int}^{min}, \inf_{\Omega_S(0)} u^0\}. \tag{4.75}$$

Corollary 4.1 (Uniqueness of classical solution of the diffusion problem)**.** *If we have two classical solutions* η_1, η_2 *in the sense of Definition 4.3 of the diffusion problem, we can plug them into the comparison principle and we get immediately* $\eta_1 \leq \eta_2$ *and* $\eta_1 \geq \eta_2$ *i.e. the solution is unique almost everywhere.*

Corollary 4.2 (Weak maximum and minimum principle for the diffusion problem)**.** [1] *Let* $\tilde{R} \in H^1$ *and* $v \in L^\infty W^{1,\infty}$. *If* $\underline{n}_{As} \in L^\infty L^2 \cap L^2 H^1$ *is a subsolution to (4.19) – (4.22) then there holds*

$$\sup_{\Omega_T} \underline{u} \leq \max\{\max_{i\in N} u_{int}(r_i), \sup_{\Omega_S(0)} u_0\} \leq \hat{F}$$

or for a supersolution $\hat{n}_{As} \in L^\infty L^2 \cap L^2 H^1$ *we have*

$$\underline{F} \leq \min\{\min_{\{i\in N\}} u_{int}(r_i), \inf_{\Omega_S(0)} u_0\} \leq \inf_{\Omega_T} \hat{u}.$$

Corollary 4.3 (Sub- and supersolution on Ω_S)**.** *Let* $\tilde{R} \in H^1$ *and* $v \in L^\infty W^{1,\infty}$. *The constant function* $\hat{F}$ *and* $\max\{n_{As}^{int,max}, sup_{\Omega_S(0)} n_{As}^0\}$, *constant in space, are supersolutions on* Ω_S, *while* $\underline{F}$ *and* $\min\{n_{As}^{int,min}, \inf_{\Omega_S(0)} n_{As}^0\}$ *are global subsolutions.*

Corollary 4.4 (Weak bounds on the solution of the diffusion problem)**.** *Let* $\tilde{R} \in H^1$ *and* $v \in L^\infty W^{1,\infty}$. *If a solution* $n_{As} \in L^\infty L^2 \cap L^2 H^1$ *exists then*

$$\underline{F} \leq \min\{\min_{\{i\in N\}} n_{As}^{int,i}, \inf_{\Omega(0)} n_{As}^0\} \leq n_{As} \leq \max\{\max_{\{i\in N\}} n_{As}^{int,i}, \sup_{\Omega(0)} n_{As}^0\} \leq \hat{F}. \tag{4.76}$$

Theorem 4.5 (Existence and uniqueness of the diffusion problem on fixed domain)**.** *We treat the more general case of the transformed diffusion problem (4.48), (4.42) – (4.44) where we allow* β *also to depend on* η.

We assume that n_{As}^{int} *is* C^2 *and we assume initial and boundary data s.t.*

$$0 \leq n_{As}^0, n_{As}^{int} \leq n_{As}^{max} := \lim_{u\to\infty} n_{As}(u).$$

Remark: by our choice of $n_{As}^{int}(r_i)$ *the last assumptions on* n_{As}^{int} *are fulfilled for arbitrary* r_i.

Let $\mathcal{T} < \infty$, *let be given the evolutions* $\tilde{R} = (R, R_{bd}) \in [H^1(0,\mathcal{T})]^{\mathcal{N}^0+1}$ *with* $\sup_{i\in N} \tilde{R}_i \leq k$, *and let*

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[1] For brevity we just use the notion “maximum principle” when we refer to the “maximum and minimum principle”.

the following smoothness assumptions on α, β, γ hold,

$$\alpha(x,t,\eta)\cdot\xi \text{ is bounded and continuous in } \eta \quad \forall(x,t)\in\Omega_S^0\times(0,\mathcal{T}),\forall\xi\in\mathbb{R}^3 \tag{4.77}$$

$$\beta(x,t,\eta) \text{ is bounded and continuous in } \eta \quad \forall(x,t)\in\Omega_S^0\times(0,\mathcal{T}), \tag{4.78}$$

$$\xi\cdot\gamma(x,t,\eta)\xi \text{ is bounded and continuous in } \eta \quad \forall(x,t)\in\Omega_S^0\times(0,\mathcal{T}),\forall\xi\in\mathbb{R}^3 \tag{4.79}$$

$$\exists C>0,\ \text{indep. of } x,t,\eta,\ \text{s. t. } \xi\cdot\gamma(x,t,\eta)\xi\geq const|\xi|^2 \quad \forall(x,t)\in\Omega_S^0\times(0,\mathcal{T}),\forall\xi\in\mathbb{R}^3. \tag{4.80}$$

1) *(Existence and uniqueness, first estimate)*

   If the initial data n_{As}^0 is in $L^2(\Omega_S(0))$ and $\tilde{f}\in L^2(0,\mathcal{T};L^2(\Omega_S(t)))$ then there exists a unique solution

   $$\tilde{n}_{As}^\varepsilon\in L^\infty(0,\mathcal{T};L^2(\Omega_S(0)))\cap L^2(0,\mathcal{T};H^1(\Omega_S(0)))$$

   of the transformed diffusion problem (4.48), (4.42) – (4.44) where we allow β to depend on x, t and η. We have the estimate

   $$\|\eta\|_{L^\infty L^2}^2+\|\nabla\eta\|_{L^2L^2}^2\leq c(\|\eta^0\|_{L^2(\Omega_S(0))}^2+\|f\|_{L^2L^2}^2) \tag{4.81}$$

   with a positive constant c depending on $\mathcal{T}$, α, β and γ.

2) *(Existence and uniqueness, second estimate)*

   If $n_{As}^0\in H^1(\Omega_S(0))$ and $\tilde{f}\in L^2(0,\mathcal{T};H^1(\Omega_S(t))$ then exists a unique solution

   $$\tilde{n}_{As}^\varepsilon\in L^\infty(0,\mathcal{T};H^1(\Omega_S(0)))\cap H^1(0,\mathcal{T};L^2(\Omega_S(0)))$$

   in particular $\partial_t n_{As}\in L^2(0,\mathcal{T};L^2(\Omega_S(t)))$ and $\Delta\tilde{n}_{As}^\varepsilon\in L^2(0,\mathcal{T};L^2(\Omega_S(t)))$. An estimate therefor is

   $$\|\nabla\eta\|_{L^\infty L^2}^2+\|\partial_t\eta\|_{L^2L^2}^2\leq c^*(\|\eta^0\|_{H^1(\Omega_S(0))}^2+\|f\|_{L^2L^2}^2) \tag{4.82}$$

   with a positive constant c^* depending on $\mathcal{T}$, α, β and γ.

   As further estimate we have

   $$\|u\|_{L^2H^2}\leq Const\|\mathcal{X}(u)(\partial_t u+v\cdot\nu)+\Xi(u)\nabla\cdot v\|_{L^2L^2}=Const\,\varepsilon^{-3/2}\|\Delta u\|_{L^2L^2} \tag{4.83}$$

   with a constant independent of ε.

3) *(Regularity result)*

   The assumptions on α, β and γ can be weakenend in the sense that measurability in t and x is enough. In particular for our PDE for diffusion in the transformed Problem E it is then enough to assume $\partial_t\tilde{U}$ and $\nabla\partial_t\tilde{U}$ to be measurable e.g. $\partial_t\tilde{U}\in L^2H^1/RD$.

   If we assume additionally $u''(\tilde{n}_{As}^\varepsilon)\geq 0$ (that can be achieved by choosing $\mathcal{J}_n$ s.t. $n_{As}^{min}\geq n_{As}(y_{min})$), initial domain $\Omega_S^0\in C^2$ and initial data $u^0\in H^1$, and if we assume for the nonlinearities,

   $$\alpha(x,t,\eta),\beta(x,t,\eta)\in L^\infty(0,\mathcal{T};\Omega_S(0)),\quad \gamma(x,t,\eta)\in L^5(0,\mathcal{T};\Omega_S(0)) \tag{4.84}$$

   and source term $\tilde{f}\in H^1$, then there exists a unique classical solution

   $$\tilde{n}_{As}^\varepsilon\in C_1^2(0,\mathcal{T};\Omega_S(0)).$$

   Since Φ is smooth this translates into

   $$n_{As}^\varepsilon\in C^1(0,\mathcal{T};C^2(\Omega_S(t))).$$

All assumptions of this theorem on smoothness and on nonlinearities are fulfilled for our concrete model, which is in particular due to $r_i \geq r_{min}$ and $|\dot{r}_i| \leq k$.

We note that, the reason for including a more general $\beta = \beta(x,t,\eta)$ is that we reduce the proof to the case of homogeneous Dirichlet boundary conditions. By this reduction such a term $\beta(x,t,\eta)$ appears in the diffusion equation, anyway.

We could apply results of parabolic theory as in [LSU88] or [RH08], but we give a direct proof for the first two statements of our theorem, since we need explicitly estimates on $\tilde{n}_{As}$, (4.81) and (4.82) later in Section 5.4.

Proof. 1) & 2) (Existence and uniqueness)

The following proof uses the weak maximum principle stated in Corollary 4.2. Roughly speaking, this principle ensures that the nonlinearity explodes only if the solution explodes.

1st step) Simplification to an equivalent problem of same type

Our proof utilises the divergence form of the PDE, i.e. the problem (4.48), (4.42) – (4.44), where we work with a general term $\tilde{f}$ on the r.h.s. This allows w.l.o.g. to work with homogeneous Dirichlet boundary conditions. Indeed this can be justified by considering an extension of the Dirichlet boundary condition n_{As}^{int} smoothly onto Ω_S^0 s.t. the Neumann boundary condition remains unchanged, again denoted by n_{As}^{int} and then substituting $\tilde{n}_{As}^{\varepsilon}$ by $\eta := \tilde{n}_{As}^{\varepsilon} - n_{As}^{int}$, which yields again a problem of same type now with unknown η since n_{As}^{int} is smooth and bounded and the strict monotonicity of u and hence of the new γ-term, which reads now $\gamma(x,t,\eta)$, is preserved. The α-term is replaced by $\alpha(x,t,\eta) - \partial_\eta \gamma(x,t,\eta)\nabla n_{As}^{int}$, β-term is replaced by $\beta(x,t) + \alpha(x,t,\eta) \cdot \nabla n_{As}^{int} + \gamma(x,t,\eta)\Delta n_{As}^{int}$ i.e. now depending on the solution η and the source term just becomes $-\partial_t n_{As}^{int} - \beta(x,t)n_{As}^{int}$. The Assumptions (4.77) – (4.80) and (4.84) hold also for substituted nonlinearities.

2nd step) Approximation scheme

We consider an implicit approximation scheme with semi-discretisation in time, the so-called Rothe's method. For details of Rothe's method we refer e.g. to [Kač85] or [Vis96], ch. II & III, which give both extensions of this method to more general monotone operators. Besides this procedure provides directly a numerical method how to find explicitly the solution.

Let t_Δ^n, $1 \leq n \leq M$, $M \in \mathbb{N}$ the time increments s.t. $\sum_{n=1}^{M} t_\Delta^n = \mathcal{T}$. Time steps are denoted by $t_n := \sum_{i=1}^{n} t_\Delta^n$, $0 \leq n \leq M$, where $t_0 = 0$ is the initial time.

In case of equidistant time steps this means $t_\Delta := t_\Delta^n = \frac{\mathcal{T}}{M}$, $t_n := n(\Delta t)$, $0 \leq n \leq M$, but we want to deal with an adaptive choice of t_Δ^n, which allows faster numeric algorithms.

We denote

$$\eta_{(M)}^n(x) := \eta(t = t_n, x).$$

Note that the lower index M at $u_{(M)}^n$ emphasises the refinement of the time approximation. Clearly $u_{(M)}^0 := u^0$ is the initial data for all $M \in \mathbb{N}$. If not necessary for understanding, we suppress in the following the index M for better readability. Analogously we define

$$\alpha^n := \alpha(t = t_n, \eta = \eta^n), \quad \beta^n := \beta(t = t_n, \eta = \eta^n), \quad \gamma^n := \gamma(t = t_n, \eta = \eta^n) \quad \forall 1 \leq n \leq M$$

and

$$f^n(x) := \frac{1}{t_\Delta^n} \int_{t_{n-1}}^{t_n} \tilde{f}(x,t)dt \quad \forall 1 \leq n \leq M \quad \forall x \in \Omega_S(0).$$

We consider the semi-discretisation of problem (4.48), (4.42) – (4.44) after reduction to homogeneous Dirichlet boundary conditions i.e. the sequence of elliptic problems with solutions η^n,

$1 \le n \le M$, so that

$$\begin{aligned}
\frac{\eta^n-\eta^{n-1}}{t_\Delta} &+ \alpha^n(x,\eta^n)\cdot\nabla\eta^n + \beta^n(x,\eta^n)\eta^n \\
&-\nabla\cdot(\gamma^n(x,\eta^n)\nabla\eta) = f^n && \text{in } \Omega_S^0, && (4.85)\\
&\partial_\nu\eta^n = 0 && \text{on } \partial\Omega^0, && (4.86)\\
&\eta^n = 0 && \text{on } I_i(0)\ \forall i\in N, && (4.87)\\
&\eta^0 = n_{As}^0 - n_{As}^{int}(t=0) && \text{in } \Omega_S(0). && (4.88)
\end{aligned}$$

We show that we can solve problem (4.85) – (4.88) step by step. Fix any $n \in \{1,...,m\}$ and assume $\eta^{n-1} \in L^2(\Omega_S(0))$. We have to determine η^n. Then t_n is fixed and existence and uniqueness of $\eta^n \in H^1(\Omega_S(0))$ follow by standard results for elliptic PDE since we have also $f^n \in L^2(\Omega_S(0))$. But for our purposes we want to get estimates over space AND time.

3rd step) *A priori* estimates

In order to derive the result given in statement 1) of the theorem we test with $t_\Delta^n\eta^n$

$$\int_{\Omega_S(0)} |\eta^n|^2 - \eta^{n-1}\eta^n + t_\Delta^n\alpha^n\cdot\nabla\eta^n\eta^n + t_\Delta^n\beta^n|\eta^n|^2 + t_\Delta^n\gamma^n|\nabla\eta^n|^2 = \int_{\Omega_S(0)} t_\Delta^n f^n\eta^n.$$

With the strict monotonicity of u in η^n we estimate for $\delta_1^n > 0$

$$\begin{aligned}
&(1-\frac{\delta_1^n}{2})\|\eta^n\|^2_{L^2(\Omega_S(0))} - t_\Delta^n\|\alpha^n\|_{L^\infty(\Omega_S(0))}\|\nabla\eta^n\|_{L^2(\Omega_S(0))}\|\eta^n\|_{L^2(\Omega_S(0))}\\
&- t_\Delta^n\|\beta^n\|_{L^\infty(\Omega_S(0))}\|\eta^n\|^2 + t_\Delta^n(\min_{\Omega_S(0)}\|\gamma^n\|)\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))}\\
&\le \frac{1}{2\delta_1^n}\|\eta^{n-1}\|^2_{L^2(\Omega_S(0))} + t_\Delta^n\|f^n\|_{L^2(\Omega_S(0))}\|\eta^n\|_{L^2(\Omega_S(0))}.
\end{aligned}$$

We introduce some abbreviations

$$\hat\alpha^n := \|\alpha^n\|_{L^\infty(\Omega_S(0);\mathbb{R}^3)}, \quad \hat\beta^n := \|\beta^n\|_{L^\infty(\Omega_S(0))}, \quad \underline{\gamma}^n := \min_{\Omega_S(0)}\|\gamma^n\|_{L^\infty(\Omega_S(0);\mathbb{R}^{3\times3})}$$

and furthermore for later

$$\hat\alpha := \max_{1\le n\le M}\hat\alpha^n, \quad \hat\beta := \max_{1\le n\le M}\hat\beta^n, \quad \underline{\gamma} := \min_{1\le n\le M}\underline{\gamma}^n.$$

We rearrange our estimate

$$\begin{aligned}
&(1-\frac{\delta_1^n}{2} - t_\Delta^n(\frac{1}{2\delta_2^n}\hat\alpha^n + \hat\beta^n + \frac{\delta_3^n}{2}))\|\eta^n\|^2_{L^2(\Omega_S(0))} + t_\Delta^n(\underline{\gamma}^n - \frac{\delta_2^n}{2}\hat\alpha^n)\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))}\\
&\le \frac{1}{2\delta_1^n}\|\eta^{n-1}\|^2_{L^2(\Omega_S(0))} + t_\Delta^n\frac{1}{2\delta_3^n}\|f^n\|^2_{L^2(\Omega_S(0))},
\end{aligned}$$

where $\delta_2^n, \delta_3^n > 0$. We choose $\delta_2^n \le \frac{\underline{\gamma}^n}{\hat\alpha^n}$.

Now summing up over n from 1 to m, $1 \le m \le M$ we get

$$\begin{aligned}
&\sum_{n=1}^m(1-\frac{\delta_1^n}{2} - t_\Delta^n(\frac{1}{2}(\frac{(\hat\alpha^n)^2}{\underline{\gamma}_n} + \delta_3^n) + \hat\beta^n))\|\eta^n\|^2_{L^2(\Omega_S(0))} + \frac{1}{2}\sum_{n=1}^m t_\Delta^n\underline{\gamma}^n\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))}\\
&\le \sum_{n=1}^m\frac{1}{2\delta_1^n}\|\eta^{n-1}\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^m t_\Delta^n\frac{1}{2\delta_3^n}\|f^n\|^2_{L^2(\Omega_S(0))}.
\end{aligned}$$

We would like to choose δ_1^n s.t. $1 - \frac{\delta_1^n}{2} - t_\Delta^n(\frac{1}{2}(\frac{(\hat{\alpha}^n)^2}{\underline{\gamma}_n} + \delta_3^n) + \hat{\beta}^n = \frac{1}{2\delta_1^n}$ in order to sum up directly, but this leads to a contradiction. Instead we choose $\delta_1^n = \delta_3^n = 1$ and find by further multiplying by 2

$$\begin{aligned}&\|\eta^m\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^m t_\Delta^n \underline{\gamma}^n \|\nabla\eta^n\|^2_{L^2(\Omega_S(0))}\\&\leq \|\eta^0\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^m t_\Delta^n (\frac{(\hat{\alpha}^n)^2}{\underline{\gamma}_n} + 1 + 2\hat{\beta}^n)\|\eta^n\|^2_{L^2(\Omega_S(0))} + \frac{t_m}{\mathcal{T}}\|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0))}.\end{aligned}$$

We choose
$$t_\Delta^n \leq \frac{1}{2}\frac{1}{\frac{(\hat{\alpha})^2}{\underline{\gamma}} + 1 + 2\hat{\beta}}.$$

We apply the discrete lemma of Gronwall. It states that for non-negative sequences b_n and u_n

$$\begin{aligned}&u_m \leq u_0 + \sum_{n=1}^m b_n u_n\\\implies\quad &u_m \leq u_0(1 + \sum_{n=1}^m b_n \prod_{l=n}^m (1-b_l)^{-1}) \overset{b_n = bt_\Delta^n \leq 1/2}{\leq} u_0(1 + b\sum_{n=1}^m t_\Delta^n \exp(\frac{3}{2}b(t_m - t_{n-1}))),\end{aligned}$$

and get

$$\begin{aligned}&\|\eta^m\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^m t_\Delta^n \underline{\gamma}^n \|\nabla\eta^n\|^2_{L^2(\Omega_S(0))}\\&\leq (1 + (\frac{(\hat{\alpha})^2}{\underline{\gamma}} + 1 + 2\hat{\beta})t_m \exp(\frac{3}{2}(\frac{(\hat{\alpha})^2}{\underline{\gamma}} + 1 + 2\hat{\beta})\mathcal{T}))(\|\eta^0\|^2_{L^2(\Omega_S(0))} + \frac{t_m}{\mathcal{T}}\|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))})\end{aligned}$$

where the r.h.s. is finite if $\mathcal{T} < \infty$ i.e.

$$\|\eta^m\|^2_{L^2(\Omega_S(0))} + \underline{\gamma}\sum_{n=1}^m t_\Delta^n \|\nabla\eta^n\|^2_{L^2(\Omega_S(0))} \leq const(\mathcal{T}, (\hat{a})^2, \hat{b}, \underline{\gamma})(\|\eta^0\|^2_{L^2(\Omega_S(0))} + \|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))}) \tag{4.89}$$

and since m, $1 \leq m \leq M$, is arbitrary

$$\begin{aligned}&\max_{1\leq n\leq M}\|\eta^n\|^2_{L^2(\Omega_S(0))} + \underline{\gamma}\sum_{n=1}^M t_\Delta^n \|\nabla\eta^n\|^2_{L^2(\Omega_S(0))}\\&\leq const(\mathcal{T}, (\hat{a})^2, \hat{b}, \underline{\gamma})(\|\eta^0\|^2_{L^2(\Omega_S(0))} + \|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))}),\end{aligned} \tag{4.90}$$

which is a discretised version of the claimed $L^\infty L^2 \cap L^2 H^1$ estimate for the PDE.

For the estimate given in 2) we test with $\frac{\eta^n - \eta^{n-1}}{\gamma^n t_\Delta^n}$

$$\begin{aligned}&\int_{\Omega_S(0)} \frac{1}{\gamma^n}\frac{|\eta^n - \eta^{n-1}|^2}{(t_\Delta^n)^2} + \frac{1}{t_\Delta^n}\frac{\alpha^n}{\gamma^n}\cdot\nabla\eta^n(\eta^n - \eta^{n-1}) + \frac{1}{t_\Delta^n}\frac{\beta^n}{\gamma^n}(|\eta^n|^2 - \eta^n\eta^{n-1})\\&+ \frac{1}{t_\Delta^n}(|\nabla\eta^n|^2 - \nabla\eta^n\cdot\nabla\eta^{n-1}) + \frac{1}{t_\Delta^n}\frac{\partial_\eta\gamma^n}{\gamma^n}(\nabla\eta^n - \nabla\eta^{n-1})\nabla\eta^n(\eta^n - \eta^{n-1}) = \int_{\Omega_S(0)} \frac{\eta^n - \eta^{n-1}}{\gamma^n t_\Delta^n} f^n.\end{aligned}$$

We estimate by the maximum principle ($\max(\eta^n - \eta^{n-1}) \leq C$)

$$\frac{\partial_\eta\gamma^n}{\gamma^n}(\nabla\eta^n - \nabla\eta^{n-1})|\nabla\eta^n(\eta^n - \eta^{n-1}) \geq -const(\frac{\partial_\eta\gamma^n}{\gamma^n})C\|\nabla\eta^n - \nabla\eta^{n-1})\|\|\nabla\eta^n\|$$

and include this term in the estimate of the $\frac{1}{t_\Delta^n}(|\nabla\eta^n|^2 - \nabla\eta^n \cdot \nabla\eta^{n-1})$ term since we assumed above $-const(\frac{\partial_\eta \gamma^n}{\gamma^n})C < 1$. We proceed as above and get for $\delta_i^n > 0$, $1 \le i \le 4$,

$$\begin{aligned}
&\frac{1}{\hat{\gamma}^n}\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} - \frac{\hat{\alpha}^n}{\underline{\gamma}^n}(\frac{\delta_1^n}{2}\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} + \frac{1}{2\delta_1^n}\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))}) \\
&- \frac{\hat{\beta}^n}{\underline{\gamma}^n}(\frac{\delta_2^n}{2}\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} + \frac{1}{2\delta_2^n}\|\eta\|^2_{L^2(\Omega_S(0))}) + \frac{1}{t_\Delta^n}((1 - \frac{\delta_3^n}{2})\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))} \\
&- \frac{1}{2\delta_3^n}\|\nabla\eta^{n-1}\|^2_{L^2(\Omega_S(0))}) \le \frac{\delta_4^n}{2\underline{\gamma}^n}\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} + \frac{1}{2\delta_4^n\underline{\gamma}^n}\|f^n\|^2_{L^2(\Omega_S(0))},
\end{aligned}$$

where we introduce

$$\hat{\gamma}^n := \max_{\Omega_S(0)}\|\gamma^n\| = \|\gamma^n\|_{L^\infty(\Omega_S(0))}, \quad \hat{\gamma} := \max_{1\le n\le M}\hat{\gamma}^n.$$

This yields by multiplying i.a. with t_Δ^n

$$\begin{aligned}
&(\frac{1}{\hat{\gamma}^n} - \frac{1}{\underline{\gamma}^n}(\frac{\delta_1^n}{2}\hat{\alpha}^n + \frac{\delta_2^n}{2}\hat{\beta}^n + \frac{\delta_4^n}{2}))t_\Delta^n\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} + ((1 - \frac{\delta_3^n}{2}) - \frac{t_\Delta^n}{2\delta_1^n}\frac{\hat{\alpha}^n}{\underline{\gamma}^n})\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))} \\
&\le \frac{1}{2\delta_3^n}\|\nabla\eta^{n-1}\|^2_{L^2(\Omega_S(0))} + \frac{t_\Delta^n}{2\delta_2^n}\frac{\hat{\beta}^n}{\underline{\gamma}^n}\|\eta^n\|^2_{L^2(\Omega_S(0))} + \frac{t_\Delta^n}{2\delta_4^n\underline{\gamma}^n}\|f^n\|_{L^2(\Omega_S(0))}.
\end{aligned}$$

We choose $\delta_3^n = 1$ and $\frac{1}{4}\frac{\underline{\gamma}^n}{\hat{\gamma}^n} \le \delta_1^n\hat{\alpha}^n + \delta_2^n\hat{\beta}^n + \delta_4^n \le \frac{1}{2}\frac{\underline{\gamma}^n}{\hat{\gamma}^n}$, multiply by 2 and sum up as above over n from 1 to m, $1 \le m \le M$,

$$\begin{aligned}
&\sum_{n=1}^m t_\Delta^n\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^m(1 - \frac{t_\Delta^n}{\delta_1^n}\frac{\hat{\alpha}^n}{\underline{\gamma}^n})\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))} \\
&\le \sum_{n=1}^m\|\nabla\eta^{n-1}\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^m\frac{t_\Delta^n}{\delta_2^n}\frac{\hat{\beta}^n}{\underline{\gamma}^n}\|\eta^n\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^m\frac{t_\Delta^n}{\delta_4^n\underline{\gamma}^n}\|f^n\|_{L^2(\Omega_S(0))},
\end{aligned} \tag{4.91}$$

which can be now reformulated with (4.89) as

$$\begin{aligned}
&\sum_{n=1}^m t_\Delta^n\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} + \|\nabla\eta^m\|^2_{L^2(\Omega_S(0))} \\
&\le \|\nabla\eta^0\|^2_{L^2(\Omega_S(0))} + \frac{4\hat{\gamma}\hat{\alpha}}{(\underline{\gamma})^2}\sum_{n=1}^m t_\Delta^n\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))} + \frac{4\hat{\gamma}}{(\underline{\gamma})^2}\|f\|_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))} \\
&\quad + \frac{4\hat{\gamma}\hat{\beta}}{(\underline{\gamma})^2}\sum_{n=1}^m t_\Delta^n(const(\mathcal{T}, \hat{a}, \hat{b}, \underline{\gamma})\|\eta^0\|^2_{L^2(\Omega_S(0))} - \sum_{l=1}^M t_\Delta^l\|\nabla\eta^l\|^2_{L^2(\Omega_S(0))}) \\
&\le \frac{4\hat{\gamma}}{(\underline{\gamma})^2}(\hat{\alpha} - t_m\hat{\beta})\sum_{n=1}^m t_\Delta^n\|\nabla\eta^n\|^2_{L^2(\Omega_S(0))} \\
&\quad + Const(\mathcal{T}, \hat{a}, \hat{b}, \underline{\gamma}, \hat{\gamma})(\|\eta^0\|^2_{H^1(\Omega_S(0))} + \|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))}).
\end{aligned}$$

Again by the discrete lemma of Gronwall or by plugging in (4.89) we finally find a bounded constant $c^*(\mathcal{T}, \hat{a}, \hat{b}, \underline{\gamma}, \hat{\gamma})$ s.t.

$$\max_{1\le m\le M}\|\nabla\eta^m\|^2_{L^2(\Omega_S(0))} + \sum_{n=1}^M t_\Delta^n\|\frac{\eta^n - \eta^{n-1}}{t_\Delta^n}\|^2_{L^2(\Omega_S(0))} \le c^*(\|\eta^0\|^2_{H^1(\Omega_S(0))} + \|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))}), \tag{4.92}$$

which is a discretised estimate of the type $L^\infty H^1 \cap H^1 L^2$.

4th step) Limit procedure

We assume that the refinement of our semi-discretisation in time $(\Delta t)^M := \max_{1\le n\le M} t^n_\Delta$ tends to zero with ratio $(\Delta t)^M \le \frac{Const}{M} \to 0$ as $M \to \infty$. We annotate that this is a restriction to an adaptive algorithm.

We have not shown yet that our discretised problem and its solution converges to our original PDE and its solution. Therefore we construct the time interpolation of our discretisation, the so-called Rothe's function

$$\eta_M := \sum_{n=1}^{M} (\eta^n + \frac{t - t_{n-1}}{t^n_\Delta}(\eta^n - \eta^{n-1}))\mathbb{I}(t)_{[t_{n-1},t_n]}$$

and as a kind of time derivative multiplied with t^n_Δ we introduce the step function

$$\check{\eta}_M := \sum_{n=1}^{M} \eta^n \mathbb{I}(t)_{(t_{n-1},t_n]} + \eta^0 \mathbb{I}(t)_0,$$

which is defined being continuous from the left. For the data we introduce

$$f_M := \sum_{n=2}^{M} f^n \mathbb{I}(t)_{(t_{n-1},t_n]} + f^1 \mathbb{I}(t)_{[0,t_1]}.$$

We rewrite the semi-discretised problem (4.85) – (4.88) with these definitions

$$\begin{aligned}
\partial_t \eta_M + \alpha^n(x,\check{\eta}_M)\cdot\nabla\check{\eta}_M + \beta^n(x,\check{\eta}_M)\check{\eta}_M & \\
-\nabla\cdot(\gamma^n(x,\check{\eta}_M)\nabla\check{\eta}_M) &= f_M && \text{in } \Omega^0_S, && (4.93)\\
\partial_\nu \check{\eta}_M &= 0 && \text{on } \partial\Omega^0, && (4.94)\\
\check{\eta}_M &= 0 && \text{on } I_i(0), && (4.95)\\
\check{\eta}^0_M &= n^0_{As} - n^{int}_{As}(t=0) && \text{in } \Omega_S(0). && (4.96)
\end{aligned}$$

We have immediately from (4.90) and (4.92) the following *a priori* estimates on η_M and $\check{\eta}_M$:

$$\|\eta_M\|_{H^1(0,\mathcal{T};L^2(\Omega_S(0)))} \le C_1, \quad \|\check{\eta}_M\|_{H^1(\Omega_S(0))} \le C_2 \quad \text{for a.a. } t \in (0,\mathcal{T})$$

uniformly in M.

We have equicontinuity of the L^2 norm of Rothe's function in time i.e.

$$\|\eta_M(t_1) - \eta_M(t_2)\|_{L^2(\Omega_S(0))} \le const_1 \|t_1 - t_2\| \tag{4.97}$$

and

$$\|\check{\eta}_M(t) - \eta_M(t)\|_{L^2(\Omega_S(0))} \le \frac{const_2}{M} \tag{4.98}$$

uniformly in m for all t, $t_i \in (0,\mathcal{T}), i \in \{1,2\}$.

Since H^1 embeds compactly into L^2, $\|\check{\eta}_M\|_{H^1(\Omega_S(0))} \le C_2$ and (4.97) we can apply the theorem of Arzelà-Ascoli, which ensures there exists $\eta \in C^0(0,\mathcal{T};L^2(\Omega_S(0)))$ and a subsequence again denoted by $\{\eta_m\}$ s.t.

$$\eta_M \to \eta \quad \text{in } C^0(0,\mathcal{T};L^2(\Omega_S(0))), \quad M \to \infty.$$

By $\|\check{\eta}_M\|_{H^1(\Omega_S(0))} \le C_2$ and (4.98) follows

$$\check{\eta}_M(t) \to \eta(t) \text{ in } H^1(\Omega_S(0)) \quad \forall t \in (0,\mathcal{T}), \quad M \to \infty. \tag{4.99}$$

Hence $\eta \in L^\infty(0,\mathcal{T};H^1(\Omega_S(0)))$.

Now (4.97) implies that $\eta(t):(0,\mathcal{T})\to L^2(\Omega_S(0))$ is Lipschitz continuous i.e.

$$\|\eta(t_1)-\eta(t_2)\|_{L^2(\Omega_S(0))} \leq const_1\|t_1-t_2\|$$

for almost all times. With Rademacher's theorem (see [Eva02], §5.8.3, Th. 6, p. 281) it follows that

$$\partial_t\eta \in L^\infty(0,\mathcal{T};L^2(\Omega_S(0))).$$

Further the $\|\partial_t\eta_M\|_{L^2(\Omega_S(0))} \leq C_1$ estimate gives

$$\partial_t\eta_M \to \partial_t\eta \quad \text{in } L^2(0,\mathcal{T};L^2(\Omega_S(0))), \quad M\to\infty. \tag{4.100}$$

5th step) Convergence of approximation scheme

We test the approximated problem (4.93) – (4.96) with $\phi \in H^1(\Omega_S(0))$ and integrate over an arbitrary time interval (t_1,t_2). We see by (4.100) and (4.99) together with the preliminary Assumptions (4.77) – (4.77) on α, β and γ, that a solution of problem (4.93) – (4.96) converges to a solution η of the original problem as $M\to\infty$.

The estimates (4.90) and (4.92) translate into the estimates

$$\begin{aligned}&\|\eta\|^2_{L^\infty(0,\mathcal{T};L^2(\Omega_S(0)))}+\underline{\gamma}\|\nabla\eta\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))}\\&\leq const(\mathcal{T},(\hat{a})^2,\hat{b},\underline{\gamma})(\|\eta^0\|^2_{L^2(\Omega_S(0))}+\|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))})\end{aligned}$$

and

$$\begin{aligned}&\|\nabla\eta\|^2_{L^\infty(0,\mathcal{T};L^2(\Omega_S(0)))}+\|\partial_t\eta\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))}\\&\leq c^*(\mathcal{T},\hat{a},\hat{b},\underline{\gamma},\hat{\gamma})(\|\eta^0\|^2_{H^1(\Omega_S(0))}+\|f\|^2_{L^2(0,\mathcal{T};L^2(\Omega_S(0)))}).\end{aligned}$$

6th step) Uniqueness

The maximum principle i.e. Corollary 4.2), which has been proved for functions in $L^\infty L^2\cap L^2H^1$, yields that a solution η is unique. Up to now we had only convergence of a subsequence of η_M and $\check{\eta}_M$ but since the limit problem has a unique solution this yields convergence of the whole sequences η_M and $\check{\eta}_M$.

7th step) Estimate on the Laplacian

We proceed as in the proof of [Eva02], Th. 5, step 3 and show (4.83). For the moment we consider the diffusion equation in u on time-dependent domain. For almost all t we test the diffusion equation with $\phi\in H^1_0(\Omega_S(t))$ and get

$$\int_{\Omega_S(t)}\varepsilon^3(\mathcal{X}(u)(\partial_t u+v\cdot\nu)+\Xi(u)\nabla\cdot v)\phi-\nabla u\cdot\nabla\phi=0.$$

For given $h=\varepsilon^3\mathcal{X}(u)(\partial_t u+v\cdot\nu)+\Xi(u)\nabla\cdot v\in L^2(\Omega_S)$ this a elliptic boundary value problem with smooth boundary and we have the standard estimate

$$\|u\|_{H^2(\Omega_S(t))}\leq Const\,\varepsilon^{3/2}\|\mathcal{X}(u)(\partial_t u+v\cdot\nu)+\Xi(u)\nabla\cdot v\|_{L^2(\Omega_S(t))}$$

with a constant, which is independent of ε, and for almost all t. The scaling of the constant can be seen analogously as in lemma 5.2 by

$$\varepsilon^3\|\partial_{x_j}\partial_{x_k}u\|^2_{L^2(\Sigma_i^\varepsilon)}\leq Const\,\varepsilon^{6-3}\|\mathcal{X}(u)(\partial_t u+v\cdot\nu)+\Xi(u)\nabla\cdot v\|^2_{L^2(\Sigma_i^\varepsilon)}.$$

Summing up over t and using the above estimates we find (4.83).

3) (Regularity)

The idea to prove better regularity, which depends on smoothness of data, is, that regularity carries over from semi-discretised problems which are elliptic, but we want to refer to an abstract result.

We apply an abstract result from [LSU88], Ch. V, §7, Th. 7.4 (p. 491) for exponent $\tilde{\beta} > 0$ and parameter $\tau = 1$ therein and the following references to literature therein on p. 492, or the survey article [LU86]. The result for Hölder continuity of solutions of a quasilinear parabolic PDE, under weakest possible assumptions on the coefficients, as far as known by the author, is given by [Lie01], Th. 7.5 and Coroll. 7.6.

Our problem in nondivergence form (4.49), (4.42) – (4.44) is a special case of the class of problems considered there. We abbreviate $p = \nabla_x \eta$ and check the premises in our reference, which follow from our Assumptions (4.77) – (4.80) and (4.84): for arbitrary η

$$0 \leq \underline{\gamma}|\xi|^2 \leq a(x,t,\eta)\xi \cdot \xi \leq \hat{\gamma}|\xi|^2 \quad \forall (x,t) \in \overline{\Omega_S(0) \times (0,\mathcal{T})},$$

and by using the monotonicity of $u'(\eta)$

$$-\eta b(x,t,\eta,p) \leq c_0 p^2 + c_1 \eta^2 + c_2 \quad \forall (x,t) \in \overline{\Omega_S(0) \times (0,\mathcal{T}))} \setminus \Omega_S(0)$$

with nonnegative constants $c_0 = \|g^{-1}\| \|u''\|_{L^\infty} \|\eta\|_{L^\infty} + \frac{1}{2}(\|\nabla_x g^{-1}\|_{L^\infty} \|u'\|_{L^\infty} + \hat{\alpha})$ ($\|\eta\|_{L^\infty} < const$ due to the maximum principle), $c_1 = \hat{\beta} + \frac{1}{2}(\|\nabla_x g^{-1}\|_{L^\infty} \|u'\|_{L^\infty} + \hat{\alpha}) + \frac{1}{2}\|\tilde{f}\|_{L^2}^2$ and $c_2 = 0$, further for bounded η and p the functions a, b are bounded. The domain $\Omega_S(0)$ is of class C^2. ☐

4.3.3. Radii evolutions

The following theorem illustrates with which regularity we have to work, in order to get classical solutions of the radii evolutions.

Theorem 4.6 (Existence and uniqueness of solutions of the ODE for free boundaries)**.** *Let* $\tilde{n}_{As} \in C^0H^2$ *and* $\tilde{U} \in (C^1H^1 \cap C^0H^2)/RD$ *be given and let the initial data* $r_i^0, i \in N(0)$ *and* R_{bd}^0 *in* $\mathcal{J}_r$*. If* $\mathbb{X}$ *is Lipschitz continuous in* r_i *and* Φ *depends smoothly on* r_i *and* $\tilde{R}$*, then the ODEs for the* $|N(t)|$ *radii* r_i *of the interfaces and the radii of the outer boundary* R_{bd} *have each a unique solution* r_i *and* R_{bd} *in* $C^1((0,\mathcal{T}) \setminus \cup_{i \in N(0)} \tau_i) \cap C^0(0,\mathcal{T})$*.*

Proof. We apply the classical Picard-Lindelöf theorem to the maps

$$r_i \to \varepsilon^3 \frac{\fint_{\bar{I}_i(0)} D\Phi^{-T}(R, R_{bd}) \nabla \tilde{u}(\tilde{n}_{As}) \cdot \tilde{\nu}}{\mathbb{X}(r_i, \fint_{\bar{I}_i(0)} \tilde{U} \cdot \nu)}, i \in N, \quad R_{bd} \to \fint_{\partial\Omega(0)} (\partial_t \tilde{U} - \tilde{U}_{\cdot||\cdot} \nabla_R \Phi(R, R_{bd}) \partial_t R) \cdot \nu, \tag{4.101}$$

which yields r_i and R_{bd} in $C^1(0,\mathcal{T})$ for $\mathcal{T} < \min_{i \in N} \tau_i$. If a droplet vanishes at time τ_i, then the time derivatives of r_i and R_{bd} have jumps in general. Hence r_i and R_{bd} globally in $H^1(0,\mathcal{T})$. ☐

4.3.4. The coupled problem

Our strategy is to exploit the estimates for the equations on fixed domain from Subsections 4.3.1 and 4.3.2, where we assumed in the mechanical BVP for the velocity that an evolution of the free boundaries $\tilde{R} \in [H^1(0,\mathcal{T})]^{\mathcal{N}^0+1}$ and a $\tilde{n}_{As} \in L^2H^1$ is given, while in the diffusion problem we assumed that $\tilde{R} \in [H^1(0,\mathcal{T})]^{\mathcal{N}^0+1}$ and $\partial_t \tilde{U}$ is given, where $\tilde{v}$ and $\nabla\tilde{v}$ are measurable e.g. $\tilde{U} \in H^1H^1/RD \cap L^2H^2/RD$.

For systems of coupled parabolic and elliptic equations without free boundaries and without mixed boundary conditions there does not seem to exist many results. Our situation can be covered by the much more general results in [AL83], [Kač90a], [Kač90b], [FK95] or [AB04], but they only consider variational solutions i.e. solutions, which are L^∞ or L^1 in time and with time-derivatives in the sense of distributions, which is not enough for our purposes. Our system on fixed domain, consisting of the equations (4.48), (4.42) – (4.44) for $\tilde{n}_{As}$ and the equations (4.26)-(4.28) for $\tilde{U}$ and (4.30) – (4.32) for $\tilde{v}$, are not included in the work of Sapa [Sap06], since this result holds only in one space dimension. A result, which comes close to what we need is [MS07], but they prove only convergence of a difference scheme and restrict to cubical domains.

We show that we can solve, at first locally, the transformed Problem E, which is stated on fixed domain, by means of Banach's fixed point theorem i.e. we prove existence of a fixed point $(\tilde{R}, \tilde{n}_{As}, \tilde{U})$ in the space

$$\mathcal{M} := \mathcal{M}_{\mathcal{T}}^{k} \times \mathcal{M}_{\mathcal{T}}^{\kappa} \times \mathcal{M}_{\mathcal{T}}^{K}$$

where

$$\begin{aligned}
\mathcal{M}_{\mathcal{T}}^{k} &:= \{\tilde{R} \in [H^1(0,\mathcal{T})]^{\mathcal{N}^0}, \sup_i \|\partial_t R_i\|_{L^2(0,\mathcal{T})} \leq k\},\\
\mathcal{M}_{\mathcal{T}}^{\kappa} &:= \{\tilde{n}_{As} \in H^1(0,\mathcal{T};L^2(\Omega_S(0))) \cap L^\infty(0,\mathcal{T};H^1(\Omega_S(0))), \|\partial_t \tilde{n}_{As}\|_{L^2L^2} + \|\nabla \tilde{n}_{As}\|_{L^\infty L^2} \leq \kappa\},\\
\mathcal{M}_{\mathcal{T}}^{K} &:= \{\tilde{U} \in L^\infty(0,\mathcal{T};C^2(\overline{\Omega_S(0)};\mathbb{R}^3)/RD) \cap H^1(0,\mathcal{T};C^1(\overline{\Omega_S(0)};\mathbb{R}^3)/RD),\\
&\qquad \|\nabla \tilde{U}\|_{L^\infty C^0} + \|\nabla \partial_t \tilde{U}\|_{L^2C^0} \leq K\}
\end{aligned}$$

with suitable constant k s.t. neither droplets do intersect each other neither intersect the outer boundary nor droplets vanish up to time $\mathcal{T}$, suitable κ s.t. the approximation (4.128) is justified and suitable K s.t. the r.h.s. of the displacement problem is of order $\mathcal{O}(\tilde{h})$ and the r.h.s. of the velocity problem is of order $\mathcal{O}(\tilde{h})k$.

Then the assumption $\tilde{v} \in L^2H^1/RD$ which is assumed for a solution of the diffusion problem in 4.3.2 is fulfilled.

Theorem 4.7 (Local existence and uniqueness for Problem E)**.** *Under the Assumptions 4.1, 4.2 and 4.4 and the assumptions on regularity and smallness of data in Theorems 4.2, 4.3 and 4.5 there exists $\mathcal{T} > 0$ s.t. a unique solution of Problem E exists:*

$$\begin{aligned}
&\tilde{n}_{As} \in H^1(0,\mathcal{T};L^2(\Omega_S(0))) \cap L^\infty(0,\mathcal{T};H^1(\Omega_S(0))),\\
&\tilde{U} \in L^\infty(0,\mathcal{T};C^2(\overline{\Omega_S(0)};\mathbb{R}^3))/RD \cap H^1(0,\mathcal{T};C^1(\overline{\Omega_S(0)};\mathbb{R}^3))/RD,\\
\textit{and } &\tilde{R} \in H^1(0,\mathcal{T})
\end{aligned}$$

and hence on time-dependent domain

$$\begin{aligned}
&n_{As} \in H^1(0,\mathcal{T};L^2(\Omega_S)) \cap L^\infty(0,\mathcal{T};H^1(\Omega_S)),\\
&U \in L^\infty(0,\mathcal{T};C^2(\overline{\Omega_S};\mathbb{R}^3))/RD \cap H^1(0,\mathcal{T};C^1(\overline{\Omega_S};\mathbb{R}^3))/RD,\\
\textit{and } &\tilde{R} \in H^1(0,\mathcal{T}).
\end{aligned}$$

Proof. We define the mapping

$$\begin{aligned}
\mathcal{F} : \mathcal{M} \to &[H^1(0,\mathcal{T})]^{\mathcal{N}^0+1} \times [H^1(0,\mathcal{T};L^2(\Omega_S(0)) \cap L^\infty(0,\mathcal{T};H^1(\Omega_S(0)))\times\\
&\times [L^\infty(0,\mathcal{T};C^2(\overline{\Omega_S(0)};\mathbb{R}^3) \cap H^1(0,\mathcal{T};C^1(\overline{\Omega_S(0)};\mathbb{R}^3))]
\end{aligned}$$

by

$$
\begin{aligned}
(\mathcal{F}(\tilde{R},\tilde{n}_{As},\tilde{U}))_0(t) &:= R^0_{bd} + \int_0^t \fint_{\partial\Omega(0)} (\partial_s \mathcal{F}_{\mathcal{N}^0+2} - (\mathcal{F}_{\mathcal{N}^0+2})_{\cdot||\cdot} \sum_{i\in N} \partial_{\mathcal{F}_i}\Phi\partial_t\mathcal{F}_i)\cdot\nu \, dA\, ds,\\
(\mathcal{F}(\tilde{R},\tilde{n}_{As},\tilde{U}))_i(t) &:= r^0_i + \varepsilon^3 \int_0^t \fint_{I_i} \frac{(D\Phi^{-T}(\tilde{R})\nabla\tilde{u}(\tilde{n}_{As}))\cdot\nu}{\mathbb{X}(r_i, \fint_{I_i}\tilde{U}\cdot\nu)} \, dA\, ds \quad \forall i\in N
\end{aligned}
$$

and $\mathcal{F}(\tilde{R},\tilde{n}_{As},\tilde{U})_{\mathcal{N}^0+1}(t)$ as the unique solution of the diffusion problem (4.33) – (4.36), wherein $\tilde{R}$ is replaced by $\mathcal{F}_i, 0\le i\le\mathcal{N}^0$ and $\tilde{U}$ is replaced by $\mathcal{F}_{\mathcal{N}^0+2}$, i.e.

$$
\begin{aligned}
&\partial_t\mathcal{F}_{\mathcal{N}^0+1} - \nabla\cdot(\gamma(x,t,\{\mathcal{F}_i\}_{0\le i\le\mathcal{N}^0+1}))\\
&\quad +\alpha(x,t,\{\mathcal{F}_i\}_{0\le i\le\mathcal{N}^0+2})\cdot\nabla\mathcal{F}_{\mathcal{N}^0+1}\\
&\qquad +\beta(x,t,\{\mathcal{F}_i\}_{0\le i\le\mathcal{N}^0+2})\mathcal{F}_{\mathcal{N}^0+1} = 0 && \text{on } \Omega_S(0), && (4.102)\\
&\partial_\nu\mathcal{F}_{\mathcal{N}^0+1} = 0 && \text{on } \partial\Omega(0), && (4.103)\\
&\mathcal{F}_{\mathcal{N}^0+1} = n^{int}_{As}(r_i) && \text{on } I_i(0)\ \forall i\in N, && (4.104)\\
&\mathcal{F}_{\mathcal{N}^0+1}(\cdot,t=0) = \tilde{n}^0_{As} && \text{in } \Omega_S(0), && (4.105)
\end{aligned}
$$

and $\mathcal{F}(\tilde{R},\tilde{n}_{As},\tilde{U})_{\mathcal{N}^0+2}(t)$ as unique solution of the mechanical problem (4.26) – (4.28), wherein $\tilde{R}$ is replaced by $\mathcal{F}_i, 0\le i\le\mathcal{N}^0$.

We have to show that $\mathcal{F}$ is a strict contractive mapping from $\mathcal{M}$ in itself for $\mathcal{T}$ small enough. Then we can apply Banach's fixed point theorem to conclude the existence and uniqueness of $\tilde{R}$, $\tilde{n}_{As}$ and $\tilde{U}$ in the given spaces.

Let $(\tilde{R}^{(1)},\eta^{(1)},\tilde{U}^{(1)}),(\tilde{R}^{(2)},\eta^{(2)},\tilde{U}^{(2)})\in\mathcal{M}$ be two pairs of solutions to the transformed Problem E. Analogously define the transformations $\Phi^{(1)}$ and $\Phi^{(2)}$ onto fixed domain corresponding to the different radii evolutions $\tilde{R}^{(1)}$ and $\tilde{R}^{(2)}$.

Let $\tilde{\sigma}_{S,(j)}$ denote the reduced Cauchy stress corresponding to the radii evolution $\tilde{R}^{(j)}$, $j=1,2$. Analogously solves $\tilde{U}^{(1)}-\tilde{U}^{(2)}$ the elliptic problem

$$
\begin{aligned}
\tilde{\sigma}^{\cdot,j}_{S,(1)}||_j(\nabla(\tilde{U}^{(1)}-\tilde{U}^{(2)})) &= (\tilde{\sigma}^{\cdot,j}_{S,(1)}||_j - \tilde{\sigma}^{\cdot,j}_{S,(2)}||_j)(\nabla(\tilde{U}^{(2)})) && \text{in } \Omega^\varepsilon_S(0),\\
\tilde{\sigma}_{S,(1)}(\nabla(\tilde{U}^{(1)}-\tilde{U}^{(2)}))\nu &= (\tilde{\sigma}_{S,(1)}-\tilde{\sigma}_{S,(2)})(\nabla(\tilde{U}^{(2)}))\nu && \text{on } \partial\Omega(0),\\
(\tilde{\sigma}_{S,(1)}(\nabla(\tilde{U}^{(1)}-\tilde{U}^{(2)}))&\\
-\frac{3k_L}{\varepsilon^3 r^{(1)}_i}\fint_{I^\varepsilon_i(0)}((\tilde{U}^{(1)}-\tilde{U}^{(2)})\cdot\nu))\nu &= (\frac{2\sigma}{r^{(1)}_i}-\frac{2\sigma}{r^{(1)}_i} - 3k_L(h^*_L(r^{(1)}_i)-h^*_L(r^{(2)}_i))\\
&\quad + (\tilde{\sigma}_{S,(1)}-\tilde{\sigma}_{S,(2)})(\nabla(\tilde{U}^{(2)}))\\
&\quad - \frac{3k_L}{\varepsilon^3}(\frac{1}{r^{(1)}_i}-\frac{1}{r^{(2)}_i})\fint_{I^\varepsilon_i(0)}(\tilde{U}^{(2)}\cdot\nu))\nu && \text{on } I^\varepsilon_i(0)\ \forall i\in N
\end{aligned}
$$

which yields with $\|\nabla\tilde{U}^{(2)}\|_{L^\infty L^2}\le K$ the estimate

$$
\|\nabla(\tilde{U}^1-\tilde{U}^2)\|_{L^2(\Omega_S(0))} \le const(k,K)\sup_{i\in\{0\}\cup N}|\tilde{R}^{(1)}_i-\tilde{R}^{(2)}_i| \tag{4.106}
$$

and

$$
\|\nabla\tilde{U}^{(1)}-\nabla\tilde{U}^{(2)}\|_{L^\infty L^2} \le const(k,K)\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{L^\infty}, \tag{4.107}
$$

respectively. Similarly we get the estimate

$$
\|D^2\tilde{U}^{(1)}-D^2\tilde{U}^{(2)}\|_{L^\infty L^2} \le const(k,K)\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{L^\infty}. \tag{4.108}
$$

$\partial_t\tilde{U}^{(1)} - \partial_t\tilde{U}^{(2)}$ solves a similar elliptic problem and with $\|\nabla\partial_t\tilde{U}^{(2)}\|_{L^\infty L^2} \leq K$ we can derive the bound

$$\|\nabla(\partial_t\tilde{U}^1 - \partial_t\tilde{U}^2)\|_{L^2(\Omega_S(0))} \leq const(k,K)(\sup_{i\in\{0\}\cup N}|\tilde{R}_i^{(1)} - \tilde{R}_i^{(2)}| + \sup_{i\in\{0\}\cup N}|\partial_t\tilde{R}_i^{(1)} - \partial_t\tilde{R}_i^{(2)}|). \quad (4.109)$$

For the velocity we get consequently

$$\|\nabla\tilde{v}^{(1)} - \nabla\tilde{v}^{(2)}\|_{L^2L^2} \leq const(k,K)(\|\tilde{R}^{(1)} - \tilde{R}^{(2)}\|_{L^\infty} + \|\partial_t\tilde{R}^{(1)} - \partial_t\tilde{R}^{(2)}\|_{L^2}). \quad (4.110)$$

We abbreviate for $j \in \{1;2\}$ according to (4.46) and (4.47)

$$\begin{aligned}&\alpha^{(j)} := \alpha(x,t,\eta^{(j)},\partial_t\tilde{U}^{(j)},\nabla\tilde{U}^{(j)},\partial_t\tilde{R}^{(j)},\tilde{R}^{(j)}), \quad \beta^{(j)} := \beta(x,t,\eta^{(j)},\nabla\cdot\partial_t\tilde{U}^j,\nabla\tilde{U}^{(j)},\tilde{R}^{(j)},\partial_t\tilde{R}^{(j)}),\\ &\gamma^{(j)} := \gamma(x,t,\eta^{(j)},\tilde{R}^{(j)})\end{aligned}$$

and furthermore we write $\tilde{f}^{(j)} := \tilde{f}(\tilde{R}^{(j)})$. Then the difference $\eta^{(1)} - \eta^{(2)}$ solves the diffusion eq.

$$\partial_t(\eta^{(1)} - \eta^{(2)}) - \nabla\cdot(\gamma^{(1)}\nabla(\eta^{(1)} - \eta^{(2)})) + \alpha^{(1)}\cdot\nabla(\eta^{(1)} - \eta^{(2)}) + \beta^{(1)}(\eta^{(1)} - \eta^{(2)}) = \mathbb{F} \quad (4.111)$$

with zero boundary conditions and zero initial data and r.h.s.

$$\mathbb{F} := \tilde{f}^{(1)} - \tilde{f}^{(2)} - \nabla\cdot(\gamma^{(1)} - \gamma^{(2)})\nabla\eta^{(2)} - (\alpha^{(1)} - \alpha^{(2)})\cdot\nabla\eta^{(2)} - (\beta^{(1)} - \beta^{(2)})\eta^{(2)}.$$

We first test by $\eta^{(1)} - \eta^{(2)}$ and then by $\partial_t(\eta^{(1)} - \eta^{(2)})$

$$\begin{aligned}&\int_0^{\mathcal{T}}\int_{\Omega_S(0)} \partial_t(\eta^{(1)} - \eta^{(2)})(\eta^{(1)} - \eta^{(2)}) + \alpha^{(1)}\cdot\nabla(\eta^{(1)} - \eta^{(2)})(\eta^{(1)} - \eta^{(2)}) + \beta^{(1)}|\eta^{(1)} - \eta^{(2)}|^2\\ &+ \gamma^{(1)}|\nabla\eta^{(1)} - \nabla\eta^{(2)}|^2 = \int_0^{\mathcal{T}}\int_{\Omega_S(0)} \mathbb{F}(\eta^{(1)} - \eta^{(2)}).\end{aligned}$$

We estimate with $\|v\|_{L^2L^\infty}, \|\nabla\cdot v\|_{L^2L^\infty} \leq const(k,K)$

$$\begin{aligned}&\|(\eta^{(1)} - \eta^{(2)})(\mathcal{T})\|_{L^2}^2 + \frac{1}{2}\|\nabla(\eta^{(1)} - \eta^{(2)})\|_{L^2L^2}^2\\ &\leq const(\{\alpha^{(j)},\beta^{(j)},\gamma^{(j)}\}_{j=1,2})\|\eta^{(1)} - \eta^{(2)}\|_{L^2L^2}^2\\ &\quad + const(\{\tilde{f}^{(j)},\alpha^{(j)},\beta^{(j)},\gamma^{(j)}\}_{j=1,2}, \|\nabla\eta^{(2)}\|_{L^\infty L^2}, \|\eta^{(2)}\|_{L^\infty L^2})(\|\tilde{R}^{(1)} - \tilde{R}^{(2)}\|_{L^\infty(0,\mathcal{T})}^2\\ &\quad + \|\partial_t\tilde{R}^{(1)} - \partial_t\tilde{R}^{(2)}\|_{L^2(0,\mathcal{T})}^2 + \|\partial_t\tilde{U}^{(1)} - \partial_t\tilde{U}^{(2)}\|_{L^2H^1}^2 + \|\tilde{U}^{(1)} - \tilde{U}^{(2)}\|_{L^2H^2}^2).\end{aligned}$$

By Gronwall we get according to (4.90)

$$\begin{aligned}&\|\eta^{(1)} - \eta^{(2)}\|_{L^\infty L^2}^2 + \|\nabla(\eta^{(1)} - \eta^{(2)})\|_{L^2L^2}^2\\ &\leq const(\tilde{f},\alpha,\beta,\gamma,\|\nabla\eta^{(2)}\|_{L^\infty L^2},\|\eta^{(2)}\|_{L^\infty L^2})(\|\tilde{R}^{(1)} - \tilde{R}^{(2)}\|_{L^\infty(0,\mathcal{T})} + \|\partial_t\tilde{R}^{(1)} - \partial_t\tilde{R}^{(2)}\|_{L^2(0,\mathcal{T})}^2\\ &\quad + \|\partial_t\tilde{U}^{(1)} - \partial_t\tilde{U}^{(2)}\|_{L^2L^2}^2 + \|\tilde{U}^{(1)} - \tilde{U}^{(2)}\|_{L^2L^2}^2)\exp(\mathcal{T}const(\alpha,\beta,\gamma))\\ &\leq const(k,\kappa,K)\exp(\mathcal{T}const(k,K))(\|\tilde{R}^{(1)} - \tilde{R}^{(2)}\|_{L^\infty(0,\mathcal{T})}^2 + \|\partial_t\tilde{R}^{(1)} - \partial_t\tilde{R}^{(2)}\|_{L^2(0,\mathcal{T})}^2\\ &\quad + \|\partial_t\tilde{U}^{(1)} - \partial_t\tilde{U}^{(2)}\|_{L^2H^1}^2 + \|\tilde{U}^{(1)} - \tilde{U}^{(2)}\|_{L^2H^2}^2).\end{aligned} \quad (4.112)$$

We test (4.111) with $\partial_t(\eta^{(1)} - \eta^{(2)})$ and get an analogous estimate

$$
\begin{aligned}
&\|(\nabla\eta^{(1)}-\nabla\eta^{(2)})(\mathcal{T})\|_{L^2}^2+\|\partial_t(\eta^{(1)}-\eta^{(2)})\|_{L^2L^2}^2\\
&\leq const(\alpha,\beta,\gamma)\|\nabla\eta^{(1)}-\nabla\eta^{(2)}\|_{L^2L^2}^2+const(\tilde{f},\alpha,\beta,\gamma,\|\nabla\eta^{(2)}\|_{L^\infty L^2},\|\eta^{(2)}\|_{L^\infty L^2})\times\\
&\quad\times(\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{L^\infty(0,\mathcal{T})}^2+\|\partial_t\tilde{R}^{(1)}-\partial_t\tilde{R}^{(2)}\|_{L^2(0,\mathcal{T})}^2+\|\partial_t\tilde{U}^{(1)}-\partial_t\tilde{U}^{(2)}\|_{L^2H^1}^2\\
&\quad+\|\tilde{U}^{(1)}-\tilde{U}^{(2)}\|_{L^2H^2}^2)
\end{aligned}
$$

and hence with (4.112) we get the estimate, *confer* (4.92),

$$
\begin{aligned}
&\|(\nabla\eta^{(1)}-\nabla\eta^{(2)})(\mathcal{T})\|_{L^2}^2+\|\partial_t(\eta^{(1)}-\eta^{(2)})\|_{L^2L^2}^2\\
&\leq const(k,\kappa,K)\exp(\mathcal{T}const(k,K))(\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{L^\infty(0,\mathcal{T})}^2+\|\partial_t\tilde{R}^{(1)}-\partial_t\tilde{R}^{(2)}\|_{L^2(0,\mathcal{T})}^2\\
&\quad+\|\partial_t\tilde{U}^{(1)}-\partial_t\tilde{U}^{(2)}\|_{L^2H^1}^2+\|\tilde{U}^{(1)}-\tilde{U}^{(2)}\|_{L^2H^2}^2).
\end{aligned}
\tag{4.113}
$$

We use the last estimate to bound $D^2(\eta^{(1)}-\eta^{(2)})$ and (4.83)

$$
\begin{aligned}
&\inf\gamma\|D^2(\eta^{(1)}-\eta^{(2)})\|_{L^2L^2}^2\\
&\leq\|\partial_t(\eta^{(1)}-\eta^{(2)})\|_{L^2L^2}^2+const(\alpha,K)\|\eta^{(1)}-\eta^{(2)}\|_{L^2L^2}^2+const(\beta,K)\|\nabla\eta^{(1)}-\nabla\eta^{(2)}\|_{L^2L^2}^2\\
&\quad+const(\tilde{f},\alpha,\beta,\gamma,\|\nabla\eta^{(2)}\|_{L^\infty L^2},\|\eta^{(2)}\|_{L^\infty L^2})(\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{L^\infty(0,\mathcal{T})}^2+\|\partial_t\tilde{R}^{(1)}-\partial_t\tilde{R}^{(2)}\|_{L^2(0,\mathcal{T})}^2\\
&\quad+\|\partial_t\tilde{U}^{(1)}-\partial_t\tilde{U}^{(2)}\|_{L^2H^1}^2+\|\tilde{U}^{(1)}-\tilde{U}^{(2)}\|_{L^2H^2}^2)\\
&\leq const(k,\kappa,K)\exp(\mathcal{T}const(k,K))\times(\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{L^\infty(0,\mathcal{T})}^2+\|\partial_t\tilde{R}^{(1)}-\partial_t\tilde{R}^{(2)}\|_{L^2(0,\mathcal{T})}^2\\
&\quad+\|\partial_t\tilde{U}^{(1)}-\partial_t\tilde{U}^{(2)}\|_{L^2H^1}^2+\|\tilde{U}^{(1)}-\tilde{U}^{(2)}\|_{L^2H^2}^2).
\end{aligned}
\tag{4.114}
$$

By exploiting $\tilde{R}_i^{(1)}(0)=\tilde{R}_i^{(2)}(0)$ and the Cauchy-Schwarz inequality we get a Poincaré inequality for the radii

$$
\begin{aligned}
\|\tilde{R}_i^{(1)}(t)-\tilde{R}_i^{(2)}(t)\|_{L^\infty(0,\mathcal{T})}&=\|\int_0^{\mathcal{T}}\partial_t(\tilde{R}_i^{(1)}-\tilde{R}_i^{(2)})\|_{L^\infty(0,\mathcal{T})}\\
&\leq\sqrt{\mathcal{T}}\|\partial_t\tilde{R}_i^{(1)}-\partial_t\tilde{R}_i^{(2)}\|_{L^2(0,\mathcal{T})}\qquad\forall i\in\{0\}\cup N.
\end{aligned}
\tag{4.115}
$$

This yields

$$
\begin{aligned}
\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{H^1(\Omega_S(0))}^2&\leq\mathcal{T}\|\tilde{R}^{(1)}-\tilde{R}^{(2)}\|_{L^\infty(\Omega_S(0))}^2+\|\partial_t\tilde{R}^{(1)}-\partial_t\tilde{R}^{(2)}\|_{L^2(\Omega_S(0))}^2\\
&\leq(1+\mathcal{T}^2)\|\partial_tR^{(1)}-\partial_tR^{(2)}\|_{L^2(\Omega_S(0))}^2.
\end{aligned}
$$

We combine our estimates (4.112), (4.113) and (4.114) with (4.107) and (4.110) get

$$
\begin{aligned}
&\|\eta^{(1)}-\eta^{(2)}\|_{H^1L^2\cap L^\infty H^1},\ \|D^2(\eta^{(1)}-\eta^{(2)})\|_{L^2L^2}\\
&\leq Const(k,\kappa,K)\exp(\mathcal{T}const(k,K))\|\partial_t\tilde{R}^{(1)}-\partial_t\tilde{R}^{(2)}\|_{L^2}.
\end{aligned}
\tag{4.116}
$$

In the following we will need the special case of the Cauchy-Schwarz inequality

$$
\int_0^{\mathcal{T}}|f|^2\leq\sqrt{\mathcal{T}}\sqrt{\int_0^{\mathcal{T}}|f|^4}
\tag{4.117}
$$

and the trace theorem (see [LSU88]),

$$
\|f\|_{L^4(0,\mathcal{T};L^2(\partial\Omega_S(0)))}\leq C(\|f\|_{L^\infty(0,\mathcal{T};L^2(\Omega_S(0)))}+\|\nabla f\|_{L^2((0,\mathcal{T})\times\Omega_S(0))})
\tag{4.118}
$$

or

$$\|\nabla g\|_{L^4(0,\mathcal{T};L^2(\partial\Omega_S(0)))} \leq C(\|\nabla g\|_{L^\infty(0,\mathcal{T};L^2(\Omega_S(0)))} + \|D^2 g\|_{L^2((0,\mathcal{T})\times\Omega_S(0))}). \tag{4.119}$$

Then for the radii components $1 \leq i \leq \mathcal{N}^0$,

$$\begin{aligned}
&\int_0^{\mathcal{T}} |\partial_t(\mathcal{F}(\tilde{R}^{(1)}, \eta^{(1)}, \tilde{U}^{(1)})_i - \mathcal{F}(\tilde{R}^{(2)}, \eta^{(2)}, \tilde{U}^{(2)})_i)|^2 ds \\
&\leq \varepsilon^3 \int_0^{\mathcal{T}} \frac{1}{|I_i(0)|^2} |\int_{I_i(0)} \left(\frac{(D\Phi^{(1)})^{-T} \nabla u(\eta^{(1)})}{\mathbb{X}(r_i^{(1)}, \fint_{I_i(0)} \tilde{U}^{(1)} \cdot \nu)} - \frac{(D\Phi^{(2)})^{-T} \nabla u(\eta^{(2)})}{\mathbb{X}(r_i^{(2)}, \fint_{I_i(0)} \tilde{U}^{(2)} \cdot \nu)} \right) \cdot \nu \, dA|^2 ds \\
&\leq \mathit{const}(\varepsilon, r_i(0), k, \mathbb{X}, u) \sqrt{T} (\|\nabla\eta^{(1)} - \nabla\eta^{(2)}\|^2_{L^4 L^2(I_i(0))} + \|D\Phi^{(1)} - D\Phi^{(2)}\|^2_{L^\infty L^\infty} \\
&\quad + |r_i^{(1)} - r_i^{(2)}|^2 + \|\tilde{U}^{(1)} - \tilde{U}^{(2)}\|^2_{L^4 L^2(I_i)}) \qquad \text{by (4.117), (4.119)} \\
&\leq \mathit{const}_2(k, \kappa, K) \sqrt{T} (\|\nabla\eta^{(1)} - \nabla\eta^{(2)}\|^2_{L^\infty L^2(\Omega_S(0))} + \|D^2\eta^{(1)} - D^2\eta^{(2)}\|^2_{L^2 L^2(\Omega_S(0))} \\
&\quad + \|\tilde{R}^{(1)} - \tilde{R}^{(2)}\|^2_{L^\infty} + \|\tilde{U}^{(1)} - \tilde{U}^{(2)}\|^2_{L^\infty L^2(\Omega_S(0))} + \|\nabla\tilde{U}^{(1)} - \nabla\tilde{U}^{(2)}\|^2_{L^2 L^2(\Omega_S(0))}) \\
&\quad \text{by (4.119), (4.118).}
\end{aligned}$$

With the estimates (4.116), (4.107), (4.108) and Korn's inequality we can bound

$$\begin{aligned}
&\int_0^{\mathcal{T}} |\partial_t(\mathcal{F}(\tilde{R}^{(1)}, \eta^{(1)}, \tilde{U}^{(1)})_i - \mathcal{F}(\tilde{R}^{(2)}, \eta^{(2)}, \tilde{U}^{(2)})_i)|^2 ds \\
&\leq \mathit{const}_3(k, \kappa, K) \sqrt{T} (1 + \exp(\mathcal{T}(\mathit{const}(k, K)))) \|\partial_t \tilde{R}^{(1)} - \partial_t \tilde{R}^{(2)}\|^2_{L^2}.
\end{aligned} \tag{4.120}$$

For small $\mathcal{T}$ we can estimate $\sqrt{\mathcal{T}} \exp(\mathcal{T} c_4) \leq c_5 \sqrt{\mathcal{T}}$ with a constant c_5 indep. of $\mathcal{T}$, s.t. we get a strict contraction for the components $\mathcal{F}_1$ to $\mathcal{F}_{\mathcal{N}^0}$.

We abbreviate $\mathcal{F}\tilde{R} := (\mathcal{F}_i)_{0 \leq i \leq \mathcal{N}^0}$ and $\mathcal{F}R := (\mathcal{F}_i)_{1 \leq i \leq \mathcal{N}^0}$. For the radius of the outer boundary we get

$$\begin{aligned}
&\int_0^{\mathcal{T}} |\partial_t(\mathcal{F}(\tilde{R}^{(1)}, \eta^{(1)}, \tilde{U}^{(1)})_0 - \mathcal{F}(\tilde{R}^{(2)}, \eta^{(2)}, \tilde{U}^{(2)})_0)|^2 ds \\
&\leq \mathit{const}(R_{bd}(0)) \int_0^{\mathcal{T}} \int_{\partial\Omega(0)} |(\partial_s \mathcal{F}^{(1)}_{\mathcal{N}^0+2} - \partial_s \mathcal{F}^{(2)}_{\mathcal{N}^0+2} - ((\mathcal{F}_{\mathcal{N}^0+2})^{(1)}_{\cdot||\cdot} - (\mathcal{F}_{\mathcal{N}^0+2})^{(2)}_{\cdot||\cdot}) \times \\
&\quad \times \nabla_{\mathcal{F}R} \Phi^{(1)} \partial_t \mathcal{F}R^{(1)} - (\mathcal{F}_{\mathcal{N}^0+2})^{(2)}_{\cdot||\cdot} (\nabla_{\mathcal{F}R} \Phi^{(1)} - \nabla_{\mathcal{F}R} \Phi^{(2)}) \partial_t \mathcal{F}R^{(1)} \\
&\quad - (\mathcal{F}_{\mathcal{N}^0+2})^{(2)}_{\cdot||\cdot} \nabla_{\mathcal{F}R} \Phi^{(2)} (\partial_t \mathcal{F}R^{(1)} - \partial_t \mathcal{F}R^{(2)})) \cdot \nu|^2 \, dA \, ds \\
&\leq \mathit{const}(k, K) \int_0^{\mathcal{T}} \int_{\partial\Omega(0)} (|\partial_s \mathcal{F}^{(1)}_{\mathcal{N}^0+2} \cdot \nu - \partial_s \mathcal{F}^{(2)}_{\mathcal{N}^0+2} \cdot \nu|^2 + |||(\mathcal{F}_{\mathcal{N}^0+2})^{(1)}_{\cdot||\cdot} - (\mathcal{F}_{\mathcal{N}^0+2})^{(2)}_{\cdot||\cdot}|||^2 \\
&\quad + \|\nabla_{\mathcal{F}R} \Phi^{(1)} - \nabla_{\mathcal{F}R} \Phi^{(2)}\|^2_{L^\infty} + |\partial_t \mathcal{F}R^{(1)} - \partial_t \mathcal{F}R^{(2)}|^2) \, dA \, ds \\
&\leq \mathit{const}(k, K)(\|\partial_t \mathcal{F}^{(1)}_{\mathcal{N}^0+2} - \partial_t \mathcal{F}^{(2)}_{\mathcal{N}^0+2}\|^2_{L^2 H^1} + \|\mathcal{F}^{(1)}_{\mathcal{N}^0+2} - \mathcal{F}^{(2)}_{\mathcal{N}^0+2}\|^2_{L^\infty H^2} \\
&\quad + \|\mathcal{F}\tilde{R}^{(1)} - \mathcal{F}\tilde{R}^{(2)}\|^2_{L^\infty(0,\mathcal{T})} + \|\partial_t \mathcal{F}R^{(1)} - \partial_t \mathcal{F}R^{(2)}\|^2_{L^2(0,\mathcal{T})})
\end{aligned} \tag{4.121}$$

where the last step follows by means of the trace theorem. $|||\cdot|||$ emphasis here the corresponding Euclidean norm for matrices. By inserting (4.109) and (4.108), where we replace $\tilde{U}$ by $\mathcal{F}_{\mathcal{N}^0+2}$ and $\tilde{R}$ by $\mathcal{F}\tilde{R}$ we get

$$\begin{aligned}
&\int_0^{\mathcal{T}} |\partial_t(\mathcal{F}(\tilde{R}^{(1)}, \eta^{(1)}, \tilde{U}^{(1)})_0 - \mathcal{F}(\tilde{R}^{(2)}, \eta^{(2)}, \tilde{U}^{(2)})_0)|^2 ds \\
&\leq \mathit{const}(k, \kappa, K)(\|\mathcal{F}\tilde{R}^{(1)} - \mathcal{F}\tilde{R}^{(2)}\|^2_{L^\infty(0,\mathcal{T})} + \|\partial_t \mathcal{F}R^{(1)} - \partial_t \mathcal{F}R^{(2)}\|^2_{L^2(0,\mathcal{T})}).
\end{aligned} \tag{4.122}$$

Now we put (4.115), where we replace $\tilde{R}$ by $\mathcal{F}\tilde{R}$, and (4.120) into (4.122) and find

$$\|\partial_t \mathcal{F}\tilde{R}_0^{(1)} - \partial_t \mathcal{F}\tilde{R}_0^{(2)}\|_{L^2}^2 \leq const(k, \kappa, K)(\mathcal{T}\|\partial_t \mathcal{F}\tilde{R}_0^{(1)} - \partial_t \mathcal{F}\tilde{R}_0^{(2)}\|_{L^2}^2 + \sqrt{\mathcal{T}}\|\partial_t R^{(1)} - \partial_t R^{(2)}\|_{L^2}^2)$$

and for sufficiently small $\mathcal{T}$ this implies

$$\|\partial_t \mathcal{F}\tilde{R}_0^{(1)} - \partial_t \mathcal{F}\tilde{R}_0^{(2)}\|_{L^2}^2 \leq const(k, \kappa, K)\sqrt{\mathcal{T}}\|\partial_t \tilde{R}^{(1)} - \partial_t \tilde{R}^{(2)}\|_{L^2}^2.$$

With the strict contractions for the components $\mathcal{F}_i$, $0 \leq i \leq \mathcal{N}^0$ and the estimate (4.113) the strict contraction follows for the component $\mathcal{F}_{\mathcal{N}^0+1}$.

We consider the last component. The regularity results given in Theorem 4.2, 3) and 4.3, 3) also hold for the differences since we consider a linear PDE and we get, because the constants, which appear, depend only on the geometry and can be bounded by k,

$$\|D^2\tilde{U}^{(1)} - D^2\tilde{U}^{(2)}\|_{C^0} \leq const(k, K)\|\tilde{R}^{(1)} - \tilde{R}^{(2)}\|_{L^\infty} \tag{4.123}$$

and

$$\|\nabla\tilde{v}^{(1)} - \nabla\tilde{v}^{(2)}\|_{C^0} \leq const(k, K)(\|\tilde{R}^{(1)} - \tilde{R}^{(2)}\|_{L^\infty} + \|\partial_t\tilde{R}^{(1)} - \partial_t\tilde{R}^{(2)}\|_{L^2}). \tag{4.124}$$

The last two equations yield the strict contractions for the component $\mathcal{F}_{\mathcal{N}^0+2}$.

If we now choose $\mathcal{T}$ sufficiently small enough then $\mathcal{F}$ is strictly contractive in $\mathcal{M}$.

Analogously we get for all $i \in N$

$$\int_0^{\mathcal{T}} |\partial_t \mathcal{F}(\tilde{R}, \eta, \tilde{U})_i|^2 dt \leq \hat{C}(k, \kappa, K)\sqrt{\mathcal{T}}\|\partial_t \tilde{R}\|_{L^2(0,\mathcal{T})}^2 \leq k$$

for sufficiently small $\mathcal{T}$ and finally by checking the other components we get that $\mathcal{F}$ maps $\mathcal{M}$ into itself. Thus we have shown, that κ and K can be bounded by k.

Hence we can indeed apply Banach's fixed point theorem which gives a unique fixed point of the evolution of the free boundaries in $\mathcal{M}$ and hence the existence of a unique solution $(\tilde{R}, \tilde{n}_{As}, \tilde{U})$ for sufficiently small $\mathcal{T}$.

Since Φ is smooth the estimates carry over to the problem on time-dependent domain and this yields the existence and uniqueness of (R, n_{As}, U) in the corresponding spaces. ☐

The upper bound K in the proof of Th. 4.7 is linked to $\mathcal{O}(\tilde{h})k$. For global existence we have to bound k uniformly in $\mathcal{T}$, which yields bounds on κ and K uniformly in $\mathcal{T}$, which is done in the next section by explicit construction of sub- and supersolutions.

We remark, that this iterative procedure, which we used for proving existence, at least locally, can be used for numerically computing solutions of our problem. Since we worked with Banach's fixed point theorem, this would allow to give an explicit error and hence how fast a numerical iteration converges to the solution.

Corollary 4.5 (Existence and uniqueness of classical solutions of Problem E)**.** *The local solution of Problem E is a classical solution i.e.* $U^\varepsilon \in C^1C^2$*,* $n_{As}^\varepsilon \in C^1C^2$ *and* $\tilde{R} \in H^1(0, \mathcal{T})$*.*

Proof. Because we have established local existence of a generalised solution with $\tilde{R} \in H^1(0, \mathcal{T})$ and $v^\varepsilon \in L^2C^2$ we get from the regularity result from Th. 4.5, 3) that $\tilde{n}_{As}^\varepsilon \in C_1^2(0, \mathcal{T}; \Omega_S(t))$. Then we get from Th. 4.6 and from Th. 4.2, 3), Th. 4.3, 3) and Th. 4.5, 3) immediately the local existence of classical solutions $\tilde{R} \in C^1(0, \mathcal{T})$ and $\tilde{U}^\varepsilon \in C^1C^2$, where $\mathcal{T}$ is sufficiently small. This carries over on $U, n_{As}, \tilde{R}$ on time-dependent domain. ☐

Directly from the estimates (4.112) and (4.113) follows

Corollary 4.6 (Well-posedness of the nonlinear diffusion problem of the transformed Problem E)**.** *Given two radii solutions* $\tilde{R}^1$ *and* $\tilde{R}^2$ *then the difference of the corresponding solutions* $\tilde{n}^1_{As} - \tilde{n}^2_{As}$ *depends continuously on the difference* $\|\tilde{R}_1 - \tilde{R}_2\|$*. Furthermore the solution* $\tilde{n}_{As}$ *depends continuously on the initial data and on the velocities.*

This shows together with the Theorem 4.5 on the existence of a unique solution that our nonlinear diffusion problem is well-posed.

Remark 4.4 (More regularity and Problem DCR)**.** *Let* $\tilde{U}_f$ *denote the solution of the full mechanical BVP of Problem DCR after transformation on fixed domain. We recall that, the solution of the mechanical BVP of the transformed Problem E is denoted by* $\tilde{U}$*. The error* $\tilde{E} := \tilde{U}_f - \tilde{U}$ *between* $\tilde{U}_f$ *and* $\tilde{U}$ *solves the problem*

$$\tilde{\sigma}_S^{\cdot;j}\|_j(\nabla\tilde{E}) = 3k_S\varepsilon^9 h^{*\prime}(\tilde{n}_{As})D\Phi^{-T}\nabla\tilde{n}_{As} \qquad \text{in } \Omega_S(0), \tag{4.125}$$

$$\tilde{\sigma}_S(\nabla\tilde{E})\nu = 3k_S\varepsilon^9 h^*(\tilde{n}_{As})\nu \qquad \text{on } \partial\Omega(0), \tag{4.126}$$

$$(\tilde{\sigma}_S(\nabla\tilde{E}) - \frac{3k_L}{\varepsilon^3 r_i}⨍_{I_i(0)}(\tilde{E}\cdot\nu))\nu = 3k_S\varepsilon^9 h^*(n^{int,i}_{As})\nu \qquad \text{on } I_i(0)\ \forall i \in N, \tag{4.127}$$

and can be estimated according to Theorem 4.2 for given $\tilde{n}_{As} \approx \tilde{n}^*_{As}(1 + \mathcal{O}(\tilde{h}))$*, where* $\tilde{n}^*_{As}$ *is* $\tilde{n}_{As}$ *without mechanical coupling on the r.h.s., by*

$$\|\tilde{E}\|_{H^1/RD} \leq \varepsilon^9 k_S Const(h^*, h^{*\prime})\|\nabla n^*_{As}\|_{L^2\Omega_S}(1 + \mathcal{O}(\tilde{h})). \tag{4.128}$$

The functions h^* *and* $h^{*\prime}$ *herein are of order* $\mathcal{O}(\tilde{h})$ *and* $\|\nabla n^*_{As}\|$ *is bounded by* k *and the initial data.*

If we could extend our fixed point argument to solutions of the diffusion BVP of Problem E i.e. $\tilde{n}_{As} \in H^1H^1$*, then the approximation of Problem DCR by Problem E would be proved rigorously.*

We might work without the change of the evolution equation of the outer boundary in Problem DCR, (3.52)*, to the equation in Problem E* (4.10) *and prove rigorously local existence, if we include the term* $(\mathbb{I} + ⨍_{\Omega(0)}(\mathcal{F}_{\mathcal{N}^0+2})_{\cdot||\cdot}\partial_{\mathcal{F}_0}\Phi)^{-1}$ *in our fixed point argument in* (4.121)*.*

For the rest of our work we consider the diffusion problem (4.4) – (4.7) for the function u, since this allows easily to compare our model with the well-known LSW theory, which is formulated in terms of the chemical potential.

4.4. Global existence and uniqueness

Since we have proven that solutions $(u, U, \tilde{R})$ exist at least for arbitrary small time intervals $(0, \mathcal{T})$, we construct super- and subsolutions and exploit the generalised Gibbs Thomson boundary condition and the Stefan condition simultaneously in order to get a bound on the maximal speed of interfaces, k, independent of $\mathcal{T}$. The monopole approximation gives us a hint how to construct this super- and subsolutions. We follow the reasoning in [Nie99], where such a bound on k is proven for the standard heat-diffusion equation.

Lemma 4.3 (Construction of supersolutions and subsolutions locally around droplets)**.** *Let* $\hat{F}$ *be the global supersolution and* $\underline{F}$ *be the global subsolution from Corollary 4.3, respectively. Let* $v \in C^0(0, \mathcal{T}; C^1(\Omega_S(t)))$*. If we assume* $\|\nabla u_0\|_{C^0(I_i)} < \varepsilon^{-3}\frac{k}{2}$ *then there exist* $\hat{K}, \underline{K} > 0$ *s.t. for* ε *sufficiently small and where* $u^{max} := \hat{F} + \varepsilon^2(\hat{F} - \underline{F})$ *and* $u^{min} := \underline{F} - \varepsilon^2(\hat{F} - \underline{F})$*:*

$$\hat{\zeta}_i(t, x) := u^{max} - \varepsilon^3 r_i(t)\frac{u^{max} - u_{int}(r_i(t))}{|x - X_i|} + \frac{\hat{K}}{2}[|x - X_i|^2 - \varepsilon^6 r_i^2(t)]$$

is a supersolution on Σ_i*, while*

$$\underline{\zeta}_i(t,x) := u^{min} - \varepsilon^3 r_i(t)\frac{u^{min} - u_{int}(r_i(t))}{|x - X_i|} - \frac{\underline{K}}{2}[|x - X_i|^2 - \varepsilon^6 r_i^2(t)]$$

is a subsolution on Σ_i *for each* $i \in N$ *for some small time interval* $[0, \tilde{\mathcal{T}}]$*.*
Furthermore the boundary condition on the interfaces matches exactly i.e. $\hat{\zeta}_i|_{I_i} = \underline{\zeta}_i|_{I_i} = u_{int}(r_i)$*.*

Proof. Let $d := \min_{i \in N} d_i$, where d_i is defined as in 3.3. In this proof we choose k s.t. $\varepsilon^3 r_i \leq \frac{1}{2} R^i_{ext}$ for all $t \in (0, \mathcal{T})$ and set $R^i_{ext} = \varepsilon \frac{d}{3}$.
We consider some arbitrary droplet i and check that $\hat{\zeta}_i$ is indeed a supersolution to u restricted on Σ_i. On the boundaries

$$\begin{aligned}
\hat{\zeta}_i(t,x)|_{I_i} &= u_{int}(r_i(t)),\\
\hat{\zeta}_i(t,x)|_{\partial\Sigma_i \setminus I_i} &= u^{max} - 3\varepsilon^2 r_i(t)\frac{u^{max} - u_{int}(r_i(t))}{d} + \frac{\hat{K}}{2}[\frac{1}{9}\varepsilon^2 d^2 - \varepsilon^6 r_i^2(t)] \geq \hat{F} \geq u|_{\partial\Sigma_i \setminus I_i},
\end{aligned}$$

where the last line holds on $A := \{t \mid \max_{i \in N} r_i < \frac{d}{6\varepsilon^2}\}$ for every $\hat{K} \geq 0$. Besides we exploited that $\hat{F}$ is a supersolution on the whole solid $\Omega_S(t)$.
If we assumed that $\varepsilon^3 \|\nabla u^0\|_{C^0(I_i)} < \frac{k}{2}$, then the Stefan condition at the initial time yields

$$|\dot{r}_i(t=0)| \leq \frac{k}{2}$$

and hence

$$|\dot{r}_i(t)| \leq k(\frac{1}{2} + \tilde{\mathcal{T}}) \leq k$$

for a time interval $[0, \tilde{\mathcal{T}}]$. We estimate on $[0, \tilde{\mathcal{T}}] \cap A$ that

$$\begin{aligned}
&\varepsilon^3(\mathcal{X}(\hat{\zeta}_i)(\partial_t \hat{\zeta}_i + v \cdot \nabla\hat{\zeta}_i) + \nabla \cdot v\, \Xi(\hat{\zeta}_i)) - \Delta\hat{\zeta}_i\\
&= \varepsilon^3 \mathcal{X}(\hat{\zeta}_i)(-\varepsilon^3 \dot{r}_i \frac{|u^{max} - u_{int}(r_i) - \partial_r u_{int}(r_i) r_i|}{|x - X_i|} - \hat{K}\varepsilon^6 r_i \dot{r}_i\\
&\quad + v \cdot (\varepsilon^3 r_i \frac{u^{max} - u_{int}(r_i)}{|x - X_i|^2} + \hat{K})(x - X_i)) + \varepsilon^3 \nabla \cdot v\, \Xi(\hat{\zeta}_i) + 3\hat{K}\\
&\geq -\varepsilon^3 \mathcal{X}(\hat{\zeta}_i) k (\frac{|u^{max} - u_{int}(r_i) - \partial_r u_{int}(r_i) r_i|}{|x - X_i|} + \hat{K}\varepsilon^3 r_i)\\
&\quad - \varepsilon^3 \|v\|_{C^0(\Omega_S(t))}(\varepsilon^3 r_i \frac{|u^{max} - u_{int}(r_i)|}{|x - X_i|} + \hat{K}|x - X_i|) - \varepsilon^3 \|\nabla \cdot v\|_{C^0(\Omega_S(t))}\, const(\Xi) + 3\hat{K}\\
&\geq -\varepsilon^3 \mathcal{X}(\hat{\zeta}_i) k (2\frac{\hat{F} - \underline{F}}{r_{min}} + |\partial_r u_{int}(r_{min})| + \varepsilon\frac{d}{6}\hat{K})\\
&\quad - \varepsilon^3(\|v\|_{C^0(\Omega_S(t))} k(2(\hat{F} - \underline{F}) - \|\nabla \cdot v\|_{C^0(\Omega_S(t))}\, const(\Xi)) + \varepsilon\frac{d}{6}\hat{K}) + 3\hat{K} \geq 0
\end{aligned}$$

for

$$\hat{K} \geq \frac{4}{3}\varepsilon^3[k[2(\hat{F} - \underline{F})(\frac{\max \mathcal{X}}{r_{min}} + \|v\|_{C^0(\Omega_S(t))}) + |\partial_r u_{int}(r_{min})|] + \|\nabla \cdot v\|_{C^0(\Omega_S(t))}\, const(\Xi)]$$

and ε small enough e.g. $\varepsilon^4 < \frac{18}{kd}$. Now $\hat{\zeta}_i$ is a supersolution and we can apply the maximum principle to deduce $\hat{\zeta}_i \geq u$ on $I_i \times [0, \tilde{\mathcal{T}}] \cap A$. Analogously the claim about the local subsolution is checked where e.g. $\underline{K} > \frac{4}{3}\varepsilon^3[k(\hat{F} - \underline{F})(\frac{\max \mathcal{X}}{r_{min}} + \|v\|_{C^0(\Omega_S(t))}) + \|\nabla \cdot v\|_{C^0(\Omega_S(t))}\, const(\Xi)]$. $\square$

Lemma 4.4 (Bound on radii and on growth of radii)**.** *Let for the initial radii hold* $\sum_i r_i^0 < \infty$ *and* $\sum_i (r_i^0)^2 < \infty$*. If* $v \in C^0(0, \mathcal{T}; C^1(\Omega_S(t)))$ *and* $\|\nabla u^0\|_{C^0(I_i)} < \varepsilon^{-3}\frac{k}{2}$ *— as in the assumptions of the last lemma —, then for sufficiently small* $\varepsilon > 0$ *there exists a constant* $K = K(\Omega(0), u^0)$*, which is independent of* $\mathcal{T}$*, s.t. for any local solution of Problem E,*

$$\max_{i \in \mathcal{N}} \|r_i\|_{L^\infty(0,\mathcal{T})} \leq K + \max_{i \in \mathcal{N}} \|r_i^0\| \tag{4.129}$$

and

$$-K \frac{|u^{min} - u_{int}(r_i)|}{r_i} \leq \dot{r}_i \leq K \frac{u^{max} - u_{int}(r_i)}{r_i}$$

and hence

$$k \leq 2|\hat{F} - \underline{F}| \frac{K}{r_i} \tag{4.130}$$

for a.a. $t \in (0, \tau_i)$ *where* τ_i *is the time when the i-th droplet vanishes as defined in* (2.3)*.*

Proof. The initial data is smooth, hence u and ∇u smooth up to $t = \tau_i$. With the maximum principle we prove with $\hat{\zeta}_i = u_{int}(r_i)$ on I_i and $\hat{\zeta}_i \geq \tilde{u}$ in $\Omega_S(t)$, which we showed in the last lemma 4.3, that

$$\nabla \tilde{u} \cdot \nu \leq \nabla \hat{\zeta}_i \cdot \nu \quad \text{on } I_i \times [0, \tilde{\mathcal{T}}] \cap A.$$

We calculate

$$\dot{r}_i(t) \leq \varepsilon^3 \nabla \hat{\zeta}_i(t,x) \cdot \nu|_{I_i} = \frac{u^{max} - u_{int}(r_i(t))}{r_i(t)} + \varepsilon^6 \hat{K} r_i(t) \quad \text{in } [0, \tilde{\mathcal{T}}] \cap A.$$

That gives with our choice of $\hat{K} = \hat{\kappa} k$ from the last lemma and $\varepsilon \leq \frac{d}{6r_i}$ small enough that

$$\dot{r}_i(t) \leq \frac{u^{max} - u_{int}(r_i(t))}{r_i(t)} \frac{1}{1 - \varepsilon^6 r_i \hat{\kappa}} \leq K \frac{u^{max} - u_{int}(r_i(t))}{r_i(t)} \quad \text{in } [0, \tilde{\mathcal{T}}] \cap A$$

e.g. with $K = \frac{1}{1 - \varepsilon^4 \frac{d}{6} \hat{\kappa}}$ only depending on data. Analogously we get

$$\dot{r}_i(t) \geq \varepsilon^3 \nabla \underline{\zeta}_i(t,x) \cdot \nu|_{I_i} = \frac{u^{min} - u_{int}(r_i(t))}{r_i(t)} - \varepsilon^6 \underline{K} r_i(t) \quad \text{in } [0, \tilde{\mathcal{T}}] \cap A$$

and since $\underline{K} < \hat{K}$, where $\underline{K}$ is chosen as in the last lemma,

$$\dot{r}_i(t) \geq K \frac{u^{min} - u_{int}(r_i(t))}{r_i(t)} \quad \text{in } [0, \tilde{\mathcal{T}}] \cap A.$$

We can iterate this procedure in $[0, \tau_1] \cap A$. By integrating up

$$r_i^2(t) = (r_i^0)^2 + 2 \int_0^t \dot{r}_i(s) r_i(s) ds \leq (r_i^0)^2 + 4K|\hat{F} - \underline{F}|t, \tag{4.131}$$

which yields $[0, \tau_1] \subset A$ i.e. the choice of ε depends only on data, in particular on $\tilde{\mathcal{T}}$, which is finite, and we get finally the bounds on $\dot{r}_i$ in $t \in [0, \tau_1]$. $\dot{r}_i$ is not necessarily smooth in τ_1.
Finally we calculate

$$r_i(t) \leq r_i^0 + 2|\hat{F} - \underline{F}| K \int_0^t \frac{1}{r_i(s)} ds \leq r_i^0 + 2|\hat{F} - \underline{F}| \frac{K}{r_{min}} t. \tag{4.132}$$

$\square$

We remark, that the constants $\hat{K}$, $\underline{K}$ and K in the last two lemmas still depend on ε.

Corollary 4.7 (Estimates on moments of radii). *Let for the initial radii hold* $\sum_i r_i^0 < \infty$ *and* $\sum_i (r_i^0)^3 < \infty$. *Under the same conditions as in the last lemma 4.4, for sufficiently small* $\varepsilon > 0$ *with same constant* $K = K(\Omega(0), u^0)$ *as above, there holds for any local solution of Problem E,*

$$\sum_{i\in N(t)} r_i^q(t)) \le Const(K, \hat{F} - \underline{F}, \sum_{i\in N(0)} r_i^0, \sum_{i\in N(0)} r_i^3) \tag{4.133}$$

for any $1 \le q \le 3$. *In particular there holds*

$$\sum_{i\in N} r_i^3 \le \sum_{i\in\mathcal{N}} (r_i^0)^3 + 6|\hat{F} - \underline{F}|K\mathcal{T}\sum_{i\in N} r_i^0 + 12|\hat{F} - \underline{F}|^2 \frac{K^2}{r_{min}}\mathcal{T}^2. \tag{4.134}$$

We have also an estimate on the zero-th moment,

$$\sum_{i\in N} 1 = \frac{\mathcal{N}(t)}{\mathcal{N}^0} \le 1. \tag{4.135}$$

Proof. We have by using (4.130) the following estimate for the volume of the droplet i,

$$r_i^3(t) = (r_i^0)^3 + 3\int_0^t \dot{r}_i(s) r_i^2(s) ds \le (r_i^0)^3 + 6|\hat{F} - \underline{F}|K \int_0^t r_i(s) ds.$$

By inserting the estimate (4.132) for r_i the estimate on volume change is

$$\sum_{i\in N(t)} r_i^3(t) \le \sum_{i\in N(0)} (r_i^0)^3 + 6|\hat{F} - \underline{F}|K\mathcal{T}\sum_{i\in N(0)} r_i^0 + 12\frac{\mathcal{N}(t)}{\mathcal{N}^0}|\hat{F} - \underline{F}|^2 \frac{K^2}{r_{min}}\mathcal{T}^2.$$

All other moments $\sum_i r_i^q$, $1 < q < 3$ can be estimated by means of the interpolation inequality

$$(\sum_{i\in N(t)} r_i^q(t))^{1/q} \le (\sum_{i\in N(t)} 1)^{\Theta}(\sum_{i\in N(t)} r_i^3(t))^{(1-\Theta)/3}, \quad \Theta := \frac{1}{2}(\frac{3}{q} - 1)$$

or

$$\sum_{i\in N(t)} r_i^q(t)) \le (\sum_{i\in N(t)} 1)^{\frac{1}{2}(3-q)}(\sum_{i\in N(t)} r_i^3(t))^{\frac{1}{2}(q-1)}. \tag{4.136}$$

The estimate (4.135) of the zero-th moment follows by our assumption, that droplets can vanish, but are not created. ☐

Due to Lemma 4.4 we can extend our fixed point iteration up to arbitrary $\mathcal{T} \le \min_{i\in N} \tau_i$ i.e. until the first droplet vanishes, which is the second crucial point, which could prevent global existence, if the new initial data at time τ_i+ is not “good” enough.

Remark 4.5 (Vanishing of droplets). *We model the vanishing of the droplet i as in Assumption 2.6. We recall that* $r_j, j \ne i$ *are continuous and that, if* $r_i = r_{min}$ *at time* τ_i, *then we restart with a new problem with initial time* τ_i *where we work with* $\mathcal{N} - 1$ *droplets, new solid* $\Omega_S^\varepsilon(\tau_i+) := \Omega_S^\varepsilon(\tau_i-) \cup \overline{\Omega_L^i(\tau_i-)}$ *and we extend our new initial data on* $\Omega_L^i(\tau_i-)$ *s.t. the conservation of mass and substance is fulfilled.*

We already have given in (2.168) an extension s.t. the new initial data $n_{As}(\cdot, \tau_i+) \in H^1(\Omega_S(\tau_i+)))$. *In particular we get since* $u(\tau_i-) \in C^1$ *in space as classical solution and*

$$\nabla u(\tau_i+, x) = u'(n_{As}(\tau_i+, x))\frac{p+1}{p+3}p\left(\frac{|x - X_i|}{r_{min}}\right)^{p-1} [[n_{As}(\tau_i-, \cdot)|_{I_i}]]_L^S \quad \forall x \in \Omega_L^i(\tau_i-) \tag{4.137}$$

with p independent of k that $|\nabla u(\tau_i+,\cdot)| \leq Const$ *with a constant independent of* k.

Theorem 4.8 (Global existence and uniqueness for Problem E)**.** *For given* $\mathcal{T} > 0$ *and* $\varepsilon > 0$ *small enough,* ε *depending on the initial geometry* $\tilde{R}^0$ *and if* $u^0 \in H^1(\Omega^0)$ *uniformly in* $\frac{1}{\varepsilon^3}$*, there exists a unique solution* $(u, U, \tilde{R})$ *of Problem E (4.1) – (4.11) for all times* $t \in (0, \mathcal{T})$.

The solution $(u, U, \tilde{R})$ *has the following properties. There exist times* $0 < \tau_1 < ... < \tau_m \leq \mathcal{T}$ *s.t.* $(u, U, \tilde{R})$ *is a classical solution on* $\cup_{t\in(\tau_{k-1},\tau_k)}\{t\} \times \Omega_S(t)$ *(i.e.* $u \in C^1(\tau_{k-1}, \tau_k; C^2(\Omega_S(t)))$, $U \in C^1(\tau_{k-1}, \tau_k; C^2(\Omega_S(t)))$ *and* $\tilde{R} \in C^1(\tau_{k-1}, \tau_k)$*) and* u *is continuous in* t *in* $L^2(\Omega_S(t))$*,* U *is continuous in* t *in* $C^2(\Omega_S(t))$ *and* $\tilde{R}$ *continuous in* t.

Furthermore $u \in L^\infty \cap H^1(0, \mathcal{T}; C^2(\Omega_S(t)))$, $U \in H^1(0, \mathcal{T}; C^2(\Omega_S(t)))$ *and* $\tilde{R} \in H^1(0, \mathcal{T})$.

Proof. Since we have shown in Lemma 4.4 that we can bound k independent of $\mathcal{T}$, our local existence result Th. 4.7 holds for $\mathcal{T} > 0$. We can extend our local classical solution up to the time $\min_{i\in N} \tau_i$, when for the first time at least the radius of one droplet is r_{min}. Let $j = \text{argmin}_{j\in N(0)}\tau_i$.

Remark 4.5 shows that in our model the new initial data is again in $H^1(\Omega_S(\tau_j+))$, since $u(t,\cdot) \to u^(\tau_j, \cdot)$ in $L^2(\Omega_S(t))$ as t to τ_j+, and furthermore $\|\nabla u(\tau_i+,\cdot)\|_{L^\infty(\Omega_S(\tau_j+))} \leq \varepsilon^{-3}\frac{k}{2}$.

With our new initial data $u(\tau_i+)$ and $\tilde{R}(\tau_i+)$ we iterate our procedure for all times up to $\mathcal{T}$. We finally get a unique solution, which is piecewise smooth as described in the statement of the theorem. ☐

We remark, that we need that $\mathcal{T} < \infty$ is given s.t. we can choose ε sufficiently small, such that no encounters occur until $\mathcal{T}$.

Chapter 5.

Rigorous Homogenisation

Now we want to pass rigorously to the limit of Problem E i.e. in regime (DC). We will see that under some reasonable additional assumptions as e.g. Assumption 5.2 we find a mean field model for the critical scaling. This mean field model is similar to the mean field model derived by formal homogenisation in Chapter 3 for the dilute scaling.

5.1. Droplet distributions

We introduce now a suitable approximation ν_ε^t of a limit distribution ν^t. Furthermore we write $\mathcal{C} := [C_0^0(\Omega(0) \times \mathcal{J}_r)] := \{\phi(x,r) \in C^0(\Omega \times \mathcal{J}_r) | \phi$ has compact support in $x \in \Omega(0)$ and in $r \in \mathcal{J}_r\}$, that is the space of test functions with compact support in the domain and in radii. Since we consider the case, where droplet centres are fixed and do not collide with the outer boundary, it is adequate to consider $x \in \Omega(0)$ and not $x \in \Omega(t)$.

Definition 5.1 (Distribution of droplets for fixed ε)**.** *Define a non-negative measure $\nu_\varepsilon^t \in \mathcal{C}' := [C_0^0(\Omega(0) \times \mathcal{J}_r)]'$ for $t \in \mathcal{J}_t$ by*

$$\fint_{\Omega(0)} \int_{r_{min}}^{\infty} f(x,r,t) d\nu_\varepsilon^t := \sum_{i \in N^\varepsilon} f(X_i, r_i, t) \tag{5.1}$$

where $f \in \mathcal{C}, t \in \mathcal{J}_t$ and $\sum_{i \in N^\varepsilon}$ as defined in (3.19). This measure is a joint distribution of particle centres and radii.

Due to our assumption (3.4) it suffices to consider the domain $\Omega(0)$ for the droplet centres X_i. Since we will find a bound (5.10), that $\dot{R}_{bd} \sim \varepsilon^3$, this is well-defined in the sense that no droplets close to the boundary intersect $\partial\Omega(t)$.

The measure ν_ε^t is nothing else than

$$d\nu_\varepsilon^t(x,r) = \sum_{i \in N^\varepsilon} \delta_{r_i(t)}(r) \delta_{X_i}(x) dr dx.$$

Or in other words, if $\omega \subset \Omega(0)$ and $(r_1, r_2) \subset \mathcal{J}_r$ then

$$\int_\omega \int_{r_1}^{r_2} d\nu^t(x,r) = \frac{\#\text{ of droplets with radius } r \in (r_1,r_2) \text{ and center } x \in \omega \text{ at fixed time } t \in \mathcal{J}_t}{\#\text{ of droplets with radius } r \in \mathcal{J}_r \text{ and center } x \in \Omega \text{ at initial time } t = 0}.$$

Note, that this measure ν_ε^t does not have a Lebesgue density.

The measure $\nu_\varepsilon^t(t=0)$ is normalised since

$$\mathbb{E}_{\nu_\varepsilon^t(t=0)}(1) := \lim_{r_{max}\to\infty} \fint_{\Omega(0)} \int_{\mathcal{J}_r} \mathbb{I}_{r\le r_{max}}(r)\, d\nu_\varepsilon^t(x,r) = \varepsilon^3 \sum_{i=1}^{\varepsilon^{-3}} 1 = 1.$$

Hence for all $\delta > 0$ there exists a r_{max} s.t. $\nu_\varepsilon^t(x,r) < \delta$ for all $r > r_{max}$.

Note that since $f(x,r,t) = 0$ for $r \le r_{min}$, droplets which have vanished do not enter into the distribution. The space $\mathcal{C}'$ can be identified with the space of non-negative Borel measures on $\Omega \times \mathcal{J}_r$.

Definition 5.2 (Admissible initial distributions)**.** *We define $\mathcal{C}_0'$, the class of admissible initial distributions as follows. $\nu_\varepsilon^0 \in \mathcal{C}_0'$ iff for all $\varepsilon > 0$:*

a) $\nu_\varepsilon^0 \in \mathcal{C}' = [C_0^0(\Omega(0) \times \mathcal{J}_r)]'$.

b) The initial distribution ν_ε^0 is normalised i.e.

$$\mathbb{E}_{\nu_\varepsilon^0}(1) = \sum_{i=1}^{\varepsilon^{-3}} 1 = 1 \text{ (Normalisation).}$$

c) ν_ε^0 has a uniformly in ε bounded mean value $\mathcal{R}_M$ of the radii

$$\mathcal{R}_M := \mathbb{E}_{\nu_\varepsilon^0}(r) = \sum_{i=1}^{\varepsilon^{-3}} r_i^0 \in (r_{min}, R_{bd}^0) \text{ (Finite mean radii),}$$

d) ν_ε^0 has a uniformly in ε bounded 3rd moment i.e.

$$\mathbb{E}_{\nu_\varepsilon^0}(r^3) = \sum_{i=1}^{\varepsilon^{-3}} (r_i^0)^3 =: \frac{3}{4\pi}\mathcal{V}_M \in (r_{min}^3, (R_{bd}^0)^3] \text{ (Finite mean volume of droplets } \mathcal{V}_M\text{),}$$

e) For initial distances between droplets there holds

$$\inf_{1\le i<j\le\varepsilon^{-3}} |X_i - X_j| > \varepsilon^2 \max_{1\le i<j\le\varepsilon^{-3}} (r_i^0 + r_j^0) \text{ (Droplets do not intersect each other),}$$

f) For initial distances between a droplet and the outer boundary there holds

$$\inf_{1\le i\le\varepsilon^{-3}} dist(X_i, \partial\Omega(0)) > \varepsilon^2 \max_{1\le i\le\varepsilon^{-3}} r_i^0 \text{ (Droplets do not intersect outer boundary).}$$

We remark, that by the definition of $\mathcal{C}'$ condition a) implies b). We give two examples for such ν_ε^0.

Example 5.1 (Discrete initial data)**.** *We consider a number of ε^{-3} droplets with a finite number $K > 1$ of non necessarily different droplet radii*

$$\nu_\varepsilon^0(r,x)dr = \frac{1}{K}\sum_{i=1}^{K}\sum_{j=1}^{\varepsilon^{-3}} \delta_{r_i^0}(r)\delta_{X_j}(x)drdx,$$

with equidistantly distributed droplets in some interval $(r_1, r_2) \in \mathcal{J}_r$ s.t. $r_i := r_1 + (i-1)\frac{r_2 - r_1}{K-1}$. The droplet centres sit on a lattice $(\varepsilon(\frac{1}{2}+k), \varepsilon(\frac{1}{2}+l), \varepsilon(\frac{1}{2}+m))$, with $k, l, m \in \mathbb{N}, 0 \le k, l, m \le \varepsilon^{-1} - 1$. This means that the K radii appear periodically w.r.t. the lattice.

Since the densities for radii and centres are independent of each other we can consider only the *marginal density w.r.t. radii i.e.*

$$[\nu_\varepsilon^t]_r dr = \frac{1}{K}\sum_{i=1}^{K} \delta_{r_i(t)}(r)dr$$

in order to get information about the radii.

We check that ν_ε^0 *is normalised and* $\mathcal{R}_M = \frac{1}{2}(r_1+r_2)$ *and* $\frac{3}{4\pi}\mathcal{V}_M = \frac{1}{4}((r_1^2+r_2^2)+\frac{(r_1-r_2)^2}{K-1}))(r_1+r_2)$. *The distances between neighbouring droplets are* ε *and the minimal distance to the outer boundary is* $\frac{\varepsilon}{2}$.

For typical data we expect $\mathcal{R}_M = \mathcal{R}_0 = 10^{-9}\mathrm{m}$, $\frac{3}{4\pi}\mathcal{V}_M = 10^{-27}\mathrm{m}^3$ and $|X_i - X_j| = 10^{-6}\mathrm{m}$ for all $1 \le i < j \le \mathcal{N}_0$. We remark that the periodicity of this example is not necessary for an admissible initial distribution.

It might be motivated to consider discrete initial data, by the fact that, droplets can grow by gaining atoms or shrink by loosing atoms and the number of atoms is a discrete variable. To each number of atoms corresponds a certain radius, which means that only certain values of radii make physically sense. But this argumentation is not mandatory, since we assume that r_i changes continuously on the other hand.

Example 5.2 (Smooth initial data)**.** *Now we assume*

$$\nu_\varepsilon^0(x,r)dr = \frac{1}{\int_{r_1}^{r_2}\nu(r)dr}\varepsilon^3\sum_{i=1}^{\varepsilon^{-3}}\nu(r)\delta_{X_i}(x)drdx,$$

with a smooth function ν *which has compact support in* $(r_1,r_2) \in \mathcal{J}_r$ *e.g. an LSW-like distribution, see [LS61]. Again the droplet centres sit on a fixed lattice* $(\frac{\varepsilon}{2},\frac{\varepsilon}{2},\frac{\varepsilon}{2}) + (\varepsilon\mathbb{Z})^3$, *where* $\mathbb{Z}$ *denotes only here the integer numbers.*

Since the densities are again independent of each other one could consider the marginal density w.r.t. radii directly

$$[\nu_\varepsilon^t]_r dr = \nu(r)dr.$$

By definition ν_ε^0 *is normalised and the integrals* $\mathcal{R}_M$ *and* $\mathcal{V}_M$ *exist. As in the last example the conditions e) and f) of Definition 5.2 are fulfilled.*

We want to fulfil the conditions of Def. 5.2 for all times t up to $\mathcal{T}$. The last two conditions can always be fulfilled by considering only ε which are sufficiently small:

Lemma 5.1 (No "encounters")**.** *For sufficiently small* ε, *depending on* $\mathcal{T}$, *eq.* (3.4) *is fulfilled i.e. the droplets* Ω_L^i *are pairwise disjoint for all* $t \in \mathcal{J}_t$ *and do not intersect* $\partial\Omega$.

Proof. Due to bounded change of volume (4.134) there holds for ε small enough and for given $\mathcal{T}$

$$\varepsilon^3 r_i \le \varepsilon^2(\sum_{i\in N^\varepsilon} r_i^3)^{1/3} \le \varepsilon^2((\sum_{i\in N^\varepsilon}(r_i^0)^3)^{1/3} + const(k)\mathcal{T})) = \varepsilon^2(\mathcal{V}_M^{1/3} + const(k)\mathcal{T}) < \frac{\varepsilon}{2} = \frac{\mathcal{D}}{2}.$$

□

Definition 5.3 (Distribution of radii growth)**.** *We define the distribution for the growth speed of radii by*

$$\fint_{\Omega(0)}\int_{\mathcal{J}_r} a_\nu^{(x)}(r,t)d\nu_\varepsilon^t \overset{(5.1)}{=} \sum_{i\in N^\varepsilon} a_\nu^{(X_i)}(r_i,t) := \sum_{i\in N^\varepsilon}\dot{r}_i(t).$$

5.2. Uniform estimates for the displacement and the velocity

We need estimates uniformly in ε on U^ε, u^ε and on moments of the radii distribution ν^t_ε in order to derive rigorously effective equations, which will turn out in particular cases to give the mean field model. There are two possible ways to derive such uniform estimates.

First we could use our approximation formulas from Subsections 3.3.1 and 3.3.2 and the corresponding corrector results, but here we have to consider also the liquid. Furthermore the approximation formulas are stated in the other i.e. the dilute scaling. The second approach is by testing the PDE directly. We follow the second approach in this section in order to get estimates on the displacement U and on the chemical potential u in Problem E, which are uniformly in the scaling parameter ε.

We extend the displacement and the Cauchy stress on Ω^ε_L and the total chemical potential and the arsenic mole density on Ω^ε_L in order to get uniform estimates.

Definition 5.4 (Extension of the solutions onto the liquid)**.** *The Cauchy stress is extended into the liquid as in (2.80) and U^ε_L is introduced as in (2.15).*

Formally we extend u^ε on Ω_L by u^ε_L, which is constant in space and then u^ε continuous on I_i. We extend n^ε_{As} by n_{As_L} on Ω^ε_L.

We remark, that it is not possible to extend the diffusion equation for u^ε into the liquid, only the local conservation of As_L could be used.

First we examine the dependence of several constants, which depend on the geometry, on ε.

Lemma 5.2 (Dependence of the constants of trace embeddings on ε)**.** *Let $f^\varepsilon \in H^1(\Omega^\varepsilon_S)$ be arbitrary.*

1) *The constant C of the trace theorem $H^1(\Sigma^\varepsilon_i) \hookrightarrow L^2(I^\varepsilon_i)$, $i \in N$,*

$$\|f^\varepsilon\|_{L^2(I^\varepsilon_i)} \leq C(I^\varepsilon_i, \Sigma^\varepsilon_i)\|f^\varepsilon\|_{L^2(\Sigma^\varepsilon_i)}$$

scales with $\varepsilon^{3/2}$ for our geometry.

2) *The constant C of the trace theorem $H^1(\Sigma^\varepsilon_0) \hookrightarrow L^2(\partial\Omega)$*

$$\|f^\varepsilon\|_{L^2(\partial\Omega)} \leq C(\partial\Omega, \Sigma^\varepsilon_0)\|f^\varepsilon\|_{L^2(\Sigma^\varepsilon_0)}$$

scales with ε^0 for our geometry.

Proof. We prove part 1). The statement 2) follows analogously.

Let for some fixed $\varepsilon = 1$ and a not on ε depending function f

$$\|f\|^2_{L^2(I^1_i)} \leq C(1)\|f\|^2_{H^1(\Sigma^1_i)} = C(1)(\|f\|^2_{L^2(\Sigma^1_i)} + \|\nabla f\|^2_{L^2(\Sigma^1_i)}), \tag{5.2}$$

where $C(1)$ is independent of ε. We scale coordinates $x \to \varepsilon x$ and radii as $r_i \to \varepsilon^3 r_i$ and define $f^\varepsilon(x) := f(\varepsilon x)$. The estimate (5.2) also holds for arbitrary ε with a constant $C(\varepsilon)$

$$\|f^\varepsilon\|^2_{L^2(I^\varepsilon_i)} \leq C(\varepsilon)(\|f^\varepsilon\|^2_{L^2(\Sigma^\varepsilon_i)} + \|\nabla f^\varepsilon\|^2_{L^2(\Sigma^1_i)}). \tag{5.3}$$

By scaling (5.2) we find

$$\varepsilon^{-6}\|f^\varepsilon\|^2_{L^2(I^\varepsilon_i)} \leq C(1)(\varepsilon^{-3}\|f^\varepsilon\|_{L^2(\Sigma^\varepsilon_i)} + \|\nabla f^\varepsilon\|_{L^2(\Sigma^\varepsilon_i)})^2$$

and hence $C(\varepsilon) \leq C(1)\,\varepsilon^3$. □

If we sum up over all ε^{-3} interfaces I_i^ε and $\partial\Omega$, then we have $H^1(\Omega_S^\varepsilon) \to L^2(\partial\Omega_S^\varepsilon)$ with a trace constant independent of ε. We remark that this a special case of a more general result from Bonder, Orive and Rossi [BOR07], which states that in our case, where we scale radii with ε^3 compared to Ω, the best Sobolev trace constant in domains with holes is in the limit $\varepsilon \to 0$ independent of ε.

Lemma 5.3 (Dependence of Korn's constant on ε). *Let $U \in H^1(\Omega_S;\mathbb{R}^3)/RD$ or $U \in H_0^1(\Omega_S;\mathbb{R}^3)$. For sufficiently small $\varepsilon > 0$ Korn's constant K, which appears in Korn's inequality $\|\nabla U\|_{L^2(\Omega)}^2 \leq K(\Omega)\|e(\nabla U)\|_{L^2(\Omega_S)}^2$, is for our geometry i.e. an open bounded domain Ω with small holes and compact closure, independent of ε.*

Proof. We see this as follows: We cover Ω_S with sets $S_j \subset \Omega_S$, which are either spherical shells around the liquid droplets or are either spheres and convex smooth domains without holes, which cover the parts of Ω_S, which remain. Since $\overline{\Omega}$ is compact we can assume that each point of Ω_S is covered by a fixed number Z of sets S_j, where Z depends on the geometry of the droplet centres X_i, but is independent of ε.
Korn's constant for spheres, convex domains and spherical shells, which have interior radii which are sufficiently smaller than the radius of the outer sphere, is bounded by $2 + d$ (see [ADP88]), in our case the dimension is $d = 3$.
For each set S_j, $1 \leq j \leq Const\,\varepsilon^{-3}$ we have the estimate

$$\|\nabla U\|_{L^2(S_j)}^2 \leq K(S)\|e(\nabla U)\|_{L^2(S_j)}^2 \leq 5\|e(\nabla U)\|_{L^2(S_j)}^2.$$

By adding up over all sets S_j we get

$$\|\nabla U\|_{L^2(\Omega_S)}^2 \leq \sum_{j=1}^{Const\,\varepsilon^{-3}} K(S_j)\|e(\nabla U)\|_{L^2(S_j)}^2 \leq 5 \sum_{j=1}^{Const\,\varepsilon^{-3}} \|e(\nabla U)\|_{L^2(S_j)}^2 \leq 5Z\|e(\nabla U)\|_{L^2(\Omega_S)}^2.$$

□

Theorem 5.1 (Uniform estimates on U and v). *We have, that the non-zero data of the displacement problem $g_0 \in L^2(\partial\Omega)$ and $g_i \in L^2(I_i)$, $i \in N$ is uniformly bounded in ε. If $\tilde{R} \in H^1(0,\mathcal{T})$ and the assumptions* (3.4) *on our geometry hold, then $U \in L^2H^1$ uniformly in ε.*

If k is uniformly bounded in ε then the non-zero data of the velocity problem $g_i^{(v)} = \partial_{r_i} g^i \dot{r}_i$, $i \in N$ is uniformly bounded in ε in $L^2(I_i)$ and $v \in L^2H^1$ uniformly in ε. In particular $\|v\|_{L^2H^1} \leq Const\,\varepsilon^3 k$, with a constant independent of ε.

Proof.

1) Displacement

We test the mechanical problem (4.1) – (4.3) with (4.15) – (4.17), extended into the liquid according to Def. 4.1, with U^ε

$$\int_\Omega \sigma_S : \nabla U = \int_{\partial\Omega} \sigma_S U \nu - \sum_{i=1}^{\mathcal{N}} \varepsilon^3 \int_{I_i} [[\sigma_S U]] \cdot \nu,$$

and plug in the constitutive laws for the Cauchy stress in solid and in the liquid, (2.77) and (2.80), and the boundary conditions on the free boundaries (4.2) and (4.3)

$$\int_{\Omega_S} -\overline{p}\,\mathrm{tr}(\nabla U) + \lambda_S[\mathrm{tr}(\nabla U)]^2 + 2\mu_S \nabla U : \nabla U + \sum_{i=1}^{\mathcal{N}} \varepsilon^6 \int_{\Omega_L^i} -(\overline{p} + 3k_L h_L^*)\mathrm{tr}(\nabla U_L) + k_L[\mathrm{tr}(\nabla U_L)]^2$$
$$= -\int_{\partial\Omega} p_0 U \cdot \nu - 2\sigma \sum_{i=1}^{\mathcal{N}} \varepsilon^3 \int_{I_i} \frac{1}{r_i} U \cdot \nu + \sum_{i=1}^{\mathcal{N}} \varepsilon^6 \int_{I_i} p_L \delta^R r_i$$

where we used the relation $e(\nabla U) : e(\nabla U) = \nabla U : \nabla U$. With (2.111) we have $U_L = a^\varepsilon_L r = (\frac{\fint_{I_i} U\cdot\nu}{\varepsilon^3 r_i} - \delta^R)r$ and we apply Gauss' theorem ($\mathrm{tr}(\nabla U_L) = \mathrm{div}(U_L)$) twice,

$$\begin{aligned}\int_{\Omega_S} (\lambda_S[\mathrm{tr}(\nabla U)]^2 + 2\mu_S \nabla U : \nabla U) - \varepsilon^6 \sum_{i=1}^{N} p_L \int_{\Omega_L^i} \mathrm{div}(U_L)\\ = \int_{\partial\Omega} (\overline{p} - p_0) U\cdot\nu - \sum_{i=1}^{\mathcal{N}} \varepsilon^6 \int_{I_i} (\frac{2\sigma}{r_i} + \overline{p}) U_{(+)} \cdot \nu + \varepsilon^6 \sum_{i=1}^{\mathcal{N}} \int_{I_i} p_L \delta^R r_i.\end{aligned}$$

Thus

$$\begin{aligned}\int_{\Omega_S} (\lambda_S[\mathrm{tr}(\nabla U)]^2 + 2\mu_S \nabla U : \nabla U) + 3k_L \sum_{i=1}^{\mathcal{N}} 4\pi r_i \varepsilon^3 (\fint_{I_i} U_{(+)} \cdot \nu)^2\\ = \int_{\partial\Omega} (\overline{p} - p_0) U\cdot\nu + \sum_{i=1}^{\mathcal{N}} \varepsilon^6 \int_{I_i} (-\frac{2\sigma}{r_i} + 3k_L(\delta^R + 3k_L h_L^*)) U_{(+)} \cdot \nu.\end{aligned}$$

Since $\overline{p}$ is constant we get by integration by parts and exploiting to have spherical droplets

$$\begin{aligned}\int_{\Omega_S} (\lambda_S[\mathrm{tr}(\nabla U)]^2 + 2\mu_S \nabla U : \nabla U) + 3k_L \sum_{i=1}^{\mathcal{N}} 4\pi r_i \varepsilon^3 (\fint_{I_i} U_{(+)} \cdot \nu)^2\\ = \int_{\partial\Omega} (\overline{p} - p_0) U\cdot\nu + \sum_{i=1}^{\mathcal{N}} \varepsilon^3 \int_{I_i} (\frac{2\sigma}{r_i} + \varepsilon^3 3k_L h_L^*) U_{(+)} \cdot \nu.\end{aligned}$$

or with (4.15) – (4.17)

$$\int_{\Omega_S} \lambda_S[\mathrm{tr}(\nabla U)]^2 + 2\mu_S \nabla U : \nabla U + 3k_L \sum_{i=1}^{N} \int_{I_i} \frac{(\fint_{I_i} U\cdot\nu)^2}{r_i} = -\int_{\partial\Omega} g_0 U\cdot\nu + \sum_{i=1}^{\mathcal{N}} \varepsilon^3 \int_{I_i} g_i U_{(+)} \cdot \nu.$$

For the moment we omit the nonnegative first and third term ($k_L > 0$, $\lambda_S > 0$) and estimate

$$\frac{2\mu}{K} \|U\|^2_{H^1} \leq (\|g_0\|_{L^2} + \sum_{i=1}^{\mathcal{N}} \varepsilon^3 \|g_i\|_{L^2}) \|U\|_{L^2}.$$

Clearly $\|U\|_{L^2(\Omega_S)} \leq \|U\|_{H^1(\Omega_S)}$. The constant of the trace theorem scales with ε^3 corresponding to Lemma 5.2, 1). Due to Lemma 5.3 Korn's constant $K > 0$ is uniformly bounded in ε. Hence with the embedding $L^2(\partial\Omega_S) \to H^1(\Omega_S)$ together with Lemma 5.2, 2), we have

$$\|U\|^2_{H^1} \leq K\tilde{C}(\|g_0\|_{L^2} + \varepsilon^6 \sum_{i=1}^{\mathcal{N}} \|g_i\|_{L^2}) \|U\|_{H^1}$$

where the $\tilde{C}$ is independent of ε. Hence

$$\|U\|_{H^1} \leq C(\{\|g_i\|_{L^2}\}_{i \in N \cup \{0\}})$$

where the constant C is independent of ε.

Besides this shows that the terms which we have neglected on the l.h.s. $\int_{\Omega_S} \lambda_S(\mathrm{tr}(\nabla U))^2$ and $\sum_{i=1}^{N} \fint_{I_i} [U\cdot\nu]^2$ are bounded as well uniformly in ε, where we use $\mu_S > 0$.

We still have to consider what happens if a droplet vanishes at time τ_i. If a droplet vanishes, then in general U is not continuous in time, but the jump $J_i := \|U\|^2_{H^1}(\Omega(\tau_i+)) - \|U\|^2_{H^1}(\Omega(\tau_i-))$ is bounded by

$$|\int_\Omega |\nabla U(\cdot,\tau_i+)|^2 - \int_\Omega |\nabla U(\cdot,\tau_i+)|^2| \leq K\tilde{C}\varepsilon^3\|g_i\|^2_{L^2})$$

since the difference solves a mechanical problem with same boundary data on the outer boundary and on the interfaces I_j, $j \neq i$. Since the number of jumps is bounded by ε^3 we can sum over all times $t \in (0, \mathcal{T})$, yielding the estimate on U.

By integrating over t from 0 to $\mathcal{T}$ we get $\|U\|_{L^2H^1}$ and $\|U\|_{C^0H^1}$ uniformly in ε.

2) Velocity

Analogously we consider the velocity, where have a similar dependence of the data on ε, if k is uniformly bounded in ε. ☐

Since we use in the following our ansatz for a formal solution of the mechanical BVP, we give this ansatz (3.59), which was stated for the dilute scaling regime, now for the critical scaling. We have to replace the power $3r-3$ of ε, which is 9 for the dilute scaling with 6 for the critical scaling. For the displacement we have

$$W(x) = \sum_{i\in N}((a+c_i)(x-X_i) + b_i\varepsilon^6 r_i^3\frac{x-X_i}{|x-X_i|^3}), \tag{5.4}$$

while for the velocity (5.5) translates into

$$\partial_t W(x) = \sum_{i\in N}(\partial_t(a+c_i)|x-X_i| + \varepsilon^6(\partial_t b_i r_i + 3b_i\dot{r}_i)\frac{r_i^2}{|x-X_i|^2})e_{r_i}. \tag{5.5}$$

where the coefficients are defined as in Appendix C.1.1.

With the last Th. 5.1 we justify the approximation of U by W in H^1 as $\varepsilon \to 0$.

Lemma 5.4 (Corrector result of the monopole approximation for the mechanical problem). *We make the same assumptions as in the last theorem. Let U be the exact solution of the mechanical problem* (4.1) – (4.3) *and W the approximation defined by (5.4), where we change the scaling from the dilute scaling to the critical scaling, which we consider now. Furthermore we neglect h^* completely corresponding to Problem E. Then the corrector $Z := U - W$ vanishes as $\varepsilon \to 0$ in the sense that $\|Z\|_{H^1(\Omega(t))} \to 0$.*

Proof. The corrector Z solves the problem

$$\begin{aligned}
\operatorname{div} \check{\sigma}_S(\nabla Z) &= 0 && \text{in } \Omega_S(t),\\
\check{\sigma}_S(\nabla Z)\nu &= (\overline{p} - p_0 - 3k_S\sum_{i\in N} a_i - 2G_S\sum_{i\in N} b_i \times \\
&\quad \times \frac{\varepsilon^9 r_i^3}{|x-X_i|^3}(1 - 3\frac{(x-X_i)\otimes(x-X_i)}{|x-X_i|^2}))\nu && \text{on } \partial\Omega(t),
\end{aligned}$$

and

$$\begin{aligned}
&(\check{\sigma}_S(\nabla Z) - \frac{3k_L}{\varepsilon^3 r_j}\fint_{I_j}(Z\cdot e_{r_j}))e_{r_j}\\
&= (\frac{2\sigma}{r_j} - 3k_L(\delta^R + h_L^*(r_i)) - 3k_S\sum_{i\in N} a_i + 4G_S b_j - 2G_S\sum_{i\neq j} b_i\frac{\varepsilon^6 r_i^3}{|x-X_i|^3}(1 - 3\frac{(x-X_i)\otimes(x-X_i)}{|x-X_i|^2})\\
&\quad + 3k_L(a_j+b_j) + 3k_L\sum_{i\neq j}(a_i + \fint_{I_j}(b_i\varepsilon^6\frac{r_i^3}{|x-X_i|^3}\frac{(x-X_i)\cdot(x-X_j)}{r_j^2})))e_{r_j} \qquad \text{on } I_j(t)\,\forall j\in N(t).
\end{aligned}$$

By choice of a_i and b_i as the corresponding coefficients of the totally radial symmetric single droplet problem this simplifies to

$$\begin{aligned} \operatorname{div} \check{\sigma}_S(\nabla Z) &= 0 && \text{in } \Omega_S(t),\\ \check{\sigma}_S(\nabla Z)\nu &= -2G_S\sum_{i\in N} b_i \frac{\varepsilon^6 r_i^3}{|x-X_i|^3}(1-3\frac{(x-X_i)\otimes(x-X_i)}{|x-X_i|^2}))\nu && \text{on } \partial\Omega(t),\\ (\check{\sigma}_S(\nabla Z)- & \\ \frac{3k_L}{\varepsilon^3 r_j}\fint_{I_j}(Z\cdot e_{r_j}))e_{r_j} &= (-2G_S\sum_{i\neq j} b_i \frac{\varepsilon^6 r_i^3}{|x-X_i|^3}(1-3\frac{(x-X_i)\otimes(x-X_i)}{|x-X_i|^2})+ & \\ &+3k_L\sum_{i\neq j}\fint_{I_j}(b_i\varepsilon^6\frac{r_i^3}{|x-X_i|^3}\frac{(x-X_i)\cdot(x-X_j)}{r_j^2}))e_{r_j} && \text{on } I_j(t) \quad \forall j\in N. \end{aligned}$$

Since we assume (3.4) we have

$$\begin{aligned} \operatorname{div} \check{\sigma}_S(\nabla Z) &= 0 && \text{in } \Omega_S(t), && (5.6)\\ \check{\sigma}_S(\nabla Z)\nu &= \mathcal{O}(\varepsilon^3)\nu && \text{on } \partial\Omega(t), && (5.7)\\ (\check{\sigma}_S(\nabla Z) - \frac{3k_L}{\varepsilon^3 r_j}\fint_{I_j}(Z\cdot e_{r_j}))e_{r_j} &= \mathcal{O}(\varepsilon^3)e_{r_j} && \text{on } I_j(t)\,\forall j\in N. && (5.8) \end{aligned}$$

In the liquid Ω_L we have

$$p_L = p_L^j(W) + p_L^j(Z) = \overline{p} - 3k_L(\frac{1}{\varepsilon^3 r_j}(\fint_{I_j}((W+Z)\cdot e_{r_j}) - \delta^R - h_L^*(r_j)) \quad \text{in } \Omega_L^j(t)\,\forall j\in N, \quad (5.9)$$

where

$$\begin{aligned} p_L^j(W) &:= \overline{p} - 3k_L(b_j - \delta^R - h_L^*(r_j) + \sum_{i\in N} a_i) && \text{in } \Omega_L^j(t)\,\forall j\in N,\\ p_L^j(Z) &:= 3k_L\sum_{i\neq j} b_i\varepsilon^6\fint_{I_j}(\frac{r_i^3}{|x-X_i|^3}\frac{(x-X_i)\cdot(x-X_j)}{r_j^2}) = \mathcal{O}(\varepsilon^3) && \text{in } \Omega_L^j(t)\,\forall j\in N. \end{aligned}$$

We can apply Th. 5.1 to the problem (5.6) – (5.8) and (5.9), which is solved by Z, and get the estimate

$$\|Z\|_{H^1(\Omega_S;\mathbb{R}^3)} \leq Const\,\varepsilon^3,$$

where the constant is independent of ε.

This yields $U - W \to 0$ in $H^1(\Omega_S)$ as $\varepsilon \to 0$ for given radii evolution. $\square$

This justifies the approximation of v by $\partial_t W$ in $H^1(\Omega_S)$, too.

Furthermore this implies with (4.10) and for a transformation Φ of the form as stated in Appendix B.1 that

$$|\dot{R}_{bd}| \leq const\,(1+\tilde{h})\,|\partial_t W|_{\partial\Omega(t)}| \leq Const\,\tilde{h}\,\varepsilon^3, \quad (5.10)$$

where the constants are independent of ε, if k is uniformly bounded in ε.

Unfortunately we cannot prove so far an estimate on $\nabla\cdot v$ in C^0 or L^∞, which is uniformly in ε, since we do not know so far, how the constants which appear in the embeddings depend exactly on the geometry and on ε.

We have to make the following

Assumption 5.1 (Scaling of constants in embeddings from Sobolev to Hölder spaces).

We assume that the geometry of Ω_S^ε allows that there exists a constant c_E s.t.

$$\|v\|_{C^1(\Omega_S^\varepsilon)} \leq c_E \|v\|_{W^{5/2,2}(\Omega_S^\varepsilon)}$$

which is used in Th. 4.1, 3) and c_E scales with $\mathcal{O}(\varepsilon^0)$ and is uniformly bounded in t.

We make an analogous assumption for

$$\|U\|_{C^2(\Omega_S^\varepsilon)} \leq c_E \|U\|_{W^{7/2,2}(\Omega_S^\varepsilon)}.$$

This assumption implies

Assumption 5.2 (Further uniform estimates on the displacement and the velocity)**.** *We assume that we can estimate*

$$\|U\|_{C^0C^2} \leq c_1 \varepsilon^0$$

and, if additionally k is uniformly bounded in ε, we have

$$\|v\|_{C^0C^1} \leq c_2 \varepsilon^0,$$

where the constants c_1 and c_2 are independent of ε and of k. This assumption seems to be plausible, if we think of our formally homogenised function W (see (5.4)*) or, if k is uniformly in ε, of our formally homogenised $\partial_t W$ (see* (5.5)*).*

5.3. Uniform estimates for the radii distribution

In this section we derive estimates on moments of the radii distribution, which are uniformly in the scaling parameter ε, under the Assumption 5.2.

We make a further assumption on the explicit form of $n_{As}^\varepsilon(u^\varepsilon)$, which is stronger than Assumption 4.2, 1) and 2).

Assumption 5.3 (Explicit form of $n_{As}^\varepsilon(u^\varepsilon)$)**.** *We assume, that*

$$n_{As}^\varepsilon(u^\varepsilon) = \overline{n}_{As}(1 + \varepsilon^9 c_1(\exp(c_2 u^\varepsilon) - 1)),$$

where c_1 and c_2 are independent of ε. This holds for our original problem by (A.21) *and* (A.17)*.*

Lemma 5.5 (Uniform estimates for new initial data after vanishing of a droplet)**.** *For the "new initial data" after the vanishing of a droplet holds*

$$\|u^\varepsilon(\tau_i)\|^2_{H^1(\Omega_S(\tau_i+))} \leq \|u^{0,\varepsilon}\|^2_{L^2(\Omega_S(0))} Const\, \varepsilon^2. \tag{5.11}$$

Proof. Let $j = \text{argmin}\ \tau_i$. After droplet j has vanished i.e. at time τ_j+ we have as new initial data $u^\varepsilon(\tau_j+)$ corresponding to the definition of $n_{As}^\varepsilon(\tau_j+)$ in Assumption 2.6 or the definition of $u^\varepsilon(\tau_j+)$ in Remark 4.5. Due to (2.169) and (2.170) we find

$$|u^\varepsilon(\tau_j+)| \leq Const(p) u_{As}^{int}(r_{min})$$

with a positive constant independent of ε. We estimate

$$\|u^\varepsilon\|^2_{L^2(\Omega_L^i(\tau_j-))} \leq \frac{4\pi}{3} \varepsilon^9 r_{min}^3\, Const(p)$$

where p can be chosen independent of ε, see (4.137). Analogously we get a uniform bound on the square of the L^2 norm of the gradient from (4.137),

$$\|\nabla u^\varepsilon\|^2_{L^2(\Omega^i_L(\tau_j-))} \leq \frac{4\pi}{3}\varepsilon^9 r^3_{min}\, Const_2(p)\ln(\frac{1}{\varepsilon}).$$

Both the L^2 norm and the L^2 norm of the gradient converge to 0 as $\varepsilon \to 0$. □

We recall, that $u_{int}(r_i)$ is bounded uniformly in ε due to its definition and to our scaling.

While in the formal homogenisation we have bounded k directly by $u_{int}(r_i)$ in (3.70), we have here to prove, since v depends on k, that the terms of the diffusion equation including v or $\nabla \cdot v$, can be neglected. We proceed as in Section 4.4 where we have constructed super- and subsolutions, which yield bounds on $k = \max_{i \in N} |\dot{r}_i|$. We show that the constant K of Lemma 4.4 yields a uniform bound on k for all ε.

Theorem 5.2 (Uniform estimate on k and on v)**.** *We assume that the initial data is uniformly bounded, s.t. $\hat{F}$ or $\underline{F}$ as defined in* (4.75) *is bounded uniformly in ε. Let Assumption 5.2 hold. Then k and $\|v\|_{C^0C^1}$ are uniformly bounded in ε.*

Proof. We start with time interval $(0, \tau_i-)$, where we assume that droplet i is the first to vanish. According to the estimate (4.130), we have

$$k(\varepsilon) \leq 2(\hat{F} - \underline{F})\frac{K(\varepsilon)}{r_{min}}$$

where we emphasise by our notation the dependence of all quantities on ε. Lemma 4.3 yields as possible choice of $K(\varepsilon)$

$$K(\varepsilon) = \frac{1}{1 - \varepsilon^4 \frac{d}{6}\hat{\kappa}(\varepsilon)}$$

where $\varepsilon^4 < \min\{(\frac{d}{6r_i})^4; \frac{18}{k(\varepsilon)d}\}$ and

$$\hat{\kappa}(\varepsilon) = \frac{4}{3}\varepsilon^3[[2(\hat{F} - \underline{F})(\frac{\max \mathcal{X}}{r_{min}} + \|v\|_{C^0(\Omega_S(t))}) + \partial_r u_{int}(r_{min})] + \frac{1}{k(\varepsilon)}\|\nabla \cdot v\|_{C^0(\Omega_S(t))}\, const(\Xi)].$$

W.l.o.g. $\hat{F} - \underline{F} \neq 0$, otherwise we would have finished our proof. We introduce the abbreviations

$$Z_1 := \frac{4(\hat{F} - \underline{F})}{r_{min}}, \qquad Z_2 := \frac{d}{9}\cdot 4(\hat{F} - \underline{F})(\frac{\max \mathcal{X}}{r_{min}} + \partial_r u_{int}(r_{min})),$$
$$Z_3 := \frac{d}{9}\cdot 4(\hat{F} - \underline{F}), \qquad Z_4 := 2\frac{d}{9}\, const(\Xi),$$

which are all strictly positive. Combining this yields

$$k(\varepsilon) \leq \frac{Z_1}{1 - \varepsilon^7[Z_2 + Z_3\|v\|_{C^0(\Omega_S(t))}] + \frac{\varepsilon^3}{k(\varepsilon)}Z_4\|\nabla \cdot v\|_{C^0(\Omega_S(t))}}, \tag{5.12}$$

which we estimate with $\varepsilon^4 < \frac{18}{k(\varepsilon)d}$

$$k(\varepsilon) \leq \frac{Z_1}{1 - \frac{\varepsilon^3}{k(\varepsilon)}(\frac{18}{d}[Z_2 + Z_3\|v\|_{C^0(\Omega_S(t))}] + Z_4\|\nabla \cdot v\|_{C^0(\Omega_S(t))})}. \tag{5.13}$$

According to Theorem 5.1 combined with Assumption 5.1 we can estimate $\|v\|_{C^0C^1} \leq Const(v)\, k$, where the constant is independent of k and ε, s.t.

$$k(\varepsilon) \leq \frac{Z_1}{1 - \frac{\varepsilon^3}{k(\varepsilon)}(\frac{18}{d}Z_2 + \frac{18}{d}(Z_3 + Z_4)Const(v)k(\varepsilon))} \leq \frac{Z_1}{1 - \frac{\varepsilon^3}{k(\varepsilon)}} \tag{5.14}$$

for sufficiently small ε.

Finally we proof our theorem by contradiction. Let $k(\varepsilon) \to \infty$ as $\varepsilon \to 0$, while $\varepsilon^4 < \frac{18}{k(\varepsilon)d}$. Then the l.h.s. goes to $+\infty$, while the r.h.s. is bounded. Hence $k(\varepsilon)$ is uniformly bounded in ε and by Theorem 5.1 this holds for $\|v\|_{L_2H_1}$, too. By Assumption 5.1 this holds for $\|v\|_{C^0C^1}$.

From the last Lemma 5.5 follows, that new initial data at time τ_i+ is again uniformly bounded in ε. □

Corollary 5.1 (Uniform maximum principle). *Since v is uniformly in ε bounded in C^0C^1, the maximum principle, Coroll. 4.2, holds for all ε and implies u^ε and n^ε_{As} uniformly bounded in $L^\infty L^\infty$.*

Lemma 5.6 (Uniform estimates on moments of the distribution of droplets). *We have*

a)

$$\fint_{\Omega(0)} \int_{\mathcal{J}_r} 1 d\nu^t_\varepsilon \leq 1, \tag{5.15}$$

b)

$$\fint_{\Omega(0)} \int_{\mathcal{J}_r} r d\nu^t_\varepsilon \leq \fint_{\Omega(0)} \int_{\mathcal{J}_r} r d\nu^0_\varepsilon + Const(\hat{F}, \underline{F}, K)t = \mathcal{R}_M + Const(\hat{F}, \underline{F}, K)t, \tag{5.16}$$

c)

$$\fint_{\Omega(0)} \int_{\mathcal{J}_r} r^2 d\nu^t_\varepsilon \leq \fint_{\Omega(0)} \int_{\mathcal{J}_r} r^2 d\nu^0_\varepsilon + Const(\hat{F}, \underline{F}, K, r_{min})t, \tag{5.17}$$

d)

$$\begin{aligned}\fint_{\Omega(0)} \int_{\mathcal{J}_r} r^3 d\nu^t_\varepsilon &\leq \fint_{\Omega(0)} \int_{\mathcal{J}_r} r^3 d\nu^0_\varepsilon + Const(\hat{F}, \underline{F}, K)(\mathcal{R}_M + Const(\hat{F}, \underline{F}, K, r_{min})t) \\ &\leq \frac{3}{4\pi}\mathcal{V}_M + Const(\hat{F}, \underline{F}, K, r_{min}, \mathcal{R}_M)t.\end{aligned} \tag{5.18}$$

Proof. k is bounded uniformly in ε due to Th. 5.2. By definition of (5.1), Corollary 4.7 and Lemma 5.5 the estimates a) – d) follow. □

We consider spherical shells $\Sigma^\varepsilon_i = B_{\varepsilon R^i_{ext}}(X_i) \setminus \overline{B_{\varepsilon^3 r_i(t)}(X_i)}$, $i \in \{1, ..., \mathcal{N}^0_\varepsilon\}$ around each droplet.

Definition 5.5 (Capacity potentials). *We define capacity potentials $\phi^{(\varepsilon)}_i$, $i \in \{1, ..., \mathcal{N}^0_\varepsilon\}$ as the unique solutions of the following problems*

$$\Delta\phi_i = 0 \qquad \text{in } \Sigma^\varepsilon_i \tag{5.19}$$

$$\phi_i = 0 \qquad \text{on } \partial B_{\varepsilon R_{ext}}(X_i) \tag{5.20}$$

$$\phi_i = 1 \qquad \text{on } \partial B_{\varepsilon^3 r_i}(X_i) \tag{5.21}$$

which can be explicitly solved,

$$\phi_i(x,t) = -\frac{\varepsilon^2 r_i(t)}{R^i_{ext}(t) - \varepsilon^2 r_i(t)} + \frac{\varepsilon^3 R^i_{ext}(t) r_i(t)}{R^i_{ext}(t) - \varepsilon^2 r_i(t)} \frac{1}{|x - X_i|} \quad \forall x \in \Sigma^\varepsilon_i(t)\ \forall t \in (0, \mathcal{T}),$$

which we extend by zero on the outside

$$\phi_i(x,t) = 0 \quad \forall x \in \mathbb{R}^3 \setminus \overline{B_{\varepsilon R^i_{ext}}(X_i)}\, \forall t \in (0,\mathcal{T}). \tag{5.22}$$

Into the interior we extend ϕ_i *by*

$$\phi_i(x,t) = 1 \quad \forall x \in B_{\varepsilon^3 r_i(t)}(X_i)\, \forall t \in (0,\mathcal{T}). \tag{5.23}$$

For all $i \in N(0)$ *we set* $R^i_{ext}(t) = R_{ext} = \frac{1}{2}$, *which is independent of time. We emphasise that this choice on* R_{ext} *is made s.t.*

$$\varepsilon^3 \max_{i\in N} r_i(t) < \varepsilon R_{ext} \leq \frac{1}{2}\min\{\min_{i\neq j, i,j\in N} |X_i - X_j|, \min_{i\in N} \ dist\ (X_i, \partial\Omega)\}$$

for sufficiently small ε *and given* $\mathcal{T}$. *For this particular* R^i_{ext} *we can write* ϕ_i *as,*

$$\phi_i(x,t) := \frac{2\varepsilon^2 r_i(t)}{1-2\varepsilon^2 r_i(t)}\left(\frac{\varepsilon}{2}\frac{1}{|x-X_i|} - 1\right). \tag{5.24}$$

This yields

$$\|\phi_i\|^2_{L^2(\Sigma^\varepsilon_i)} = \int_{\Sigma^\varepsilon_i} |\phi_i|^2 dz = \frac{2\pi}{3}\varepsilon^4 r_i(1-2\varepsilon^2 r_i) \leq \frac{2\pi}{3}\varepsilon^4 r_i \tag{5.25}$$

and

$$\|\nabla\phi_i\|^2_{L^2(\Sigma^\varepsilon_i)} = 4\pi\frac{\varepsilon^3 r_i}{1-2\varepsilon^2 r_i} \leq 2\pi\varepsilon^3 r_i, \tag{5.26}$$

where the upper bounds hold for sufficiently small $\varepsilon > 0$.

Lemma 5.7 (A further control on growth of radii)**.** *If* k *is bounded uniformly in* ε, *then we have the following control uniformly in* ε

$$\sum_i r_i^3 |\dot{r}_i|^2 \leq const. \tag{5.27}$$

Proof. That the estimate is uniformly in ε follows directly from the uniform estimate on $\sum_{i\in N} r_i^3$ proved in Lemma 5.6 under our assumptions on admissible initial distributions ν^0_ε. In particular ν^0_ε has compact support in r for all ε. ☐

The condition on k i.e. the uniform estimate on $\dot{r}_i$ is fulfilled as proved in Theorem 5.2. The control (5.27) translates into the following estimate for the distribution ν^t_ε, uniform in ε.

Corollary 5.2 (Uniform estimates on moments of the distribution of radii velocities for finite ε)**.** *Under the same assumptions as in the last lemma*

$$\fint_{\Omega(0)} \int_{\mathcal{J}_r} r^3 a_\nu(r,t)^2 d\nu^t_\varepsilon \leq const, \tag{5.28}$$

where the constant is independent of ε.

Now we rewrite the Stefan condition (4.8) for (DC) in terms of ν^t_ε.

Lemma 5.8 (Stefan conditions for (DC) for the distribution of droplets for fixed ε)**.** *Eq. (4.8), the Stefan condition for regime (DC), reads in terms of* ν^t_ε

$$\partial_t \nu^t_\varepsilon(x,r) = -\partial_r\left(\varepsilon^3 \frac{\fint_{\partial B_{\varepsilon^3 r}(x)} \nabla u^\varepsilon(x,t)\cdot\nu(x,t)dA(x,t)}{\mathbb{X}(r, \fint_{\partial B_{\varepsilon^3 r}(x)} U^\varepsilon(x,t)\cdot\nu)}\nu^t_\varepsilon(x,r)\right). \tag{5.29}$$

which holds in sense of distributions i.e. in $[C^\infty(0,\mathcal{T})\times\mathcal{C}]'$.

The initial condition (4.9) reads now

$$\nu_\varepsilon^t(t=0)(x,r)=\nu_\varepsilon^0(x,r):=\sum_{i=1}^{\varepsilon^{-3}}\delta_{X_i}(x)\delta_{r_i^0}(r).$$

Proof. By (5.1) we have

$$\begin{aligned}0&=\int_0^\infty\partial_t\sum_{i\in N^\varepsilon}\beta(t)\zeta(X_i,r_i)=\int_0^\infty\sum_{i\in N^\varepsilon}(\partial_t\beta(t)\zeta(X_i,r_i)+\beta(t)\partial_r\zeta(X_i,r_i)a_\nu(r_i,t))\\&=\int_0^\infty(\partial_t\beta(t)\fint_{\Omega(0)}\int_{\mathcal{J}_r}\zeta(x,r)\nu_\varepsilon^t(x,r)dxdr+\beta(t)\fint_{\Omega(0)}\int_{\mathcal{J}_r}\partial_r\zeta(x,r)a_\nu(r,t)\nu_\varepsilon^t(x,r)dxdr)dt\end{aligned}\tag{5.30}$$

for all test functions $\beta\in C^\infty(0,\mathcal{T})$ and $\zeta\in\mathcal{C}$. Then we integrate further by parts and find the statement about the Stefan condition. The initial condition is obtained directly from (5.1). ☐

5.4. Uniform estimates for the chemical potential

Theorem 5.3 (Uniform *a posteriori* estimates on u^ε or n_{As}^ε)**.** *If Assumption 5.2 holds, if the assumptions of Th. 5.1 hold, if Assumption 5.3 holds and if*

$$0<\mathcal{X}'(u^\varepsilon)\le\varepsilon^p\overline{Y}\max_{x\in\Omega_S}u^\varepsilon\tag{5.31}$$

for sufficiently small ε, *then* $u^\varepsilon\in L^\infty L^\infty\cap L^2H^1$ *and* $n_{As}^\varepsilon\in L^\infty L^\infty\cap L^2H^1$ *uniformly in* ε.

A posteriori estimate means that we can use the Stefan condition (4.8) and the boundary condition (4.6) simultaneously since we have already demonstrated existence of such a solution in Chapter 4.

The assumption (5.31) is fulfilled for typical data, see (A.20).

Proof. For better readability we drop the indices "ε" in this proof. First we consider only times $t<\inf_i\tau_i$, since we have to be careful if a droplet vanishes.

We recall that $\|u\|_{L^\infty L^\infty}$ is uniformly bounded in ε due to Corollary 5.1. We test the diffusion equation (4.4) on Ω_S with $\frac{u}{\mathcal{X}(u)}$ and get with the homogeneous Neumann b.c. on $\partial\Omega$, (4.5),

$$\int_{\Omega_S(t)}\varepsilon^3(\partial_tu+v\cdot\nabla u)u+\varepsilon^3\nabla\cdot v\,\frac{\Xi(u)}{\mathcal{X}(u)}u+\nabla u\cdot\nabla\frac{u}{\mathcal{X}(u)}\,dx+4\pi\varepsilon^3\sum_{i\in N}r_i^2\fint_{I_i}\partial_\nu u\frac{u}{\mathcal{X}(u)}\,dA=0.$$

With the boundary condition (4.6) and the Stefan condition (4.8) we have

$$\begin{aligned}\int_{\Omega_S(t)}\frac{\varepsilon^3}{2}\partial_t|u|^2+\varepsilon^3v\cdot\nabla u\,u+\varepsilon^3\nabla\cdot v\,\frac{\Xi(u)}{\mathcal{X}(u)}u+(1-\frac{\mathcal{X}'(u)}{\mathcal{X}(u)}u)\frac{1}{\mathcal{X}(u)}|\nabla u|^2\,dx&\\+4\pi\sum_{i\in N}r_i^2\dot r_i\frac{\mathbb{X}(r_i,U_M^i)}{\mathcal{X}(u_{int}(r_i))}u_{int}(r_i)=0.&\end{aligned}$$

Due to the maximum principle (Corollary 5.1), eq. (5.31) and Assumption 4.2, 1) we have $\mathcal{X}'(u)u\le$ *Const* ε^9 with a constant independent of ε and get the estimate

$$\int_{\Omega_S(t)}\frac{\varepsilon^3}{2}\partial_t|u|^2+\frac{\varepsilon^3}{2}v\cdot\nabla|u|^2+\varepsilon^3\nabla\cdot v\,\frac{\Xi(u)}{\mathcal{X}(u)}u+\frac{1}{2\mathcal{X}(u)}|\nabla u|^2\,dx+4\pi\sum_{i\in N}r_i^2\dot r_i\frac{\mathbb{X}(r_i,U_M^i)}{\mathcal{X}(u_{int}(r_i))}u_{int}(r_i)\le0$$

for sufficiently small ε. We apply Reynolds' transport theorem

$$\frac{\varepsilon^3}{2}\partial_t \int_{\Omega_S(t)} |u|^2\, dx - \frac{\varepsilon^3}{2}\int_{\partial\Omega(t)} |u|^2 \dot{R}_{bd}\, dA + \int_{\Omega_S(t)} \varepsilon^3 v\cdot\nabla u\, u + \varepsilon^3 \nabla\cdot v\, \frac{\Xi(u)}{\mathcal{X}(u)} u\, dx$$
$$+ \int_{\Omega_S(t)} \frac{1}{2\mathcal{X}(u)}|\nabla u|^2\, dx + 4\pi \sum_{i\in N} (\frac{\varepsilon^6}{2} + \frac{\mathbb{X}(r_i, U_M^i)}{\mathcal{X}(u_{int}(r_i))u_{int}(r_i)}) u_{int}(r_i)^2 \dot{r}_i r_i^2 \le 0.$$

According to Assumptions 4.2 – 4.4 we can split up

$$\frac{\varepsilon^6}{2} u_{int}(r_i)^2 + \frac{\mathbb{X}(r_i, \fint_{I_i} U\cdot\nu)}{\mathcal{X}(u_{int}(r_i))} u_{int}(r_i) = \mathbb{A}_1 - \mathbb{A}_2(r_i, \fint_{I_i} U\cdot\nu),$$

where $\mathbb{A}_1$ is a strictly positive constant and $\mathbb{A}_2$ is a strictly positive bounded function, such that we get

$$\frac{\varepsilon^3}{2}\partial_t \int_{\Omega_S(t)} |u|^2\, dx + \int_{\Omega_S(t)} \frac{1}{2\mathcal{X}(u)}|\nabla u|^2\, dx + 4\pi\mathbb{A}_1 \sum_{i\in N} \dot{r}_i r_i^2$$
$$\le \frac{\varepsilon^3}{2}\int_{\partial\Omega(t)} |u|^2 \dot{R}_{bd}\, dA - \varepsilon^3 \int_{\Omega_S(t)} (v\cdot\nabla u + \nabla\cdot v\, \frac{\Xi(u)}{\mathcal{X}(u)})\, u\, dx + 4\pi \sum_{i\in N} \mathbb{A}_2(r_i, U_M^i)\dot{r}_i r_i^2.$$

We integrate over the time interval $(0,t)$, use again Assumption 4.2, 1) and estimate with $|\dot{R}_{bd}| \le \varepsilon^3 k$, $|\dot{r}_i| \le k$ and the monotonicity of u_{int},

$$\frac{\varepsilon^3}{2}\int_{\Omega_S(t)} |u|^2\, dx + \frac{1}{2\max\mathcal{X}}\int_0^t \int_{\Omega_S(s)} |\nabla u|^2\, dx\, ds + \frac{4\pi}{3}\mathbb{A}_1 \sum_{i\in N(t)} r_i(t)^3$$
$$\le \frac{\varepsilon^3}{2}\int_{\Omega_S(0)} |u^0|^2\, dx + \frac{4\pi}{3}\mathbb{A}_1 \sum_{i\in N(0)} (r_i^0)^3 + \frac{\varepsilon^6}{2} k\, const(\partial\Omega(0), k)\|u\|^2_{L^\infty L^\infty}$$
$$+ \varepsilon^3 \|v\|_{L^\infty L^\infty} (\int_0^t \int_{\Omega_S(s)} |u|^2\, dx\, ds)^{1/2} (\int_0^t \int_{\Omega_S(s)} |\nabla u|^2\, dx\, ds)^{1/2}$$
$$+ \varepsilon^3 \|\nabla\cdot v\|_{L^2L^2}\|u\|_{L^2L^2} \frac{\max\Xi}{\min\mathcal{X}} + 2\pi \int_0^t \sum_{i\in N} r_i^2 ds\, const(\mathcal{X}, \mathbb{X}, u_{int}(r_{min}), r_i^0)k.$$

Let $\tau_j = \inf_i \tau_i$. Because the last estimate holds for all $t\in(0,\tau_j)$ we get with Young's inequality and the maximum principle

$$\frac{\varepsilon^3}{2}\sup_{t\in(0,\tau_j)} \int_{\Omega_S(t)} |u|^2\, dx + \frac{1}{2}(\frac{1}{\max\mathcal{X}(u)} - \varepsilon^3\|v\|_{L^\infty L^\infty}) \int_0^{\tau_j} \int_{\Omega_S(s)} |\nabla u|^2\, dx\, ds$$
$$+ \frac{4\pi}{3}\mathbb{A}_1 \sup_{t\in(0,\tau_j)} \sum_{i\in N(t)} r_i(t)^3$$
$$\le \frac{\varepsilon^3}{2}\int_{\Omega_S(0)} |u^0|^2\, dx + \frac{4\pi}{3}\mathbb{A}_1 \sum_{i\in N(0)} (r_i^0)^3 + \frac{\varepsilon^3}{2}(\varepsilon^3 k\, const(\partial\Omega(0), k) + (\|v\|_{L^\infty L^\infty} + \frac{\max\Xi}{\min\mathcal{X}})\times$$
$$\times\, const(\Omega(0), k))\|u\|^2_{L^\infty L^\infty} + \frac{\varepsilon^3}{2}\frac{\max\Xi}{\min\mathcal{X}}\|\nabla\cdot v\|^2_{L^2L^2} + 2\pi \int_0^t \sum_{i\in N} r_i^2 ds\, const(\mathcal{X}, \mathbb{X}, u_{int}(r_{min}), r_i^0)k.$$

The L^2-norm of the new initial data $u^0(\tau_j)$ is bounded by $\varepsilon^3 Const(k)$, where the constant is independent of ε, see Lemma 5.5, and the radii of the surviving droplets, i.e. of the droplets $N(\tau_j+)$, are continuous. This yields for all $t\in(0,\mathcal{T})$, since we extend u by the constant u_L into

Ω_L, for sufficiently small ε the estimate

$$\begin{aligned}
&\int_0^{\tau_j} \int_{\Omega(s)} |\nabla u|^2 \, dx \, ds \\
&\leq 4 \max \mathcal{X}(u) \left\{ \frac{4\pi}{3} \mathbb{A}_1 \sum_{i \in N(0)} (r_i^0)^3 + \varepsilon^3 Const(\|u^0\|_{L^2}, \|v\|_{L^\infty L^\infty}, \|\nabla \cdot v\|_{L^2 L^2}, k, \Xi, \mathcal{X}) \right. \\
&\quad \left. + 2\pi\tau_j \, const \, (\sum_{i \in N(0)} (r_i^0)^2, \sum_{i \in N(0)} r_i^0, k, u_{int}, \mathcal{X}, \mathbb{X}) \right\},
\end{aligned} \tag{5.32}$$

which is uniform in ε. From Assumption 5.3 we find the estimates for n_{As} as described.

We remark that, we could choose $\mathbb{A}_1 = 0$ in order to proof the theorem. But introducing $\mathbb{A}_1 > 0$ yields a further estimate on the 3^{rd} moment of the radii distribution and shows the correspondance with the estimate given in the study of Niethammer ([Nie99], lemma 16). □

We remark, that $\|\nabla u^\varepsilon\|^2_{L^2(\Omega_\mathcal{T})}$ corresponds to the difference of availability $\mathcal{A}(0) - \mathcal{A}(t)$ in regime (DC), see Appendix A.7, eq. (A.32).

We prove now a uniform estimate on $\partial_t u^\varepsilon$ on time-dependent domain.

Theorem 5.4 (Uniform *a posteriori* estimates on $\partial_t u^\varepsilon$ and Δu^ε)**.** *Let $u^\varepsilon \in C_1^2(0, \mathcal{T}; \Omega_S)$ and $u^\varepsilon|_{\Omega_L^i} = u_{int}(r_i)$. We assume* (5.10)*. If Assumption 5.2, if Assumption 5.3 and the assumptions of Th. 5.1 hold, then for sufficiently small ε and sufficiently small $\tilde{h}$ we have $\partial_t u^\varepsilon \in L^2(\Omega_\mathcal{T})$ and $\Delta u^\varepsilon \in L^2(\Omega_\mathcal{T})$ with a uniform estimate in ε. Then we have $\partial_t n_{As}(u^\varepsilon) \in L^2(\Omega_\mathcal{T})$, uniformly in ε.*

Proof. Again we drop within this proof the index "ε". First we consider also times $t \in (0, \tilde{t})$, $\tilde{t} < \min_i \tau_i$. We test Problem E with $\partial_t u - \Delta u$ and integrate the $\Delta u \, \partial_t u$-term by parts, where we use (4.5):

$$\begin{aligned}
\int_{\Omega_S(t)} \varepsilon^3 \mathcal{X}(u) |\partial_t u|^2 + (\varepsilon^3 (\mathcal{X}(u) v \cdot \nabla u) + \varepsilon^3 \nabla \cdot v \, \Xi(u))(\partial_t u - \Delta u) + \nabla u \cdot \nabla(\partial_t u) + |\Delta u|^2 \, dx \\
+ 4\pi\varepsilon^3 \sum_{i \in N} r_i^2 \fint_{I_i(t)} \partial_\nu u \, \partial_t u = 0.
\end{aligned}$$

Since we have classical solutions $u \in C_1^2(0, \mathcal{T}; \Omega_S)$ for each fixed $\varepsilon > 0$ we have $\nabla \partial_t u = \partial_t \nabla u$ and $\partial_t u|_{I_i} = u'_{int}(r_i) \dot{r}_i$, which yields with (4.8)

$$\begin{aligned}
\int_{\Omega_S(t)} \varepsilon^3 \mathcal{X}(u) |\partial_t u|^2 + |\Delta u|^2 + (\varepsilon^3 \mathcal{X}(u) v \cdot \nabla u + \varepsilon^3 \nabla \cdot v \, \Xi(u))(\partial_t u - \Delta u) + \frac{1}{2} \partial_t |\nabla u|^2 \, dx \\
+ 4\pi \sum_{i \in N} r_i^2 |\dot{r}_i|^2 \mathbb{X}(r_i, U_M^i) u'_{int}(r_i) = 0.
\end{aligned}$$

We apply Reynolds' transport theorem to the term with $\partial_t |\nabla u|^2$ and using Assumption 4.2, 1) we estimate

$$\begin{aligned}
&\varepsilon^3 \min \mathcal{X} \int_{\Omega_S(t)} |\partial_t u|^2 \, dx + \int_{\Omega_S(t)} |\Delta u|^2 \, dx + \varepsilon^3 \int_{\Omega_S(t)} \mathcal{X}(u) v \cdot \nabla u (\partial_t u - \Delta u) \, dx \\
&+ \varepsilon^3 \int_{\Omega_S(t)} \nabla \cdot v \, \Xi(u)(\partial_t u - \Delta u) \, dx + \frac{1}{2} \partial_t \int_{\Omega_S(t)} |\nabla u|^2 \, dx \\
&- \int_{\partial\Omega_S(t)} |\nabla u|^2 \dot{R}_{bd} \, dA + 4\pi \sum_{i \in N} (\varepsilon^3 r_i^2 \dot{r}_i \fint_{I_i(t)} |\nabla u|^2 dA + \frac{1}{3} |\partial_t r_i^3|^2 \mathbb{X}(r_i, U_M^i) u'_{int}(r_i)) \leq 0.
\end{aligned}$$

We estimate the third and forth term by the Cauchy-Schwarz inequality and use for the fifth and sixth term the trace theorem, where for the dependence of the embedding constants we refer to Lemma 5.2,

$$\begin{aligned}
&\varepsilon^3 \min \mathcal{X} \|\partial_t u\|^2_{L^2(\Omega_S(t))} + \|\Delta u\|^2_{L^2(\Omega_S(t))} + \frac{1}{2}\partial_t \|\nabla u\|^2_{L^2(\Omega_S(t))} + \frac{4\pi}{3}\sum_{i\in N} |\partial_t r_i^3|^2 \mathbb{X}(r_i, U_M^i) u'_{int}(r_i) \\
&\le \varepsilon^3 \max \mathcal{X} \|v\|_{L^\infty(\Omega_S(t))} \|\nabla u\|_{L^2(\Omega_S(t))} (\|\partial_t u\|_{L^2(\Omega_S(t))} + \|\Delta u\|_{L^2(\Omega_S(t))}) + \varepsilon^3 \max \Xi \|\nabla \cdot v\|_{L^2(\Omega_S(t))} \times \\
&\quad \times (\|\partial_t u\|_{L^2(\Omega_S(t))} + \|\Delta u\|_{L^2(\Omega_S(t))}) + C(\partial\Omega(t))|\dot{R}_{bd}| (\|\nabla u\|^2_{L^2(\Omega_S(t))} + \|D^2 u\|^2_{L^2(\Omega_S(t))}) \\
&\quad + \varepsilon^6 \sum_{i\in N} C(I_i(t)) k (\|\nabla u\|^2_{L^2(\Omega_S(t))} + \|D^2 u\|^2_{L^2(\Omega_S(t))}),
\end{aligned}$$

where the constants are independent of ε. Then we estimate with the bound (5.10), $|\dot{R}_{bd}| \le \varepsilon^3 \tilde{h} k$,

$$C(\partial\Omega(t))|\dot{R}_{bd}| + \varepsilon^9 \sum_{i\in N} C(I_i(t)) k \le \varepsilon^3 (\tilde{h} + \varepsilon^3) C_{tr},$$

with a constant $C_{tr}(\Omega_S(0), k)$ independent of ε and $\tilde{h}$. We use the bound (4.83) on $D^2 u$, we integrate over the time interval $(0, t)$, we use again Assumption 4.2, 1) and we estimate with Young's inequality the first and second term of the r.h.s.

$$\begin{aligned}
&\varepsilon^3 \min \mathcal{X} \|\partial_t u\|^2_{L^2 L^2} + \|\Delta u\|^2_{L^2 L^2} + \frac{1}{2} \|\nabla u(t)\|^2_{L^2(\Omega_S(t))} \\
&\le \frac{1}{2} \|\nabla u^0\|^2_{L^2(\Omega_S(0))} + \frac{\varepsilon^3}{2} (\frac{2}{\min \mathcal{X}} + 2)(\max \mathcal{X})^2 \|v\|^2_{L^\infty L^\infty} \|\nabla u\|^2_{L^2 L^2} + \frac{\varepsilon^3}{2} \min \mathcal{X} \|\partial_t u\|^2_{L^2 L^2} \\
&\quad + \frac{\varepsilon^3}{2} \|\Delta u\|^2_{L^2 L^2} + \varepsilon^3 (\frac{2}{\min \mathcal{X}} + 2)(\max \Xi)^2 \|\nabla \cdot v\|^2_{L^2 L^2} \\
&\quad + \frac{4\pi}{3} \max \mathbb{X}\, |u'_{int}(r_{min})| \int_0^t \sum_{i\in N} |\partial_t (r_i^3)|^2 + \varepsilon^3 (\tilde{h} + \varepsilon^3)\, C_{tr} \|\nabla u\|^2_{L^2 L^2} + (\tilde{h} + \varepsilon^3)\, C_{tr} \|\Delta u\|^2_{L^2 L^2}.
\end{aligned}$$

We compensate the $\varepsilon^3 \|\partial_t u\|_{L^2 L^2}$ and $\|\Delta u\|_{L^2 L^2}$ terms of the r.h.s. and for sufficiently small ε and for $\tilde{h} C_{tr} \le 1/4$ we can estimate the last two terms of the last equation by the other terms on the r.h.s.:

$$\begin{aligned}
&\varepsilon^3 \frac{\min \mathcal{X}}{2} \|\partial_t u\|^2_{L^2 L^2} + \frac{1}{2} \|\Delta u\|^2_{L^2 L^2} + \frac{1}{2} \|\nabla u(t)\|^2_{L^2(\Omega_S(t))} \\
&\le \|\nabla u^0\|^2_{L^2(\Omega_S(0))} + \varepsilon^3 (C_{tr} + (2 + \frac{2}{\min \mathcal{X}}) \max \mathcal{X}^2 \|v\|^2_{L^\infty L^\infty}) \|\nabla u\|^2_{L^2 L^2} \\
&\quad + \varepsilon^3 (2 + \frac{2}{\min \mathcal{X}}) \max \Xi^2 \|\nabla \cdot v\|^2_{L^2 L^2} + \frac{4\pi}{3} \max \mathbb{X}\, |u'_{int}(r_{min})| \int_0^t \sum_{i\in N} |\partial_t (r_i^3)|^2.
\end{aligned}$$

We multiply by two and apply the lemma of Gronwall to the terms with $\|\nabla u\|^2_{L^2(\Omega_S(t))}$ and get

$$\begin{aligned}
&\varepsilon^3 \min \mathcal{X} \|\partial_t u\|^2_{L^2 L^2} + \|\Delta u\|^2_{L^2 L^2} + \|\nabla u\|^2_{L^2(\Omega_S(t))} \\
&\le \exp(2\varepsilon^3\, (C_{tr} + (2 + \frac{2}{\min \mathcal{X}}) \max \mathcal{X}^2 \|v\|^2_{L^\infty L^\infty}) t) (\|\nabla u^0\|^2_{L^2(\Omega_S(0))} \\
&\quad + \varepsilon^3\, (2 + \frac{2}{\min \mathcal{X}}) \max \mathcal{X}^2 \|\nabla \cdot v\|^2_{L^2 L^2} + \frac{8\pi}{3} \max \mathbb{X}\, |u'_{int}(r_{min})| \int_0^t \sum_{i\in N} |\partial_t (r_i^3)|^2).
\end{aligned}$$

W.l.o.g. $\tau_j = \inf_i \tau_i$. The last inequality holds for all $t \in (0, \tau_j)$. Furthermore we use $|\dot{r}_i| \le k$ and our assumptions and find

$$\begin{aligned}&\varepsilon^3 \min \mathcal{X}\|\partial_t u\|^2_{L^2L^2} + \|\Delta u\|^2_{L^2L^2} + \sup_{t\in(0,\tau_j)} \|\nabla u(t)\|^2_{L^2(\Omega_S(t))}\\ &\le \exp(\varepsilon^3\, Const(\mathcal{X}, \Xi, \|v\|^2_{L^\infty L^\infty}, \Omega_S(0), k)\tau_j)\; const(\|\nabla u^0\|^2_{L^2(\Omega_S(t))}, \varepsilon^3\|\nabla\cdot v\|^2_{L^2L^2}, I(0), k^6),\end{aligned} \tag{5.33}$$

where the first constant is independent of ε due to Assumption 5.2 and the assumption on the initial data. The last estimate is extended into the liquid since $|\partial_t u_L| = |u'_{int}(r_i)\dot r_i| \le const\, k$ and $\nabla u_L = 0$,

$$\varepsilon^3 \min \mathcal{X}\|\partial_t u\|^2_{L^2(\Omega_{\tau_j})} + \|\Delta u\|^2_{L^2(\Omega_{\tau_j})} + \sup_{t\in(0,\tau_j)} \|\nabla u(t)\|^2_{L^2(\Omega(0))} \le \exp(\varepsilon^3\, c_I(\tau_j)\tau_j)\; c_{II}(t),$$

where the constants, in which norms enter up to a time t, are

$$c_I(t) := c_I(\mathcal{X}, \Xi, \|v\|^2_{L^\infty(\Omega_t)}, \Omega_S(0), k), \quad c_{II}(t) := c_{II}(\|\nabla u^0\|^2_{L^2(\Omega(0))}, \varepsilon^3\|\nabla\cdot v\|^2_{L^2(\Omega_t)}, I(0), k^6).$$

Since the sum over all jumps $[\|\nabla u\|_{L^2(\Omega_S(t))}]^{\tau_i-}_{\tau_i+}$ at times τ_i, $i \in N(0)$, when droplets vanish, are uniformly bounded in ε, see Lemma 5.5, we extend the estimate (5.33) for all times $t \in (0, \mathcal{T})$ and finally get the estimates on $\partial_t u$ and Δu in $L^2(\Omega_{\mathcal{T}})$ and ∇u in $L^\infty(0, \mathcal{T}; L^2(\Omega(t)))$, which are uniform in ε,

$$\varepsilon^3 \min \mathcal{X}\|\partial_t u\|^2_{L^2(\Omega_{\mathcal{T}})} + \|\Delta u\|^2_{L^2(\Omega_{\mathcal{T}})} + \|\nabla u(t)\|^2_{L^\infty(0,\mathcal{T};L^2(\Omega(t)))} \le \exp(\varepsilon^3\, c_I(\mathcal{T}))\; c_{II}(\mathcal{T}).$$

Finally this translates into the corresponding estimate on $\partial_t n_{As}(u)$. □

We remark that, the proof relies on having in our specific situation a factor ε^3 on the l.h.s. of the diffusion equation, $\dot R_{bd} \sim \tilde h \varepsilon^3$ and $r_i \sim \varepsilon^3$, otherwise we could not compensate the boundary terms which enter by applying the transport theorem.

5.5. Existence of the homogenisation limits

We recall that we have uniform estimates on u^ε, U^ε and estimates on the distribution of droplets ν^t_ε from Sections 5.4, 5.2, and 5.3, which allow to conclude the existence of a limit distribution ν^t and limits u^∞ and U^∞.

Theorem 5.5 (Existence of homogenisation limits). *For all $t \in \mathcal{J}_t = (0, \mathcal{T})$:*

1) *There exists a subsequence, again denoted by ν^t_ε and a weakly continuous map $\mathcal{J}_t \to \mathcal{C}', t \mapsto \nu_t$ s.t. as $\varepsilon \to 0$*

$$\fint_{\Omega(0)} \int_{\mathcal{J}_r} f d\nu^t_\varepsilon \to \fint_{\Omega(0)} \int_{\mathcal{J}_r} f d\nu^t \quad \text{locally uniformly in } t \quad \forall f \in \mathcal{C}. \tag{5.34}$$

   The limit measure ν could be defective, but

$$\fint_{\Omega(0)} \int_{\mathcal{J}_r} r d\nu^t \le 1.$$

   For the volume of the liquid we have

$$\fint_{\Omega(0)} \int_{\mathcal{J}_r} r^3 d\nu^t_\varepsilon \le \fint_{\Omega(0)} \int_{\mathcal{J}_r} r^3 d\nu^t_0 + const(\nu^t_0, \overline{u}_0). \tag{5.35}$$

   The limit ν^t is better than ν in the sense, that it has a Lebesgue density w.r.t. x for all t, if *the distribution of initially given centres X_i is regular.*

2) *We have strongly $R_{bd} \to R_{bd}(0)$ in $L^\infty(0,\mathcal{T})$ and $\mathbb{I}_{\Omega^\varepsilon} \to \mathbb{I}_{\Omega(0)}(x)$ strongly in $L^\infty((0,\mathcal{T} \times \mathbb{R}^3)$, where $\mathbb{I}_S(0)$ denotes the characteristic function of a set S.*

3) *There exists a measurable map $\mathcal{J}_t \to H^1(\Omega(0)), t \mapsto u^\infty(t)$ s.t. $u^\varepsilon \to u^\infty$ strongly in L^2L^2 and weakly in $L^\infty H^1$.*

4) *There exists a measurable map $\mathcal{J}_t \to C^2(\Omega(0)), t \mapsto U^\infty(t)$ and a measurable map $\mathcal{J}_t \to C^2(\Omega(t)), t \mapsto v^\infty(t)$ s.t. $U^\varepsilon \to U^\infty$ and $v^\varepsilon \to v^\infty$ strongly in L^2L^2 and weakly in L^2H^1.*

Proof.
1) (Limit distribution of radii)

Here our proofs follow [Nie04a].

Step A: Weak Hölder regularity of the family $\{\nu_\varepsilon^t\}_t$ in time.

Let $f \in \mathcal{C}$. With (5.30) and the Cauchy-Schwarz inequality follows

$$\begin{aligned}
&|\fint_{\Omega(0)} \int_{\mathcal{J}_r} f d\nu_\varepsilon^{t_1} - \fint_{\Omega(0)} \int_{\mathcal{J}_r} f d\nu_\varepsilon^{t_2}| = |\int_{t_1}^{t_2} \frac{d}{dt}(\fint_{\Omega(0)} \int_{\mathcal{J}_r} f d\nu_t^\varepsilon dt| = |\int_{t_1}^{t_2} (\fint_{\Omega(0)} \int_{\mathcal{J}_r} \partial_r f a_\nu d\nu_t^\varepsilon dt| \\
&\leq |t_1 - t_2|^{1/2} (\int_{t_1}^{t_2} \int_0^\infty \int_{\mathcal{J}_r} r^3 a_\nu(r,t)^2 d\nu_\varepsilon^t)^{1/2} \sup_{r \in \mathcal{J}_r} |\partial_r f| r^{-3/2} \\
&\leq |t_1 - t_2|^{1/2} \frac{Const(f,k)}{\min_{r,X} \mathbb{X}(r, \fint_{B_r(X)} U^\varepsilon \cdot \nu)}
\end{aligned}$$

which is due to the fact that (5.15) and (5.28) are uniformly bounded in ε.

Step B: Convergence of $\{\nu_\varepsilon^t\}_t$, locally uniform in time.

From (5.15) and step A we get by the theorem of Arzelà-Ascoli existence of a weakly continuous family $\{\nu^t\}_t$ s.t. for a subsequence the equation (5.34) holds for f in a countable subset of $\mathcal{C} \cap C^\infty(\Omega(0) \times \mathcal{J}_r)$. By means of (5.15) we see that we can enlarge the result to all $f \in \mathcal{C}$.

Step C: Tightness of ν_ε^t w.r.t. radii.

We show that for given $\delta > 0, \tilde{\mathcal{T}} > 0$, there exists $r_{\tilde{\mathcal{T}}}$ s.t.

$$\sup_{t \in (0,\tilde{\mathcal{T}})} \int_{r > r_{\tilde{\mathcal{T}}}} r^3 d\nu_\varepsilon^t < \delta. \tag{5.36}$$

Let η be a smooth cut-off function, s.t. $\eta = 1$ for all $r > r_{\tilde{\mathcal{T}}}$ and $\eta = 0$ for all $r < \frac{1}{2} r_{\tilde{\mathcal{T}}}$. We calculate

$$\begin{aligned}
\frac{d}{dt} \int_0^\infty \eta r^3 d\nu_t^\varepsilon &\leq |\sum_{i=1}^{\mathcal{N}^\varepsilon} (\eta'(r_i) r_i^3 + 2\eta r_i^2) \dot{r}_i| && \text{by (5.1)} \\
&\leq (\sum_{i=1}^{\mathcal{N}^\varepsilon} |\dot{r}_i|^2 r_i^3)^{1/2} (\sum_{i=1}^{\mathcal{N}^\varepsilon} (|\eta'(r_i)^2| r_i^3 + \eta^2))^{1/2} && \text{by Cauchy-Schwarz}
\end{aligned} \tag{5.37}$$

We estimate the second factor

$$\sum_{i=1}^{\mathcal{N}^\varepsilon} (|\eta'(r_i)^2| r_i^3 + \eta^2) \leq \sum_{i=1}^{\mathcal{N}^\varepsilon} (\frac{C_\eta^2}{r_{\tilde{\mathcal{T}}}^2} |\eta'(r_i)^2| r_i^3 + \frac{1}{r_{\tilde{\mathcal{T}}}^3} \sum_{i=1}^{\mathcal{N}^\varepsilon} r_i^3) \qquad \text{by the def. of } \eta. \tag{5.38}$$

We put (5.38) into (5.37) and get

$$\frac{d}{dt}\int_0^\infty \eta r^3 d\nu_t^\varepsilon \le (\sum_{i\in N^\varepsilon} |\dot{r}_i|^2 r_i^3)^{1/2} \frac{Const_1}{r_{\tilde{\mathcal{T}}}^{3/2}} \qquad \text{by Lemma 5.6 b) \& c).}$$

By integrating up over $t \in (0, \tilde{t})$, $\tilde{t} \in (0, \tilde{\mathcal{T}})$ together with $r_{\tilde{\mathcal{T}}}|_{\mathcal{T}=0} = \sup_{i\in N(0)} r_i^0$ we get

$$\int_0^\infty \eta r^3 d\nu_{\tilde{t}}^\varepsilon \le \frac{Const_2 \tilde{\mathcal{T}}}{r_{\tilde{\mathcal{T}}}^{3/2}} \qquad \text{by Def. 5.2, d) and by (5.27).}$$

By taking the supremum over all $\tilde{t} \in (0, \mathcal{T})$ and choosing $r_{\tilde{\mathcal{T}}} \ge (\frac{Const_2 \mathcal{T}}{\delta})^{2/3}$ we have proved (5.36). Together with Corollary 4.7 and Def. 5.2, d) we get $\fint_{\Omega(0)} \int_{\mathcal{J}_r} r^3 d\nu_\varepsilon^t \le \fint_{\Omega(0)} \int_{\mathcal{J}_r} r^3 d\nu_0^t + const(\nu_0^t, \overline{u}_0)$. From (5.15) we get $\fint_{\Omega(0)} \int_{\mathcal{J}_r} d\nu^t \le 1$ for all $t \in \mathcal{J}_t$.

Step D: First we want to show that the marginal of ν^t w.r.t. x has a bounded Lebesgue density i.e. there exists a constant c_L s.t.

$$\fint_\Omega \int_{\mathcal{J}_r} \zeta \, d\nu^t \le c_L \fint_\Omega \zeta \, dx$$

for all nonnegative $\zeta \in C^0(\Omega(0))$ and all $t \in [0, \infty)$.

We consider a fixed $\zeta \in C^1(\Omega(0))$. We estimate for all $i \in N$

$$\zeta(X_i) \le const_1 \frac{\int_{B_{\varepsilon^3 r_i}(X_i)} \zeta \, dx}{|B_{\varepsilon^3 r_i}(X_i)|} \le \frac{const_2}{\varepsilon^3 r_i} \int_{B_{\varepsilon^3 r_i}(X_i)} \zeta \, dx.$$

This implies

$$\fint_{\Omega(0)} \zeta \, d\nu_\varepsilon^t = \varepsilon^3 \sum_{i\in N^\varepsilon} \zeta(X_i) \le \frac{const_2}{r_{min}} \sum_{i\in N^\varepsilon} \int_{B_{\varepsilon^3 r_i}(X_i)} \zeta \, dx \le \frac{const_2}{r_{min}} \int_{\Omega(0)} \zeta \, dx,$$

since ε is sufficiently small enough to avoid collisions. The result for general ζ follows by approximation.

2) (Limit domain)

The bound (5.10) yields $\dot{R}_{bd}^\infty := \lim_{\varepsilon\to 0} \dot{R}_{bd} = 0$ i.e. $\lim_{\varepsilon\to 0} R_{bd} = R_{bd}(0)$ and in particular $\Omega^\infty = \Omega(0)$, i.e. $\mathbb{I}_{\Omega^\varepsilon}(\cdot) \to \mathbb{I}_{\Omega(0)}(\cdot)$ strongly in $L^\infty((0, \mathcal{T} \times \mathbb{R}^3)$.

3) (Limit of the chemical potential)

Since ∇u^ε is uniformly bounded in L^2L^2, see Th. 5.3, we get the existence of a suitable subsequence which converges in L^2L^2. By the Rellich-Kondrachov theorem, see the book of Alt ([Alt99], A 6.4), we get strong convergence of u^ε in L^2L^2. Hence $u^\varepsilon \rightharpoonup u^\infty$ in L^2H^1. That in the limit we have $\Omega(0)$ as domain follows from 2).

We remark, that our estimate from Th. 5.3 relies on $\mathcal{T} < \infty$ so the convergence in time cannot be extended to infinite times.

4) (Limit of the mechanical displacement and velocity)

Analogously to 3) we find from Th. 5.1 that $U^\varepsilon \rightharpoonup U^\infty$ in L^2H^1 for a suitable subsequence. We recall that we fix the representant in the class of equivalence RD. And from Th. 5.1 together with Th. 5.2 we get $v^\varepsilon \rightharpoonup v^\infty$ in L^2H^1, where we deal with a fixed representant in the class of equivalence RD_t. $\square$

5.6. Homogenised problem with kinetic equation

We derive the corresponding limit problems for regime (DC), which are solved by u^∞, U^∞ and ν^t. We can determine the solution only of the mechanical part of this coupled limit problems and find so a good approximation to our original mechanical problems with fixed ε. Thus we consider the homogenisation of the mechanical boundary value problem at first.

Theorem 5.6 (Homogenised mechanical BVP). *Let ν_ε^t and ν_∞^t from Theorem 5.5 be given and t be fixed. Then the limit U^∞ solves the following limit problem,*

$$-\nabla \cdot (\lambda_S tr(U^\infty)\mathbb{I}_3 + 2\mu_S e(\nabla U^\infty)) = 0 \qquad \forall x \in \Omega(0), \tag{5.39}$$

$$(\lambda_S tr(\nabla U^\infty)\mathbb{I}_3 + 2\mu_S e(\nabla U^\infty))\nu = (\overline{p} - p_0)\nu \qquad \forall x \in \partial\Omega(0). \tag{5.40}$$

We find $U^\infty = (\overline{p} - p_0)x$ and $\sigma_S(U^\infty) = \frac{\overline{p}-p_0}{3k_S})\mathbb{I}_3$ where this solution is unique up to all infinitesimal rigid displacements RD as defined in Def. 2.1.

The homogenised velocity BVP is

$$-\nabla \cdot (\lambda_S tr(v^\infty)\mathbb{I}_3 + 2\mu_S e(\nabla v^\infty)) = 0 \qquad \forall x \in \Omega(0), \tag{5.41}$$

$$(\lambda_S tr(v^\infty)\mathbb{I}_3 + 2\mu_S e(\nabla v^\infty))\nu = 0 \qquad \forall x \in \partial\Omega(0), \tag{5.42}$$

which has the solution $v^\infty = 0$.

The limit problems hold in sense of distributions i.e. for all test functions in $C^\infty(\Omega^\infty; \mathbb{R}^3)$.

Since the limit problem for U^∞ is uniquely solvable for fixed representatives in the class of equivalence RD and for v^∞ uniquely solvable in the class of equivalence RD_t, this yields not only convergence of a subsequence, but strong convergence of $U^\varepsilon \to U^\infty$ in L^2H^1 and strong convergence of $v^\varepsilon \to v^\infty$ in L^2H^1.

We see that $v^\infty = \partial_t U^\infty$, i.e. the homogenisation limit and the time derivative commute, what cannot be expected in general. Furthermore for boundary values on the interfaces we have $r_i^{-1}U^\varepsilon|_{I_i} \cdot \nu \to a^\dagger + b^\dagger(r_i)$ strongly in L^2.

Proof. We recall, that the time-dependent domain $\Omega^\varepsilon(t)$ enters in the mechanical BVP only as parameter. We test the mechanical BVP with an arbitrary function $\Phi \in C^\infty(\Omega^\varepsilon; \mathbb{R}^3)$ and integrate by parts

$$\begin{aligned}
0 &= \int_{\Omega^\varepsilon} \nabla \cdot (\lambda_S tr(\nabla U^\varepsilon)\mathbb{I}_3 + 2\mu_S e(\nabla U^\varepsilon))\Phi dx \\
&= -\int_{\Omega^\varepsilon} (\lambda_S tr(\nabla U^\varepsilon)\mathbb{I}_3 + 2\mu_S e(\nabla U^\varepsilon)) \cdot \nabla\Phi dx \\
&\quad - \int_{\partial\Omega^\varepsilon} (\overline{p} - p_0)\Phi dA + \sum_{i \in N^\varepsilon} \int_{I_i} (3k_L(-\varepsilon^3(\delta^R + h_L^*(r_i) + \frac{U^\varepsilon \cdot \nu}{r_i}) + \varepsilon^3 \frac{2\sigma}{r_i} + p_L)\Phi dA \\
&= -\int_{\Omega^\varepsilon} (\lambda_S tr(\nabla U^\varepsilon)\mathbb{I}_3 + 2\mu_S e(\nabla U^\varepsilon)) \cdot \nabla\Phi dx \\
&\quad - \int_{\partial\Omega^\varepsilon} (\overline{p} - p_0)\Phi dA + \varepsilon^3 \sum_{i \in N^\varepsilon} \int_{I_i} (-\overline{p} + \frac{2\sigma}{r_i})\Phi dA.
\end{aligned}$$

As $\varepsilon \to 0$ this converges with the uniform bound on $U^\varepsilon \in H^1$ and since σ_S is linear in ∇U^ε, to

$$0 = -\int_{\Omega^\infty} (\lambda_S tr(\nabla U^\infty)\mathbb{I}_3 + 2\mu_S e(\nabla U^\infty)) \cdot \nabla\Phi - \int_{\partial\Omega^\infty} (\overline{p} - p_0)\Phi dA$$

and by integrating by parts back we find the homogenised mechanical BVP. Analogously the result for the velocity problem follows.

We get by the corrector result of the mechanical monopole approximation, see Lemma 5.4, that

$$\lim_{\varepsilon\to 0} \fint_{I_i} \frac{U^\varepsilon}{\varepsilon^3 r_i} \to a^\dagger + b^\dagger(r),$$

where $a^\dagger$ as in (3.61) and $b^\dagger$ as in (3.63). ☐

Lemma 5.9 (Convergence of the nonlinearities)**.** *From Th. 5.5 follows*

1) *The function $\mathcal{X}$, which is nonlinear in u^ε, converges strongly to a constant $\mathcal{X}^\infty$ as u^ε to u^∞ strongly in L^2.*
2) *The function $\mathbb{X}$, which can depend nonlinear on $\fint_{I^i} U^\varepsilon \cdot \nu$, converges to a function $\mathbb{X}^\infty$, which depends only on r_i. This holds for arbitrary $r_i \in \mathcal{J}_r$, hence we can consider $\mathbb{X}^\infty$ as function of $r \in \mathcal{J}_r$.*
3) *The function Ξ converges strongly to a constant Ξ^∞ as u^ε to u^∞ strongly in L^2.*

Proof. We note, that in general nonlinear functions are not continuous w.r.t. weak convergence. But here we have:

1) According to Assumption 5.31 we have $\mathcal{X}(u^\varepsilon) = Const(1 + \varepsilon^9 \overline{Y} y(u^\varepsilon))$ and y is continuous. We use, that the maximum principle is uniformly in ε (see Corollary 5.1) and estimate
$$\|\mathcal{X}(u^\varepsilon)\|_{L^\infty} \le Const(1 + \varepsilon^9 \overline{Y} const|u^\varepsilon|_{L^\infty}) \le Const(1 + const_2 \varepsilon) \tag{5.43}$$
with constants independent of ε. Thus $\|\mathcal{X}(u^\varepsilon) - Const\|_{L^\infty} \to 0$ as $\varepsilon \to 0$.
2) Due to Th. 5.6 together with Assumption 5.2 we have strong convergence of $r_i^{-1} U^\varepsilon|_{I_i} \to a^\dagger + b^\dagger(r_i)$. Inserting this into $\mathbb{X}$ yields $\mathbb{X}^\infty(r_i) = \mathbb{X}(r_i, a^\dagger + b^\dagger(r_i))$ for every r_i.
3) Follows analogously as 1).

☐

Theorem 5.7 (Problem EH for the homogenised functions in regime (DC))**.** *Let for the data hold $u^0_\varepsilon \to u^0_\infty$ in L^2, $\nu^0_\varepsilon \to \nu^0$ in $[\mathcal{C}]'$ as $\varepsilon \to 0$ then the limits u^∞, U^∞ and ν^t_∞ from Theorem 5.5 solve the following limit problems, which we refer to as the **Problem EH**.*

The homogenised diffusion problem is

$$-\Delta u^\infty + 4\pi \int_{\mathcal{J}_r} r(u^\infty - u_{int}(r))d\nu^t = 0 \qquad \forall x \in \Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.44}$$

$$\nabla u^\infty \cdot \nu = 0 \qquad \forall x \in \partial\Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.45}$$

$$u^\infty(\cdot, t=0) = u^0_\infty \qquad \forall x \in \Omega(0), \tag{5.46}$$

*where u^∞ depends on time and varies in space as ν^t. The Stefan condition translates into an evolution equation for the density, a so-called **kinetic equation**,*

$$\partial_t \nu^t + \partial_r\left(\nu^t \frac{u^\infty - u_{int}(r)}{r\mathbb{X}^\infty(r)}\right) = 0 \qquad \forall x \in \Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.47}$$

$$\nu^t|_{t=0} = \nu^0 \qquad \forall x \in \Omega(0). \tag{5.48}$$

The limit diffusion equation (5.44) *holds for all test functions $\zeta \in H^1$ and for a.e. $t \in \mathcal{J}_t$ i.e.*

$$\int_{\Omega(0)} \nabla u^\infty \cdot \nabla\zeta\, dx = 4\pi \fint_{\Omega(0)} \int_{\mathcal{J}_r} r(u^\infty - u_{int}(r))\, d\nu^t.$$

The kinetic equation (5.47) *holds in the following weak sense*

$$\frac{d}{dt} \fint_{\Omega(0)} \int_{\mathcal{J}_r} \xi \, d\nu^t = \fint_{\Omega(0)} \int_{\mathcal{J}_r} \partial_r \xi \frac{u^\infty - u_{int}(r)}{r\mathbb{X}^\infty(r)} \, d\nu^t$$

distributionally in $t \in \mathcal{J}_t$ *for all test functions* $\xi \in C^\infty(\Omega^\infty; \mathbb{R})$*.*

The homogenised mechanical BVP and the homogenised velocity problem, as derived in Th. 5.6, have the explicit solution

$$U^\infty = (\overline{p} - p_0)x \qquad \forall x \in \Omega(0) \, \forall t \in \mathcal{J}_t, \tag{5.49}$$

$$v^\infty = 0 \qquad \forall x \in \Omega(0) \, \forall t \in \mathcal{J}_t. \tag{5.50}$$

and enter as parameters.

By the homogenisation procedure our Problem E has simplified to a limit problem (5.44) – (5.48) for u^∞ and ν^t, which is a inhomogeneous Laplace equation for u^∞ coupled to the kinetic equation for ν^t.

Proof. From Th. 5.5 we have the strong convergence of u^ε in L^2 and weak convergence of u^ε in H^1 to the limit u^∞.

We consider again capacity potentials ϕ_i of $B_{\varepsilon^3 r_i}(X_i)$ with respect to $B_{\varepsilon/2}(X_i)$ for all $i \in \{1, ..., \mathcal{N}^0\}$ as defined in Def. 5.5. With the help of these capacity potentials we can test the diffusion problem in a neighbourhood of the droplets, i.e. in Σ_i^ε and examine what happens when droplets "shrink" to points in the limit $\varepsilon \to 0$.

Step 1: Boundary conditions on the interface

Let $\zeta \in C_0^\infty(\mathcal{J}_r)$ and $\Phi \in \mathcal{C}$. We show

$$-\int_{\mathcal{J}_t} \zeta \sum_{i \in N^\varepsilon} \Phi(X_i, r_i) \int_{I_i} u^\varepsilon \nabla \phi_i \cdot \nu \, dt \to 4\pi \int_{\mathcal{J}_t} \zeta \int_{\mathcal{J}_r} \Phi r u^\infty d\nu^t dt. \tag{5.51}$$

W.l.o.g. $R_{ext}^i = \frac{1}{2}$. Additionally to the capacity potentials we define other test functions ψ_i for all $i \in \{1, ..., \mathcal{N}_\varepsilon^0\}$ on $B_{\varepsilon R_{ext}^i}(X_i)$ by

$$\psi_i(x,t) := 4r_i(\varepsilon^2 (R_{ext}^i)^2 - |x - X_i|^2) = r_i(\varepsilon^2 - 4|x - X_i|^2),$$

which we extend with zero outside of $B_{\varepsilon R_{ext}^i}(X_i)$. We see

$$|\psi| \leq \varepsilon^2 r_i. \tag{5.52}$$

We find $\partial_{|x-X_i|}\psi_i = -8r_i|x - X_i|$ and hence ψ_i has the following properties:

$$\begin{aligned} \partial_\nu \psi_i = -4\varepsilon r_i = 4r_i^2(1 - 2\varepsilon^2 r_i)\partial_\nu \phi \quad \forall x \in \partial\Sigma_i^\varepsilon \setminus I_i^\varepsilon, \\ \|\nabla \psi_i\|_{L^\infty(B_{\varepsilon R_{ext}^i}(X_i))} \leq 4\varepsilon r_i, \end{aligned} \tag{5.53}$$

$$\Delta \psi_i = \frac{2}{|x - X_i|}\partial_{|x-X_i|}\psi_i + \partial_{|x-X_i|}^2 \psi_i = -24 r_i.$$

Furthermore

$$D_t \psi_i = \dot{r}_i(\varepsilon^2 - 4|x - X_i|^2) - 8 r_i v^\varepsilon \cdot (x - X_i), \tag{5.54}$$

$$|D_t \psi_i| \leq \varepsilon(k\varepsilon(1 - 4\varepsilon^4 r_i^2) + 4r_i \|v^\varepsilon\|_{L^\infty}) \leq const \, \varepsilon \tag{5.55}$$

with a constant independent of ε.

We test the diffusion equation with $-\psi_i$ in Σ_i^ε and integrate by parts,

$$\begin{aligned} &-\int_{\Sigma_i^\varepsilon}(\varepsilon^3 D_t n_{As}(u^\varepsilon)+\varepsilon^3 n_{As}(u^\varepsilon)\nabla\cdot v)\psi_i = -\int_{\Sigma_i^\varepsilon}\Delta u^\varepsilon\psi_i \\ &=\int_{\Sigma_i^\varepsilon}\nabla\cdot(u^\varepsilon\nabla\psi_i)-u^\varepsilon\Delta\psi_i=\int_{\partial\Sigma_i^\varepsilon\setminus I_i^\varepsilon}u^\varepsilon\partial_\nu\psi_i+24r_i\int_{\Sigma_i^\varepsilon}u^\varepsilon-\int_{I_i}u^\varepsilon\partial_\nu\psi_i. \end{aligned} \tag{5.56}$$

On $\Omega_L^{i,\varepsilon}$ we use Def. 5.4 for $u^\varepsilon|_{\Omega_L^{i,\varepsilon}}$ and add a creative zero

$$0=-\int_{\Omega_L^{i,\varepsilon}}\Delta u^\varepsilon\psi_i=\int_{\Omega_L^{i,\varepsilon}}\nabla\cdot(u^\varepsilon\nabla\psi_i)-u^\varepsilon\Delta\psi_i=\int_{I_i^\varepsilon}u^\varepsilon\partial_\nu\psi_i+24r_i\int_{\Omega_L^{i,\varepsilon}}u^\varepsilon$$

and get together with (5.56)

$$-\int_{\Sigma_i^\varepsilon}(\varepsilon^3 D_t n_{As}(u^\varepsilon)+\varepsilon^3 n_{As}(u^\varepsilon)\nabla\cdot v)\psi_i=\int_{\partial\Sigma_i\setminus I_i}u^\varepsilon\partial_\nu\psi_i+24r_i\int_{B_{\varepsilon R^i_{ext}}(X_i)}u^\varepsilon.$$

We integrate over time ($\tau_i\notin(t_1,t_2)\ \forall i\in N^\varepsilon$), add up and get the following estimate

$$\begin{aligned} &\left|\int_{t_1}^{t_2}\sum_{i\in N^\varepsilon}\Phi(X_i,r_i)\left\{\int_{\partial\Sigma_i^\varepsilon\setminus I_i^\varepsilon}u^\varepsilon\partial_\nu\psi_i+24r_i\int_{B_{\varepsilon R^i_{ext}}(X_i)}u^\varepsilon\right\}\right| \\ &\le\sum_{i\in N^\varepsilon}\Phi(X_i,r_i)\left(\left|\left[\int_{\Sigma_i^\varepsilon}n_{As}(u^\varepsilon)\right]_{t_1}^{t_2}\right|\max_i|\psi_i^\varepsilon|+\left|\int_{t_1}^{t_2}\int_{\Sigma_i^\varepsilon}n_{As}(u)D_t\psi_i\right|\right) \\ &\le\|\Phi\|_{C^0(\mathbb{R}^3\times\mathcal{J}_r)}\left(\|n_{As}(u^\varepsilon)\|_{L^\infty(\Omega_S^\varepsilon)}\max_i\|\psi_i\|_{C^0(\Omega_{\mathcal{T}}^\varepsilon)}+\varepsilon^3\|n_{As}(u^\varepsilon)\|_{L^\infty(\Omega_{S,\mathcal{T}}^\varepsilon)}\max_i\|D_t\psi_i\|_{C^0(\Omega_{\mathcal{T}}^\varepsilon)}\right). \end{aligned}$$

We use (5.52), (5.53) and that, n_{As} is uniformly bounded. Let $t_1=0$, $t_2=\mathcal{T}$. Then we have

$$\int_0^{\mathcal{T}}\sum_{i\in N^\varepsilon}\Phi(X_i,r_i)\left\{\int_{\partial\Sigma_i\setminus I_i}u^\varepsilon\partial_\nu\psi_i+24r_i\int_{B_{R^i_{ext}}(X_i)}u^\varepsilon\right\}\le C\,\varepsilon^2$$

with a constant C independent of ε.

We define now

$$\Psi^\varepsilon(x,t):=24\sum_{i\in N^\varepsilon}r_i(t)\Phi(X_i,r_i(t))\mathbb{I}_{B_{\varepsilon R^i_{ext}}(X_i)}(x),$$

and see with

$$\lim_{\varepsilon\to0}\Big(\frac{1}{\varepsilon^3}\int_{B_{\varepsilon R^i_{ext}}(X_i)}\Psi^\varepsilon\zeta\Big)=\frac{4\pi}{3\cdot2^3}24r_i\,\zeta(X_i)$$

for arbitrary $\zeta\in C_0^\infty(\mathbb{R}^3)$ that

$$\int_{\mathcal{J}_t}\int_{\Omega^\varepsilon}\Psi^\varepsilon\xi dxdt\to4\pi\int_{\mathcal{J}_t}\fint_{\Omega(0)}\int_{\mathcal{J}_r}r\xi d\nu_t dt$$

as $\varepsilon\to0$ for arbitrary test functions $\xi\in C_0^\infty(\Omega\times\mathcal{J}_t)$.

We want to pass to the limit in the term

$$\int_0^{\mathcal{T}}\int_{\Omega^\varepsilon}\Psi^\varepsilon u^\varepsilon dxdt, \tag{5.57}$$

where both sequences are only weakly convergent, but $\mathbb{I}_{\Omega^\varepsilon} \to \mathbb{I}_{\Omega(0)}$ strongly.

Now we can apply the theorem of compensated compactness as stated in [CD99], Th. 13.10, to (5.57), where we exploit, that u^ε is "good" in x, while Ψ^ε is "good" in t. Therefore we write $\Psi^\varepsilon u^\varepsilon$ as scalar product of $W^\varepsilon = (\Psi^\varepsilon, 1, 1, 1)^T$ and $V^\varepsilon = (u^\varepsilon, 0, 0, 0)$ and consider for the moment as coordinates (t, x_1, x_2, x_3). div W^ε is bounded in $L^2((0,\infty) \times Z)$ by $\partial_t \Psi^\varepsilon$ and the embedding $L^2(Z) \hookrightarrow H^{-1}(Z)$ is compact. curl V^ε is antisymmetric, with the only non-zero entries $(\text{curl } V^\varepsilon)_{1,2} = -(\text{curl } V^\varepsilon)_{2,1} = \partial_{x_1} u^\varepsilon$, $(\text{curl } V^\varepsilon)_{1,3} = -(\text{curl } V^\varepsilon)_{3,1} = \partial_{x_2} u^\varepsilon$ and $(\text{curl } V^\varepsilon)_{1,4} = -(\text{curl } V^\varepsilon)_{4,1} = \partial_{x_3} u^\varepsilon$. curl V^ε is bounded in $[L^2((0,\infty) \times Z)]^{4\times 4}$ by $2 \int_0^\infty \int_Z |\nabla u^\varepsilon|^2$. Hence we find

$$\int_0^{\mathcal{T}} \int_{\Omega^\varepsilon} \Psi^\varepsilon u^\varepsilon = \int_0^{\mathcal{T}} \int_{\Omega^\varepsilon} W^\varepsilon \cdot V^\varepsilon \to \int_0^{\mathcal{T}} \int_{\Omega^\varepsilon} W^\infty \cdot V^\infty = 4\pi \int_{\mathcal{J}_t} \fint_{\Omega(0)} \int_{\mathcal{J}_r} r u^\infty d\nu_t dt$$

and have demonstrated (5.51).

Step 2: The kinetic equation

By suitably inserting the capacity potential ϕ_i and by integration by parts we get

$$\begin{aligned}
\int_{I_i^\varepsilon} \nabla u^\varepsilon \cdot \nu &= \int_{I_i^\varepsilon} \nabla u^\varepsilon \cdot \nu \phi_i = -\int_{\Sigma_i^\varepsilon} \nabla u^\varepsilon \cdot \nabla \phi_i - \Delta u^\varepsilon \phi_i \\
&= \int_{\Sigma_i^\varepsilon} u^\varepsilon \Delta \phi_i - \int_{\Sigma_i^\varepsilon} \Delta u^\varepsilon \phi_i - \int_{\partial \Sigma_i^\varepsilon \setminus I_i^\varepsilon} u^\varepsilon \nabla \phi_i \cdot \nu + \int_{I_i^\varepsilon} u_{int}(r_i) \nabla \phi_i \cdot \nu \\
&= -\int_{\Sigma_i^\varepsilon} \varepsilon^3 (\mathcal{X}(u^\varepsilon)(\partial_t u^\varepsilon + v^\varepsilon \cdot \nabla u^\varepsilon) + \nabla \cdot v^\varepsilon \, \Xi(u^\varepsilon)) \phi_i - \int_{\partial \Sigma_i^\varepsilon \setminus I_i^\varepsilon} u^\varepsilon \nabla \phi_i \cdot \nu \\
&\quad - \frac{4\pi\varepsilon^3}{1 - 2\varepsilon^2 r_i} r_i u_{int}(r_i),
\end{aligned} \tag{5.58}$$

where in the last step we use (5.19). Let $\Phi \in \mathcal{C}$. We differentiate the discrete distribution w.r.t. time,

$$\begin{aligned}
&\frac{d}{dt} \sum_{i \in N^\varepsilon} \Phi(X_i, r_i) \\
&= \sum_{i \in N^\varepsilon} \partial_r \Phi(X_i, r_i) \dot{r}_i = \sum_{i \in N^\varepsilon} \partial_r \Phi(X_i, r_i) \frac{\varepsilon^3}{4\pi\varepsilon^6 r_i^2 \mathbb{X}(r_i, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} \int_{I_i^\varepsilon} \nabla u^\varepsilon \cdot \nu \, dA \\
&= -\sum_{i \in N^\varepsilon} \partial_r \Phi(X_i, r_i) \frac{1}{4\pi\varepsilon^3 r_i^2 \mathbb{X}(r_i, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} \int_{\partial \Sigma_i^\varepsilon \setminus I_i^\varepsilon} u^\varepsilon \nabla \phi_i \cdot \nu \, dA \qquad \text{by (5.58)} \\
&\quad - \sum_{i \in N^\varepsilon} \partial_r \Phi(X_i, r_i) \frac{u_{int}(r_i)}{r_i \mathbb{X}(r_i, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} \frac{1}{1 - 2\varepsilon^2 r_i} \\
&\quad - \sum_{i \in N^\varepsilon} \partial_r \Phi(X_i, r_i) \frac{1}{4\pi r_i^2 \mathbb{X}(r_i, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} \int_{\Sigma_i^\varepsilon} (\mathcal{X}(u^\varepsilon)(\partial_t u^\varepsilon + v \cdot \nabla u^\varepsilon) + \nabla \cdot v \, \Xi(u^\varepsilon)) \phi_i \, dx.
\end{aligned} \tag{5.59}$$

We estimate the term

$$\begin{aligned}
&\sum_{i \in N^\varepsilon} \partial_r \Phi(X_i, r_i) \frac{1}{4\pi r_i^2 \mathbb{X}(r_i, \fint_{I_i^\varepsilon} U^\varepsilon \cdot \nu)} \int_{\Sigma_i^\varepsilon} (\mathcal{X}(u^\varepsilon)(\partial_t u^\varepsilon + v \cdot \nabla u^\varepsilon) + \nabla \cdot v \, \Xi(u^\varepsilon)) \phi_i \, dx \\
&\le \frac{\|\partial_r \Phi\|_{C^0(\Omega(0))}}{4\pi r_{min}^{3/2} \min \mathbb{X}} \sqrt{2\pi \frac{\varepsilon^3}{3}} \sup_i (\max \mathcal{X} (\|\partial_t u^\varepsilon\|_{L^2(\Sigma_i^\varepsilon)} + \|v^\varepsilon\|_{L^\infty(\Sigma_i^\varepsilon)} \|\nabla u^\varepsilon\|_{L^2(\Sigma_i^\varepsilon)}) + \max \Xi \, \|v^\varepsilon\|_{L^2(\Sigma_i^\varepsilon)}),
\end{aligned}$$

where we use (5.25). Hence this volume integral vanishes as $\varepsilon \to 0$. With step 1 and with Lemma

5.9, 2) for the convergence of $\mathbb{X}$ the equation (5.59) converges with Th. 5.2 and Th. 5.4 to

$$\partial_t \int_{\mathcal{J}_r} \Phi(X_i, r_i) d\nu^t = \int_{\mathcal{J}_r} \partial_r \Phi(X_i, r_i) \frac{u^\infty - u_{int}(r)}{r \mathbb{X}^\infty(r)} d\nu^t$$

forall $\Phi \in \mathcal{C}$ and hence the given kinetic equation holds in sense of distributions i.e. in $\mathcal{C}'$.

Step 3: The diffusion equation

Let again $\zeta \in C_0^\infty(\mathcal{J}_t)$, $\Phi \in \mathcal{C}$. We test the diffusion equation with $\zeta\Phi$ and integrate the third term by parts:

$$\begin{aligned} 0 &= \int_{\mathcal{J}_t} \int_{\Omega_S^\varepsilon} (\varepsilon^3 D_t n_{As}(u^\varepsilon) + \varepsilon^3 n_{As}(u^\varepsilon) \nabla \cdot v^\varepsilon - \Delta u^\varepsilon) \zeta \Phi \, dx \, dt \\ &= \int_{\mathcal{J}_t} \zeta \{ \int_{\Omega_S^\varepsilon} \varepsilon^3 (D_t n_{As}(u^\varepsilon) + \varepsilon^3 n_{As}(u^\varepsilon) \nabla \cdot v^\varepsilon) \Phi + \nabla u^\varepsilon \cdot \nabla \Phi dx + \varepsilon^3 \sum_{i \in N^\varepsilon} \int_{I_i} \nabla u^\varepsilon \cdot \nu \Phi \, dA \} dt. \end{aligned}$$

We choose Φ s.t. $\Phi|_{I_i} = const(i)$ and get by (5.58)

$$\begin{aligned} 0 = \int_{\mathcal{J}_t} \zeta \Bigg\{ & \int_{\Omega_S^\varepsilon} \varepsilon^3 (\mathcal{X}(u^\varepsilon)(\partial_t u^\varepsilon + \nabla u^\varepsilon \cdot v^\varepsilon) + \nabla \cdot v^\varepsilon \, \Xi(u^\varepsilon)) \Phi + \nabla u^\varepsilon \cdot \nabla \Phi \, dx \\ & + \sum_{i \in N^\varepsilon} \left(\int_{I_i^\varepsilon} u_{int}(r_i) \partial_r \phi_i \Phi \, dA - \int_{\partial \Sigma_i^\varepsilon \setminus I_i^\varepsilon} u^\varepsilon \partial_r \phi_i \, dA \, \Phi|_{I_i} \right) \Bigg\} dt. \end{aligned} \tag{5.60}$$

Since u^ε in $L^2 H^1$ and $\mathbb{I}_{\Omega_S^\varepsilon} \to \mathbb{I}_{\Omega(0)}$ strongly and since $\partial_t u^\varepsilon$ is uniformly bounded according to Th. 5.4 this converges with step 1 to

$$0 = \int_{\mathcal{J}_t} \zeta \int_{\Omega(0)} \nabla u^\varepsilon \cdot \nabla \Phi \, dx \, dt - 4\pi \int_{\mathcal{J}_t} \zeta \fint_{\Omega(0)} \int_{\mathcal{J}_r} (u^\infty - u_{int}(r)) r \Phi \, d\nu^t \, dx \, dt, \tag{5.61}$$

from where we get

$$\begin{aligned} -\Delta u^\infty + 4\pi \int_{\mathcal{J}_r} r(u^\infty - u_{int}(r)) d\nu^t &= 0 \qquad && \forall x \in \Omega(0) \, \forall t \in \mathcal{J}_t, \\ \partial_\nu u^\infty &= 0 && \forall x \in \partial\Omega(0) \, \forall t \in \mathcal{J}_t. \end{aligned}$$

This yields that $u^\infty(t)$ does depend on x and t. ☐

Corollary 5.3 (Conservation of mass and substance)**.** *We have* $n_{As} \to \overline{n}_{As}^\infty(1 - 3a^\dagger)$*,* $n_{Ga} \to \overline{n}_{Ga}^\infty(1 - 3a^\dagger)$ *and* $\rho_S \to \overline{\rho}_S^\infty(1 - 3a^\dagger)$ *strongly in* $L^\infty L^\infty$ *as* $\varepsilon \to 0$*. The conservation of As, Ga and mass is preserved under the limit i.e.*

$$|\Omega(0)| \, \overline{n}_{As}^\infty (1 - \frac{\overline{p} - p_0}{k_S}) = N_0^R X_0, \tag{5.62}$$

$$|\Omega(0)| \, \overline{n}_{Ga}^\infty (1 - \frac{\overline{p} - p_0}{k_S}) = N_0^R (1 - X_0), \tag{5.63}$$

$$|\Omega(0)| \, \overline{\rho}_S^\infty (1 - \frac{\overline{p} - p_0}{k_S}) = N_0^R M(X_0). \tag{5.64}$$

Proof. We see immediately that the global conservation for As, Ga and mass hold for all ε due to (2.38) and (2.40) or due to (3.71) and (3.72). Note that since $\overline{Y} \sim \varepsilon^9$ the reference values $\overline{n}_{As}$, $\overline{n}_{Ga}$ and ρ_S depend on ε, too.

This yields $| \int_\Omega n_{As} dx - N_0^R X_0 | \to 0$ in L^1 as $\varepsilon \to 0$. We know from Assumption 5.3 that $n_{As} \to \overline{n}_{As}^\infty (1 - 3\mathrm{tr}(\nabla U^\infty))$ strongly since u^ε is bounded uniformly by the maximum principle (Coroll. 5.1) and since U^∞ exists. Furthermore $\nabla U^\infty = 3a^\dagger$. In particular n_{As_L} is bounded and we have (5.35). By the dominated convergence theorem $|\Omega|\overline{n}_{As} = N_0^R X_0$ follows. The other estimates are shown analogously. $\square$

Assumption 5.4 (The homogenised problem in the dilute scaling regime)**.** *For the dilute scaling regime we expect to find the following problem.*

Let for the data hold $u_\varepsilon^0 \to u_\infty^0$ *in* L^2, $\nu_\varepsilon^0 \to \nu^0$ *in* $[\mathcal{C}]'$ *as* $\varepsilon \to 0$ *then there exist limits* $u^\infty \in W^{1,\infty}$, U^∞ *and* ν_∞^t *as in Theorem 5.5 of the critical regime. They solve the following limit problems.*

The homogenised diffusion problem is

$$\Delta u^\infty = 0 \qquad \forall x \in \Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.65}$$
$$\nabla u^\infty \cdot \nu = 0 \qquad \forall x \in \partial\Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.66}$$

i.e. u^∞ *is constant in space and depends only on time and is determined by the next order equation*

$$\mathcal{X}^\infty \partial_t u^\infty + 4\pi \int_{\mathcal{J}_r} r(u^\infty - u_{int}(r))d\nu^t = 0 \qquad \forall x \in \Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.67}$$
$$u^\infty(\cdot, t=0) = u_\infty^0 \qquad \forall x \in \Omega(0). \tag{5.68}$$

The Stefan condition translates into an evolution equation for the density, a so-called ***kinetic equation****,*

$$\partial_t \nu^t + \partial_r\Big(\nu^t \frac{u^\infty - u_{int}(r)}{r\mathbb{X}^\infty(r)}\Big) = 0 \qquad \forall x \in \Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.69}$$
$$\nu^t|_{t=0} = \nu^0 \qquad \forall x \in \Omega(0). \tag{5.70}$$

The homogenised mechanical BVP and the homogenised velocity problem, are identical as derived in Th. 5.6 for the critical scaling, and have the explicit solution

$$U^\infty = (\overline{p} - p_0)x \qquad \forall x \in \Omega(0)\ \forall t \in \mathcal{J}_t, \tag{5.71}$$
$$v^\infty = 0 \qquad \forall x \in \Omega(0)\ \forall t \in \mathcal{J}_t. \tag{5.72}$$

5.7. Analysis of the homogenised problem

We do not consider existence and uniqueness for the full problem (5.44) – (5.48) in this study, but examine a special case later in Chapter 6. A result in a situation similar to this problem is the result of Niethammer and Velázquez [NV04]. Under suitable assumptions we can prove a partial result.

We rewrite the kinetic equation (5.47) in the form

$$\partial_t \nu^t + \partial_r a_{\nu^t} \nu^t + a_{\nu^t} \partial_r \nu^t = 0. \tag{5.73}$$

Theorem 5.8 (Existence and uniqueness of solutions ν^t of the kinetic equation)**.** *Given initial data* $\nu^0 \in C^1(\mathcal{J}_r)$ *and if* u^∞ *is uniformly continuous in t then exists a unique solution* ν^t *of (5.73) in* $C^2(\mathcal{J}_r \times \mathcal{J}_t)$.

Proof. The kinetic equation (5.73) is linear in $\nu^t = \nu^t(r)$, $\partial_t \nu^t$ and $\partial_r \nu^t$, whereas the coefficients in front of $\partial_r \nu^t$ or ν^t, namely a_{ν^t} or $\partial_r a_{\nu^t}$, are weakly nonlinear, because these coefficients depend still on non-local terms of the type $\int_{\mathcal{J}_r} \nu^t dr$, $\int_{\mathcal{J}_r} r^3 \nu^t dr$.

Such a first-order PDE with weakly nonlinear coefficient in front of $\partial_r \nu^t$ (where in our situation the dependence of a_{ν^t} on ν^t is the same for all r for fixed t), has as ODE for its characteristic r_{r^0} emanating from r^0, where $r^0 \in J$ arbitrary,

$$\dot{r}_{r^0}(t) = a_{\nu^t}(r_{r^0}(t)), \tag{5.74}$$

$$r_{r^0}(0) = r^0, \tag{5.75}$$

like in case of linear first-order PDE. The coefficient in front of $\partial_t \nu^t$ is 1, which implies that we have always noncharacteristic boundary conditions and hence guarantees, that we can continue the characteristics of this ODE for all times $t \in \mathcal{J}_t$.

The local existence theorem as proved in the book of Evans [Eva02], p.107, Th.2 and its application to the linear case in [Eva02], p.110, 3.2.5.a corresponds exactly to our situation.

According to the theorem of Picard-Lindelöf (since a_{ν^t} is smooth and in particular Lipschitz-continuous in r_{r^0} and uniformly continuous in t) the characteristic equations (5.74) and (5.75) have a unique solution for all times $t \in \mathcal{J}_t$.

Characteristics also cannot cross (i.e. for finite times), because this would contradict the uniqueness of the characteristics. ☐

5.8. Special initial data for the homogenised problem

At first we consider the critical scaling regime in the case of the discrete initial data from Example 5.1. By our homogenisation we have passed from Problem E, which is a modification of Problem DCR in regime (DC), with a finite number of droplets at initial time $\mathcal{N}_\varepsilon^0$, to an infinite-dimensional system in the limit $\mathcal{N}^0 \to \infty$.

Lemma 5.10 (Discrete initial data and the mean field model in the critical scaling regime).
If we have discrete initial data

$$\nu^0(r) = \frac{1}{K}\sum_{i=1}^{K} \delta_{r_i^0}(r), \tag{5.76}$$

then the infinite-dimensional dynamical system i.e. the kinetic equation (5.47) *and the homogenised mean field equation* (5.44) *reduce to a mean field model for regime (DC) in the critical scaling, but with a different equation for the mean field than* (3.78) *in the dilute regime. This mean field model is*

$$\Delta u^\infty = 4\pi \frac{1}{K}\sum_{i=1}^{K} r_i(u^\infty - u_{int}(r_i)) \qquad \forall x \in \Omega(0), \tag{5.77}$$

$$\partial_\nu u^\infty = 0 \qquad \forall x \in \partial\Omega(0), \tag{5.78}$$

$$\dot{r}_j = \frac{u^\infty - u_{int}(r_j)}{r_j \mathbb{X}^\infty(r_j)} \qquad \forall j \in \{1, ..., K\},\ r_j(t) > r_{min}, \forall x \in \Omega(0), \tag{5.79}$$

for all $t \in (0, \mathcal{T})$ *together with the initial conditions* (3.51) *and* (5.46).

Proof. We insert (5.76) into (5.47) and test with $r\eta$, η a smooth cut-off function s.t. $\eta = 1$ for $r \in (r_{min} + \delta, \max_i r_i^0 + \delta)$ and $\eta = 0$ for $r \le r_{min}$ and $r \ge \max_i r_i^0 + 2\delta$, where $\delta > 0$ is arbitrary. By intergration by parts we get for sufficiently small times $t \le t_\delta$

$$\partial_t r_i(t) - \frac{u^\infty(t) - u_{int}(r_i(t))}{r_i(t)\mathbb{X}^\infty(r_i(t))} = 0$$

for all i, $r_i > r_{min}$. Thus the distribution is of the form $\nu^t(r) = \frac{1}{K}\sum_{i=1}^{K} \delta_{r_i(t)}(r)$ for $t \in [0, t_\delta]$ and by iteration of this form for all times $t \in [0, \mathcal{T})$. (5.44) reads now

$$-\Delta u^{\infty} + 4\pi \frac{1}{K} \sum_{i=1}^{K} r_i (u^{\infty} - u_{int}(r_i)) = 0.$$

□

We now consider the dilute scaling. Our result will be, that we can identify u^{∞} with the $\overline{u}$ in our mean field model in case of discrete initial data, as introduced in Example 5.1, and if we set $h^* = 0$ in our "ad-hoc" mean field model from Subsection 3.3.5.

Lemma 5.11 (Discrete initial data and the mean field model in the dilute scaling regime)**.** *If we have discrete initial data* (5.76) *then the kinetic equation* (5.69) *and the homogenised mean field equation* (5.65) *reduce to the mean field model for regime (DC),* (3.70) *and* (3.78)*.*

Proof. We proceed as in the last lemma and we get for all i with $r_i(t) > r_{min}$

$$\partial_t r_i(t) - \frac{u^{\infty}(t) - u_{int}(r_i(t))}{r_i(t) \mathbb{X}^{\infty}(r_i(t))}) = 0.$$

Thus the distribution is of the form $\nu^t(r) = \frac{1}{K} \sum_{i=1}^{K} \delta_{r_i(t)}(r)$ for all times $t \in (0, \mathcal{T})$. (5.65) reads now

$$\mathcal{X}^{\infty} \partial_t u^{\infty}(t) + 4\pi \frac{1}{K} \sum_{i=1}^{K} r_i (u^{\infty}(t) - u_{int}(r_i)) = 0.$$

If we identify u^{∞} with our heuristically derived mean field $\overline{u}$ of the mean field model for regime (DC) from Subsection 3.3.5 and further identify $\mathbb{X}^{\infty}$ with $\overline{\mathbb{X}}$ and $\mathcal{X}^{\infty}$ with $\overline{\mathcal{X}}$, then the infinite-dimensional system reduces to the mean field model for regime (DC). □

We emphasise, that u^{∞} depends on t and x.

Chapter 6.

Analysis of mean field models

Despite our coupled PDEs could be solved numerically by the approximation scheme, which we used in Section 4.3 to prove existence and uniqueness, this procedure is quite slow and we are interested in simulations of several thousand droplets, which is a realistic number in experiments, see Section 3.5. As we considered in Chapter 3 we can exploit the scaling behaviour of our system and look, what happens if we make the scaling parameter ε arbitrarily small. This leads to so called mean field models, which are first order approximations in ε of the full Problems D and DI.

We recall that the mean field models on one hand are received from our Problems D or DI by formal homogenisation for the dilute scaling regime in Sections 3.3 and 3.4. On the other hand, in case of regime (DC) in the critical scaling, mean field models from Problem E are obtained by inserting special initial data into the kinetic equation, which we rigorously derived in Chapter 5, for ε_0, see Section 5.8.

In this chapter we consider the full mean field model including terms with h^* derived by formal homogenisation from the full Problems D or DI in the dilute scaling regime. We consider numerical simulations for fixed $\varepsilon = \varepsilon_0 = 10^{-1}$.

According to our discussion in Section 3.5 we would have to consider $\mathcal{N}^0 = N_0^0 \varepsilon_0^{-3} \approx 4200$ precipitates (see also Table 3.1) and K different droplet radii, if we assume an initial distribution of radii of the type of Example 5.1. Since it turns out, that we can only run simulations in reasonable time for small numbers of K we consider only the case of $K \leq 20$ and assume that these K droplets are periodically distributed. By abuse of notation we write in the following $\mathcal{N}^0 = K$ and $N(t) = \{i \in \{1, ..., K\} | r_i(t) > r_{min}\}$.

In the following we demonstrate, that these mean field models, which are macroscopic models, can not only be simulated much easier and faster, but the analysis of these models gives also some insight on the macroscopic behaviour of the system e.g. equilibria and its stability. We consider the mean field models with variables r_i and $\overline{u}$ i.e. (3.70) and (3.78) for regime (DC) as well as (2.163) and (3.85) for regime (IC).

6.1. The mean field problems

The systems of ODEs (3.70) and (3.78) as well as (2.164) and (3.85) are autonomous. Our models lead hence to the analysis of dynamical systems, which we call the **mean field problems**.

Definition 6.1 (Mean field problems)**.**

$$\dot{r}_i(t)=\mathcal{H}(r_i(t),\overline{u}(t)) \qquad \forall i\in\{1,...,\mathcal{N}(t)\} \quad \forall t\in(0,\mathcal{T}), \tag{6.1}$$

$$\dot{\overline{u}}(t)=\mathcal{G}(\{r_i(t)\}_{1\leq i\leq\mathcal{N}},\overline{u}(t)) \qquad \forall t\in(0,\mathcal{T}), \tag{6.2}$$

where in the regime (DC)

$$\mathcal{H}:=\frac{\overline{u}-u_{int}(r_i)}{r_i\overline{\mathbb{X}}(r_i)},$$
$$\mathcal{G}:=-4\pi\frac{\sum_{i\in N}r_i(\overline{u}-u_{int}(r_i))}{\overline{\mathcal{X}}(\overline{u})|\Omega_S(\{r_i(t)\},\overline{u})|},$$

while in the regime (IC)

$$\mathcal{H}:=\frac{\overline{u}-\overline{u_L}(\overline{u},r_i)}{\overline{\mathbb{Z}}(\overline{u},r_i)}$$
$$\mathcal{G}:=-4\pi\frac{\sum_{i\in N}r_i^2(\overline{u}-\overline{u_L}(\overline{u},r_i))\frac{\mathbb{Z}(r_i)}{\mathbb{X}(r_i)}}{\overline{\mathcal{X}}(\overline{u})|\Omega_S(\{r_i(t)\},\overline{u})|},$$

together with the initial conditions

$$r_i(t=0)=r_i^0, \quad \forall i\in\{1,...,\mathcal{N}^0\}, \quad \overline{u}(t=0)=\overline{u}^0. \tag{6.3}$$

is called the mean field problem.

All other quantities e.g. R_{bd} are determined in this model by explicit formula.

Remark 6.1 (Discussion of small volume fraction for fixed ε_0)**.** *The reason for considering* $|\Omega_S|$ *instead of* $|\Omega|$ *in the denominator of the mean field problems i.e. we do not neglect the terms* $\varepsilon^9\sum_{i\in N}r_i^3$*, is that stable radii exist, which are of order* $\mathcal{D}$ *(see Fig. 6.2), and which have non-vanishing volume fraction. This means, that terms* $\varepsilon^9\sum_{i\in N}r_i^3$ *yield a significant correction for the particular choice of* ε_0*, while other terms are of higher order.*

In the following we consider everything in unscaled dimensionful quantities, unless otherwise stated.

The ODEs (6.2) for regime (DC) and regime (IC) have jumping coefficients if and only if a droplet vanishes i.e. the right hand side is not Lipschitz continuous in r_i and $\overline{u}$ for all times. Hence we cannot apply the theorem of Picard-Lindelöf directly, in order to conclude existence and uniqueness of a solution $\overline{u}$ for all times directly. But we get

Lemma 6.1 (Existence and uniqueness for the mean field problem)**.** *There exists a unique smooth solution* $(\overline{u},r_i)$ *of the dynamical system (6.1) – (6.3) for all* $t\in(0,\mathcal{T})\setminus\cup_{i\in N(0)}\tau_i$ *which is at least continuous for all* $t\in(0,\mathcal{T})$*.*

Proof. We check that the r.h.s. is Lipschitz continuous in r_i and $\overline{u}$ as long as no droplet vanishes. If we reach $t=\tau_i$ for some $i\in N(0)$ we start at time τ_i+ again with new initial data and $N(\tau_i+):=N(\tau_i^-)\setminus\{i\}$ and get again a smooth solution. Hence the global solution is smooth for all times $t\neq\tau_i, i\in N(0)$ and at least continuous in τ_i, $i\in N(0)$. □

We assume for the rest of this chapter that for regime (IC) we can approximate

$$\overline{u}-\overline{u_L}(\overline{u},r_i)\approx\overline{u}-u_{int}(r_i). \tag{6.4}$$

This can be motivated by the approximation (3.88), if we assume $\mathbb{H}_{\tilde{\mu}}/\mathbb{H}_{\tilde{m}} = 1$ and inserting therein the approximation (2.167) for X_L^A. The approximation (6.4) allows in particular to treat the two regimes (DC) and (IC) simultaneously in this chapter.
In order to compare the mean field $\overline{u}$ with radii r_i we rewrite $\overline{u}$ in terms of a radius:

Definition 6.2 (Mean field radius)**.** *We define the mean field radius as*

$$\overline{r}(t) := \begin{cases} r_{min} & ; \quad \overline{u}(t) \in [u_{int}(r_{min}), +\infty), \\ u_{int}^{-1}(\overline{u}(t)); & \quad \overline{u}(t) \in (\lim_{r\to+\infty} u_{int}(r), u_{int}(r_{min})), \\ +\infty & ; \quad \overline{u}(t) \in (-\infty, \lim_{r\to+\infty} u_{int}(r)]. \end{cases} \tag{6.5}$$

Since $u_{int} : r \in \mathcal{J}_r \to (\lim_{r\to+\infty} u_{int}(r), u_{int}(r_{min}))$ is continuous and strictly monotone the mean field radius $\overline{r}$ is well-defined.

This allows to rewrite (6.2) and our dynamical system can now be formulated as

$$\dot{r}_i(t) = \mathcal{H}_2(r_i(t), \overline{r}(t)) \qquad \forall i \in \{1, ..., \mathcal{N}(t)\} \quad \forall t \in (0, \mathcal{T}), \tag{6.6}$$

$$\dot{\overline{r}}(t) = \mathcal{G}_2(\{r_i(t)\}_{1\le i\le\mathcal{N}}, \overline{r}(t)) \qquad \forall t \in (0, \mathcal{T}), \tag{6.7}$$

where we define for regime (DC)

$$\mathcal{H}_2 = \frac{u_{int}(\overline{r}) - u_{int}(r_i)}{r_i\overline{\mathbb{X}}(r_i)}, \quad \mathcal{G}_2 = u_{int}^{-1\prime}(u_{int}(\overline{r}))\mathcal{G} = \frac{4\pi}{|u'_{int}(\overline{r})|}\frac{\sum_{i\in N} r_i(u_{int}(\overline{r}) - u_{int}(r_i))}{\overline{\mathcal{X}}(\overline{r})|\Omega_S(\{r_i(t)\}, \overline{r})|}$$

where we use $u'_{int}(r) < 0$ or for (IC)

$$\mathcal{H}_2 = \frac{u_{int}(\overline{r}) - u_{int}(r_i)}{\overline{\mathbb{Z}}(\overline{u}, r_i)}, \quad \mathcal{G}_2 = \frac{4\pi}{|u'_{int}(\overline{r})|}\frac{\sum_{i\in N} r_i^2(\overline{u} - u_{int}(r_i))\frac{\overline{\mathbb{X}}(\overline{r}, r_i)}{\overline{\mathbb{Z}}(\overline{r}, r_i)}}{\overline{\mathcal{X}}(\overline{r})|\Omega_S(\{r_i(t)\}, \overline{r})|},$$

with initial conditions

$$r_i(t=0) = r_i^0, \quad \forall i \in \{1, ..., \mathcal{N}^0\}, \quad \overline{r}(t=0) = \overline{r}^0 := u_{int}^{-1}(\overline{u}^0). \tag{6.8}$$

We do not change notation of $\mathbb{X}$ (for (IC)), $\mathbb{Z}$, $\overline{\mathcal{X}}$ and $|\Omega_S|$, though they are now functions in $\overline{r}$ instead of $\overline{u}$.
There holds a maximum principle for $\overline{u}$ or for the "critical" radius of the dynamical system, which is $\overline{r}$. We prove the maximum principle in Lemma 6.4.

Remark 6.2 (Mean field problem with approximation of u_{int})**.** *In Appendix C.1.2 we show, that our strictly monotone functions y_{int} or u_{int} can be approximated for small mechanical terms. By (C.38) we approximate $y_{int}(r_i) \approx 1 + \tilde{c}_1 + \frac{\tilde{c}_2}{r_i}$ with strictly positive constants e.g. $\tilde{c}_1 \approx 0.05$ and $\tilde{c}_2 \approx \frac{2\sigma}{RTn_G^R} \approx 0.55$ and together with (A.17) we find $u_{int}(r_i) \approx \frac{1+\tilde{\mu}}{\tilde{\mu}}(\tilde{c}_1 + \frac{\tilde{c}_2}{r_i}) \approx c_1 + \frac{c_2}{r_i}$ with $c_1 \approx 0.1$ and $c_2 \approx 1.1$. This approximation allows later to compare our results with the results of classical LSW theory. If we assume*

$$u_{int}(r) = c_1 + \frac{c_2}{r}, \tag{6.9}$$

i.e. $c_1 := \lim_{r\to+\infty} u_{int}(r)$, then $\overline{r} = \frac{c_2}{\overline{u}-c_1}$. Furthermore we approximate $\overline{\mathbb{X}}(r_i) \approx \overline{\mathbb{X}}(1) =: \overline{\mathbb{X}}_c$ since this functions depends "weakly" on its arguments. Then the ODEs read for regime (DC)

$$\dot{r}_i = c_2\frac{\frac{1}{\overline{r}} - \frac{1}{r_i}}{r_i\overline{\mathbb{X}}(r_i)} = c_2\frac{r_i - \overline{r}}{r_i^2\overline{r}\overline{\mathbb{X}}_c} \qquad \forall i \in \{1, ..., \mathcal{N}(t)\} \quad \forall t \in (0, \mathcal{T}), \tag{6.10}$$

$$\dot{\overline{r}} = 4\pi\frac{\overline{r}\sum_{i\in N}(r_i - \overline{r})}{\overline{\mathcal{X}}(\overline{r})|\Omega_S(\{r_i\}, \overline{r})|} \qquad \forall t \in (0, \mathcal{T}) \tag{6.11}$$

and c_1 drops out completely.

For (IC) our approximations are with $\overline{\mathbb{Z}}(\overline{u}, r_i) \approx \overline{\mathbb{Z}}(u_{int}(1), 1) =: \overline{\mathbb{Z}}_c$

$$\dot{r}_i = c_2 \frac{\frac{1}{\overline{\overline{r}}} - \frac{1}{r_i}}{\overline{\overline{\mathbb{Z}}}_c} = c_2 \frac{r_i - \overline{r}}{r_i \overline{r} \overline{\overline{\mathbb{Z}}}_c} \qquad \forall i \in \{1, ..., \mathcal{N}(t)\} \quad \forall t \in (0, \mathcal{T}) \tag{6.12}$$

$$\dot{\overline{r}} = 4\pi \frac{\overline{r} \sum_{i \in N} r_i (r_i - \overline{r}) \frac{\overline{\mathbb{X}}_c}{\overline{\overline{\mathbb{Z}}}_c}}{\overline{\mathcal{X}}(\overline{r}) |\Omega_S(\{r_i\}, \overline{r})|} \qquad \forall t \in (0, \mathcal{T}) \tag{6.13}$$

First we examine the system of coupled ODEs (6.6) – (6.8) analytically.

6.2. Available free energy for mean field models

In this section we work with scales and with dimensions.

For the approximation of the availability by the mean field models holds

Lemma 6.2 (Availability for mean field model)**.**

1) The availability for the mean field model, which we get by plugging in the approximation of u by u_A, of U by W and the corresponding approximations of the Stefan condition, is for both regimes (DC) and (IC) non-increasing with time.

2) We have as explicit formula for the availability for the mean field model in the regimes (DC)

$$\begin{aligned} \mathcal{A}^\varepsilon = {} & |\Omega|(R_{bd})[p_0 - \overline{p} + (\mu_{Ga_S}^{chem}(1 - X_S) + \mu_{As_S}^{chem} X_S)(\overline{u})(3 - Y_V) n_G^R (1 - \frac{p_0 - \overline{p}}{k_S})] \\ & + \frac{4\pi}{3} \varepsilon^9 \sum_{i \in N} r_i^3 (\mu_{Ga_S}^{chem} - \mu_{As_S}^{chem})(\overline{u})(X_S(\overline{u}) - X_L^i)(3 - \overline{Y}_V) n_G^R \\ & + 4\pi\varepsilon^9 \sum_{i \in N} r_i^2 (1 - \frac{2}{3} \frac{\overline{\rho}_L}{\overline{\rho}_S}) \sigma^R, \end{aligned} \tag{6.14}$$

while in regime (IC)

$$\begin{aligned} \mathcal{A}^\varepsilon = {} & |\Omega|(R_{bd})[p_0 - \overline{p} + (\mu_{Ga_S}^{chem}(1 - X_S) + \mu_{As_S}^{chem} X_S)(\overline{u})(3 - Y_V) n_G^R (1 - \frac{p_0 - \overline{p}}{k_S})] \\ & + \frac{4\pi}{3} \varepsilon^9 \sum_{i \in N} r_i^3 [(\mu_{Ga_S}^{chem} - \mu_{As_S}^{chem})(\overline{u})(X_S(\overline{u}) - X_L^i) \\ & \quad + (v_{Ga_L}^\nu(\dot{r}_i)(1 - X_L^i) + v_{As_L}^\nu(\dot{r}_i) X_L^i - \dot{r}_i)](3 - \overline{Y}_V) n_G^R \\ & + 4\pi\varepsilon^9 \sum_{i \in N} r_i^2 (1 - \frac{2}{3} \frac{\overline{\rho}_L}{\overline{\rho}_S}) \sigma^R. \end{aligned} \tag{6.15}$$

Proof.
1) Follows directly from (A.32) which reads for our mean field problems for regime (DC)

$$\frac{d}{dt} \mathcal{A}^\varepsilon = - \int_{\Omega_S} |\nabla u_A|^2 \leq 0.$$

For the regime (IC) this reads

$$\frac{d}{dt} \mathcal{A}^\varepsilon = -4\pi \sum_{i \in N} r_i^2 (([[\mu_{As}]](u_A, r_i) + 4 G_S b_i \frac{1}{\overline{\rho}_S})^2 + ([[\mu_{Ga}]](u_A, r_i) + 4 G_S b_i \frac{\tilde{\mu}}{\overline{\rho}_S})^2) \leq 0.$$

2) First consider the regime (DC). With the mean field model the availability (A.35) simplifies to

$$\begin{aligned}\mathcal{A}^\varepsilon = {} & |\Omega|(R_{bd})[p_0 - \overline{p} + (\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As})(\overline{u}) n_G^R (1-3a)] \\ & + \frac{4\pi}{3}\varepsilon^9 \sum_{i\in N} r_i^3 [-(\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As})(\overline{u}) n_G^R (1-3a) \\ & + ((\mu_{Ga_S}^{chem}(\overline{u})(1-X_L^i) + \mu_{As_S}^{chem}(\overline{u}) X_L^i) n_G^R (3-\overline{Y}_V)(1-3(a_L^i - \delta^R - h_L^*(r_i))) \\ & + 3k_L(\delta^R + h_L^*(r_i) - \frac{\overline{\rho}_L}{\overline{\rho}_S}(a+b_i)))] \\ & + 4\pi\varepsilon^9 \sum_{i\in N} r_i^2 (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma^R\end{aligned} \tag{6.16}$$

and with the definition of X_S this can be rewritten as

$$\begin{aligned}\mathcal{A}^\varepsilon = {} & |\Omega|(R_{bd})[p_0 - \overline{p} + (\mu_{Ga_S}^{chem}(1-X_S) + \mu_{As_S}^{chem} X_S)(\overline{u})(3-Y_V) n_G^R] \\ & + \frac{4\pi}{3}\varepsilon^9 \sum_{i\in N} r_i^3 [(\mu_{Ga_S}^{chem} - \mu_{As_S}^{chem})(\overline{u})(X_S(\overline{u})\frac{3-Y_V(\overline{u})}{3-\overline{Y}_V}(1-3a) - X_L^i(1-3(a_L^i - \delta^R - h_L^*(r_i)))) \\ & + r_i^3[\mu_{Ga_S}^{chem}(\overline{u}) 3(a - a_L^i + \delta^R + h_L^*(r_i))](3-\overline{Y}_V) n_G^R + 3k_L(\delta^R + h_L^*(r_i) - \frac{\overline{\rho}_L}{\overline{\rho}_S}(a_L^i - \delta^R))] \\ & + 4\pi\varepsilon^9 \sum_{i\in N} r_i^2 (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma^R\end{aligned}$$

By neglecting higher order terms in $\tilde{h}$ and ε we receive (6.14).

For regime (IC) we have

$$\begin{aligned}\mathcal{A}^\varepsilon = {} & |\Omega|(R_{bd})(p_0 - \overline{p}) + (|\Omega|(R_{bd}) - \frac{4\pi}{3}\varepsilon^9 \sum_{i\in N} r_i^3)(\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As})(\overline{u}) n_G^R (1-3a) \\ & + \frac{4\pi}{3}\varepsilon^9 \sum_{i\in N} r_i^3 ((\mu_{Ga_S}^{chem}(1-X_L^i) + \mu_{As_S}^{chem} X_L^i)(3-\overline{Y}_V) n_G^R (1 - 3(a+b_i) + 3h_L^*(r_i))) \\ & + (v_{Ga_L}(\dot{r}_i)\cdot\nu(1-X_L^i) + v_{As_L}(\dot{r}_i)\cdot\nu X_L^i - \dot{r}_i)(3-\overline{Y}_V) n_G^R (1-3(a_L^i + \delta^R - {h_L^*}^i)) \\ & + 3k_L(\delta^R + h_L^*(r_i) - \frac{\overline{\rho}_L}{\overline{\rho}_S}(a+b_i)))] \\ & + 4\pi\varepsilon^9 \sum_{i\in N} r_i^2 (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma^R\end{aligned}$$

and in our approximation this yields finally (6.15). □

The explicit formulas for the availability (6.14) and (6.15) allows in principle to determine stable and unstable equilibria as maxima, minima and saddle points of the availability.

6.3. Stability and instability of a finite number of liquid droplets

A natural question to ask is how the dynamical system deduced from the mean field model evolves with time. Here we consider the case of a finite number of liquid droplets $\mathcal{N}^0$ at initial time. In this section we classify stationary solutions or equivalently referred to as equilibrium of the mean field model and discuss their stability. Finally we determine the long-time behaviour of the system.

Definition 6.3 (Stationary solution or equilibrium). *We define as stationary solution a time-independent radii distribution* $\{r_i^\infty\}_{1\le i\le\mathcal{N}^\infty}, r_i^\infty \in \mathcal{J}_r$*, a fixed mean field* $\overline{u}$*, a fixed domain* Ω^∞ *and*

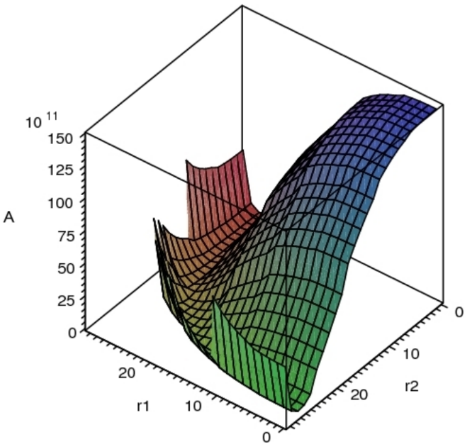

Figure 6.1.: Availability [in 10^{-27} N m] versus radii [in 10^{-9} m] for the mean field model of a system with $\mathcal{N}^0 = 2$ and here $N_0^R = 2.39 \cdot 10^{-14}$mol, $p_0 = 10^5\,\mathrm{N\,m}^{-2}$. The equilibrium $(r_1 = r_{crit}^2, r_2 = r_{crit}^2)$ is unstable, $(r_1 = r_{crit}^1, r_2 = 0)$, $(r_1 = 0, r_2 = r_{crit}^1)$ and $(r_1 = r_{stab}^2, r_2 = r_{stab}^2)$ are metastable saddle points and $(r_1 = r_{stab}^1, r_2 = 0)$, $(r_1 = 0, r_2 = r_{stab}^2)$ are stable equilibria.

a fixed number of particles $\mathcal{N}^\infty$ *such that*

$$\begin{aligned} 0 &= \mathcal{H}(r_i^\infty, \overline{u}^\infty) && \forall i \in \{1, ..., \mathcal{N}^\infty\}, \\ 0 &= \mathcal{G}(\{r_i^\infty\}_{1 \le i \le \mathcal{N}^\infty}, \overline{u}^\infty), \end{aligned}$$

i.e. we require

$$\dot{r}_i(t) = 0, \quad \dot{\overline{u}}(t) = 0, \quad \frac{d}{dt}|\Omega(t)| = 0, \quad \mathcal{N} = const. \tag{6.17}$$

We abbreviate the fraction of droplets, which exist at time t or in an equilibrium, w.r.t. the number of droplets at initial time $t = 0$ by $\eta(t) := \frac{\mathcal{N}(t)}{\mathcal{N}(0)}$ or $\eta^\infty := \frac{\mathcal{N}^\infty}{\mathcal{N}(0)}$.

We can calculate explicitly equilibria $\{r_i^\infty\}_{1 \le i \le \mathcal{N}^\infty}$, $\overline{u}^\infty$, Ω^∞ and $\mathcal{N}^\infty$.

Lemma 6.3 (Necessary and sufficient conditions on equilibria)**.** *For both regimes (DC) and (IC) there holds:*

1) We have equilibria i.e. the conditions (6.17) hold with $\mathcal{N}^\infty \in \{1, ..., \mathcal{N}^0\}$ *droplets, iff*

$$r_i^\infty = u_{int}^{-1}(\overline{u}^\infty) =: r_{stat} \quad \forall i \in N(t), \tag{6.18}$$

$$\overline{u}^\infty = X_S^{-1}\Big(\frac{X_0 - \frac{4\pi}{3}\eta^\infty r_{stat}^3 X_L(r_{stat})\frac{n_L(r_{stat})}{N_0^R}}{1 - \frac{4\pi}{3}\eta^\infty r_{stat}^3 \frac{n_L(r_{stat})}{N_0^R}}\Big), \tag{6.19}$$

$$|\Omega^{R,\infty}| = \frac{|\Omega^\infty|}{\mathcal{N}^0} = \frac{1}{\rho_S^A(\overline{u}^\infty)}[M_0^R - \frac{4\pi}{3}\eta^\infty r_{stat}^3 \rho_L(r_{stat})] + \frac{4\pi}{3}\eta^\infty r_{stat}^3. \tag{6.20}$$

Therefore we do not make any assumption on the shape of Ω^∞*. If* $\Omega_0 = B_{R_{bd}}(0)$ *then (6.20) is equivalent to*

$$R_{bd}^\infty = \sqrt[3]{\frac{3}{4\pi}|\Omega^\infty|} = \sqrt[3]{\mathcal{N}^0\Big(\frac{1}{\rho_S^A(\overline{u}^\infty)}[\frac{3}{4\pi}M_0^R - \eta^\infty r_{stat}^3 \rho_L(r_{stat})] + \eta^\infty r_{stat}^3\Big)}.$$

2) If we assume that $\overline{u}^{\infty}$ *is concave as function of* r_{stat}*, if we assume that* u_{int} *is convex in* r_{stat} *and if* $\lim_{r\to\infty} X_S(u_{int}(r)) < X_0$*, then the condition (6.18) has two solutions for the stationary radius* r_{stat} *for sufficiently large* N_0^R*,*

$$r_{stat} \in \{r_{crit}^{(\mathcal{N}^\infty)}, r_{stab}^{(\mathcal{N}^\infty)}\}.$$

3) In the special case $\mathcal{N}^\infty = 0$ *we have equilibria iff*

$$\overline{u}^{\infty} = X_S^{-1}(X_0), \tag{6.21}$$

$$|\Omega^{R,\infty}| = \frac{|\Omega^\infty|}{\mathcal{N}^0} = \frac{M_0^R}{\rho_S^A(\overline{u}^\infty)}. \tag{6.22}$$

Proof.
1) We have due to the Stefan condition (2.153)

$$\overline{u} = u_{int}(r_i^\infty) \qquad \forall i \in \{1,...,\mathcal{N}^\infty\}$$

and because u_{int} is continuous and strictly monotone in the radius this holds iff all stationary radii are identical.

Plugging this into (3.73) and (3.74) together with (3.78) and (3.76) yields the other two conditions.

2) The conservation of As (3.71) simplifies by plugging in (6.18) to

$$N_0^R X_0 = (N_0^R - \frac{4\pi}{3} r_{stat}^3 n_L(r_{stat})) X_S(\overline{u}^\infty) + \frac{4\pi}{3}\eta^\infty r_{stat}^3 n_L(r_{stat}) X_L(r_{stat}),$$

that can be expressed, since X_S is continuous and strictly monotone, as

$$X_S(\overline{u}^\infty(r_{stat})) = \frac{X_0 N_0^R - \frac{4\pi}{3}\eta^\infty r_{stat}^3 n_L(r_{stat}) X_L(r_{stat})}{N_0^R - \frac{4\pi}{3}\eta^\infty r_{stat}^3 n_L(r_{stat})}. \tag{6.23}$$

The possible values of r_{stat} can be determined as intersections of $X_S(u^\infty(r_{stat}))$ with $X_S(u_{int}(r_{stat}))$.

$X_S(u^\infty)$ is concave and strictly monotone decreasing in r_{stat}, while $X_S(u_{int}(r_{stat}))$ is convex and strictly monotone decreasing in r_{stat}, see Fig. 6.2 and Fig. 6.3. Therewith the difference $\Psi_\Delta := X_S(u^\infty) - X_S(u_{int})$ is concave with $\Psi_\Delta(r_{stat} = 0) = X_0 - X_S(u_{int}(0)) < 0$ and $\Psi_\Delta(r_{stat} = r_{max}) = -X_S(u_{int}(r_{max})) < 0$. The equation $\Psi_\Delta = 0$ has hence either exactly 0, 1 or 2 solutions depending on the sign of $\Psi_\Delta(r_d)$ where

$$r_d := \max_{r_{stat}\in(r_{min},r_{max})} r_{stat}$$

We consider the family of concave curves $\Psi_\Delta(r_{stat}; c_\Delta)$ which are continuously differentiable in the parameter $c_\Delta := \frac{\eta^\infty}{N_0^R}$ and have the common point $\Psi_\Delta(r_{stat} = 0; c_\Delta) = X_0 - X_S(u_{int}(0)) < 0$. If we derive Ψ_Δ w.r.t. the parameter c_Δ we find for fixed r_{stat}

$$\partial_{c_\Delta}\Psi_\Delta(r_{stat}) = \frac{4\pi}{3} r_{stat}^3 n_L(r_{stat}) \frac{X_0 - X_L(r_{stat})}{(1 - \frac{4\pi}{3}\eta^\infty r_{stat}^3 \frac{n_L(r_{stat})}{N_0^R})^2} < 0$$

since $X_L \geq \overline{X}_L$ according to Lemma 2.4 and $\overline{X}_L > X_0$. We have $\Psi_\Delta(r_{stat}; 0) = X_0 - X_S(u_{int})$ which gets positive for a $r_{stat} < u_{int}^{-1}(X_S^{-1}(X_0)) = r_{max}$ where we use our assumption $X_0 > \lim_{r\to\infty} X_S(u_{int}(r))$. By the intermediate value theorem there exists c_Δ^* s.t. $\Psi_\Delta(r_{stat}; c_\Delta^*) > 0$ for a points r_{stat}. Hence for $c_\Delta < c_\Delta^*$ and since the curves are concave we can find two intersection points i.e. solutions of (6.18), which we denominate with r_{crit} and r_{stab} where $0 < r_{crit} < r_{stab} < r_{max}$.

By some asymptotics or numerically we see that for $\frac{\eta^\infty}{N_0^R} < \frac{1}{N_0^R}$, N_0^R sufficiently large, which is a

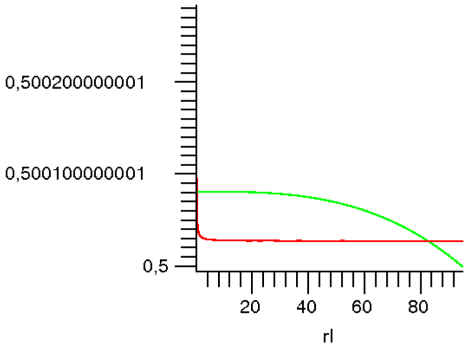

Figure 6.2.: $X_S(u_{int}(r_{stat}))$ and $X_S(\overline{u}^\infty(r_{stat}))$ (red/green line). The equilibria for $\mathcal{N}^\infty = 1$ for the total number of atoms $N_0 = 20\ N_0^R$ i.e. $\mathcal{N}^0 = 20$, are given as intersections.

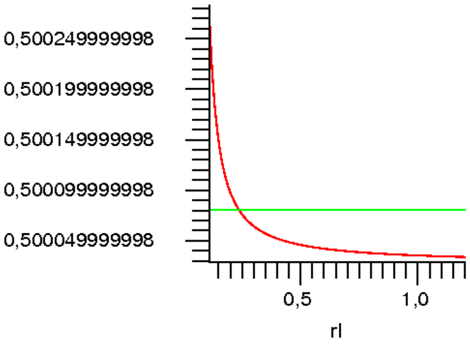

Figure 6.3.: Zoom of Fig. 6.2 for small radii, the intersection gives the critical radius r_{crit}. In both figures radii are measured in units of $\mathcal{R}_0 = 10^{-9}$m.

reasonable assumption in our model, $\Psi_\Delta > 0$, see Fig. 6.4. We note that, we see from Fig. 6.4 that we cannot assume vanishing liquid volume fraction in the formulas for $\Omega(t)$ and $\overline{u}(t)$, as pointed out in Remark 6.1.

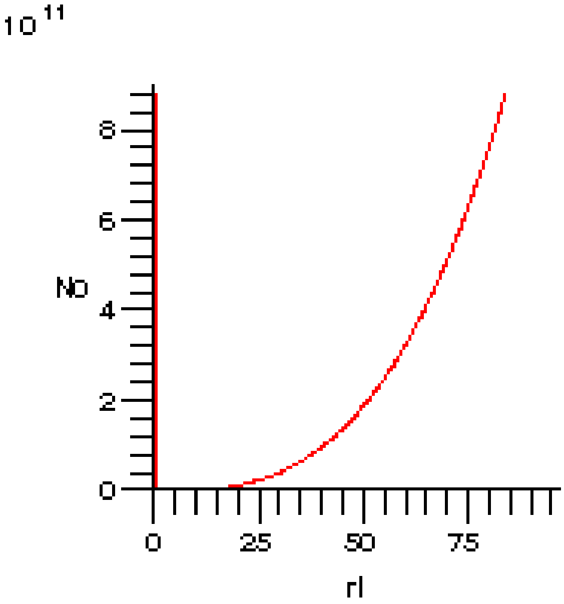

Figure 6.4.: The equilibria r_{crit} and r_{stab} [in 10^{-9} m] depend on N_0 [in units of 1] for $\mathcal{N}^\infty = 1$.

We remark, that the reason, why we abbreviate the smaller equilibrium radius $r_{crit}^{\mathcal{N}^\infty}$ as "critical" radius, is that, that for a single droplet i.e. $\mathcal{N}^\infty = 1$ these droplets are critical in the sense that, if we disturb r_{crit} a little bit, the system goes away from this radius, see the plot of $\dot{r_1}$ against r_1 in Fig. 6.5.

Precisely this instability is due to change of sign from $-$ to $+$ in the Stefan condition at r_{crit}, while for r_{stab} the change of sign is from $+$ to $-$, hence r_{stab} is stable for $\mathcal{N}^\infty = 1$.

3) Is a special case of 1) and 2) where (6.18) is no condition since $N(t) = \emptyset$ and $\eta^\infty = 0$. $\square$

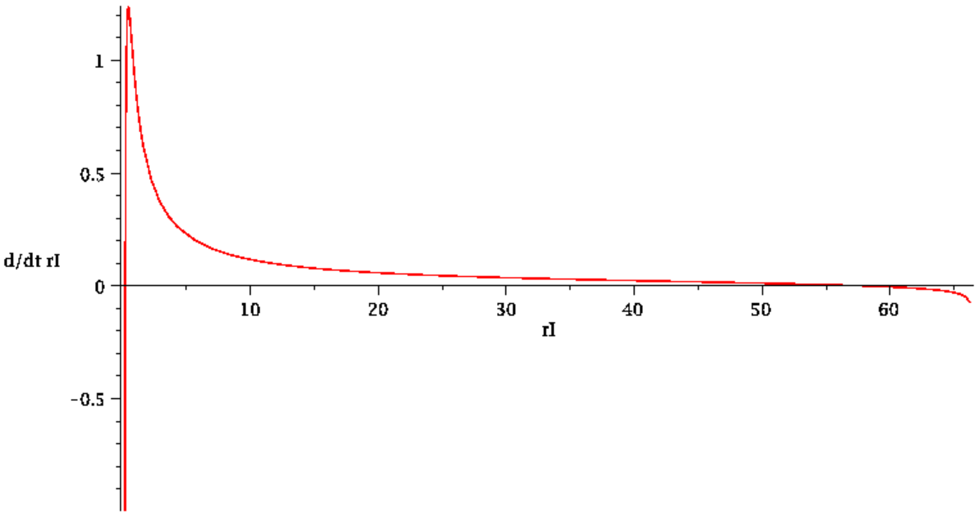

Figure 6.5.: Plot of a typical Stefan condition of regime (DC) for $\mathcal{N}(t) = 1$ i.e. $\dot{r}_i$ in units of $[1 \text{ nm } (10^{-6} \text{ s})^{-1}]$ as function of r_i in [1 nm] in case of $N_0 = 2.39 \cdot 10^{-14}$mol.

Remark: If there exists no intersection at all, then $\dot{r}_i < 0$ i.e. the system reduces the number of droplets until at least one intersection exists or until $\mathcal{N}^\infty = 0$. If there exists exactly one intersection i.e. $r_{stat} = r_{crit} = r_{stab}$ then the Stefan condition has no change of sign and hence r_{stat} is unstable, a “saddle”.

Note that this cannot be enlarged at once for $\mathcal{N}^\infty > 1$. But for many droplets we will prove in the following rigorously that r_{crit} stays critical. For the moment this can be motivated numerically by the fact that r_{crit} is almost independent of $\mathcal{N}^\infty$, but what can we say about stability of r_{stab}?

We use in the next theorem the definitions of instability, asymptotic stability and stability as defined by Walter [Wal00].

Theorem 6.1 (Stability of equilibria of the mean field problems)**.** *We consider $\mathcal{N}^\infty$ droplets and work in this theorem with typical material data as given in Appendix D and with the stated approximations of $\mathbb{X}$, $\mathbb{Z}$ and $\mathcal{X}$.*

Critical radii ($r_{crit} \approx 0.2 \cdot 10^{-10} m$) are always unstable.

Other stationary radii are unstable for $\mathcal{N}^\infty > 1$ and asymptotically stable for $\mathcal{N}^\infty = 1$.

For $\mathcal{N}^\infty = 0$ the system is stable, but not asymptotically stable.

We emphasise that this result holds for both regimes (DC) or (IC). Hence we cannot decide from the equilibria if we are in regime (DC) or (IC) or a combination of both i.e. regime (DC & IC).

Proof. We want to apply the theorem of Poincaré-Lyapunov (see [Wal00], S. 278/9, *Sätze VII + VIII*) i.e. we examine the stability of the dynamical system $\{\mathcal{G}, \mathcal{H}\}$ by linearisation around the stationary radii r_{stat}.

We introduce the abbreviations

$$d_i := r_i - r_{stat} \quad \forall i \in N, \quad \overline{d} := \overline{r} - r_{stat}.$$

Furthermore we write

$$\omega(\{r_i\}_{i \in N}, \overline{r}(t)) = \frac{1}{4\pi} \overline{\mathcal{X}} |\Omega_S(\{r_i\}, \overline{r})|.$$

In this new variables $\{d_i\}_{i\in N}, \overline{d}$ the linearised system is for (DC)

$$\dot{d}_i = \frac{u'_{int}(r_{stat})(\overline{d} - d_i)}{r_{stat}\mathbb{X}(r_{stat})} + o(d_i^2, \overline{d}^2, d_i\overline{d}) \quad \forall i \in N, \tag{6.24}$$

$$\dot{\overline{d}} = \frac{1}{u'_{int}(r_{stat})}\dot{\overline{u}} = -\frac{r_{stat}}{\omega(r_{stat})}(\eta^\infty\overline{d} - \frac{1}{\mathcal{N}^0}\sum_{i\in N} d_i) + o(d_i^2, \overline{d}^2, d_i\overline{d}), \tag{6.25}$$

where we use $\overline{u}^\infty = u_{int}(r_{stat})$. $\omega(r_{stat})$ here is just short for $\omega(\{r_i = r_{stat}\}_{i\in N}, \overline{r} = r_{stat})$.

The system (6.24) and (6.25) can be written in the form

$$\dot{D} = AD$$

with A an $(\mathcal{N}^\infty + 1) \times (\mathcal{N}^\infty + 1)$ matrix which represents the coupling of the liquid droplets via the solid matrix mean field. The entries of the $\mathcal{N}^\infty + 1$ vector D are the $\mathcal{N}^\infty$ distances of the equilibrium to the radii r_i and to the mean field radius $\overline{r}$. More precisely

$$\begin{array}{rlrll}
(D)_i := d_i & \forall i \in N, & (D)_{\mathcal{N}^\infty+1} := \overline{d}, & & \\
(A)_{i,j} := \delta^{ij}A_1 & \forall i, j \in N, & (A)_{i,\mathcal{N}^\infty+1} := -A_1 & & \forall i \in N, \\
(A)_{\mathcal{N}^\infty+1,j} := \frac{1}{\mathcal{N}^0}A_2 & \forall j \in N, & (A)_{\mathcal{N}^\infty+1,\mathcal{N}^\infty+1} := -\eta^\infty A_2, & &
\end{array}$$

where

$$A_1 := -\frac{u'_{int}(r_{stat})}{r_{stat}\mathbb{X}(r_{stat})}, \quad A_2 := \frac{r_{stat}}{\omega(r_{stat})}. \tag{6.26}$$

For (IC) we can argue as for regime (DC), but we have instead of (6.24) and (6.25)

$$\begin{aligned}
\dot{d}_i &= \frac{u'_{int}(r_{stat})(\overline{d} - d_i)}{\mathbb{Z}(u_{int}(r_{stat}), r_{stat})} + o(d_i^2, \overline{d}^2, d_i\overline{d}) \quad \forall i \in N, \\
\dot{\overline{d}} &= \frac{1}{u'_{int}(r_{stat})}\dot{\overline{u}} = -\frac{r_{stat}}{\omega(r_{stat})}\frac{\mathbb{X}(u_{int}(r_{stat}), r_{stat})}{\mathbb{Z}(u_{int}(r_{stat}), r_{stat})}(\eta^\infty\overline{d} - \frac{1}{\mathcal{N}^0}\sum_{i\in N} d_i)^2 + o(d_i^2, \overline{d}^2, d_i\overline{d}).
\end{aligned}$$

and instead of (6.26)

$$A_1 := -\frac{u'_{int}(r_{stat})(\overline{d} - d_i)}{\mathbb{Z}(u_{int}(r_{stat}), r_{stat})}, \quad A_2 := \frac{r_{stat}}{\omega(r_{stat})}\frac{\mathbb{X}(u_{int}(r_{stat}), r_{stat})}{\mathbb{Z}(u_{int}(r_{stat}), r_{stat})}.$$

Due to the special structure of the matrix A we can prove by induction over $\mathcal{N}^\infty$, for $\mathcal{N}^\infty \geq 1$

$$\det(A - \lambda\mathbb{I}_{\mathcal{N}+1}) = \lambda(\lambda + \eta^\infty A_2 - A_1)(A_1 - \lambda)^{\mathcal{N}^\infty - 1}.$$

For $\mathcal{N}^\infty = 0$ the only eigenvalue is 0.

Hence the spectrum of A consists of eigenvalues 0, $A_1 - \eta^\infty A_2$ and $\mathcal{N}^\infty - 1$ times the eigenvalue A_1. Since u_{int} is monotone decreasing $A_1 > 0$ and since

$$\omega(r_{stat}) = \frac{1 - \tilde{\nu}}{4\pi}[M_0^R - \frac{4\pi}{3}\eta^\infty r_{stat}^3\rho_L(r_{stat})]P'(u_{int}(r_{stat})) \geq 0$$

together with our assumptions on $\mathbb{X}$ for (DC) or on $\mathbb{X}$ and $\mathbb{Z}$ for (IC) we have $A_2 > 0$.

Due to definition of η^∞ we have

$$A_1 > A_1 - \eta^\infty A_2 > A_1 - A_2.$$

We have $sign(A_1 - \eta^\infty A_2) = sign(-u'_{int}(r_{stat})\omega(r_{stat}) - \eta^\infty r_{stat}^2 \mathbb{X}(r_{stat}, u_{int}(r_{stat}))$ for example for (DC). By plugging in concrete values for r_{stat} we see that $A_1 - A_2 > 0$ for $r_{stat} = r_{crit}$ and $A_1 - \eta^\infty A_2 < 0$ for $r_{stat} = r_{stab}$ for typical material data in case of both regimes.

We conclude that A has at least one strictly positive eigenvalue $\lambda = A_1$ unless $\mathcal{N} = 0, 1$. Hence r_{stab} is unstable if $\mathcal{N}^\infty > 2$, and r_{crit} is always unstable.

The theorem of Poincaré-Lyapunov gives us no information about stability if $\max_\lambda \mathrm{Re}(\lambda) = 0$. But for $\mathcal{N}^\infty = 1$ we already know that r_{stab} is asymptotically stable and for $\mathcal{N}^\infty = 0$ the system is also stable, since droplets cannot appear in our model and hence $\overline{u} = const$, but not asymptotically stable.

Critical droplets are maxima of the availability, other stationary radii ($\mathcal{N} > 1$) are saddles and in the special case of $\mathcal{N} = 1$ or $\mathcal{N} = 0$ we have minima of the energy. The case of no droplet is a absolute minimum, but it is not clear if the system can go to the global minimum, since it would have to pass a "barrier of critical radii" which has relatively high energy. This depends on the initial energy. ☐

We remark, that the choice of considering the mean field problem (6.6)-(6.8) with an "artificially" introduced ODE for the mean field radius enabled this form of the proof. Otherwise it is in general difficult to calculate the eigenvalues.

Remark 6.3 (Availability of equilibria)**.** *Alternatively we could prove the last theorem by determining maxima, minima and saddle points of the Lyapunov function $\mathcal{A}$.*

The initially given value of the availability $\mathcal{A}(0)$ allows to determine which equilibria are possible, i.e. these are equilibria with available free energy $\mathcal{A}_{eq} \leq \mathcal{A}(t) \leq \mathcal{A}(0)$.

We emphasise that we work here contrary to Section 6.2 in a notation without ε. For equilibria the equations (6.14) *and* (6.15) *simplify by using in particular* (6.20) *in our approximation as*

$$\begin{aligned}
\mathcal{A} = {} & \frac{M(X_0)}{M(X_S)} N_0^R \left[\frac{p_0 - \overline{p}}{(3 - \overline{Y}_V) n_G^R} + (\mu_{Ga_S}^{chem}(1 - X_S) + \mu_{As_S}^{chem} X_S)(u_{int}(r_{stat})) \right] \\
& + \frac{4\pi}{3} \eta^\infty r_{stat}^3 [(1 - \frac{\overline{\rho}_L}{\overline{\rho}_S})(p_0 - \overline{p}) \\
& + ((\mu_{Ga_S}^{chem}(u_{int}(r_{stat}))(1 - X_L(r_{stat})) + \mu_{As_S}^{chem}(u_{int}(r_{stat})) X_L(r_{stat})) \\
& - \frac{\overline{\rho}_L}{\overline{\rho}_S} (\mu_{Ga_S}^{chem}(1 - X_S) + \mu_{As_S}^{chem} X_S)(u_{int}(r_{stat})))(3 - \overline{Y}_V)) n_G^R] \\
& + 4\pi \eta^\infty r_{stat}^2 (1 - \frac{2}{3} \frac{\overline{\rho}_L}{\overline{\rho}_S}) \sigma^R.
\end{aligned}$$

Another representation of this formula is more suitabel to compare with the result in [DD08]. By starting from (6.16) *together with* (2.56) *and* (2.57) *and with the further approximation $\frac{\overline{\rho}_L}{\overline{\rho}_S} \approx 1$ we get*

$$\begin{aligned}
\mathcal{A} = {} & |\Omega_S|(R_{bd}, \{r_i\}_{i \in N})(\mu_{Ga_S} Y_{Ga} + \mu_{As_S} Y_{As})(\overline{u}) n_G^R (1 - 3a) \\
& + \frac{4\pi}{3} \sum_{i \in N} r_i^3 ((\mu_{Ga_L}(\overline{u})(1 - X_L^i) + \mu_{As_L}(\overline{u}) X_L^i) n_L^R (1 - 3(a_L^i - h_L^*(r_i))) \\
& + \frac{4\pi}{3} \sum_{i \in N} r_i^3 \nu \cdot \sigma_S^{<\cdot,\cdot>} \nu|_{I_i} + \frac{4\pi}{3} \sum_{i \in N} r_i^2 \sigma^R
\end{aligned}$$

where $\mathcal{A}$ corresponds to the formula stated in [DD08], eq. (8.13).

6.4. Convergence to equilibria

Unfortunately we do not have in general some monotonicity of the mean field in time, but we can state some positivity result for $\overline{u}$.

Lemma 6.4 (Maximum principle and monotonicity result for the mean field)**.** *Assume* $\mathcal{N} \geq 1$.

1) *If* $\overline{u} \leq \min_{\mathcal{J}_r}(u_{int})$ *then* $\dot{\overline{u}} > 0$. *In particular* $\overline{u}^0 > \min_{\mathcal{J}_r}(u_{int})$ *implies* $\overline{u} > \min_{\mathcal{J}_r}(u_{int})$ *for all times* $t \in (0, \mathcal{T})$.
2) *If* $\overline{u} \geq \max_{\mathcal{J}_r}(u_{int})$ *then* $\dot{\overline{u}} < 0$. *In particular* $\overline{u}^0 < \max_{\mathcal{J}_r}(u_{int})$ *implies* $\overline{u} < \max_{\mathcal{J}_r}(u_{int})$ *for all times* $t \in (0, \mathcal{T})$.

Proof. We start from (6.1) which we rewrite as

$$\dot{\overline{u}}(t) = \frac{s(t)}{\omega(t)},$$

where $\omega(t) = \overline{\mathcal{X}}(\overline{u}(t))|\Omega_S(t)|$, $s(t) :=\sum_{i\in N} \nu_i(t, \overline{u}(t))(\overline{u}(t) - u_{int}(r_i(t))$ with strictly positive weights ν_i. For regime (DC) we have $\nu_i = 4\pi r_i$ and for regime (IC) we have $\nu_i = 4\pi r_i^2 \frac{\overline{\mathbb{X}}(\overline{u},r_i)}{\overline{\mathbb{Z}}(\overline{u},r_i)}$. The denominator ω is strictly positive for fixed $\mathcal{T}$ due to estimate (5.18) for the 3rd moment of the radii distribution. We examine the sign of s.

If $\overline{u} \leq \min_{\mathcal{J}_r}(u_{int})$ all summands are nonpositive and hence $\dot{\overline{u}} > 0$ until $\overline{u} > \min_{i\in N(t)}(u_{int})$ by continuity of $\overline{u}$. Analogously, if $\overline{u} \geq \max_{\mathcal{J}_r}(u_{int})$ all summands are nonnegative and hence $\dot{\overline{u}} < 0$ until $\overline{u} > \max_{i\in N(t)}(u_{int})$. ☐

Hence we can assume w.l.o.g. $\overline{u} \in (\min_{\mathcal{J}_r}(u_{int}), \max_{\mathcal{J}_r}(u_{int}))$.

Lemma 6.5 (Intersection of characteristics)**.** *We interpret the mean field radius* $\overline{r}(t) = r_{\overline{r}^0}$ *as a characteristic for the ODE (6.7) emanating from* $\overline{r}(0) = \overline{r}^0$. *Consider* $r_i(t) = r_{r_i^0}(t)$ *as the characteristics of the ODEs (6.6) with starting point* r_i^0 *respectively.*

1) *Two characteristics of radii,* r_i *and* r_j, $i \neq j$ *do not cross unless* $r_i^0 = r_j^0$. *In the last case the characteristics coincide.*
2) *We consider the approximation* $u_{int}(r) = c_1 + c_2/r$. *If there is only one droplet left, w.l.o.g. droplet* 1 *and droplet* 2 *has vanished at time* τ_2 *and* $\overline{r}(\tau_2+) = r_1(\tau_2+)$, *then the characteristic of the mean field radius* $\overline{r}(t)$ *approaches the characteristic* $r_1(t)$ *in infinite time or* $r_1(t)$ *vanishes in finite time.*

Proof. Part 1) follows as for the infinite-dimensional case. We show 2). We work with (6.10) and (6.11) for (DC) and (6.12) and (6.13) for (IC) i.e. in our situation of only one remaining droplet the ODE system is for (DC)

$$\dot{r}_1 = c_2 \frac{r_1 - \overline{r}}{r_1^2 \overline{r} \overline{\mathbb{X}}_c}, \quad \dot{\overline{r}} = 4\pi \frac{\overline{r}(r_1 - \overline{r})}{\overline{\mathcal{X}}(\overline{r})|\Omega_S(r_1, \overline{r})|}$$

or for (IC)

$$\dot{r}_1 = c_2 \frac{r_1 - \overline{r}}{r_1 \overline{r} \overline{\mathbb{Z}}_c}, \quad \dot{\overline{r}} = 4\pi \frac{\overline{r} r_1 (r_1 - \overline{r}) \frac{\overline{\mathbb{X}}_c}{\overline{\mathbb{Z}}_c}}{\overline{\mathcal{X}}(\overline{r})|\Omega_S(r_1, \overline{r})|}.$$

This yields for (DC) and (IC) the **same** relation between radius r_1 and mean field radius

$$\dot{r}_1 = \frac{c_2}{4\pi} \frac{\overline{\mathcal{X}}(\overline{r})|\Omega_S(r_1, \overline{r})|}{r_1^2 \overline{r}^2 \overline{\mathbb{X}}_c} \dot{\overline{r}}.$$

We abbreviate $f_d := \frac{c_2}{4\pi} \frac{\overline{\mathcal{X}}(\overline{r})|\Omega_S(r_1,\overline{r})|}{r_1^2 \overline{r}^2 \overline{\mathbb{X}}_c}$. We consider $d_1 = r_1 - \overline{r}$ and get for both regimes

$$\dot{d}_1 = (f_d - 1)\dot{\overline{r}} = \frac{1}{f_d}(f_d - 1)\dot{r}_1. \tag{6.27}$$

Let $d_1 > 0$ then $\dot{\overline{r}} > 0$ and $\dot{r}_1 > 0$ by the Stefan condition (6.10) or (6.12). For sufficiently large $\overline{r}$ and r_1 we get that $f_d \to 0$ and hence $\dot{d}_1 < 0$ and finally $r_1 - \overline{r} \to 0$.

Otherwise let $d_1 < 0$ then $\dot{\overline{r}} < 0$ and $\dot{r}_1 < 0$. For sufficiently small $\overline{r}$ and r_1 we get $f_d > 1$ and d_1 gets smaller until $r_1 = \overline{r}$ unless r_1 has vanished before. ☐

W.l.o.g. we can assume $r_1^0 \geq ... \geq r_i^0 \geq ... \geq r_{\mathcal{N}^0}^0 \quad \forall i \in N$. Due to the last lemma 6.5 characteristics do not cross and the ranking of droplets is preserved with time i.e. $r_1 \geq ... \geq r_i \geq ... \geq r_{\mathcal{N}} \quad \forall i \in N \quad \forall t \in \mathcal{J}_t$ where droplets with the highest indices vanish next, which is practical for a numerical algorithm.

Remark 6.4 (Convergence to equilibria). *The last results suggest that we have the following qualitative behaviour of the droplet evolution. Droplets with $r_i^0 < \overline{r}^0$ vanish at first. If there are only droplets with $r_i^0 < \overline{r}^0$ all droplets vanish. If there exist droplets with $r_j^0 > \overline{r}^0$ then the mean field radius is changing faster than the radii (see Remark 6.6) and is expected to run to a radius close to a new "metastable" equilibrium*

$$\overline{r} = u_{int}^{-1} \left(\frac{\sum_i u_{int}(r_i) r_i}{\sum_i r_i} \right) \approx \sum_i r_i \quad \textit{by } (6.9) \tag{6.28}$$

for (DC) or

$$\overline{r} = u_{int}^{-1} \left(\frac{\sum_i u_{int}(r_i) r_i^2 \frac{\overline{\mathbb{X}}(u_{int}(\overline{r}), r_i)}{\overline{\mathbb{Z}}(\overline{u}, r_i)}}{\sum_i r_i^2 \frac{\overline{\mathbb{X}}(u_{int}(\overline{r}), r_i)}{\overline{\mathbb{Z}}(\overline{u}, r_i)}} \right) \approx \frac{\sum_i r_i}{\sum_i r_i^2}$$

for (IC), where the last approximations is corresponding to Remark 6.2.

The droplets which are crossed by the mean field from below shrink. This succession starts again after a droplet has vanished, until only one droplet is left, unless we get stuck in a metastable state e.g. run "occasionally" into a critical radius. Then the mean field goes into the stable equilibrium $\overline{r} = r_1$. Our numerical simulations, which are documented in the next section, exhibit the behaviour, which is described in this remark.

Remark 6.5 (Self-similarity of the mean field problem and stable radii). *If we assume $\overline{\mathbb{X}}$ and $\overline{\mathbb{Z}}$ to be constant in the mean field models, then the candidate for the re-scaling for self-similar behaviour would be $t \sim \varepsilon_*^2$ and $r_i \sim \varepsilon_*$ for regime (DC) or $t \sim \varepsilon_*$ and $r_i \sim \varepsilon_*$ for regime (IC).*

But due to the existence of stable radii we cannot expect to find self-similar solutions which hold for all times. However, we emphasise that the existence of a stable radius is only ensured for $\mathcal{N}^0 < \infty$.

6.5. Typical time-lags, within droplets vanish

For given diffusion coefficient D or bulk mobilities B^D and B^I we found for our original system in Section 3.5 as time scale of Problem D, for the regime (DC), $\tau_0 = 10^{-6}$ s or as time scale of Problem DI, for the regime (IC), $\tau_0^I = 10^{-12}$ s.

Remark 6.6 (Time scales of the mean field problems)**.** *For regime (DC) the typical time scales in the mean field model in the equations* (6.10) *are*

$$\mathbf{T}_i := \frac{\overline{\mathbb{X}}_c}{c_2} \frac{\overline{r} r_i^2}{|r_i - \overline{r}|} \frac{1}{\mathcal{R}^2} \tau_0 \quad \forall i \in N,$$

while for (6.11) *we find as typical time scale*

$$\mathbf{T}_m := \overline{Y} \frac{1}{c_2 |\sum_{i \in N} (r_i - \overline{r})|} \frac{R_{bd}^3}{\mathcal{R}^2} \tau_0.$$

For regime (IC) we have as approximation for the time scales of (6.12)

$$\mathbf{T}_i^I := \frac{\overline{\mathbb{Z}}_c}{c_2} \frac{\overline{r} r_i}{|r_i - \overline{r}|} \frac{1}{\mathcal{R}} \tau_0^I \quad \forall i \in N$$

or for the time scales of (6.13)

$$\mathbf{T}_m^I := \frac{1}{c_2 |\sum_{i \in N} r_i (r_i - \overline{r}) \frac{\overline{\mathbb{X}}_c}{\overline{\mathbb{Z}}_c}|} \frac{R_{bd}^3}{\mathcal{R}} \tau_0^I.$$

From (3.79) *we find approximately as time scale for the change of volume i.e. for the change of* R_{bd} *for regime (DC) or (IC)*

$$\mathbf{T}_{bd} \propto \varepsilon^{-9} \mathbf{T}_i \textit{ or } \mathbf{T}_{bd}^I \propto \varepsilon^{-9} \mathbf{T}_i^I,$$

that shows again, that in both regimes the change of the outer boundary takes place on a time scale which is of order ε^9 *slower. This allows for the rest of this section to approximate* $R_{bd} \approx R_{bd}(0) = 10^3$.

For regime (DC) we consider a droplet r_j which is going to vanish i.e. $r_j < \overline{r}$ and assume that the mean field radius is close to the initial mean value of radii, $\overline{r} \approx \mathcal{R}_M$ and that all of the other droplets are not about to vanish or vanish much slower, $\sum_{i \in N} r_i \approx \mathcal{R}_M$. Then the radius r_j changes within times of $\frac{\overline{\mathbb{X}}_c}{c_2} \frac{\mathcal{R}_M}{\mathcal{R}_M - r_j} \frac{r_j^2}{\mathcal{R}_M^2} \tau_0$, while the mean field varies within times of $\overline{Y} \frac{1}{c_2} \frac{\mathcal{N}}{\mathcal{R}_M - r_j} \frac{10^9}{\mathcal{R}_M^2} \tau_0$. We see that the mean field is by a factor $\frac{\overline{Y}}{\overline{\mathbb{X}}_c \mathcal{R}_M} \frac{\mathcal{N}}{r_j^2} \approx 10^5 \frac{\mathcal{N}}{\mathcal{R}_M r_j^2}$ slower.

This allows a rough estimate for τ_j i.e. for the time until first droplets vanish. We approximate $\dot{r}_j \approx -\frac{c_2}{\overline{\mathbb{X}}_c} \frac{\mathcal{R}_M - r_j}{\mathcal{R}_M r_j^2}$. We consider droplets with $\mathcal{R}_M = 1$. We solve the approximated ODE for the initial condition $r_j(0) = r_j^0 \approx 0.9 \mathcal{R}_M = 0.9$.

We cannot solve this ODE analytically, but a solution of this ODE has to fulfil

$$F(r_j(t)) - F(r_j(0)) = \frac{c_2}{\overline{\mathbb{X}}_c} t, \quad F(r) := \mathcal{R}_M (\frac{1}{2} r^2 + \mathcal{R}_M r + \mathcal{R}_M^2 \ln(\mathcal{R}_M - r))$$

which yields

$$\begin{aligned} \tau_j &= (F(r_{min} - F(r_j^0))) \frac{\overline{\mathbb{X}}_c}{c_2} \tau_0 = -\mathcal{R}_M (\frac{1}{2} ((r_j^0)^2 - r_{min})^2 + \mathcal{R}_M (r_j^0 - r_{min}) + \mathcal{R}_M^2 \ln(\frac{\mathcal{R}_M - r_j^0}{\mathcal{R}_M - r_{min}})) \\ &\approx 9.944 \cdot 10^{-1} \, [10^{-6} \, \mathrm{s}], \end{aligned} \tag{6.29}$$

if we assume $\frac{c_2}{\overline{\mathbb{X}}_c} \approx 1$. If $\mathcal{R}_M = 100$ then we have $\tau_j = 9.976 \cdot 10^5 \, [10^{-6} \, \mathrm{s}]$. We recall that these times are measured in units of $\tau_0 = 10^{-6}$ s.

Analogously for regime (IC) a vanishing droplet changes within times of $\frac{\overline{\mathbb{Z}}_c}{c_2}\frac{\mathcal{R}_M}{\mathcal{R}_M-r_j}\frac{r_j}{\mathcal{R}_M}\tau_0$, while the mean field changes on the time scale $\frac{1}{c_2}\frac{\mathcal{N}}{(\mathcal{R}_M-r_j)\frac{\overline{\mathbb{X}}_c}{\overline{\mathbb{Z}}_c}}\frac{10^9}{\mathcal{R}_M}\tau_0$ and we get for a solution of the ODE $\dot{r}_j \approx -\frac{c_2}{\overline{\mathbb{Z}}_c}\frac{\mathcal{R}_M-r_j}{\mathcal{R}_M r_j}$

$$G(r_j(t)) - G(r_j(0)) = \frac{c_2}{\overline{\mathbb{Z}}_c}t, \quad G(r) := \mathcal{R}_M(r + \mathcal{R}_M \ln(\mathcal{R}_M - r))$$

and thus

$$\tau_j = (G(r_{min}) - G(r_j^0))\frac{\overline{\mathbb{Z}}_c}{c_2} = -\mathcal{R}_M(r_j^0 - r_{min} + \mathcal{R}_M \ln(\frac{\mathcal{R}_M - r_j^0}{\mathcal{R}_M - r_{min}})) \qquad (6.30)$$

$$\approx 1.379\ [10^{-12}\ \mathrm{s}]$$

if we assume $\frac{c_2}{\overline{\mathbb{Z}}_c} \approx 1$. For $\mathcal{R}_M = 100$ we find $\tau_j = 1.402 \cdot 10^4\ [10^{-12}\ \mathrm{s}]$.

We see that, in the (IC) regime it takes longer until droplets vanish, if we had the same time scale i.e. $\tau_0 = \tau_0^I$, see also Fig. 6.6 for different $\mathcal{R}_M$ around 1. For larger $\mathcal{R}_M$ the regime (DC) yields a longer time-lag τ_j.

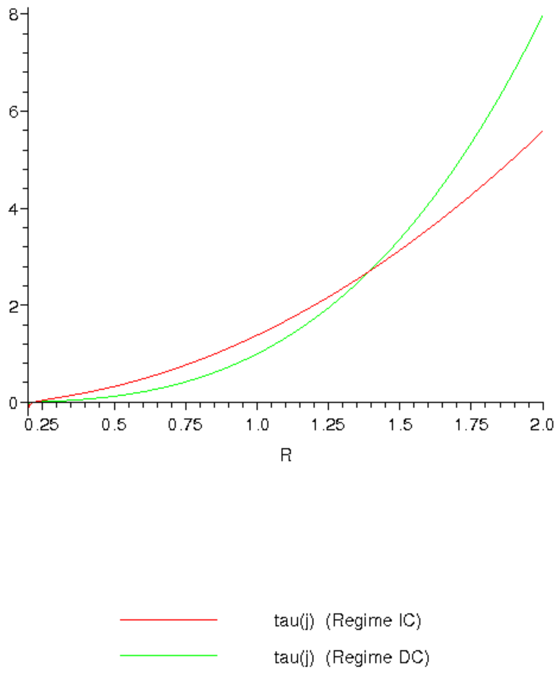

Figure 6.6.: Time-lag τ_j of a droplet with initial radius $r_j^0 = 0.9\mathcal{R}_{(M)}$ versus initial mean radius $\mathcal{R}_{(M)}$ for regime (DC) and (IC). For smaller $\mathcal{R}_{(M)}$ we have larger time-lags for (IC), for larger $\mathcal{R}_{(M)}$ for (DC).

But if we take the time scales as calculated in Section 3.5 than clearly the (IC) regime is important for smaller times around 10^{-12}s, while the (DC) regime is dominant for larger times 10^{-6} s.

In experiments larger times τ_j are observed. Steinegger [Ste01] considers exposure times of the wafer under heat treatment between 600s = 10min and 7200min = 5d and in this span of time droplets of radii size of about 10^{-7}m are observed to vanish. The reason to consider droplets, which are a factor 100 larger, is due to the fact that it is not clear if too small droplets can be detected at all in experiments.

If we considered regime (DC) for $D = 10^{-16}\mathrm{m}^2\mathrm{s}^{-1}$ then we would get $\tau_0 = 10^{-2}\mathrm{s}$ and according to (6.29) that $\tau_j = 9.976 \cdot 10^3\mathrm{s} \approx 2\mathrm{h}57\mathrm{min}$ for $r_j^0 = 100$.

For regime (IC) we conclude that for $r_j^0 = 100$ we get $\tau_j = 1.402 \cdot 10^4\mathrm{s} \approx 1\mathrm{d}14\mathrm{h}39\mathrm{min}$ if $\tau_0^I = 1\mathrm{s}$ or $B^I = 9.8 \cdot 10^{-24}\mathrm{mol\ nm}^{-2}\mathrm{s}^{-1}$.

We recall that the scale $\mathcal{R}_0$ is fixed by the critical radius and the minimal radius, which are about 1nm.

We consider the behaviour of vanishing droplets by numerical simulations of the mean field models in the next Section 6.6 for $D = 10^{-12}\mathrm{m}^2\mathrm{s}^{-1}$ as before, while for (IC) we consider $B^I = 10^{-23}\mathrm{mol\ nm}^{-2}\mathrm{s}^{-1}$ which is a factor 10^9 larger than the interface mobility computed from (3.93), since the latter value gives a time scale far away from times in experiments.

An ansatz of a quasi-stationary mean field radius i.e. assuming

$$\overline{r} = \sum_{i \in N} r_i,$$

approximates the situation $\mathbf{T}_i^I \ll \mathbf{T}_m^{(I)}$ well, but not the situation $\mathbf{T}_i^{(I)} \gg \mathbf{T}_m^{(I)}$. This shows that we cannot work with a quasi-stationary version of the mean field equation (6.2) neither in regime (DC) nor in regime (IC).

6.6. Numerical simulations of mean field models

We analyse the system of coupled ODE (6.6) – (6.8) for regimes (DC) and (IC) numerically in order to get more insight into the qualitative behaviour of our effective equations with time. Analogously we could simulate numerically the system of coupled ODE (6.6) with initial conditions (6.8), where the mean field radius is determined by (3.71) or alternatively the system (6.6) – (6.8) and (3.74).

The mean field model is an approximation for the full problem. We consider typical material data as given for $T = 1100$ K in Appendix D for our numerical simulations of the evolution of radii $r_i(t)$ and the critical mean field radius $\overline{r}(t)$ and keep track of the outer boundary $R_{bd}(t)$, too.

An aim of our simulations is to compare the regimes (DC) vs. (IC) and to decide by the typical values for times τ_j, when droplets vanish, whether the physical processes are in the regime (DC) or (IC).

Data which has large influence on the simulations are N_0^R, which yields with other parameters the initial value $\overline{r}^0$, further the mobilities B^D or B^I and the surface tension σ. Furthermore we see a large influence of the shape of the initial radii $r_i^0, i \in N(0)$ on the evolution.

The next simulations are due to an implementation in MATLAB. The following numerical simulations, see Fig. 6.7 – Fig. 6.9 examine the influence of the regimes on the times τ_j, where we have taken $N_0^R = 1.267 \cdot 10^{-10}\mathrm{mol}$, in order to be able to consider larger stable droplets, and initial radii between $350 \cdot 10^{-9}\mathrm{m}$ and $390 \cdot 10^{-9}\mathrm{m}$ for (IC) $\mathcal{N}^0 = 3$ and (DC) or between $350 \cdot 10^{-9}\mathrm{m}$ and $390 \cdot 10^{-9}\mathrm{m}$ for (IC) and $\mathcal{N}^0 = 20$, equidistantly distributed with a slight stochastic perturbation. Surface tension and other material data are chosen as given in Appendix D. For (DC) we have simulated with bulk mobility $B = 3.7 \cdot 10^{-8}\mathrm{mol\ m}^{-1}\mathrm{s}^{-1}$ (which corresponds to $D = 10^{-12}\mathrm{m}^2\mathrm{s}^{-1}$). For (IC) we have taken $B^I = 10^{-23}\mathrm{mol\ nm}^{-2}\mathrm{s}^{-1}$ instead of the value from (3.93).

Remark 6.7 (Criterion for (DC) or (IC)). *One notices a difference in the behaviour of the mean field radius between regime (DC) and regime (IC). For the first regime $\overline{r}$ shrinks, while a droplet is about to vanish and for the second regime $\overline{r}$ grows in this case, which is probably due to the different powers r_i in the mean field ODEs (3.78) and (3.85). This gives another criteria to decide, which of the two regimes corresponds to experiments.*

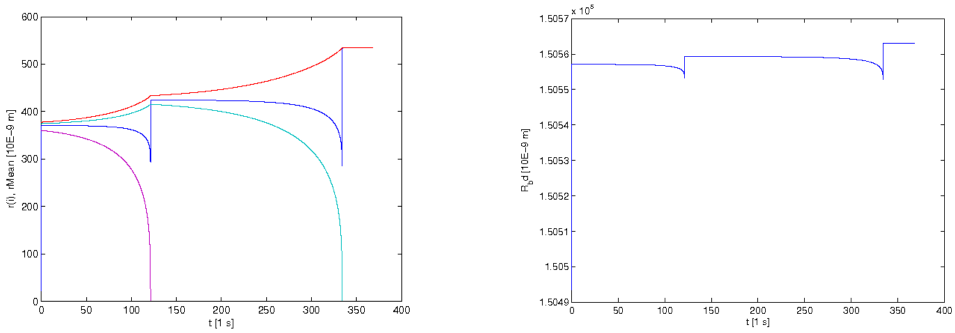

Figure 6.7.: Simulation for regime (DC) with $\mathcal{N}_0 = 3$ and $N_0^R = 1.27 \cdot 10^{-10}$mol.

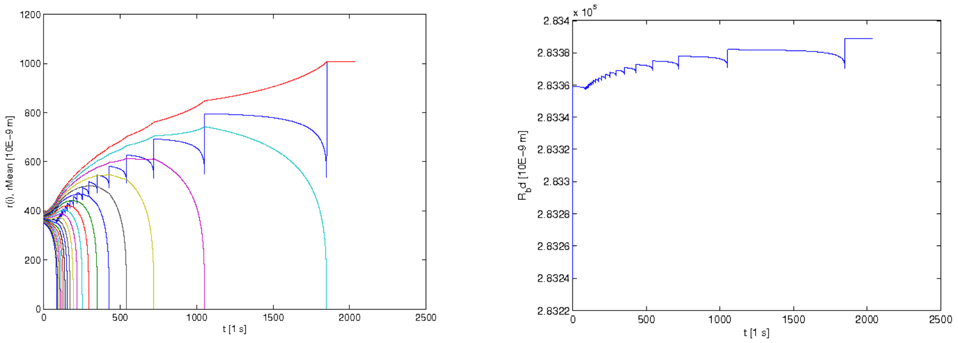

Figure 6.8.: Simulation for regime (DC) with $\mathcal{N}_0 = 20$, $N_0^R = 1.27 \cdot 10^{-10}$mol.

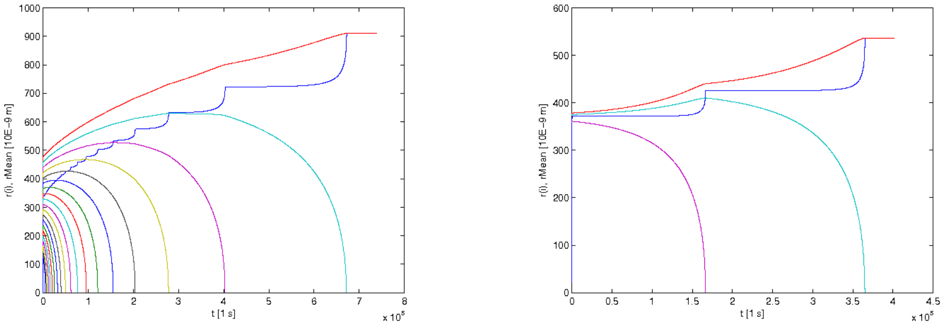

Figure 6.9.: Simul. f. reg. (IC) with $\mathcal{N}^0 = 3$ and $\mathcal{N}^0 = 20$, $N_0^R = 1.27 \cdot 10^{-10}$mol.

Since the database is insufficient, see Remark 3.4, we cannot exclude one of the regimes by the time-lags τ_j. But in principle, if a value for D or B^I is known within a smaller range, it might be possible to decide, in which regime the experiments take place.

For the influence of the initial distribution see Fig. 6.10. If the variance of the initial distribution ν^0 is small, the resulting times τ_i are larger.

If N_0^R is large enough or the initial radii are small (e.g. around $0.25 \cdot 10^{-10}$ m) all droplets can vanish, which is not possible with a quasi-stationary version of a mean field problem $\dot{\overline{u}} = 0$, see an example in Fig. 6.11, where we remind that $0.2 \cdot 10^{-9}$m is the minimal radius.

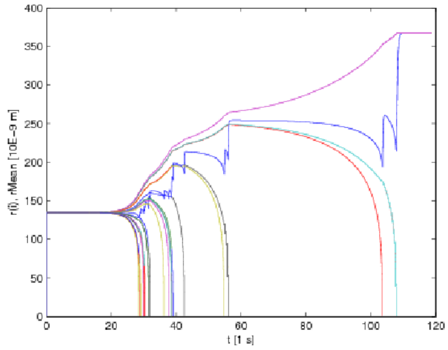

Figure 6.10.: Simulation for regime (DC) with $\mathcal{N}_0 = 20$ and $N_0^R = 1.27 \cdot 10^{-10}$mol, initial droplets concentrated around 135± 1 nm.

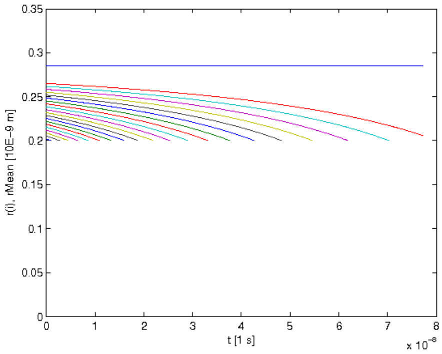

Figure 6.11.: Simulation for regime (DC) with $\mathcal{N}_0 = 20$ and $N_0^R = 1.27 \cdot 10^{-10}$mol. All droplets vanish. At 0.2 nm is the minimal radius r_{min}.

For the relation of time scaling and radii scaling in the mean field model for regime (IC) see Fig. 6.12.

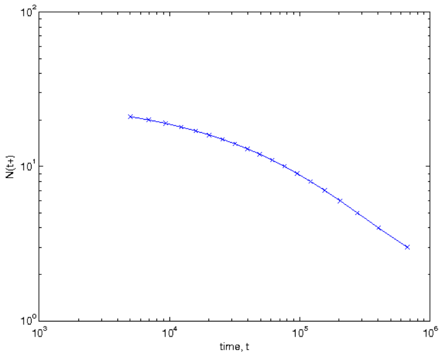

Figure 6.12.: Simulation for regime (IC) with $\mathcal{N}_0 = 20$ and $N_0^R = 1.27 \cdot 10^{-10}$mol, plot of τ_i against droplet number i on a log-log scale. All but one droplet vanish.

A simulation with MAPLE 11 with close up of the "swinging-in process" of a mean field within shorter times than vanishing of a droplets is shown in Fig. 6.13. The initial data consists of $\mathcal{N}^0 = 20$ equidistantly distributed droplet radii, which are bigger than the mean field radius of the system $\overline{r}^0 := u_{int}^{-1}(\overline{u}^0)$ at initial time. The mean field radius is critical in the sense, that radii which are smaller at time t shrink at time t, while bigger radii grow. Droplets r_i^0 which are smaller than $\overline{r}^0$ would vanish almost immediately.

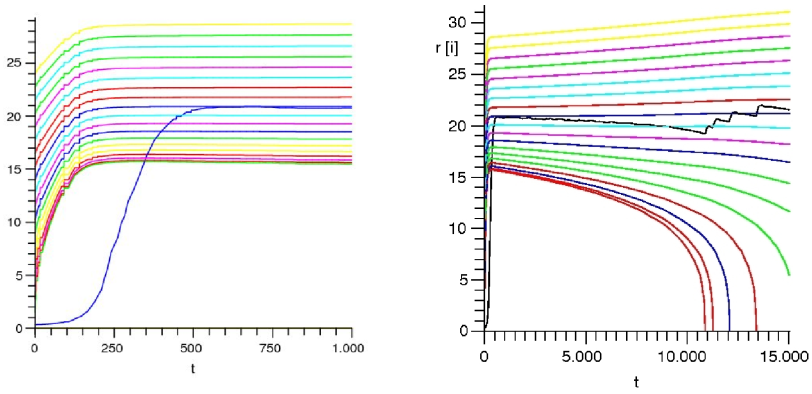

Figure 6.13.: Evolution of radii $r_i[10^{-9}\mathrm{m}]$ and mean field radius $\overline{r}[10^{-9}\mathrm{m}]$ (inverse mean field) by time t $[10^{-6}\,\mathrm{s}]$ for initial number of droplets $\mathcal{N}^0 = 20$, $N_0^R = 2.39 \cdot 10^{-14}\,\mathrm{mol}$ and $B = 22\,\mathrm{nm}^{-1}\mu\mathrm{s}^{-1}$. Left hand side: At the beginning the mean field goes into a meta stable state. Right hand side: At larger times droplets smaller than $\overline{r}$ vanish, while bigger droplets grow until a droplet disappears. If a droplet vanishes the mean field and equivalently $\dot{\overline{r}}$ has a jump.

Our numerics suggest that our dynamical system exhibits two different time scales, a short and a long time behaviour, see the discussion at the beginning of Section 6.5. Our simulations are in agreement with equilibria as determined in Lemma 6.3. Furthermore our simulations are consistent with the stability result Theorem 6.1, with Lemma 6.4, with Lemma 6.5 and with the Remark 6.4.

Remark 6.8 (Numerical implementation of the algorithm)**.** *Our algorithm implemented in MAPLE 11.0 (Release Feb 2007) runs relatively "slowly", although some improvised adaptivity was used. Our implementation in MATLAB 7.6.0 (R2008a) which uses odesolve45 as solver for the coupled ODE system is faster.*

The speed of the algorithms could be improved by amelioration of the algorithm e.g. by exploiting further adaptive controls of time steps or by implementation in a more suitable programming language e.g. C or FORTRAN.

We emphasise that the focus of this work is not the numerical treatment but the analysis of the problem of precipitation in solid crystals. Numerics are only used in order to check the relevance of our model, where we compare main features like qualitative behaviour with time, values for equilibria and the stability of equilibria.

Chapter 7.

Conclusion

In this thesis we have derived a free boundary problem from a thermodynamically consistent model for precipitation in crystalline gallium arsenide, which consists of PDEs and ODEs with a small scaling parameter ε — a nonlinear parabolic problem, an elliptic mechanical problem and ODEs for the free boundaries. This problem corresponds to the diffusion-controlled regime of interface motion. Furthermore there is another regime, the interface-controlled regime of interface motion, which consists of coupled ODEs. We have shown that for both regimes there are different interesting scaling regimes and we have examined the dilute and the critical scaling regime.

For sufficiently small ε we proved global existence and uniqueness of the coupled problem in the diffusion-controlled regime for the critical scaling. Under suitable assumptions on the dependence of the geometry on ε we homogenised the coupled problem and obtained for discrete initial data the mean field model, a system of coupled ODEs.

For the dilute scaling we derived for both regimes of interface motion a mean field model by formal homogenisation. The analysis of the mean field model, which we considered in the dilute scaling, allows further insight into the evolution of the liquid droplets. We have given necessary criteria for equilibria and discussed stability issues. An important result is that stable states of the mean field model are only possible for one or no droplet.

We remark, that the assumption of working on a spherical domain Ω is no restriction, since by using suitable mappings our results can be transformed to any other smooth and simply-connected domain.

At first we compare our result with known classical models, which are presented in Section 1.2, like the Mullins-Sekerka model, the Lifshitz-Slyozov-Wagner model and thermodynamically-consistent generalisations of these models. Then we interpret our results in the experimental context in Section 7.2.

7.1. Relation to classical results

7.1.1. Comparison with classical sharp-interface models

The availabilities of the sharp-interface limits (1.8) or (1.9) look similar to the available free energy (2.43) in our situation. We recall that the derivation of the equations (2.173) – (2.183) in this work relies on the available free energy (2.43), which is, expressed in our unknowns u, U, $\{r_i\}$ and R_{bd}, of the form

$$\mathcal{A}(u,U,\{r_i\},R_{bd}) = \int_{\Omega_S(\{r_i\},R_{bd})} \rho_S(U(x))\psi_S(u(x),U(x))\,dx \\ + \sum_{i\in N}\int_{\Omega_L^i(r_i)} \rho_L(U_L(x))\psi_L(U_L(x),r_i)\,dx + \sum_{i\in N}\int_{I_i(r_i)} \sigma\,dx + p_0|\Omega(R_{bd})|$$

with $\rho_S = \overline{\rho}_S(1-\mathrm{tr}(\nabla U))$ and $\rho_L = \overline{\rho}_L(1-\mathrm{tr}(\nabla U_L))$.

Our model for fixed ε can be considered as a generalisation of the Mullins-Sekerka model in the following sense. The (MS) model is the sharp-interface limit of the Cahn-Hilliard equation, while our model is a sharp-interface model, which is derived from a thermodynamically consistent free energy and additionally includes bulk stresses in case of pressure control. One can expect that our model can be derived from a phase-field model similar to the Cahn-Larché equation, see (1.9).

We recall, that the availability (2.43), which has been used in our model, is deduced from first principles [DD08]. In this study we put the model of Dreyer and Duderstadt in a mathematical form, including in particular the introduction of a suitable total chemical potential u in (2.91) so that we could prove existence and uniqueness of Problem E.

The main differences of our model to (MS) are, that in the classical model there exists no minimal droplet radius r_{min}, the outer boundary is fixed and the volume of droplets is conserved. Furthermore we deal with a more general boundary condition on the interfaces (2.177) instead of the Gibbs-Thomson law (1.5).

7.1.2. Comparison with classical Lifshitz-Slyozov-Wagner model

We compare our mean field model for (DC), which is the homogenised model (5.44) – (5.48) in the case of specific initial data (5.76), with (LSW). Unlike (LSW) our model is derived from a thermodynamically consistent sharp interface model and for the situation of constant external pressure and not for constant total volume. Our Stefan condition has an additional factor $\mathbb{X}$ in the denominator, which can be approximated by a constant only for relatively large radii, $r_i \gg r_{min}$. The incorporation of mechanical stresses in our model, while in classical LSW theory only surface tension is considered, has influence on $\mathbb{X}$ and hence on the dynamics and the stability of the system of differential equations. The fact that the outer boundary is a free boundary has no influence on the homogenised model, since $\dot{R}_{bd} \to 0$ as $\varepsilon \to 0$.

By neglecting mechanical bulk stresses, i.e. setting $U = (0,0,0)^T$ everywhere and setting $[[\rho]]_{I_i} = 1$, which corresponds to consider only one substance and not two substances as in our case, we find the (MS) model, where we extend u by u_L into the liquid. In the limit of vanishing scaling parameter and considering the quasi-stationary version of the ODE (6.2) for regime (DC) we find the formulas of the classical (LSW) theory.

We point out the differences and similarities of our scaling to the classical limit (MS) to (LSW) as considered for the dilute scaling in [Nie99] and [Nie00]. In these articles one scales $u_{int}(r_i) = r_i^{-1} \sim \frac{1}{\varepsilon^4}$ and $\sigma \equiv 1$ and later rescales u. This is due to the fact that in the classical Mullins-Sekerka model there exists no minimal radius r_{min}, but in our model the chemical potential on the interface u_{int} does not explode for $r \to r_{min}$. If we re-examine our results with neglecting the mechanics we find, as expected, agreement with her results [Nie99].

Later Niethammer and Otto derived the limit (MS) → (LSW) for the critical scaling elegantly by exploiting the gradient flow structure of the classical (MS) model [NO01]. However, for our situation it is not clear, whether the homogenisation can also be proved by means of a gradient flow.

7.2. Consequences for experiments

We emphasise that the applicability of our analysis to experimental situations relies on the assumption that the length of the wafer $\mathcal{L}_0$, typical particle distances $\mathcal{D}_0$ and typical radii $\mathcal{R}_0$ are related to each other as

$$\mathcal{L}_0 \approx \varepsilon_0^{-1}\mathcal{D}_0 \approx \varepsilon_0^{-3}\mathcal{R}_0 \text{ or } \mathcal{L}_0 \approx \varepsilon_0^{-1}\mathcal{D}_0 \approx \varepsilon_0^{-4}\mathcal{R}_0 \tag{7.1}$$

for some $\varepsilon_0 \ll 1$. We remark that our scaling of radii $r_i \sim \varepsilon^4$ is the dilute scaling i.e. we find $\Delta u^\infty = 0$ in the homogenisation limit and the boundary values of the radii enter in the next order equation for $\partial_t u^\infty$. The critical scaling is $r_i \sim \varepsilon^3$ and yields an inhomogeneous Laplace equation for u^∞ in the limit.

We recall, that we have considered the dilute regime in our numerical simulations, which seems to fit well to experiments. From the exact determination of the length scales one could decide, if one is in a critical or dilute or another scaling regime.

7.2.1. Regime (DC) or regime (IC)

We recall that it is unclear from experiments, if the evolution of our droplets takes place in a diffusion-controlled regime of interface motion (DC) or in an interface-controlled regime of interface motion (IC) or a combination of both, regime (DC & IC). Our theoretical considerations led to macroscopic equations, which we have simulated numerically.

Let us assume that (7.1) is fulfilled for our original experimental problem. A criterion to decide between (DC) and (IC) is given in Remark 6.7: We see that the evolution of the mean field $\overline{u}$ and the corresponding $\overline{r}$ with time has a qualitatively different behaviour as seen in Fig. 6.7 and Fig. 6.8 of simulations for a (DC) regime compared with Fig. 6.9 of a simulation in the (IC) regime. This might be possible to decide by measurements.

If we believe in the value for the diffusion constant given by Steinegger, see (3.91), the too small vanishing times τ_i of droplets suggest that the (DC) regime has to be excluded. This means that diffusion-controlled motion happens on a faster time-scale than experiments and only the (IC) regime remains as a possibility.

Another model for precipitation in crystalline solids is a model of Becker-Döring type, as derived in [DD06] and analysed mathematically in [HNN06]. But comparison of the time scales on which droplets vanish in a Becker-Döring model, suggests that diffusion models are more appropriate to describe the precipitation in GaAs observed in experiments.

7.2.2. How to enforce droplets to disappear?

The results of Chapter 6 suggest that for $\mathcal{T}$ large enough at most one droplet remains, depending on the initial data, but in practice the necessary $\mathcal{T}$ might be too large.

The model considered in this study suggests that the main “adjustment screw” for experiments might be the outer pressure p_0 and the temperature T, at which the heat treatment takes place. Almost all material parameters depend significantly on T. However, the influence of p_0 is marginal since it enters only at $\mathcal{O}(\tilde{h})$ in the resulting dynamical system (6.1) and (6.2) for regime (IC). So it remains the possibility to find a suitable T s.t. the time scale for the evolution of droplets $\mathbf{T}_i$ gets as short as possible or that, in light of equation (2.62), B^I becomes maximal.

The idea of limiting the precipitation to a homogeneous droplet distribution, in order to get a better GaAs waver, seems not be promising on a long-time scale, since only one or no droplet is stable.

However, if one knows, how to enforce droplets to disappear, then the mechanical properties of the produced galliumarsenide waver might be ameliorated.

7.3. Outlook

In this section we compile some open tasks and further ideas.

7.3.1. Generalisation on precipitation in other crystalline solids

One can hope to generalise the models in this paper to other semiconductors or semi-insulators, in particular compounds of the group III and V of the table of elements e.g. AlAs, InP and compounds of GaAs and AlAs.

We would like to consider the more general case of precipitation in an arbitrary crystalline solid and ask under which assumptions our mathematical model of coupled PDEs and ODEs, which was derived so far for GaAs, could describe this situation as well.

Therefore we recall the main assumptions, which hold for GaAs:

* We assume constant temperature, which seems to be always appropriate to the experimental situation of a relatively thin wafer.
* The cubic anisotropy of the crystal is negligible.
* In the Freiberg model Ga atoms appear only on one sublattice. In the crystal each sublattice has the same number of lattice sites, confer (2.4).
* For the mobilities of vacancies the inequalities $B_V \gg B$ and $B_V^i \gg B_{As}^i, B_{Ga}^i$ both hold. Thus vacancies are in quasi-stationary equilibrium.
* The chemical potentials $\{\mu_{As_a}\}_{a \in \mathbf{as}}, \mu_{Ga_\alpha}, \mu_{As_L}, \mu_{Ga_L}$ have some monotone behaviour w.r.t. their arguments, see Appendix A.3.
* The mean value X_0 is prescribed in order to guarantee semi-insulating behaviour.
* Displacement gradients are sufficiently small such that we can work with the theory of linear elasticity.

The other main assumptions of our model are:

* We assume a misfit situation with (2.109), $\overline{n}_L < \overline{n}_S$, and that an argument, which is similar to the Eshelby argument, like (2.112) holds.
* We restricted our analysis to the case of spherical droplets.

We recall that in Assumption 2.4 we restricted us to consider arsenic-rich liquid droplets. From the production of stoichiometric GaAs crystals out of a gallium-rich melt, it is suggested that it would be interesting to consider also gallium rich liquid inclusions in our framework, see Kießling et al. [KAI$^+$08].

However, the question, whether there is another semi-insulating crystal with two different substances for which these assumptions are fulfilled, remains open.

7.3.2. Different modelling of the surrounding gaseous phase

Our approach allows us to consider inhomogeneous distributions of droplets. For example in experiments more droplets are initially present at the upper part of the crystal, where it is in contact with a gas atmosphere, than in the rest of the crystal.

In this study we have assumed that on its outer boundary the GaAs crystal is only in contact with an inert gas. If we assume that there is a net exchange between the crystal and the surrounding gas, then it is necessary to drop the global conservation of mass and substance. Then the homogeneous Neumann boundary condition (2.178) on the outer boundary is replaced by

$$u = u_{out}(t) \quad \text{on } \partial\Omega(t)\, \forall t \in (0, \mathcal{T}),$$

where u_{out} is a given time-dependent function. This allows a control of the system by choice of a suitable u_{out}.

7.3.3. Further analysis

Since the homogenisation for the interface-controlled motion of free boundaries i.e. for regime (IC) is not proved rigorously, this remains an open task, but we expect, that the proof could be developed along the lines of the proof given in this thesis for (DC).

In this thesis we refer several times to results from regularity theory for elliptic and parabolic equations. Unfortunately there do not seem to be any existing regularity results, which fit well to this special case of coupled elliptic equations for the displacement (4.1) and a nonlinear parabolic equation for the chemical potential (4.4), where the time derivative of the displacement enters into the parabolic equation as a convective term. Application of stronger results would allow a generalisation of the obtained results and the avoidance of the Assumption 5.1.

In order to model the vanishing of a liquid droplet in the solid crystal we have introduced a minimal radius of the droplets, see Subsection 2.6.7. In experiments the external pressure, the surface tension and the minimal radius are usually of such a size that displacement gradients are small enough in order to work with linear elasticity. It might be interesting for the future and for still higher precision or for more general situations to also allow large displacement gradients. This requires the theory of nonlinear elasticity. Since similar results as in linear elasticity exist [Cia98], we expect that some of the results given in this thesis may be extended to the nonlinear case.

The concept of Kohn-Otto bounds [KO02] is that, if certain inequalities and differential inequalities for an energy and a generalised length scale hold, then exists a fastest possible decay rate of the energy with time. This is applied to the classical LSW model and an LSW model with degenerated mobility. An interesting question is, whether for our more complex available free energy $\mathcal{A}$ and for a suitable generalised length scale their result could be applied to our mean field model.

The homogenised model for smooth initial data is an infinite-dimensional dynamical system including mechanical stresses. Further analysis of the full dynamical system (5.44) – (5.48) for smooth initial data is consequently important to understand. The convergence to equilibria and the dependence of the long time behaviour on the initial data for the infinite-dimensional system is another open task. The hope is that this can be done by means of the thermodynamically consistent Lyapunov function $\mathcal{A}$ rewritten for the homogenised model. For the LSW model, rigorous results in this direction have been obtained by Niethammer and Pego [NP99], [NP01].

Appendix A.

Further details of the modelling

In this appendix we give auxiliary calculations for the modelling explicitly and we check that some assumptions of Chapter 2 are fulfilled for the reduced Freiberg model by plugging in material data.

A.1. Global conservation laws

Lemma A.1 (Global conservation laws and side conditions)**.** *The side conditions (2.29) – (2.31), (2.35) – (2.37) and the local conservation laws (2.17) – (2.20) imply the global conservation laws (2.38) – (2.40).*

Proof. Calculation of the conservation of total mass yields by applying the transport theorem

$$\begin{aligned}\frac{d}{dt}\int_{\Omega(t)}\rho &= \int_{\Omega(t)}\partial_t\rho + \int_{\partial\Omega(t)}\rho w - \int_{I(t)}[[\rho]]w\cdot\nu \\ &= \int_{\partial\Omega(t)}\rho(w-v)\cdot\nu - \int_{I(t)}([[\rho]]w - [[\rho v]])\cdot\nu \qquad \text{by (2.20)} \qquad (\text{A.1})\end{aligned}$$

Analogously checking of conservation of As gives

$$\begin{aligned}&\frac{d}{dt}\int_{\Omega(t)}n_{As} = \int_{\Omega(t)}\partial_t n_{As} + \int_{\partial\Omega(t)}n_{As}w - \int_{I(t)}[[n_{As}]]w\cdot\nu \\ &= \int_{\Omega(t)}-\nabla\cdot j + \int_{\partial\Omega(t)}n_{As}(w-v)\cdot\nu - \int_{I(t)}([[n_{As}]]w - [[n_{As}v]])\cdot\nu \qquad \text{by (2.17)} \\ &= \int_{\partial\Omega(t)}(-j + n_{As}(w-v))\cdot\nu - \int_{I(t)}(-[[j]] + [[n_{As}]]w - [[n_{As}v]])\cdot\nu \qquad \text{by Gauss' th.} \qquad (\text{A.2})\end{aligned}$$

We see that (A.1) and (A.2) are zero if we assume (2.37), (2.31), (2.35) and (2.29). □

Remark, for a radial symmetric single droplet problem and with Fick's law we find

$$\dot{R}_{bd} = v|_{\partial\Omega(t)}\cdot\nu, \quad \partial_\nu u|_{\partial\Omega} = 0. \qquad (\text{A.3})$$

A.2. Reduction of concentrations by chemical equilibrium

We prove Lemma 2.2, which we state here again:

Lemma A.2. *For $y \in \mathscr{J}_y := (0, \zeta)$, where $\zeta := \min\{(y \in (0, \frac{1}{\overline{Y}}) | (1 - C_1)C_2^2 - (C_1(1 + C_3 - 2C_2) + 3C_2)C_2\overline{Y}y - (C_1(1 - C_2)(C_3 - C_2) - 3C_2^2)(\overline{Y}y)^2 - C_2^2(\overline{Y}y)^3), \frac{1}{\overline{Y}}\}$ we can express uniquely $y_a, a \in \mathbf{a_S} \setminus \{As_\gamma\}$ as rational functions in y which are well defined i.e. $y_a \in (0, \frac{1}{\overline{Y}_a}), a \in \mathbf{a_S} \setminus \{As_\gamma\}$. For typical experimental data we have the estimate $\zeta \leq \frac{1}{3\overline{Y}}$.*

Proof. Written for relative lattice occupancies the equations (2.96) – (2.98) give together with (2.82)

$$y_{V_\alpha} y_{V_\beta} y_{V_\gamma} = 1, \quad \frac{y_{As_\beta}}{y_{V_\beta}} = \frac{y_{As_\alpha}}{y_{V_\alpha}}, \quad \frac{y_{As_\beta}}{y_{V_\beta}} = \frac{y}{y_{V_\gamma}}.$$

Since we do not know exactly $\overline{Y}_a$ for all $a \in \mathbf{a_S}$, we can also exploit (2.96) – (2.98) to get some estimates between this constants, which rely on our model. We point out that the modelling is built up on the reduced Freiberg model, where as mentioned above α is the gallium-rich sublattice, β is predominantly occupied by As, while γ is almost empty i.e. $Y_{V_\alpha}, Y_{As_\alpha} \ll Y_{Ga_\alpha}$, $Y_{V_\beta} \ll Y_{As_\beta}$, $Y \ll Y_{V_\gamma}$. Since we have

$$\begin{aligned}
C_1 &= \overline{Y}_{V_\alpha}\overline{Y}_{V_\beta}(1 - \overline{Y}),\\
C_2 &= \frac{\overline{YY}_{V_\beta}}{1 - (\overline{Y} + \overline{Y}_{V_\beta} - \overline{YY}_{V_\beta})} \approx \overline{YY}_{V_\beta}(1 + \overline{Y} + \overline{Y}_{V_\beta} - \overline{YY}_{V_\beta}) + \mathcal{O}(\overline{YY}_{V_\beta}(\overline{Y} + \overline{Y}_{V_\beta} - \overline{YY}_{V_\beta})^2),\\
C_3 &= \frac{\overline{Y}_{As_\alpha}\overline{Y}_{V_\beta}}{\overline{Y}_{V_\alpha}(1 - \overline{Y}_{V_\beta})} \approx \frac{\overline{Y}_{As_\alpha}\overline{Y}_{V_\beta}}{\overline{Y}_{V_\alpha}}(1 + \overline{Y}_{V_\beta}) + \mathcal{O}(\frac{\overline{Y}_{As_\alpha}\overline{Y}_{V_\beta}}{\overline{Y}_{V_\alpha}}\overline{Y}^2_{V_\beta}),
\end{aligned}$$

typical values for the constants $C_i, i \in \{1; 2; 3\}$ hence fulfil

$$0 < C_1 < 1, C_1 \ll C_3, \quad 0 < C_2 \ll 1 \tag{A.4}$$

and with the additional assumptions $Y_{V_\alpha} \ll Y_{As_\alpha}, Y_{V_\alpha} \ll Y$, which fits to experimental data, we finally get

$$0 < C_1 \ll C_2 \ll 1, \quad 0 < C_1 < C_2 \ll C_3. \tag{A.5}$$

We remark that for typical temperatures $\overline{Y} = \mathcal{O}(10^{-4})$, $C_1 = \mathcal{O}(10^{-30})$, $C_2 = \mathcal{O}(10^{-14})$ and $C_3 = \mathcal{O}(10^2)$ are upper bounds.

We introduce some abbreviations in order to avoid too long formulas:

$$\begin{aligned}
&E(y) := 1 - \overline{Y}y, \qquad A(y) := C_2 + (1 - C_2)\overline{Y}y, \qquad G(y) := C_2 + (C_3 - C_2)\overline{Y}y,\\
&\hat{G}(y) := C_2^2 E(y)^3 - C_1 A(y) G(y)\\
&\quad = (1 - C_1)C_2^2 - (C_1(1 + C_3 - 2C_2) + 3C_2)C_2\overline{Y}y\\
&\qquad - (C_1(1 - C_2)(C_3 - C_2) - 3C_2^2)(\overline{Y}y)^2 - C_2^2(\overline{Y}y)^3.
\end{aligned}$$

At first we reduce the absolute lattice occupancies to one independent variable, for experimental reasons we have chosen $Y = Y_{As_\gamma}$.

$$\begin{aligned}
(2.95.1) \quad &\Longleftrightarrow \quad & Y_{V_\gamma} &= 1 - \overline{Y}y = E(y),\\
(2.95.2) \quad &\overset{(2.97)}{\Longrightarrow} \quad & Y_{V_\beta} &= \frac{C_2(1 - \overline{Y}y)}{C_2 + (1 - C_2)\overline{Y}y} = \frac{C_2 E(y)}{A(y)},\\
&\overset{(2.96)}{\Longrightarrow} \quad & Y_{V_\alpha} &= \frac{C_1(C_2 + (1 - C_2)\overline{Y}y)}{C_2(1 - \overline{Y}y)^2} = \frac{C_1 A(y)}{C_2 E(y)^2},\\
&\overset{(2.95.2)}{\Longrightarrow} \quad & Y_{As_\beta} &= \frac{\overline{Y}y}{C_2 + (1 - C_2)\overline{Y}y} = \frac{\overline{Y}y}{A(y)},
\end{aligned}$$

$$\overset{(2.98)}{\Longrightarrow} \qquad Y_{As_\alpha} = \frac{C_1C_3\overline{Y}y(C_2+(1-C_2)\overline{Y}y)}{C_2^2(1-\overline{Y}y)^3} = \frac{C_1C_3\overline{Y}yA(y)}{C_2^2E(y)^3}$$

$$\overset{(2.95.3)}{\Longrightarrow} \qquad Y_{Ga_\alpha} = \frac{C_2^2E(y)^3 - C_1A(y)G(y)}{C_2^2E(y)^3} = \frac{\hat{G}(y)}{C_2^2E(y)^3}.$$

By inserting $y \equiv 1$ we get the formulas for the reference values $\overline{Y}_a$, $a \in \mathbf{a_S}$, and so we get the reduction of the relative lattice occupancies just by division.

$$\begin{aligned}
y_{V_\gamma} &= \frac{1-\overline{Y}y}{1-\overline{Y}} = \frac{E(y)}{E(1)},\\
y_{V_\beta} &= \frac{(1-\overline{Y}y)(C_2+(1-C_2)\overline{Y})}{(1-\overline{Y})(C_2+(1-C_2)\overline{Y}y)} = \frac{E(y)A(1)}{E(1)A(y)},\\
y_{V_\alpha} &= \frac{(C_2+(1-C_2)\overline{Y}y)(1-\overline{Y})^2}{(C_2+(1-C_2)\overline{Y})(1-\overline{Y}y)^2} = \frac{A(y)E(1)^2}{A(1)E(y)^2},\\
y_{As_\beta} &= \frac{y(C_2+(1-C_2)\overline{Y})}{(C_2+(1-C_2)\overline{Y}y)} = \frac{yA(1)}{A(y)},\\
y_{As_\alpha} &= \frac{y(C_2+(1-C_2)\overline{Y}y)(1-\overline{Y})^3}{(C_2+(1-C_2)\overline{Y})(1-\overline{Y}y)^3} = \frac{yA(y)E(1)^3}{A(1)E(y)^3}\\
y_{Ga_\alpha} &= \frac{(C_2^2E(y)^3 - C_1A(y)G(y))E(1)^3}{(C_2^2E(1)^3 - C_1A(1)G(1))E(y)^3} = \frac{\hat{G}(y)E(1)^3}{\hat{G}(1)E(y)^3}
\end{aligned}$$

We now discuss the three polynomials E, A and $\hat{G}$, considering at first $y \in D_0$. We denote partial derivatives of a function f with respect to y by $f'(y)$.

E is linear, strictly monotone decreasing with $E'(y) = -\overline{Y}$. The range is $(0,1)$ and particularly E has no zeros in D_0.

A is linear, strictly monotone (increasing) under the assumption from above that $C_2 < 1$ with $A'(y) = (1-C_2)\overline{Y}$. The range is $(C_2, 1)$ and A has no zeros too.

We consider now $\hat{G}$. Due to the estimates for the constants (A.4) and (A.5) we see immediately that the first coefficient is positive, the second and the forth one are negative. Furthermore by assuming e.g.

$$C_1C_3 > 6C_2^2, \tag{A.6}$$

that is justified since we have typically $\overline{Y}_{As_\alpha} \gg \overline{Y}^2$, we get that the third coefficient is negative. Unfortunately $\hat{G}$ has one or three zeros in $(0, 1/\overline{Y})$ as we can see by change of sign of the continuous function $\hat{G}$ for instance by evaluating $\hat{G}$ for $y \to 0$ or $y \to 1/\overline{Y}$:

$$\lim_{y\to 0}\hat{G}(y) = (1-C_1)C_2^2 > 0, \qquad \lim_{y\to 1/\overline{Y}}\hat{G}(y) = -C_1C_3 < 0.$$

A negative lattice occupancy y_{Ga_α} makes no sense in our model.

If we consider the first and second derivatives of $\hat{G}$,

$$\begin{aligned}
\hat{G}'(y) &= -(C_1(1+C_3-2C_2)+3C_2)C_2\overline{Y} - 2(C_1(1-C_2)(C_3-C_2)-3C_2^2)\overline{Y}^2y - 3C_2^2\overline{Y}^3y^2,\\
\hat{G}''(y) &= -2(C_1(1-C_2)(C_3-C_2)-3C_2^2)\overline{Y}^2 - 6C_2^2\overline{Y}^3y < 0 \quad \forall y, y > -1/\overline{Y}.
\end{aligned}$$

$\hat{G}$ is strictly monotone decreasing for all $Y \in (0,1)$ and since $\hat{G}$ is concave we see, that there exists one and only one zero in D_0. Hence chemical equilibrium can be realised only for small values of

y_{Ga_α} or y. From now on we work with $y \in \mathcal{J}_y := (0, \zeta)$ where $\zeta := (y \in (0,1) | \hat{G}(y) = 0)$.

We can make a rough estimate of ζ by using the fact that the tangent of a concave function always lies beyond the function itself. By using (A.5) we get

$$\zeta < \frac{(1-C_1)C_2}{C_1(1+C_3-2C_2)+3C_2} \frac{1}{\overline{Y}} \leq \frac{1}{3\overline{Y}}.$$

$\square$

Since Y_{As} and $3 - Y_V$ appear several times in this study, we give explicit formulas:

$$Y_{As} = \sum_{b \in L} Y_{As_b} = \frac{C_1 C_3 \overline{Y} y A(y)^2 + C_2^2 E(y)^3 \overline{Y} y (1 + A(y))}{C_2^2 A(y) E(y)^3}, \tag{A.7}$$

$$Y_V = \sum_{b \in L} Y_{V_b} = \frac{C_1 A(y)^2 + C_2 E(y)^3 (C_2 + A(y))}{C_2 A(y) E(y)^2}. \tag{A.8}$$

A.3. Monotonicity of chemical potentials and of the mole fraction of As in the solid

We show in this section in particular that u and X_S are strictly monotone in y. In this section we use the notation of Section A.2.

Lemma A.3 (Monotonicity of chemical potentials in the solid). *W.l.o.g. we assume* (2.88).

1) u^{chem}_{As} *as defined in* (2.90) *has range in* $(0, RT\ln(\frac{\zeta}{1-\overline{Y}\zeta}))$, *is continuous and strictly monotone in* y *on* $\mathcal{J}_y$.

2) u^{chem}_{Ga} *as defined in* (2.89) *has range in* $(-\infty, RT\ln(\frac{(1-C_1)C_2 E(1) A(1)}{\hat{G}(1)}))$, *is continuous and strictly monotone decreasing in* y *on* $\mathcal{J}_y$ *if* (A.4) *holds.*

3) u *as defined in* (2.91) *has range in* $\mathbb{R}$, *is continuous and strictly monotone in* y *on* $\mathcal{J}_y$ *if* $\tilde{\mu} > \frac{1}{3}$ *and* (A.4) *holds.*

Proof. 1) We have

$$\mu^{chem}_{As}(y) = RT\ln(\frac{y}{y_{V_\gamma}(y)}) = RT\ln(\frac{yE(1)}{E(y)})$$

and we see that $\mu^{chem}_{As}(0) = 0$ and $\mu^{chem}_{As}(\zeta) = RT\ln(\frac{\zeta}{1-\overline{Y}\zeta}) \leq RT\ln(\frac{1}{2\overline{Y}})$. We calculate

$$\frac{1}{RT}\mu'_{As}(y) = \frac{1}{y} + \frac{\overline{Y}}{E(y)} = \frac{1}{yE(y)} > 0,$$

where $y < \zeta \leq \frac{1}{3\overline{Y}} \leq \frac{\tilde{\mu}}{\overline{Y}} < \frac{1}{\overline{Y}}$.

2) There holds

$$\frac{1}{RT}\mu^{chem}_{Ga}(y) = \frac{y_{Ga_\alpha}}{y_{V_\alpha}(y)} = \ln(\frac{\hat{G}(y)E(1)A(1)}{\hat{G}(1)E(y)A(y)})$$

and $\lim_{y\to 0} \mu^{chem}_{Ga}(y) = RT\ln(\frac{(1-C_1)C_2 E(1) A(1)}{\hat{G}(1)}) > 0$ and $\lim_{y \to \zeta} \mu^{chem}_{Ga}(y) = -\infty$. With (A.4) we have $\hat{G}(y) > 0$ and $\hat{G}'(y) < 0$ according to the proof of Lemma A.2 and find

$$\frac{1}{RT}\mu'_{Ga}(y) \overset{\hat{G}, -\hat{G}'>0}{<} \frac{\overline{Y}}{E(y)} - \frac{A'(y)}{A(y)} = -\overline{Y}\frac{1 - 2C_2 - 2(1-C_2)\overline{Y}y}{(1-\overline{Y}y)(C_2 + (1-C_2)\overline{Y}y)} < 0$$

for $y \in \mathcal{J}_y$.

3) We have $u(y) = RT\ln(S(y))$ according to (2.93) with S as defined in (2.92). From 1) & 2) follows $\lim_{y\to 0} u(y) = 0$ and $\lim_{y\to\zeta} u(y) = +\infty$. 1) & 2) yields directly for the sign of derivative

$$\mathcal{A}(y) := (\ln(S(y)))' = \frac{1}{y} + (1 - \frac{1}{\tilde{\mu}})\frac{\overline{Y}}{E(y)} + \frac{1}{\tilde{\mu}}(\frac{(1-C_2)\overline{Y}}{A(y)} - \frac{\hat{G}'(y)}{\hat{G}(y)}) > 0. \tag{A.9}$$

□

Lemma A.4 (Monotonicity of chemical potentials in the liquid)**.** *We assume* $L_1 > 0$ *and* $L_0+3L_1 < 0$*, which holds for typical values for* L_0 *and* L_1*, see Appendix D. Then with* (2.88)

1) $u^{chem}_{As_L}$ *as defined in* (2.85) *has range in* $(0, RT\ln(\frac{1}{\overline{X}_L}) - (L_0 + L_1(1-4\overline{X}_L))(1-\overline{X}_L)^2)$*, is continuous and strictly monotone in* X_L *on* $\mathcal{J}_{X_L} = (\overline{X}_L(1-\tilde{h}), 1)$*.*

2) $u^{chem}_{Ga_L}$ *as defined in* (2.84) *has range in* $(-\infty, 0)$*, is continuous and strictly monotone decreasing in* X_L *on* $\mathcal{J}_{X_L}$*.*

3) u_L *as defined in* (2.94) *has range in* $(RT\ln(\frac{1}{\overline{X}_L}) - (L_0+L_1(1-4\overline{X}_L))(1-\overline{X}_L)^2, \infty)$*, is continuous and strictly monotone in* X_L *on* $\mathcal{J}_{X_L}$*.*

Proof. The statements about continuity and range are seen directly.

Under our assumptions on L_0 and L_1 we get by calculation that

$$\mu^{chem\,\prime}_{Ga_L}(X_L) = -\frac{RT}{1-X_L} + 2(L_0+3L_1)X_L - 12L_1X_L^2 < 0, \tag{A.10}$$

$$\mu^{chem\,\prime}_{As_L}(X_L) = \frac{RT}{X_L} - 2(L_0+3L_1)(1-X_L) + 3L_1X_L(5-4X_L) > 0. \tag{A.11}$$

Hence u_L is strictly increasing and we check that it has range as given. □

Lemma A.5. X_S *as defined in* (2.7) *in the solid has range in* $(X_0, 1)$*, is continuous and strictly monotone in* y *on* $\mathcal{J}_y$*.*

Proof. At first we have a closer look at $X_S(y)$:

$$\begin{aligned} X_S(y) &= \frac{C_1C_3\overline{Y}yA(y)^2 + C_2^2E(y)^3\overline{Y}y(1+A(y))}{C_1C_3\overline{Y}yA(y)^2 + C_2^2E(y)^3\overline{Y}y(1+A(y)) + \hat{G}(y)A(y)} \\ &= \frac{\overline{Y}y}{C_2E(y)}\frac{C_1C_3A(y)^2 + C_2^2E(y)^3(1+A(y))}{C_2E(y)^2\overline{Y}y(1+A(y)) + C_2E(y)^2A(y) - C_1A(y)^2} \end{aligned} \tag{A.12}$$

To verify the monotonicity of X_S we declare some abbreviations

$$\tau(y) := \frac{Y_{As}}{Y_{Ga_\alpha}}, \quad Y_{As} = Y_{As_\alpha} + Y_{As_\beta} + Y_{As_\gamma},$$

$$\mathcal{U}(y) := \frac{Y_{As}Y_{Ga_\alpha}}{(Y_{As}+Y_{Ga_\alpha})^2}, \quad \text{in particular } \mathcal{U}(y) > 0.$$

We get $X'_S(y) = \frac{Y'_{As}Y_{Ga_\alpha} - Y_{As}Y'_{Ga_\alpha}}{(Y_{As}+Y_{Ga_\alpha})^2} \frac{Y_{As}Y_{Ga_\alpha}}{(Y_{As}+Y_{Ga_\alpha})^2}(\frac{Y'_{As}}{Y_{As}} - \frac{Y'_{Ga_\alpha}}{Y'_{Ga_\alpha}}) = \mathcal{U}(y)(\ln(\tau(y)))'$. So the sign of $X'_S(y)$ depends on $\ln(\tau(y))'$. We reduce first the fraction

$$\tau(y) = \overline{Y}y\frac{C_1C_3A(y)^2 + C_2^2E(y)^3(1+A(y))}{\hat{G}(y)A(y)}$$

and use then standard calculus for logarithms

$$
\begin{aligned}
(\ln\tau(y))' &= (\ln\overline{Y}y)' - (\ln A(y))' + (\ln H(y))' - (\ln\hat{G}(y))' && \text{(A.13)}\\
&= \frac{1}{y} - \frac{(1-C_2)\overline{Y}}{C_2+(1-C_2)\overline{Y}y} + (\ln H(y))' - (\ln\hat{G}(y))' && \text{(A.14)}\\
&= \frac{C_2}{y(C_2+(1-C_2)\overline{Y}y)} + \frac{H'(y)\hat{G}(y)-H(y)\hat{G}'(y)}{H(y)\hat{G}(y)}, && \text{(A.15)}
\end{aligned}
$$

where we defined

$$
\begin{aligned}
H(y) &:= C_1C_3A(y)^2 + C_2^2E(y)^3(1+A(y))\\
&= C_2^2(1+C_1C_3+C_2) - 2C_2(C_2(1+C_1C_3+2C_2)-C_1C_3)\overline{Y}y\\
&\quad + (C_1C_3(1-C_2)^2+6C_2^3(T))\overline{Y}^2y^2 + 2C_2^2(1-2C_2)\overline{Y}^3y^3 - C_2^2(1-C_2)\overline{Y}^4y^4\\
&\gtrapprox 0 \quad \forall y \le \frac{C_2(1+C_1C_3+C_2)}{2(C_2(1+C_1C_3+2C_2)-C_1C_3)\overline{Y}} \in (\frac{1}{3\overline{Y}},\frac{1}{4\overline{Y}}),
\end{aligned}
$$

and so the latter “$\le$“ is fulfilled if $y\in\mathcal{J}_y$. We consider

$$
\begin{aligned}
H'(y) &= -2C_2(C_2(1+C_1C_3+2C_2)-C_1C_3)\overline{Y} + 2(C_1C_3(1-C_2)^2+6C_2^3)\overline{Y}^2y\\
&\quad + 6C_2^2(1-2C_2)\overline{Y}^3y^2 - 4C_2^2(1-C_2)\overline{Y}^4y^3.
\end{aligned}
$$

We note that the coefficients of H and hence also of H' are of same order, that justifies to consider only the first terms of the development.

Let h_k the coefficient in the polynomial H in a expansion w.r.t. $y^k, k\in\mathbb{N}_0$. It is *a priori* not clear, what is the sign of $2h_1 := -2C_2(C_2(1+C_1C_3+2C_2)-C_1C_3)$, which appears as first coefficient in H', i.e. the sign of H' for small y. If the coefficient h_1 is nonnegative we are already finished with (A.14) since $\hat{G}>0$ and $\hat{G}'<0$ for $y\in\mathcal{J}_y$. We now examine, what happens if $h_1<0$ (that holds for numerical data). Then

$$
H'(y) \lessapprox 0 \quad \forall y \le \frac{C_2}{\overline{Y}}\frac{C_2(1+C_1C_3+2C_2)-C_1C_3}{C_1C_3(1-C_2)^2+6C_2^3}
$$

and compute now

$$
\begin{aligned}
&H'(y)\hat{G}(y) - H(y)\hat{G}'(y)\\
&= C_2^3(C_1+C_2(1-(1-2C_1)C_2)+C_1C_2+C_1C_3(3-C_1)+2C_1C_2C_3+C_1^2C_3^2)\overline{Y}\\
&\quad + 2C_2^2(-C_1^2C_3+C_1^2C_3^2-2C_1C_2C_3+C_1^2C_2C_3-C_1^2C_2C_3^2-3C_1C_2^2C_3+3C_2^3-C_1C_2+\\
&\qquad + 2C_1C_3-5C_1C_2^3-3C_2^2)\overline{Y}^2y\\
&\quad - C_2(-2C_1^2C_2C_3+2C_1C_2^2C_3-2C_1C_2^2-C_1^2C_2^2C_3^2-20C_1C_2^4+2C_1^2C_2C_3^2+10C_1C_2^3+\\
&\qquad + C_1^2C_3+C_1^2C_2^2C_3-4C_1C_2^3C_3-C_1^2C_3^2-15C_2^3+5C_1C_2C_3+15C_2^4)\overline{Y}^3y^2\\
&\quad - 4C_2^3(C_1+5C_1C_2^2+5C_2-5C_1C_2-5C_2^2-C_1C_2C_3)\overline{Y}^4y^3\\
&\quad + C_2^2(1-C_2)(-10C_1C_2^2+15C_2^2+6C_1C_2C_3+5C_1C_2-C_1C_3)\overline{Y}^5y^4\\
&\quad + 2C_2^2(1-C_2)(C_1C_2^2-3C_2^2-C_1C_2-C_1C_2C_3+C_1C_3)\overline{Y}^6y^5\\
&\quad + C_2^4(1-C_2)\overline{Y}^7y^6.
\end{aligned}
$$

It follows in linear approximation $H'(y) > 0$ since the coefficients in order 1 and y are positive. The positivity of the second coefficient follows (by using the additional assumption (A.6)) from:

$$C_1(C_3 - C_2) + C_1(C_3(\frac{1}{2} - 3C_2^2 + C_1(-1 + C_3(1 - C_2)) + C_2) - 5C_2^3) + \frac{1}{2}(C_1C_3 - 6C_2^2) + 3C_2^3 > 0.$$

Hence $H'(y)\hat{G}(y) - H(y)\hat{G}'(y) > 0$ on $\mathcal{J}_y$ and we get $X_S'(y) > 0$ from (A.15). $\square$

Since X_S is continuous this allows us in principle to express $y \in \mathcal{J}_y$ uniquely as a function of X_S.

A.4. An approximation of terms of the diffusion problem for small lattice occupancies

In this appendix we calculate explicit approximation formulas in case of the reduced Freiberg model by using in particular $\overline{Y} \ll 1$. These approximations are important for quantities of the homogenised model since in the limit $\overline{Y} \to 0$. We assume in the following that $y \ll const\varepsilon^0 \ll \zeta$. The approximations are needed for approximations used in Subsection C.1.2 and for the formal homogenisation but not anywhere else in this study.

We make a development of the nonlinearities $\mathcal{X}$ and $\mathcal{A}$ of the diffusion problem in y and consider only the dominant terms of $\mathcal{X}$ and $\mathcal{A}$.

At first we make a development of $\mathcal{A}(y) = \ln'(S(y))$ in $Y = y\overline{Y}$. We start with (A.9)

$$\mathcal{A}(y) = \frac{1}{y} + \frac{\overline{Y}}{E(y)} + \frac{1}{\tilde{\mu}}(\frac{(1 - C_2)\overline{Y}}{A(y)} - \frac{\overline{Y}}{E(y)} + \frac{\hat{G}'(y)}{\hat{G}(y)}).$$

We use $C_2 \ll \overline{Y}y \ll 1$ and $C_2 \ll \overline{Y}^3$ and get the following Taylor series

$$\begin{aligned}
\frac{1}{E(y)} &= \frac{1}{1 - \overline{Y}y} = 1 + \overline{Y}y + \mathcal{O}((\overline{Y}y)^2),\\
\frac{1 - C_2}{A(y)} &= \frac{1}{\overline{Y}y(1 + \frac{C_2}{(1-C_2)\overline{Y}y})} = \frac{1}{\overline{Y}y} - \frac{C_2}{(1 - C_2)(\overline{Y}y)^2} + \mathcal{O}(\frac{C_2^2}{(1 - C_2)(\overline{Y}y)^2})\\
&\approx \frac{1}{\overline{Y}y} + \mathcal{O}(\frac{C_2}{(\overline{Y}y)^2})
\end{aligned}$$

and

$$\begin{aligned}
&\frac{\hat{G}'(y)}{\hat{G}(y)}\\
&= \frac{-3C_2^2\overline{Y}E(y)^2 - C_1(1 - C_2)\overline{Y}G(y) - C_1(C_3 - C_2)\overline{Y}A(y)}{C_2^2E(y)^3 - C_1A(y)G(y)}\\
&= -\frac{(3C_2^2 + C_1C_2(1 + C_3 - 2C_2))\overline{Y} + (-3C_2^2 + 2C_1(1 - C_2)(C_3 - C_2))\overline{Y}^2y + \mathcal{O}((\overline{Y}y)^2)}{(1 - C_1)C_2^2 - (C_1(1 + C_3 - 2C_2) + 3C_2)C_2\overline{Y}y + \mathcal{O}((\overline{Y}y)^2)}\\
&\overset{(*)}{=} -((3C_2^2 + C_1C_2(1 + C_3 - 2C_2))\overline{Y} + 2(C_1(1 - C_2)(C_3 - C_2) - 3C_2^2)\overline{Y}^2y)\times\\
&\quad \times \frac{1}{(1 - C_1)C_2^2}(1 + \frac{C_1(1 + C_3 - 2C_2) + 3C_2}{(1 - C_1)C_2}\overline{Y}y) + \mathcal{O}((\overline{Y}y)^2)
\end{aligned}$$

where we used that $\frac{C_1(1+C_3-2C_2)+3C_2}{(1-C_1)C_2} \approx 3$ in order to justify the approximation (*). This yields

$$\begin{aligned}
&\frac{\hat{G}'(y)}{\hat{G}(y)} \\
&= -\frac{3C_2 + C_1(1+C_3-2C_2)}{(1-C_1)C_2}\overline{Y} \\
&- (\frac{(3C_2 + C_1(1+C_3-2C_2))^2 + 2(1-C_1)(C_1(1-C_2)(C_3-C_2) - 3C_2^2)}{(1-C_1)^2C_2^2})\overline{Y}^2 y \\
&+ \mathcal{O}((\overline{Y}y)^2) \\
&= -\frac{3C_2 + C_1(1+C_3-2C_2)}{(1-C_1)C_2}\overline{Y} \\
&- (\frac{3C_2^2 + 4C_1C_2 + f^2C_1^2 + 4C_1C_2^2 - 2C_1^2C_2 + 2C_1^2C_2^2 + (2C_1 + 4C_1C_2)C_3 + C_1^2C_3^2}{(1-C_1)^2C_2^2})\overline{Y}^2 y \\
&+ \mathcal{O}((\overline{Y}y)^2).
\end{aligned}$$

We put this together

$$\begin{aligned}
\mathcal{A}(y) &= \frac{1}{y} - (\frac{1}{\tilde{\mu}} - 1)\frac{\overline{Y}}{E(y)} + \frac{1}{\tilde{\mu}}(\frac{(1-C_2)\overline{Y}}{A(y)} + \frac{\hat{G}'(y)}{\hat{G}(y)}) \\
&= (\frac{1}{\overline{Y}y} - (\frac{1}{\tilde{\mu}} - 1) + \frac{1}{\tilde{\mu}}\frac{1}{\overline{Y}y} - \frac{1}{\tilde{\mu}}\frac{3C_2 + C_1(1+C_3-2C_2)}{(1-C_1)C_2} + \mathcal{O}(\overline{Y}y))\overline{Y} \\
&= (1 + \frac{1}{\tilde{\mu}})\frac{1}{y} - (\frac{1}{\tilde{\mu}}\frac{4C_2 + C_1(1+C_3-3C_2)}{(1-C_1)C_2} - 1)\overline{Y} + \mathcal{O}(\overline{Y}^2 y) \\
&= (1 + \frac{1}{\tilde{\mu}})\frac{1}{y} - (\frac{4}{\tilde{\mu}} - 1)\overline{Y} + \mathcal{O}(\overline{Y}^2 y). \qquad \text{(A.16)}
\end{aligned}$$

The dominant term turns out to be $(1+\frac{1}{\tilde{\mu}})\frac{1}{y}$.

We use (A.16) in order to give an approximation for the total chemical potential u, too:

$$\begin{aligned}
u(y) = \ln(S(y)) = \int_1^y \mathcal{A}(\tilde{y})d\tilde{y} &= \frac{1+\tilde{\mu}}{\tilde{\mu}}\ln(y) - (\frac{4}{\tilde{\mu}} - 1)\overline{Y}(y-1) + \mathcal{O}(\overline{Y}^2 y) \\
\iff \quad S(y) &= y^{\frac{1+\tilde{\mu}}{\tilde{\mu}}}\exp(-(\frac{4}{\tilde{\mu}} - 1)\overline{Y}(y-1) + \mathcal{O}(\overline{Y}^2 y)) \\
&= y^{\frac{1+\tilde{\mu}}{\tilde{\mu}}}(1 - (\frac{4}{\tilde{\mu}} - 1)\overline{Y}(y-1) + \mathcal{O}(\overline{Y}^2 y)) = y^{\frac{1+\tilde{\mu}}{\tilde{\mu}}} + \mathcal{O}(\overline{Y}y).
\end{aligned}$$

This implies in $\mathcal{O}(\overline{Y}y)$ if $y \in \mathcal{D}_y$

$$u(y) = \frac{1+\tilde{\mu}}{\tilde{\mu}}\ln(y) \qquad \text{(A.17)}$$

and

$$y(u) = \exp(\frac{\tilde{\mu}}{1+\tilde{\mu}}u),$$

which yields

$$y'(u) = \frac{\tilde{\mu}}{1+\tilde{\mu}}\exp(\frac{\tilde{\mu}}{1+\tilde{\mu}}u) = \frac{\tilde{\mu}}{1+\tilde{\mu}}y(u).$$

We proceed as above, now with $\mathcal{X}(y) := \rho_S(y)P'(X_S(y))X_S'(y)$. We have the Taylor series

$$
\begin{aligned}
&X_S(y)\\
&= \frac{\overline{Y}yH(y)}{\overline{Y}yH(y) + \hat{G}(y)A(y)}\\
&= \overline{Y}y(C_2^2(1 + C_1C_3 + C_2) - 2C_2(C_2(1 + C_1C_3 + 2C_2) - C_1C_3)\overline{Y}y + (C_1C_3(1 - C_2)^2 + 6C_2^3)\\
&\times (\overline{Y}y)^2)/(C_2^3(1 - C_1) + C_2^2(2 - 3C_2)(1 - C_1)\overline{Y}y - C_2(C_2(5 - 2C_2) + C_1(1 - 4C_2 - 3C_2^2))(\overline{Y}y)^2 +\\
&+ C_2(C_2(3 + 2C_2) + C_1(1 - 2C_2 + C_2^2))(\overline{Y}y)^3)\\
&+ \mathcal{O}((\overline{Y}y)^3)\\
&\overset{C_2 \ll (\overline{Y}y)^2}{=} \frac{1}{C_2}(C_2^2(1 + C_1C_3 + C_2) - 2C_2(C_2(1 + C_1C_3 + 2C_2) - C_1C_3)\overline{Y}y +\\
&+ (C_1C_3(1 - C_2)^2 + 6C_2^3)(\overline{Y}y)^2)/\\
&/(C_2(2 - 3C_2)(1 - C_1) - (C_2(5 - 2C_2) + C_1(1 - 4C_2 - 3C_2^2))\overline{Y}y +\\
&+ (C_2(3 + 2C_2) + C_1(1 - 2C_2 + C_2^2))(\overline{Y}y)^2)\\
&+ \mathcal{O}(\frac{C_2}{\overline{Y}y})\\
&= \frac{1}{(2 - 3C_2)(1 - C_1)} \times\\
&\frac{1 + C_1C_3 + C_2 - 2(1 + C_1C_3 + 2C_2 - \frac{C_1}{C_2}C_3)\overline{Y}y + (\frac{C_1C_3}{C_2^2}(1 - C_2)^2 + 6C_2)\overline{Y}y^2}{1 - \frac{(C_2(5-2C_2)+C_1(1-4C_2-3C_2^2))}{C_2(2-3C_2)(1-C_1)}\overline{Y}y + \frac{(C_2(3+2C_2)+C_1(1-C_2)^2)}{C_2(2-3C_2)(1-C_1)}(\overline{Y}y)^2}\\
&+ \mathcal{O}(\frac{C_2}{\overline{Y}y})\\
&= \frac{1}{2}\frac{1 - 2\overline{Y}y + \frac{C_1C_3}{C_2^2}(\overline{Y}y)^2}{1 - \frac{(C_2(5-2C_2)+C_1(1-4C_2-3C_2^2))}{C_2(2-3C_2)(1-C_1)}\overline{Y}y + \frac{(C_2(3+2C_2)+C_1(1-C_2)^2)}{C_2(2-3C_2)(1-C_1)}(\overline{Y}y)^2} + \mathcal{O}(\frac{C_2}{\overline{Y}y})\\
&= (\frac{1}{2} - \overline{Y}y + \frac{C_1C_3}{2C_2^2}\overline{Y}y^2)(1 + \frac{5}{2}\overline{Y}y + \frac{19}{4}(\overline{Y}y)^2) + \mathcal{O}(\frac{C_2}{\overline{Y}y})\\
&= \frac{1}{2} + \frac{1}{4}\overline{Y}y + (\frac{C_1C_3}{2C_2^2} - \frac{1}{8})(\overline{Y}y)^2 + \mathcal{O}(\frac{C_2}{\overline{Y}y}) \qquad \text{(A.18)}
\end{aligned}
$$

In the expansion for X_S we considered terms up to second order since we will also need $X_S'(y)$,

$$X_S'(y) = \frac{1}{4}\overline{Y} + (\frac{C_1C_3}{C_2^2} - \frac{1}{4})\overline{Y}^2y + \mathcal{O}(\frac{C_2}{\overline{Y}^3y^2}).$$

We substitute the development (A.18) for $X_S(y)$ into

$$
\begin{aligned}
P'(X_S(y)) &= \frac{\tilde{\mu}}{(X_S(y) + \tilde{\mu}(1 - X_S(y)))^2} = \frac{\tilde{\mu}}{(\frac{1}{2}(1 + \tilde{\mu}) + \frac{1}{4}(1 - \tilde{\mu})\overline{Y}y)^2} + \mathcal{O}(\frac{C_2^2}{(\overline{Y}y)^2})\\
&= \frac{4\tilde{\mu}}{(1 + \tilde{\mu})^2}(1 - \frac{1 - \tilde{\mu}}{1 + \tilde{\mu}}\overline{Y}y) + \mathcal{O}((\overline{Y}y)^2).
\end{aligned}
$$

Finally with

$$\rho_S = \overline{\rho}_S(1 - \operatorname{tr}(\nabla U))$$

we get

$$\begin{aligned}\mathcal{X}(y) &= \frac{1}{M_{As}}\rho_S P'(X_S(y))X_S'(y)\\ &= \frac{1}{M_{As}}\overline{\rho}_S(1-\mathrm{tr}(\nabla U))\frac{1}{(1+\tilde{\mu})^2}(1-\frac{1-\tilde{\mu}}{1+\tilde{\mu}}\overline{Y}y)(1+(4\frac{C_1C_3}{C_2^2}-1)\overline{Y}y)\overline{Y}+\mathcal{O}(\frac{C_2}{(\overline{Y}y)^2}) \qquad (A.19)\\ &= \frac{1}{M_{As}}\overline{\rho}_S(1-\mathrm{tr}(\nabla U))\frac{1}{(1+\tilde{\mu})^2}(1+[4\frac{C_1C_3}{C_2^2}-\frac{2}{1+\tilde{\mu}}]\overline{Y}y)\overline{Y}+\mathcal{O}(\frac{C_2}{(\overline{Y}y)^2}).\end{aligned}$$

For the derivative we get

$$\mathcal{X}'(y) = \frac{1}{M_{As}}\overline{\rho}_S(1-\mathrm{tr}(\nabla U))\frac{1}{(1+\tilde{\mu})^2}[4\frac{C_1C_3}{C_2^2}-\frac{2}{1+\tilde{\mu}}]\overline{Y}^2+\mathcal{O}(\overline{Y}^3y) > 0, \qquad (A.20)$$

where the strict positivity follows from Assumption 2.1 and (A.6).

For illustration, the approximated mobility is

$$B_a \approx \frac{B(1+3a)}{\overline{n}_G(\overline{Y}_{As}+\tilde{\mu}\overline{Y}_{Ga})}\frac{(1+\tilde{\mu})^3}{\tilde{\mu}}\frac{1}{\overline{\overline{Y}}}.$$

Furthermore we give an approximation for n^*_{As} for small $\overline{Y}$. We start from (A.7) and keep leading order terms in $\overline{Y}$ and assume $C_2 \ll \overline{Y}y$

$$\begin{aligned}Y_{As}(y) &\approx \frac{C_1C_3\overline{Y}y(C_2+\overline{Y}y)^2+C_2^2(1-3\overline{Y}y)\overline{Y}y(1+\overline{Y}y)}{C_2^2(C_2+\overline{Y}y)(1-3\overline{Y}y)}\\ &\approx [\frac{C_1C_3}{C_2^2}\overline{Y}y(C_2+\overline{Y}y)^2+(1-3\overline{Y}y)\overline{Y}y(1+\overline{Y}y)]\frac{1}{\overline{\overline{Y}}y}(1+3\overline{Y}y)\\ &\approx \frac{C_1C_3}{C_2^2}(1+3\overline{Y}y)(\overline{Y}y)^2+1+\overline{Y}y\\ &\approx 1+\overline{Y}y+\frac{C_1C_3}{C_2^2}(\overline{Y}y)^2,\end{aligned}$$

which is strictly monotone in y. We have

$$\overline{Y}_{As} = Y_{As}(1) = 1+\overline{Y}+\frac{C_1C_3}{C_2^2}\overline{Y}^2.$$

Analogously we find $3-Y_V = 2+\overline{Y}y+\mathcal{O}((\overline{Y}y)^2)$.

Thus in our approximation we find

$$n^*_{As}(y) = Y_{As}(y)\overline{n}_G = (1+\overline{Y}y)\overline{n_G} = (1+\overline{Y}(y-1))\overline{n}_{As}. \qquad (A.21)$$

A.5. Boundary conditions on interfaces

We can prove Assumption 2.4 in case of a single droplet problem (SDP). Numerically this assumption seems to hold in general. We motivate Assumption 2.4 for a formal asymptotic expansion, which reduces for sufficiently small ε to a superposition of many single droplet problems.

Lemma A.6 (Well-posedness of boundary conditions on interfaces). *We assume (2.130) to hold. 1) If* $r_i > r_{min} \geq \frac{2\sigma}{4G_S+3k_L}$, $\overline{X}_L \geq \frac{1}{2}$, $1 > \tilde{\mu} > \frac{1}{3}$ *and* $\tilde{m} > 1$, *then exists a unique solution to* $(u_{int}, X_L) \in (1, const(r_{min}, \tilde{h})) \times \mathcal{J}_{X_L}$ *of the interface conditions (2.128) and (2.129) for all* *parameters* $r_I \in J_r = (r_{min}, r_{max})$ *and solutions* U *of the mechanical BVP (where in particular the data of the mechanical BVP has to be in our approximation of* $\mathcal{O}(\tilde{h})$*).*

2) u_{int} *and* X_L *depend smoothly on* r_i *and on* $\|U\|_{H^1}$*.*

Proof. 1) As first step we summarise the monotonicities of chemical potentials.

Due to Lemma A.3 and since the proof works analogously if we replace $\tilde{\mu}$ by $\tilde{m}$ and S by $\tilde{S}$, we have that u and analogously $\tilde{u}$ clearly have range in $\mathbb{R}$, are continuous and strictly monotone in y on $\mathcal{J}_y$ if $\tilde{\mu} > \frac{1}{3}$ or $\tilde{m} > \frac{1}{3}$. Thus u is invertible on $\mathbb{R}$.

The monotony of u_L^{chem} is proved in Lemma A.4 and follows analogously for $\tilde{u}_L^{chem}$.

2) We now consider (2.133) and (2.134) i.e.

$$\begin{aligned} u_{int}^{\varepsilon}(r_I) &= (\tilde{u}^{chem})^{-1}[\tilde{u}_L^{chem}(X_L(r_I)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I}], \\ 0 &= \tilde{u}_L^{chem}(X_L(r_I)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} - \tilde{u}^{chem}(u_L^{chem}(X_L(r_I)) \\ &\quad + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h_L^*(X_L(r_I)) - a_L(X_L(r_i), r_I, U_M^i, (\nabla U)_M^i)))). \end{aligned}$$

The first equation can be solved if the second yields a unique X_L. We define

$$\begin{aligned} \Phi(X_L(r_I), r_I, U_M^i, (\nabla U)_M^i)) = \tilde{u}_L^{chem}(X_L(r_I)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} - \tilde{u}^{chem}(u_L^{chem}(X_L(r_I)) \\ + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h_L^*(X_L(r_I)) - a_L(X_L(r_I), r_I, U_M^i, (\nabla U)_M^i))). \end{aligned}$$

and prove by the intermediate value theorem that Φ has for all of the parameters a unique solution.

By means of the asymptotic expansion of Chapter 3 we can prove this. Then the problem reduces to consider a single droplet problem, for which we refer to Appendix C.1.2. ☐

A.6. The denominator of the Stefan condition

In this section we show that $\mathbb{X}$ as defined in (2.156) can be rewritten in the approximation of small displacement gradients as (2.157). We demonstrate that $\mathbb{X}$ is strictly positive for all arguments and motivate that $\mathbb{X}$ is strictly monotone decreasing in r_i.

In Section 2 we derive (2.160) and assume then, that we can write $\partial_t \rho_L = \partial_{r_i} \rho_L \dot{r}_i$ and $\partial_t n_{As_L} = \partial_{r_i} n_{As_L}$. We show this in the following by algebraic considerations in our approximation and state (2.157).

First we calculate explicit formulas for $\partial_t a_L$ and $\partial_t X_L$. Since a_L is a function in r_I and U_M^i, according to (2.111), we have

$$\partial_t a_L = \frac{v_M^i}{r_i} - \frac{U_M^i}{r_i^2}\dot{r}_i$$

but v_M^i still depends on $\partial_t \rho_L$ and hence on $\partial_t a_L$. Due to (2.134) for the rest of this proof we can consider X_L to be a function in r_i and a_L and thus

$$\partial_t X_L = \partial_{r_i} X_L \dot{r}_i + \partial_{a_L} X_L \partial_t a_L.$$

We calculate

$$\partial_t \rho_L = -3\overline{\rho}_L \partial_t a_L = -3\overline{\rho}_L \left(\frac{v_M^i}{r_i} - \frac{U_M^i}{r_i^2}\dot{r}_i \right) = -\overline{\rho}_L((1 - \frac{\rho_L}{\rho_S})\frac{3}{r_i}\dot{r}_i - \frac{\partial_t \rho_L}{\rho_S} - 3\frac{U_M^i}{r_i^2}\dot{r}_i)$$

where we plug in (2.159) in the last step. We solve the equation for $\partial_t \rho_L$ and get

$$\begin{aligned}\partial_t \rho_L &= -\frac{\overline{\rho}_L(1-\frac{\rho_L}{\rho_S}-\frac{U_M^i}{r_i})}{1-\frac{\overline{\rho}_L}{\rho_S}}\frac{3}{r_i}\dot{r}_i = -\overline{\rho}_L(1+\frac{\frac{\overline{\rho}_L}{\rho_S}3a_L-\frac{U_M^i}{r_i}}{1-\frac{\overline{\rho}_L}{\rho_S}})\frac{3}{r_i}\dot{r}_i \qquad (A.22)\\ &= -\overline{\rho}_L(1+\frac{(3\frac{\overline{\rho}_L}{\rho_S}-1)\frac{U_M^i}{r_i}-3\frac{\overline{\rho}_L}{\rho_S}\delta^R}{1-\frac{\overline{\rho}_L}{\rho_S}})\frac{3}{r_i}\dot{r}_i \qquad \text{by (2.111)}\end{aligned}$$

or in our approximation

$$\partial_t a_L = (1+\frac{(3\frac{\overline{\rho}_L}{\overline{\rho}_S}-1)\frac{U_M^i}{r_i}-3\frac{\overline{\rho}_L}{\overline{\rho}_S}\delta^R}{1-\frac{\overline{\rho}_L}{\overline{\rho}_S}})\frac{\dot{r}_i}{r_i}. \qquad (A.23)$$

On the other hand if we calculate

$$\partial_t \rho_L = \partial_t n_L M(X_L) + n_L \partial_t M(X_L) = -3\overline{n}_L M(X_L)(\partial_t a_L - h_L^{*\prime}\partial_t X_L) + n_L M_{As}(1-\tilde{\mu})\partial_t X_L$$

and we get with (A.22) and with

$$h_L^{*\prime}(X_L) = -\frac{1}{3(1-h_L^*)^2}\frac{M_{As}(1-\tilde{\mu})}{M(\overline{X}_L)} \qquad (A.24)$$

that

$$\partial_t X_L = \frac{3(\overline{X}_L - X_L)}{1-3a_L+h_L^*}\partial_t a_L = 3(\overline{X}_L - X_L)(1+3a_L-h_L^*)(1+\frac{(3\frac{\overline{\rho}_L}{\rho_S}-1)\frac{U_M^i}{r_i}-3\frac{\overline{\rho}_L}{\rho_S}\delta^R}{1-\frac{\overline{\rho}_L}{\rho_S}})\frac{\dot{r}_i}{r_i}, \qquad (A.25)$$

whereas in the last step we use (A.23) and our approximation in $\mathcal{O}(\tilde{h})$.

We get

$$\begin{aligned}&\partial_t n_{As_L} - \frac{n_{As}}{\rho_S}\partial_t \rho_L\\ &= -3\overline{n}_L X_L(\partial_t a_L - h_L^{*\prime}\partial_t X_L) + \overline{n}_L(1-3a_L+3h_L^*)\partial_t X_L + 3\frac{n_{As}}{\rho_S}\overline{\rho}_L\partial_t a_L\\ &= [-3\overline{n}_L X_L(1+\frac{1}{3(1-h_L^*)^2}\frac{M_{As}(1-\tilde{\mu})}{M(\overline{X}_L)}\frac{3(\overline{X}_L - X_L)}{1-3a_L+h_L^*}) + \overline{n}_L(1-3a_L+3h_L^*)\frac{3(\overline{X}_L - X_L)}{1-3a_L+h_L^*}\\ &\quad + 3\frac{n_{As}}{\rho_S}\overline{\rho}_L]\partial_t a_L\\ &= 3\overline{n}_L[-X_L(1+(1+3a_L-3h_L^*)(1-\frac{M(X_L)}{M(\overline{X}_L)})) + (1+2h_L^*)(\overline{X}_L - X_L) + \frac{n_{As}}{\rho_S}M(\overline{X}_L)]\partial_t a_L\\ &= 3\overline{n}_L[\overline{X}_L - 2X_L + \frac{\overline{n}_{As}}{\overline{\rho}_S}M(\overline{X}_L)]\partial_t a_L = -3[2\overline{n}_L X_L - \overline{n}_{As_L} - \frac{\overline{n}_{As}}{\overline{\rho}_S}\overline{\rho}_L]\partial_t a_L\end{aligned}$$

by (A.24) and (A.25) and using several times our approximation.

Then

$$\dot{r}_i = \frac{\frac{B}{RT}\fint_{I_i}\partial_\nu u}{\mathbb{X}(r_i, U_M^i)}$$

where

$$\mathbb{X}(r_i, U_M^i) = -n_{As}\frac{\rho_-}{\rho_+} + n_{As_-} - [2\overline{n}_L X_L - \overline{n}_{As_L} - \frac{\overline{n}_{As}}{\overline{\rho}_S}\overline{\rho}_L](1+\frac{(3\frac{\overline{\rho}_L}{\overline{\rho}_S}-1)\frac{U_M^i}{r_i}-3\frac{\overline{\rho}_L}{\overline{\rho}_S}\delta^R}{1-\frac{\overline{\rho}_L}{\overline{\rho}_S}})$$

and in our approximation, where we can not exclude the case $\varrho = 1 - \frac{\overline{\rho}_L}{\overline{\rho}_S} \approx \mathcal{O}(\tilde{h})$ (this is plausible for our material data, which is given in Appendix D), this simplifies in our approximation to

$$\begin{aligned}
\mathbb{X}(r_i, U_M^i) &= -n_{As}\frac{\rho_-}{\rho_+} + n_{As_-} - [2\overline{n}_L X_L - \overline{n}_{As_L} - \frac{\overline{n}_{As}}{\overline{\rho}_S}\overline{\rho}_L](1 + \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}) \\
&= (\overline{n}_G \overline{Y}_{As} - n_G Y_{As})\frac{\overline{\rho}_L}{\overline{\rho}_S} + (n_L - \overline{n}_L)X_L + \overline{n}_L(X_L - \overline{X}_L) \\
&\quad - [\overline{n_L}(2X_L - \overline{X}_L - \overline{X}_S)]\frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho} \\
&= \overline{n}_G(3 - \overline{Y}_V)[(\overline{X}_S - X_S)\frac{\overline{\rho}_L}{\overline{\rho}_S} + (X_L - \overline{X}_L)(1 - \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}) + (\overline{X}_S - X_L)\frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}]
\end{aligned}$$

which is (2.157). With $X_L - \overline{X}_L = \mathcal{O}(\tilde{h}^{1/2})$ and $y - 1 = \mathcal{O}(\tilde{h}^{1/2})$ eq. (2.157) is in our approximation

$$\mathbb{X} \approx \overline{n}_G(3 - \overline{Y}_V)[(\overline{X}_S - X_S)\frac{\overline{\rho}_L}{\overline{\rho}_S} + (X_L - \overline{X}_L)(1 - \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}) + (\overline{X}_S - X_L)\frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}]$$

which is bigger than $\tilde{h}$ and strictly positive for typical material data i.e.

$$\mathbb{X} > \overline{n}_G(3 - \overline{Y}_V)(\overline{X}_L - \overline{X}_S)\frac{3\delta^R}{\varrho} \approx \mathcal{O}(1) > 0$$

since always $\overline{X}_L > \overline{X}_S$.

By plugging into (2.157) the ansatz $y - 1 = c_Y^1 + \frac{c_Y^2}{r_i}$ and $X_L - \overline{X}_L = c_X^1 + \frac{c_X^2}{r_i}$ (see Section A.5) with positive constants c_X^1, c_X^2, c_Y^1 and c_Y^2 we get

$$\mathbb{X} \approx \overline{n}_G(3 - \overline{Y}_V)[-X_S'(1)(c_Y^1 + \frac{c_Y^2}{r_i})\frac{\overline{\rho}_L}{\overline{\rho}_S} + (c_X^1 + \frac{c_X^2}{r_i})(1 - \frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}) + (\overline{X}_S - X_L)\frac{2\frac{U_M^i}{r_i} - 3\delta^R}{\varrho}]$$

which is monotone in r_i since $c_X^1, c_Y^1, U_M^i = \mathcal{O}(\tilde{h})$, $c_X^2, c_Y^2 = \mathcal{O}(1)$, $c_X^2 \geq 0.1$, $c_Y^2 \leq 9$ and $0 < X_S'(y) \ll 1$.

Hence

$$0 < \overline{n}_G(3 - \overline{Y}_V)(\overline{X}_L - \overline{X}_S)\frac{3\delta^R}{\varrho}(1 + \mathcal{O}(\tilde{h})) \leq \mathbb{X} \leq \mathbb{X}(r_{min}, U_M^i(r_i = r_{min})(1 + \mathcal{O}(\tilde{h})) < \infty. \quad \text{(A.26)}$$

A.7. Proof of the availability result

Theorem A.1 (Lyapunov function). *Assume Problem B or BI has a smooth solution and assume in particular that $\partial\Omega$ and I_i for all $i \in N$ are spheres. We assume the Helmholtz energy density $\rho\psi$ to fulfil the relations (A.28) and (A.29), we use local conservation of substance and we assume all assumptions which we made so far on material parameters to hold.*

Then the availability is decreasing in time i.e. there holds

$$\frac{d}{dt}\mathcal{A} \leq 0 \quad \forall t \neq \tau_i, i \in N(0) \quad \text{(A.27)}$$

where the availability is modelled at τ_i as in (2.171). The therin appearing "availability of two single atoms" $\mathcal{A}_i^d$ as defined by (2.172) is well-defined.

The availability is bounded from below and by adding up a suitable constant we can achieve that

$$\mathcal{A} = 0$$

for a equilibrium. Hence $\mathcal{A}$ is a Lyapunov function in sense of [Wal00] w.r.t. this equilibrium.

We prove 3) for regime (DC) and prove 1) & 2) for all regimes.

Proof. 1) We derive (2.45) w.r.t. time for arbitrary $t \in (0, \mathcal{T}) \setminus \cup_{i=1}^{\mathcal{N}(0)} \tau_i$ and apply the transport theorem which reads for closed surfaces A as $\frac{d}{dt}\int_A da = 2\int_A k_M w \cdot \nu_+ da$

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = &\int_{\Omega_S} \frac{d}{dt}(\rho_S\psi_S) + \sum_{i\in N}\int_{\Omega_L^i} \frac{d}{dt}(\rho_L^i\psi_L^i) \\ &+ \int_{\partial\Omega}(\rho_S\psi_S + p_0)v\cdot\nu + \sum_{i\in N}\int_{I_i}(\rho_L^i\psi_L^i - \rho_S\psi_S + 2\sigma k_M)w\cdot\nu_+.\end{aligned}$$

With the help of the continuity equation (2.20) this is rewritten as

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = &\int_{\Omega_S} D_t(\rho_S\psi_S) - D_t\rho_S\psi_S + \sum_{i\in N}\int_{\Omega_L^i} D_t(\rho_L^i\psi_L^i) - D_t\rho_L^i\psi_L^i \\ &+ \int_{\partial\Omega}((\rho_S\psi_S)(w-v) + p_0 w)\cdot\nu - \sum_{i\in N}\int_{I_i}([[\rho\psi]]w - [[\rho\psi v]] - 2\sigma k_M w)\cdot\nu_+.\end{aligned}$$

We introduce the common notation $A : B = \mathrm{tr}(A^T B) = \sum_{i,j=1}^{3} A^{ji}B^{ij}$ for two matrices $A, B \in \mathbb{R}^{n\times n}$, here always $n = 3$.

Due to several identities from mechanics, e.g. the Gibbs-Duhem equation (2.44), there holds (see [DD08], eq.(A 4))

$$D_t(\rho_S\psi_S) = \sum_{a\in\mathbf{a_S}} \mu_a D_t n_a - \frac{p}{\rho_S} D_t\rho_S + \sigma_S : \nabla v \tag{A.28}$$

and

$$D_t(\rho_L\psi_L) = \sum_{a\in\mathbf{a_L}} \mu_a D_t n_a - \frac{p_L}{\rho_L} D_t\rho_L - p_L\mathbb{I} : \nabla v_L. \tag{A.29}$$

Together with the definition of the specific free enthalpy $g := \psi + \frac{p}{\rho}$ we obtain

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = &\int_{\Omega_S} \sum_{a\in\mathbf{a_S}} \mu_a D_t n_a - g D_t\rho + \sigma_S : \nabla v \\ &+ \sum_{i\in N}\int_{\Omega_L^i} \sum_{a\in\mathbf{a_L}} \mu_a D_t n_a - g D_t\rho - p_L \mathrm{tr}(\nabla v_L) \\ &+ \int_{\partial\Omega}((\rho_S\psi_S)(w-v) + p_0 w)\cdot\nu - \sum_{i\in N}\int_{I_i}([[\rho\psi]]w - [[\rho\psi v]] - 2\sigma k_M w)\cdot\nu_+.\end{aligned}$$

We consider the mechanical contributions and exploit the mechanical BVP (2.51) – (2.55),

$$\begin{aligned}&\int_{\Omega_S} \sigma_S : \nabla v - \sum_{i\in N}\int_{\Omega_L^i} p_L \mathrm{tr}(\nabla v_L) \\ &= -\int_{\Omega_S}(\nabla\cdot\sigma_S)\cdot v + \sum_{i\in N}\int_{\Omega_L^i}\nabla p_L\cdot v_L + \int_{\partial\Omega}\sigma_S v\cdot\nu - \sum_{i\in N}\int_{I_i}(\sigma_S v_+ + p_L v_-)\cdot\nu_+ \\ &= -\int_{\partial\Omega} p_0 v\cdot\nu - \sum_{i\in N}\int_{I_i}(\sigma_S[[v]] + 2\sigma k_M v_-)\cdot\nu_+,\end{aligned}$$

where we used on $\partial\Omega_S$

$$\sigma_S v \cdot \nu = \sigma_S((v \cdot \nu)\nu + (v \cdot \tilde{\tau}_1)\tilde{\tau}_1 + (v \cdot \tilde{\tau}_2)\tilde{\tau}_2) \cdot \nu = \sigma_S \nu \cdot \nu (v \cdot \nu).$$

Hence

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = & \int_{\Omega_S} \sum_{a \in \mathbf{a_S}} \mu_a D_t n_a - g D_t \rho + \sum_{i \in N} \int_{\Omega_L^i} \sum_{a \in \mathbf{a_L}} \mu_a D_t n_a - g D_t \rho \\ & + \int_{\partial\Omega} (\rho_S \psi_S + p_0)(w - v) \cdot \nu \\ & - \sum_{i \in N} \int_{I_i} ([[\rho\psi]]w - [[\rho\psi v]] + \sigma_S[[v]] - 2\sigma k_M (w - v_-)) \cdot \nu_+ .\end{aligned}$$

With the Gibbs-Duhem equation (2.44) $g = \rho \sum_{a \in \mathbf{a_b}} \mu_a n_a$, $b \in \{S, L\}$, local conservation of substance (2.17) and (2.18) and local conservation of mass (2.20) and the definition of the diffusion fluxes j_a we find, since we assumed chemical equilibrium i.e. no chemical reactions take place,

$$\sum_{a \in \mathbf{a_S}} \mu_a D_t n_a - g D_t \rho = \sum_{a \in \mathbf{a_S}} \mu_a (D_t n_a - \frac{n_a}{\rho} D_t \rho) = - \sum_{a \in \mathbf{a_S}} \mu_a \nabla \cdot j_a$$

and an analogous formula in the liquid. We get

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = & - \int_{\Omega_S} \sum_{a \in \mathbf{a_S}} \mu_a \nabla \cdot j_a - \sum_{i \in N} \int_{\Omega_L^i} \sum_{a \in \mathbf{a_L}} \mu_a \nabla \cdot j_a + \int_{\partial\Omega} (\sum_{a \in \mathbf{a_S}} \mu_a n_a)(w - v) \cdot \nu \\ & - \sum_{i \in N} \int_{I_i} ((\sum_{a \in \mathbf{a_S}} \mu_a n_a - \sum_{a \in \mathbf{a_L}} \mu_a n_a - \sigma_S^{<\cdot,\cdot>})w \\ & - (\sum_{a \in \mathbf{a_S}} \mu_a n_a v_+ - \sum_{a \in \mathbf{a_L}} \mu_a n_a v_- - \sigma_S^{<\cdot,\cdot>})v_+)) \cdot \nu_+\end{aligned}$$

where we further used the Gibbs-Duhem equation (2.44) under the surface integrals and again (2.51) – (2.55) and (2.16). Note that in particular

$$[[p]] = p_S - p_L = \nu_+ \sigma_S^{<\cdot,\cdot>} \nu_+ - 2\sigma k_M . \tag{A.30}$$

Assuming a homogeneous spherical liquid droplet, which allows to use Gauss' theorem, with use of $w = \dot{r}_i \nu$ and together with the interfacial conditions (2.56) and (2.57) where we consider at first both regimes (DC) & (IC) simultaneously, we have

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = & - \int_{\Omega_S} \sum_{a \in \mathbf{a_S}} \mu_a \nabla \cdot j_a - \sum_{i \in N} (\mu_{As_S} \int_{I_i} j_{As_L} \cdot \nu_+ + \mu_{Ga_S} \int_{I_i} j_{Ga_L} \cdot \nu_+ \\ & - (\frac{1}{\rho_S^i} \fint_{I_i} \nu_+ \cdot \sigma_S^{<\cdot,\cdot>} \nu_+ \sum_{a \in \mathbf{a_L}} M_a - \sum_{a \in \mathbf{a_L}} \frac{RT}{B_a^I} (v_a - w) n_a) \int_{I_i} j_a \cdot \nu_+) \\ & + \int_{\partial\Omega} (\sum_{a \in \mathbf{a_S}} \mu_a n_a)(w - v) \cdot \nu + \sum_{i \in N} \int_{I_i} (\mu_{As_S} n_{As_L} + \mu_{Ga_S} n_{Ga_L} \\ & + (1 - \frac{\rho_L^i}{\rho_S^i}) \fint_{I_i} \nu_+ \sigma_S^{<\cdot,\cdot>} \nu_+ + \sum_{a \in \mathbf{a_L}} \frac{RT}{B_a^I} (v_a - w) n_a^2 - \sum_{a \in \mathbf{a_S}} \mu_a n_a) w \cdot \nu_+ \\ & + (\sum_{a \in \mathbf{a_S}} \mu_a n_a v_+ - (\mu_{As_S} n_{As_L} + \mu_{Ga_S} n_{Ga_L}) v_- - (v_+ - \frac{\rho_L^i}{\rho_S^i} v_-) \fint_{I_i} \nu_+ \cdot \sigma_S^{<\cdot,\cdot>} \nu_+) \cdot \nu_+ \\ & - \sum_{a \in \mathbf{a_L}} \frac{RT}{B_a^I} (v_a - w) n_a^2 v_- \cdot \nu_+\end{aligned}$$

and with (2.24), (2.25), $B_a^I =: n_a B_*^I$ and the definition of u, (2.91),

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = &-\int_{\Omega_S}\sum_{a\in\mathbf{as}}\mu_a\nabla\cdot j_a - \sum_{i\in N}(u^i_{int}\int_{I_i} j_{As_L}\cdot\nu_+ + \frac{RT}{B^I_*}\int_{I_i}(v_{As_L} - \frac{1}{\tilde{\mu}}v_{Ga_L} - (1-\frac{1}{\tilde{\mu}})w)j_{As_L}\cdot\nu_+) \\ &+ \int_{\partial\Omega}(\sum_{a\in\mathbf{as}}\mu_a n_a)(w-v)\cdot\nu + \sum_{i\in N}\int_{I_i}(\sum_{a\in\mathbf{as}}\mu_a n_a(-w+v_+) \\ &- (\mu_{As_S}n_{As_L} + \mu_{Ga_S}n_{Ga_L})(-w+v_-) + \fint_{I_i}\nu_+\cdot\sigma_S^{<\cdot,\cdot>}\nu_+(w - v_+ + \frac{\rho^i_L}{\rho^i_S}(-w+v_-))\cdot\nu_+ \\ &- \frac{RT}{B^I_*}((v_{As_L}-w)n_{As_L} + (v_{Ga_L}-w)n_{Ga_L})(v_- - w)).\end{aligned}$$

We now exploit chemical equilibrium to express $\sum_{a\in\mathbf{as}}\mu_a n_a$ as a function of the total chemical potential u, first (2.95), then (2.96) and finally (2.97) and (2.98).

$$\begin{aligned}\sum_{a\in\mathbf{as}}\mu_a n_a &= (\mu_{Ga_\alpha}Y_{Ga_\alpha} + \mu_{As_\alpha}Y_{As_\alpha} + \mu_{As_\beta}Y_{As_\beta} + \mu_{As_\gamma}Y + \mu_{V_\alpha}Y_{V_\alpha} + \mu_{V_\beta}Y_{V_\beta} + \mu_{V_\gamma}Y_{V_\gamma})n_G \\ &= (\mu_{Ga_\alpha}Y_{Ga_\alpha} + \mu_{As_\alpha}Y_{As_\alpha} + \mu_{As_\beta}Y_{As_\beta} + \mu_{As_\gamma}Y + \mu_{V_\alpha}(1 - Y_{As_\alpha} - Y_{Ga_\alpha}) \\ &\quad + \mu_{V_\beta}(1 - Y_{As_\beta}) + \mu_{V_\gamma}(1-Y))n_G \\ &= ((\mu_{Ga_\alpha} - \mu_{V_\alpha})Y_{Ga_\alpha} + (\mu_{As_\alpha} - \mu_{V_\alpha})Y_{As_\alpha} + (\mu_{As_\beta} - \mu_{\mu_{V_\beta}})Y_{As_\beta} + (\mu_{As_\gamma} - \mu_{V_\gamma})Y)n_G \\ &= (\mu_{Ga_S}Y_{Ga_\alpha} + \mu_{As_S}Y_{As})n_G = \mu_{Ga_S}n_{Ga_S} + \mu_{As_S}n_{As_S}.\end{aligned} \tag{A.31}$$

Therefore with (2.26), (2.96) – (2.98) and finally with (2.24) there results

$$\begin{aligned}\sum_{a\in\mathbf{as}}\mu_a\nabla\cdot j_a &= \mu_{Ga_\alpha}\nabla\cdot j_{Ga} + \mu_{As_\alpha}\nabla\cdot j_{As_\alpha} + \mu_{As_\beta}\nabla\cdot j_{As_\beta} + \mu_{As_\gamma}\nabla\cdot j_{As_\gamma} \\ &\quad + \mu_{V_\alpha}\nabla\cdot(j_{As_\gamma} + j_{V_\gamma} - j_{As_\alpha} - j_{Ga}) + \mu_{V_\beta}\nabla\cdot(j_{As_\gamma} + j_{V_\gamma} - j_{As_\beta}) + \mu_{V_\gamma}\nabla\cdot j_{V_\gamma} \\ &= (\mu_{Ga_\alpha} - \mu_{V_\alpha})\nabla\cdot j_{Ga} + (\mu_{As_\alpha} - \mu_{V_\alpha})\nabla\cdot j_{As_\alpha} + (\mu_{As_\beta} - \mu_{V_\beta})\nabla\cdot j_{As_\beta} \\ &\quad + (\mu_{As_\gamma} - \mu_{V_\gamma})\nabla\cdot j_{As_\gamma} \\ &= (-\frac{1}{\tilde{\mu}}\mu_{Ga_S} + \mu_{As_S})\nabla\cdot j_{As} = u\nabla\cdot j_{As}.\end{aligned}$$

We have now

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = &-\int_{\Omega_S}u\nabla\cdot j_{As} - \sum_{i\in N}(u^i_{int}\int_{I_i} j_{As_L}\cdot\nu_+ \\ &+ \frac{RT}{B^I_*}\int_{I_i}((v_{As_L}-w)(v_{As_L}-v_-)n_{As_L} + (v_{Ga_L}-w)(v_{Ga_L}-v_-)n_{Ga_L}) \\ &+ \int_{\partial\Omega}(\mu_{Ga_S}n_{Ga_S} + \mu_{As_S}n_{As_S})(w-v)\cdot\nu \\ &+ \sum_{i\in N}\int_{I_i}(\mu_{Ga_S}(-[[n_{Ga}]]w + [[n_{Ga}v]]) + \mu_{As_S}(-[[n_{As}]]w + [[n_{As}v]]) \\ &+ \frac{\fint_{I_i}\nu_+\cdot\sigma_S^{<\cdot,\cdot>}\nu_+}{\rho^i_S}([[\rho]]w - [[\rho v]]))\cdot\nu_+ \\ &- \sum_{i\in N}\frac{RT}{B^I_*}\int_{I_i}((v_{As_L}-w)n_{As_L} + (v_{Ga_L}-w)n_{Ga_L})(v_- - w)).\end{aligned}$$

We can simplify further by applying conditions for the change of interface (2.158),

$$\fint_{I_i} w\cdot\nu_{(+)} = -\frac{(\frac{B}{RT}\fint_{I_i}\nabla u + j_{As_L})\cdot\nu}{[[n_{As}]]} + \frac{\fint_{I_i}[[n_{As}v]]\cdot\nu_+}{[[n_{As}]]} \quad \text{on } I_i(t) \quad \forall i\in N(t) \quad \text{for a.a. } t\in(0,\mathcal{T}),$$

and (2.31) which translates into

$$\fint_{I_i} w\cdot\nu_{(+)} = \frac{\fint_{I_i}[[\rho v]]\cdot\nu_+}{[[\rho]]} \quad \text{on } I_i(t) \quad \forall i\in N(t) \quad \text{for a.a. } t\in(0,\mathcal{T}).$$

We find

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = &-\int_{\Omega_S} u\nabla\cdot j_{As} - \sum_{i\in N}(u^i_{int}\int_{I_i} j_{As_L}\cdot\nu_+ \\ &+\int_{\partial\Omega}(\mu_{Ga_S}n_{Ga_S}+\mu_{As_S}n_{As_S})(w-v)\cdot\nu + \frac{B}{RT}\sum_{i\in N}\int_{I_i}(-\frac{1}{\tilde\mu}\mu_{Ga_S}+\mu_{As_S})\nabla u\cdot\nu_+ \\ &+\sum_{i\in N}\int_{I_i}(-\frac{1}{\tilde\mu}\mu_{Ga_S}+\mu_{As_S})j_{As_L}\cdot\nu_+ - \frac{RT}{B^I_*}\sum_{i\in N}\int_{I_i}(|v_{As_L}-w|^2 n_{As_L}+|v_{Ga_L}-w|^2 n_{Ga_L})\end{aligned}$$

and we obtain by further using Fick's law (2.59) and since the terms with j_{As_L} cancel out, that

$$\begin{aligned}\frac{d}{dt}\mathcal{A} = &\frac{B}{RT}\int_{\Omega_S} u\Delta u + \int_{\partial\Omega}(\mu_{Ga_S}n_{Ga_S}+\mu_{As_S}n_{As_S})(w-v)\cdot\nu + \frac{B}{RT}\sum_{i\in N}\int_{I_i} u^i_{int}\nabla u\cdot\nu_+ \\ &-\frac{RT}{B^I_*}\sum_{i\in N}\int_{I_i}(\frac{|\dot{\mathcal{N}}_{As}|^2}{n_{As_L}}+\frac{|\dot{\mathcal{N}}_{Ga}|^2}{n_{Ga_L}})\end{aligned}$$

and finally by integration by parts where we use (2.178)

$$\frac{d}{dt}\mathcal{A} = -\frac{B}{RT}\int_{\Omega_S}|\nabla u|^2+\int_{\partial\Omega}(\mu_{Ga_S}n_{Ga_S}+\mu_{As_S}n_{As_S})(w-v)\cdot\nu - RT\sum_{i\in N}\int_{I_i}(\frac{1}{B^I_{As}}|\dot{\mathcal{N}}_{As}|^2+\frac{1}{B^I_{Ga}}|\dot{\mathcal{N}}_{Ga}|^2).$$

If we assume $n_{As}|_{\partial\Omega} = const$ (that implies $\mu^{chem}_{As}|_{\partial\Omega} = const$, while $\mu^{mech}_{As}|_{\partial\Omega} = const$ since $p|_{\partial\Omega} = p_0$) and $n_{Ga}|_{\partial\Omega} = const$ with $w\cdot\nu = v\cdot\nu + \mathcal{O}(\tilde\varepsilon)$ according to Lemma 3.1 there results with further exploiting (2.28)

$$\frac{d}{dt}\mathcal{A} = -\frac{B}{RT}\int_{\Omega_S}|\nabla u|^2 - \frac{1}{RT}\sum_{i\in N}\int_{I_i}(B^I_{As}([[\mu_{As}]]-\frac{M_{As}}{\rho_S}\sigma_S^{<\cdot,\cdot>})^2+B^I_{Ga}([[\mu_{Ga}]]-\frac{M_{Ga}}{\rho_S}\sigma_S^{<\cdot,\cdot>})^2)\le 0, \tag{A.32}$$

which is always nonpositive. In the regime (DC) the last term vanishes while in (IC) the first term is zero (after suitable rescaling of time).

This can be rewritten as

$$\frac{d}{dt}\mathcal{A} = \frac{B}{RT}\int_{\Omega_S} u\Delta u + \sum_{i\in N}\int_{I_i} u^i_{int}\dot r_i \mathbb{X}(r_i,\fint_{I_i} U\cdot\nu) - \frac{RT}{B^I_*}\sum_{i\in N}\int_{I_i}(\frac{|\dot{\mathcal{N}}_{As}|^2}{n_{As_L}}+\frac{|\dot{\mathcal{N}}_{Ga}|^2}{n_{Ga_L}}).$$

2) We use the formula (2.45) for $\mathcal{A}$ in order to consider the availability at time τ_i. With (A.31)

$$\begin{aligned}\mathcal{A} = &\int_{\Omega_S}\mu_{Ga_S}n_{Ga_S}+\mu_{As_S}n_{As_S}+p_0-p_S \\ &+\sum_{i\in N}\int_{\Omega^i_L}\mu_{Ga_L}n_{Ga_L}+\mu_{As_L}n_{As_L}+p_0-p^i_L+\sum_{i\in N}\int_{I_i}\sigma.\end{aligned}$$

By plugging in the mechanical parts of the chemical potentials and the assumption of spherical homogeneous droplets and (2.79) for p_L in we have

$$\begin{aligned}\mathcal{A} = &\int_{\Omega_S} \mu_{Ga_S}^{chem} n_{Ga_S} + \mu_{As_S}^{chem} n_{As_S} + p_0 - \overline{p} \\ &+ \sum_{i\in N} \int_{\Omega_L^i} \mu_{Ga_L}^{chem} n_{Ga_L} + \mu_{As_L}^{chem} n_{As_L} + \frac{n_L}{\overline{n}_L} 3k_L(h_L^* - h_L) + p_0 - \overline{p} + 3k_L(h_L - h_L^*) + \sum_{i\in N} \int_{I_i} \sigma,\end{aligned}$$

that simplifies in our approximation to

$$\mathcal{A} = |\Omega|(p_0 - \overline{p}) + \int_{\Omega_S} \mu_{Ga_S}^{chem} n_{Ga_S} + \mu_{As_S}^{chem} n_{As_S} + \sum_{i\in N} \int_{\Omega_L^i} \mu_{Ga_L}^{chem} n_{Ga_L} + \mu_{As_L}^{chem} n_{As_L} + \sum_{i\in N} \int_{I_i} \sigma.$$

With the modelling of a dissolving droplet as in Subsection 2.6.7, where we indicate functions at time τ_i+ by an index $+$ and at time τ_i- by an index $-$, we have

$$\mathcal{A}_i^d = \mathcal{A}(\tau_i+) - \mathcal{A}(\tau_i-) = \int_{\Omega_L^i} (\mu_{Ga_S}^{chem^+} n_{Ga}^+ - \mu_{Ga_L}^{chem^-} n_{Ga_L}^-) + (\mu_{As_S}^{chem^+} n_{As}^+ - \mu_{As_L}^{chem^-}) n_{As_L}^- - \int_{I_i} \sigma \tag{A.33}$$

(A.33) shows that $\mathcal{A}_i^d$ is finite, depends only on the time τ_i+ and varies in terms of order $\mathcal{O}(\tilde{h})$ for each droplet i.

If we neglect the regularisation for $n_{As}(\tau_i+)$ as in (2.168) and for the resulting $n_{Ga}(\tau_i+)$ and assume $n_{As}(\tau_i+) \approx n_{As_L}(\tau_i-)$ and $n_{As}(\tau_i+) \approx n_{As_L}(\tau_i-)$ we get

$$\mathcal{A}_i^d = \mathcal{A}(\tau_i+) - \mathcal{A}(\tau_i-) = \int_{\Omega_L^i} (\mu_{Ga_S}^{chem^+} - \mu_{Ga_L}^{chem^-}) n_{Ga_L}^- + (\mu_{As_S}^{chem^+} - \mu_{As_L}^{chem^-}) n_{As_L}^- - \int_{I_i} \sigma \tag{A.34}$$

Clearly the last term is negative. Numerically we see that the other terms are expected to be also negative, but this is not important for the rest of the study.

3) We calculate explicitly $\mathcal{A}$ as expression in the variables $u, U, \{r_i\}$ and R_{bd}.

We start from (2.45). With (A.31) together with the interfacial conditions (2.56) and (2.56)

$$\begin{aligned}\mathcal{A} = &\int_{\Omega_S} \mu_{Ga_S} n_{Ga_S} + \mu_{As_S} n_{As_S} + p_0 - p_S \\ &+ \sum_{i\in N} \int_{\Omega_L^i} ((\mu_{Ga_S} - \frac{M_{Ga}}{\rho_S^i} \nu_+ \sigma_S^{<\cdot,\cdot>} \nu_+ + \frac{RT}{B_*^I} (v_{Ga_L} - w) \cdot \nu_+) n_{Ga_L} \\ &+ (\mu_{As_S} - \frac{M_{As}}{\rho_S^i} \nu_+ \sigma_S^{<\cdot,\cdot>} \nu_+ + \frac{RT}{B_*^I} (v_{As_L} - w) \cdot \nu_+) n_{As_L}) + p_0 - p_L^i) + \sum_{i\in N} \int_{I_i} \sigma.\end{aligned}$$

By plugging in the mechanical parts of the chemical potentials and the assumption of spherical homogeneous droplets we have

$$\begin{aligned}\mathcal{A} = &\int_{\Omega_S} (\mu_{Ga_S}^{chem} (1 - X_S) + \mu_{As_S}^{chem} X_S) n_S + p_S - \overline{p} + p_0 - p_S \\ &+ \sum_{i\in N} \int_{\Omega_L^i} ((\mu_{Ga_S}^{chem} (1 - X_L^i) + \mu_{As_S}^{chem} X_L^i) n_L^i + \frac{RT}{B_*^I} (v_{Ga_L} (1 - X_L^i) + v_{As_L} X_L^i - w) \cdot \nu_+ n_L^i \\ &+ \frac{\rho_L^i}{\rho_S^i} (p_S - \overline{p} - \nu_+ \sigma_S^{<\cdot,\cdot>} \nu_+) + p_0 - p_L^i) + \sum_{i\in N} \int_{I_i} \sigma.\end{aligned}$$

Now we exploit (A.30)

$$\begin{aligned}\mathcal{A} = &\int_{\Omega_S} (\mu_{Ga_S}^{chem}(1-X_S) + \mu_{As_S}^{chem} X_S) n_S + p_0 - \overline{p} \\ &+ \sum_{i\in N} \int_{\Omega_L^i} ((\mu_{Ga_S}^{chem}(1-X_L^i) + \mu_{As_S}^{chem} X_L^i) n_L^i + \frac{RT}{B_*^I}(v_{Ga_L}(1-X_L^i) + v_{As_L} X_L^i - w)\cdot \nu_+ n_L^i \\ &+ (\frac{\rho_L^i}{\rho_S^i} - 1)(p_L^i - \overline{p}) + p_0 - \overline{p}) + 4\pi \sum_{i\in N} r_i^2 (1 - \frac{2}{3}\frac{\rho_L^i}{\rho_S^i})\sigma\end{aligned}$$

and with (2.115) together with some rearranging

$$\begin{aligned}\mathcal{A} = &\int_{\Omega} p_0 - \overline{p} + \int_{\Omega_S} (\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As}) n_G \\ &+ \sum_{i\in N} \int_{\Omega_L^i} ((\mu_{Ga_S}^{chem}(1-X_L^i) + \mu_{As_S}^{chem} X_L^i) n_L^i + \frac{RT}{B_*^I}(v_{Ga_L}(1-X_L^i) + v_{As_L} X_L^i - w)\cdot \nu_+ n_L^i \\ &- 3k_L(\frac{\rho_L^i}{\rho_S^i} - 1)(\frac{\fint_{I_i} U\cdot\nu}{r_i} - \delta^R - h_L^*(X_L^i)) + 4\pi \sum_{i\in N} r_i^2 (1 - \frac{2}{3}\frac{\rho_L^i}{\rho_S^i})\sigma.\end{aligned}$$

Eliminating n_G and n_L by (2.75.1) and (2.112) and with $\frac{\rho_L^i}{\rho_S^i} = \frac{\overline{\rho}_L}{\overline{\rho}_S}(1 - 3\frac{\fint_{I_i} U\cdot\nu}{r_i} + 3\delta^R + 3\mathrm{tr}(\nabla U))$ in our approximation

$$\begin{aligned}\mathcal{A} = &\int_{\Omega} p_0 - \overline{p} \\ &+ \int_{\Omega_S} (\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As}) n_G^R (1 - \mathrm{tr}(\nabla U) + 3h^*) \\ &+ \sum_{i\in N} \int_{\Omega_L^i} ((\mu_{Ga_S}^{chem}(1-X_L^i) + \mu_{As_S}^{chem} X_L^i)(3 - \overline{Y}_V) n_G^R (1 - 3\frac{\fint_{I_i} U\cdot\nu}{r_i} + 3h_L^*)) \\ &+ \frac{RT}{B_*^I}(v_{Ga_L}(1-X_L^i) + v_{As_L} X_L^i - w)\cdot \nu_+ n_L^i - 3k_L(\frac{\overline{\rho}_L}{\overline{\rho}_S}(\frac{\fint_{I_i} U\cdot\nu}{r_i} - \delta^R - h_L^*(X_L^i)) \\ &+ 4\pi \sum_{i\in N} r_i^2 (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma.\end{aligned}$$

The (IC) term is bounded where we use $|\dot{r}_i| \leq k$. We let this term now → 0.

Finally with dependencies on variables u, U, r_i and R_{bd}

$$\begin{aligned}\mathcal{A} = &|\Omega|(R_{bd})(p_0 - \overline{p}) \\ &+ \int_{\Omega_S(R_{bd},\{r_i\})} (\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As})(u) n_G^R (1 - \mathrm{tr}(\nabla U) + 3h^*(u)) \\ &+ \frac{4\pi}{3} \sum_{i\in N} r_i^3 ((\mu_{Ga_S}^{chem}(1-X_L^i) + \mu_{As_S}^{chem} X_L^i)(r_i) n_G^R (3 - \overline{Y}_V)(1 - 3\frac{\fint_{I_i} U\cdot\nu}{r_i} + 3h_L^*(X_L(r_i)))) \\ &+ 3k_L(\delta^R + h_L^*(X_L^i)) + 4\pi \sum_{i\in N} r_i^2 [-k_L \frac{\overline{\rho}_L}{\overline{\rho}_S} \fint_{I_i} U\cdot\nu + (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma]\end{aligned} \tag{A.35}$$

or alternatively

$$
\begin{aligned}
\mathcal{A} = {} & |\Omega|(R_{bd})(p_0 - \overline{p}) + \int_{\Omega_S(R_{bd},\{r_i\})} \mu_{Ga_S}^{chem}(u) n_G^R (1 - \operatorname{tr}(\nabla U) + 3h^*(u)) \\
& + \frac{4\pi}{3} \sum_{i \in N} r_i^3 \mu_{Ga_S}^{chem}(r_i) n_G^R (3 - \overline{Y}_V)(1 - 3\frac{\fint_{I_i} U \cdot \nu}{r_i} + 3h_L^*(X_L(r_i)))) \\
& + \int_{\Omega_S(R_{bd},\{r_i\})} [(-\mu_{Ga_S}^{chem} + \mu_{As_S}^{chem}) X_S](u) n_G^R (1 - \operatorname{tr}(\nabla U) + 3h^*(u)) \\
& + \frac{4\pi}{3} \sum_{i \in N} r_i^3 [(-\mu_{Ga_S}^{chem} + \mu_{As_S}^{chem}) X_L^i)(r_i) n_G^R (3 - \overline{Y}_V)(1 - 3\frac{\fint_{I_i} U \cdot \nu}{r_i} + 3h_L^*(X_L(r_i)))) \\
& + 3k_L(\delta^R + h_L^*(X_L^i)) + 4\pi \sum_{i \in N} r_i^2 [-k_L \frac{\overline{\rho}_L}{\overline{\rho}_S} \fint_{I_i} U \cdot \nu + (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma].
\end{aligned}
$$

The last could also be written by formal extension of $\mu_{a_S}^{chem}$ constant onto the liquid and by means of notation of extended h, h^* and X and $n_{\cdot} := n_{S/L}$ as

$$
\begin{aligned}
\mathcal{A} = {} & |\Omega|(p_0 - \overline{p}) + \int_{\Omega} \mu_{Ga_S}^{chem} n_{\cdot}^R (1 - 3h + 3h^*) + \int_{\Omega} (-\mu_{Ga_S}^{chem} + \mu_{As_S}^{chem}) X n_{\cdot}^R (1 - 3h + 3h^*) \\
& + 4\pi \sum_{i \in N} r_i^3 k_L (\delta^R + h_L^*) + 4\pi \sum_{i \in N} r_i^2 [-k_L \frac{\overline{\rho}_L}{\overline{\rho}_S} \fint_{I_i} U \cdot \nu + (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma].
\end{aligned}
$$

We use (A.35) in order to show that $\mathcal{A}$ is bounded. Due to 1) & 2) it suffices to give a bound from below in the case that a solutions exist.

We can estimate the mechanical terms in n_G if we are in approximation of small displacement gradients and if $n_G^R = \mathcal{O}(1)$.

$$
\begin{aligned}
\mathcal{A} \geq {} & |\Omega|(R_{bd})(p_0 - \overline{p}) + \int_{\Omega_S(R_{bd},\{r_i\})} (\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As})(u) n_G^R (1 + \mathcal{O}(\tilde{h})) \\
& + \frac{4\pi}{3} \sum_{i \in N} r_i^3 ((\mu_{Ga_S}^{chem}(1 - X_L^i) + \mu_{As_S}^{chem} X_L^i)(r_i) n_G^R (1 + \mathcal{O}(\tilde{h}))(3 - \overline{Y}_V) \\
& + 3k_L(\delta^R + h_L^*(X_L^i)) + 4\pi \sum_{i \in N} r_i^2 [-k_L \frac{\overline{\rho}_L}{\overline{\rho}_S} \fint_{I_i} U \cdot \nu + (1 - \frac{2}{3}\frac{\overline{\rho}_L}{\overline{\rho}_S})\sigma].
\end{aligned}
$$

The first term is strictly positive since we have $|\Omega| \geq 0$, also the first term with $X_L > \overline{X}_L$. The last term of the last line is bounded below and if $\sigma > 0$ and $\overline{\rho}_L \leq \frac{3}{2}\overline{\rho}_S)$ then this term is nonnegative. The term $\fint_{I_i} U \cdot \nu$ has no sign, but it is bounded by $3k_L \max\{\frac{\overline{p} - p_0}{3k_S}, \frac{2\sigma}{3k_L r_{min}}, \delta^R, h_L^*(X_L), h^*(X_S)\}$. This leaves with $k_L < k_S$, $\sum_{i \in N} |I_i| < |\Omega|$ and $h^* \leq h_L^*$

$$
\begin{aligned}
\mathcal{A} > {} & \int_{\Omega_S(R_{bd},\{r_i\})} (\mu_{Ga_S}^{chem} Y_{Ga} + \mu_{As_S}^{chem} Y_{As})(u) n_G^R (1 + \mathcal{O}(\tilde{h})) \\
& + \frac{4\pi}{3} \sum_{i \in N} r_i^3 ((\mu_{Ga_S}^{chem}(1 - X_L^i) + \mu_{As_S}^{chem} X_L^i)(r_i) n_G^R (1 + \mathcal{O}(\tilde{h}))(3 - \overline{Y}_V) + 4\pi \sum_{i \in N} r_i^3 |\mathcal{O}(\tilde{h})|.
\end{aligned}
$$

The first two terms with chemical potentials are nonnegative since $\overline{X}_L \leq X_L < 1$ and $1 \leq y < \zeta$. Hence

$$
\mathcal{A} > 4\pi \sum_{i \in N} r_i^3 k_L |\mathcal{O}(\tilde{h})| \geq 0 > -\infty.
$$

$\square$

Appendix B.

Transformation on fixed domain

B.1. Construction of a transformation on fixed domain

We construct explicitly a transformation Φ of the type, which we used in Section 4.2.

Therefore we split $\Omega_S^\varepsilon(t)$ in spherical shells around the droplets, $\Sigma_i^\varepsilon(t) = B_{\varepsilon R_{ext}^i(t)}(X_i) \setminus \overline{B_{\varepsilon^3 r_i(t)}(X_i)}$, a boundary layer shell of thickness of order ε around the free outer boundary defined by $\Sigma_0^\varepsilon(t) := B_{R_{bd}(t)}(0) \setminus \overline{B_{R_{bl}(t)}(0)}$, and denote the rest by $F_0^\varepsilon(t) := \Omega_S^\varepsilon(t) \setminus \overline{\cup_{i=0}^{\mathcal{N}} \Sigma_i^\varepsilon(t)}$. In this section we use again the notation of Section 4.2.

We assume that $R_{ext}^i(t)$ are small enough resp. $R_{bl}(t)$ is large enough such that up to time $\mathcal{T}$ neither spherical shells Σ_i^ε intersect each other nor the boundary layer shell and any other shell intersect. Further $\mathcal{T}$ should be small enough that both the boundary layer shell and the other shells have strictly positive thickness.

Now we transform the Σ_i^ε onto the fixed domains $\Sigma_i^\varepsilon(t=0) := B_{\varepsilon R_{ext}^i(0)}(X_i) \setminus \overline{B_{\varepsilon^3 r_i^0}(X_i)}$, $i \in N^\varepsilon$ resp. $\Sigma_0^\varepsilon(t=0) := B_{R_{bd}(t)}(0) \setminus \overline{B_{R_{bl}(0)}(0)}$ and analogously we rescale $\Omega_S^\varepsilon(t)$ onto $\Omega_S^\varepsilon(0) := \Omega(t = 0) \setminus \overline{\cup_{i=1}^{\mathcal{N}} B_{r_i^0}(X_i)}$ by means of

$$\Phi(\cdot, t) : \begin{cases} z \mapsto x := z & , \quad z \in F_0^\varepsilon(t=0), \\ z \mapsto x := q_t(|z|)\frac{z}{|z|} & , \quad z \in \Sigma_0^\varepsilon(t=0), \\ z \mapsto x := X_i + p_t(|z - X_i|)\frac{z-X_i}{|z-X_i|}, & \quad z \in \Sigma_i^\varepsilon(t=0) \,\forall i \in N^\varepsilon, \end{cases}$$

where q_t is a function which fulfils $q_t(R_{bl}(0)) = R_{bl}(t)$, $q_t(R_{bd}(0)) = R_{bd}(t)$ and where p_t is a function which fulfils $p_t(\varepsilon^3 r_i^0) = \varepsilon^3 r^i(t)$, $p_t(\varepsilon R_{ext}^i(0)) = \varepsilon R_{ext}^i(t)$ s.t. q_t resp. p_t are continuous.

In principle we could assume existence of such a transformation Φ since all boundaries are smooth and by decomposition of unity we could locally map balls of the original domain onto the time-dependent domain, analogously we proceed at points close to the boundaries and then put these maps together to get the sought-after Φ. But since Φ is time-dependent and we need in the following $\partial_t \Phi$ to be continuous on $\Omega_S^\varepsilon(0)$ we construct explicitly the transformation. We calculate

$$(D\Phi(z,t))_{ij} := \begin{cases} \delta^{ij} & , \quad z \in F_0^\varepsilon(t=0), \\ \frac{q_t(|z|)}{|z|}(\delta^{ij} - \frac{z_i z_j}{|z|^2}) + \partial_\rho q_t(|z|)\frac{z_i z_j}{|z|^2} & , \quad z \in \Sigma_0^\varepsilon(t=0), \\ \frac{p_t(|z-X_l|)}{|z-X_l|}(\delta^{i,j} - \frac{(z_i-[X_l]_i)(z_j-[X_l]_j)}{|z-X_l|^2}) & \\ +\partial_\rho p_t(|z - X_l|)\frac{(z_i-[X_l]_i)(z_j-[X_l]_j)}{|z-X_l|^2} & , \quad z \in \Sigma_l^\varepsilon(t=0) \,\forall l \in N^\varepsilon. \end{cases}$$

where $1 \leq i, j \leq 3$, hence for continuity of $D\Phi$, $\partial_\rho q_t(R_{bl}(0)) = \partial_\rho p_t(\varepsilon R_{ext}^l(0)) = 1 \,\forall l \in N^\varepsilon$.

Remark: this yields for the metric tensor

$$g_{ij} := \begin{cases} \delta^{ij} & , \quad z \in F_0^\varepsilon(t=0), \\ (\frac{q_t(|z|)}{|z|})^2(\delta^{ij} - \frac{z_i z_j}{|z|^2}) + (\partial_\rho q_t(|z|))^2 \frac{z_i z_j}{|z|^2}, & \quad z \in \Sigma_0^\varepsilon(t=0), \\ (\frac{p_t(|z-X_l|)}{|z-X_l|})^2(\delta^{i,j} - \frac{(z_i-[X_l]_i)(z_j-[X_l]_j)}{|z-X_l|^2}) & \\ +(\partial_\rho p_t(|z-X_l|))^2 \frac{(z_i-[X_l]_i)(z_j-[X_l]_j)}{|z-X_l|^2} & , \quad z \in \Sigma_l^\varepsilon(t=0)\ \forall l \in N^\varepsilon. \end{cases}$$

Furthermore

$$\partial_{kj}\Phi(z,t)_i := \begin{cases} 0 & , z \in F_0^\varepsilon(0), \\ (\partial_\rho q_t(|z|) - \frac{q_t(|z|)}{|z|})(\delta^{i,j} z_k + \delta^{jk} z_i + \delta^{ki} z_j - 3\frac{z_i z_j z_k}{|z|^2})\frac{1}{|z|^2} & \\ +\partial_{\rho,\rho} q_t(|z|)\frac{z_i z_j z_k}{|z|^3} & , z \in \Sigma_0^\varepsilon(0), \\ (\partial_\rho p_t(|z-X_l|) - \frac{p_t(|z-X_l|)}{|z-X_l|})(\delta^{ij}(z_k - [X_l]_k) + \delta^{j,k}(z_i - [X_l]_i) & \\ +\delta^{ki}(z_j - [X_l]_j) - 3\frac{(z_i-[X_l]_i)(z_j-[X_l]_j)(z_k-[X_l]_k)}{|z-X_l|^2})\frac{1}{|z-X_l|^2} & \\ +\partial_{\rho,\rho} p_t(|z-X_l|)\frac{(z_i-[X_l]_i)(z_j-[X_l]_j)(z_k-[X_l]_k)}{|z-X_l|^3} & , z \in \Sigma_l^\varepsilon(0)\ \forall l \in N^\varepsilon, \end{cases}$$

where $1 \leq i,j,k \leq 3$, hence we need $\partial_{\rho,\rho} q_t(R_{bl}(0)) = \partial_{\rho,\rho} p_t(\varepsilon R^l_{ext}(0)) = 0\ \forall l \in N^\varepsilon$.

We introduce as abbreviations for the thickness of the shells $\lambda^i(t) := \varepsilon(R^i_{ext}(t) - \varepsilon^2 r_i(t))$, $\lambda^i_0 := \varepsilon(R^i_{ext}(0) - \varepsilon^2 r^0_i)$, $\lambda^0(t) := R_{bd}(t) - R_{bl}(t)$ and $\lambda^0_0 := R_{bd}(0) - R_{bl}(0)$.

We achieve that Φ is C^2 in space by taking Newton's interpolation with polynomials up to order 3, and get finally

$$q_t(\rho) := R_{bd}(t) - \frac{\lambda^0(t)}{\lambda^0_0}(R_{bd}(0) - \rho)[1 + (\frac{1}{\lambda^0(t)} - \frac{1}{\lambda^0_0})(\rho - R_{bl}(0))(1 - \frac{1}{\lambda^0_0}(\rho - R_{bl}(0)))]$$

resp.

$$p_t(\rho) := \varepsilon^3 r_i(t) + \frac{\lambda^i(t)}{\lambda^i_0}(\rho - \varepsilon^3 r^0_i)[1 + (\frac{1}{\lambda^i_0} - \frac{1}{\lambda^i(t)})(\varepsilon R^i_{ext}(0) - \rho)(1 + \frac{1}{\lambda^i_0}(\varepsilon R^i_{ext}(0) - \rho))]$$

where we can take $\rho \in \mathbb{R}^+$.

We remark, that in principle for $1 \leq k < \infty$ we achieve that Φ is C^k in space by taking Newton's interpolation with polynomials of order $k+1$, with $q_t^{(l)}(R_{bl}(0)) = 0$ and $p_t^{(l)}(\varepsilon R^i_{ext}(0)) = 0$ for $l \geq 2$. We check, that for suitable small ε, we have that $D\Phi > 0$.

Furthermore we want to have $\partial_t q_t(R_{bl}(0)) = \dot{R}_{bl}(t) = 0$ and $\partial_t p_t(\varepsilon R^i_{ext}(0)) = \varepsilon \dot{R}^i_{ext}(t) = 0$ i.e. $R_{bl}(t) := R_{bl}(0)$ resp. $R_{ext}(t) = R_{ext}(0)$ in order to guarantee that the time-derivative of Φ is at least continuous in space and as smooth in time as R_{bd} resp. r_i. We have even that $\partial_t^k \Phi$, $k \geq 0$ are continuous in space

$$\partial_t \Phi(z,t) := \begin{cases} 0 & , \quad z \in F_0^\varepsilon(t=0), \\ \dot{R}_{bd}(t)\partial_{R_{bd}(t)} q_t(|z|)\frac{z}{|z|} & , \quad z \in \Sigma_0^\varepsilon(t=0), \\ \dot{r}_i(t)\partial_{r_i(t)} p_t(|z-X_i|)\frac{z-X_i}{|z-X_i|}, & \quad z \in \Sigma_i^\varepsilon(t=0),\ i \in N^\varepsilon \end{cases}$$

that simplifies to

$$\partial_t \Phi(z,t) := \begin{cases} 0 & , \quad z \in F_0^\varepsilon(t=0), \\ \dot{R}_{bd}(t)(\frac{\rho - R_{bl}(0)}{\lambda^0_0})^3 \frac{z}{|z|} & , \quad z \in \Sigma_0^\varepsilon(t=0), \\ \dot{r}_i(t)(\frac{\varepsilon R^i_{ext}(0) - \rho}{\lambda^i_0})^3 \frac{z-X_i}{|z-X_i|}, & \quad z \in \Sigma_i^\varepsilon(t=0),\ i \in N^\varepsilon. \end{cases}$$

If we want to exploit any specific properties of the transformation Φ we will work in the following with q_t resp. p_t.

Remark: By convolution with suitable mollifiers we could improve the regularity of Φ up to C^∞. It suffices for our purposes to assume that Φ and analogously Φ^{-1} is C^2 in space, because this implies that Christoffel symbols are C^0, and Φ to be as good in time as $\tilde{R}$.

B.2. Transformation of a stress tensor

Now we derive briefly the transformation formulas of the reduced Cauchy stress $\hat{\sigma}_S$ to arbitrary curvilinear coordinates, which are given in detail in [Cia00]. In order to determine the transformation behaviour of this Cauchy stress tensor, we recall its definition:

$$\check{\sigma}_S^{ij}(\nabla U^\varepsilon) := K^{ijkl} e_{ij}(\nabla U^\varepsilon)$$

where the components of the stiffness tensor K are defined by (2.78), which transform contravariantly and in our new coordinates they read

$$\tilde{K}^{ijkl} = \lambda_S g^{ij} g^{kl} + \mu_S (g^{ik} g^{jl} + g^{il} g^{jk}).$$

Hence with (4.24)

$$\tilde{\sigma}_S^{ij}(\nabla \tilde{U}^\varepsilon) = \lambda_S g^{ij} e_{k||l}(\nabla \tilde{U}^\varepsilon)\, g^{kl} + \mu_S (g^{ik} e_{k||l}(\tilde{U}^\varepsilon)\, g^{jl} + g^{il} e_{l||k}(\nabla \tilde{U}^\varepsilon)\, g^{jk}) \tag{B.1}$$

for components, or rewritten

$$\tilde{\sigma}_S(\nabla \tilde{U}^\varepsilon) = \lambda_S g^{-1} (e_{.||.}(\nabla \tilde{U}^\varepsilon) : g^{-1}) + 2\mu_S \operatorname{sym}(g^{-1} e_{.||.}(\nabla \tilde{U}^\varepsilon)\, g^{-T}).$$

Hence the components of the reduced Cauchy stress tensor transform contravariantly, i.e.

$$\check{\sigma}_S(\cdot) = D\Phi^T \tilde{\sigma}_S(\cdot) D\Phi,$$

or written in components we have

$$\check{\sigma}_S^{\tilde{i}\tilde{j}}(\cdot) = [g_{\tilde{i}}]^i \tilde{\sigma}_S^{ij}(\cdot) [g_{\tilde{j}}]^j.$$

B.3. Derivation of the transformed problem for the velocity

Here we derive in details the derivation of the problem for the velocity after transformation on fixed domain, given in (4.30) – (4.32). We do not assume here (2.13) i.e. $v = \partial_t U$ and start with the definition $v = (\mathbb{I}_3 + \nabla U)\partial_t U$. We will see at the end of this section that $\partial_t U = \mathcal{O}(\|\nabla U\|)$ hence we can always work in our approximation of small displacement gradients with

$$v^\varepsilon = \partial_t U^\varepsilon.$$

We examine the dependence of the mechanical BVP in time in order to get a problem for the transformed barycentric velocity field

$$\tilde{v}^\varepsilon = \partial_t \tilde{U}^\varepsilon + D\Phi^{-T} \nabla \tilde{U}^\varepsilon D\Phi^{-1} (\partial_t \tilde{U}^\varepsilon - \partial_t \Phi)$$

or

$$[\tilde{v}^\varepsilon]^i = \partial_t [\tilde{U}^\varepsilon]^i + [g^i(x)]_{\tilde{i}} \tilde{U}^\varepsilon_{\tilde{i}||\tilde{j}} [g^k(x)]_{\tilde{j}} (\partial_t [\tilde{U}^\varepsilon]^k - \partial_t \Phi^k)$$

in the approximation of small displacement gradients.

Therefore we consider difference quotients $\frac{\tilde{U}^\varepsilon(t+h)-\tilde{U}^\varepsilon(t)}{h}$. Then we can exchange the ∇ and the difference quotient and for letting $h \to 0$ we assume that the limits of the right hand sides exist. Hence we can differentiate (4.26) – (4.28) w.r.t. time and find the following problem for $\eta := \partial_t \tilde{U}^\varepsilon$.

$$\begin{aligned}
\tilde{\sigma}_S^{\cdot\cdot}\|_{\cdot}(\nabla\eta) &= -(\text{div }(\partial_t\tilde{\sigma}_S)(\nabla\tilde{U}^\varepsilon) + \partial_t\Gamma^{\cdot}_{pj}\tilde{\sigma}_S^{pj}(\nabla\tilde{U}^\varepsilon) \\
&\quad + \partial_t\Gamma^{j}_{jp}\tilde{\sigma}_S^{\cdot p}(\nabla\tilde{U}^\varepsilon)) \\
&\quad + \partial_t\tilde{f} + 3k_S[h^{*\prime\prime}(\tilde{u}^\varepsilon)D\Phi^{-T}\nabla\tilde{u}^\varepsilon\partial_t\tilde{u}^\varepsilon \\
&\quad + h^{*\prime}(\tilde{u}^\varepsilon)[\partial_t D\Phi^{-T}\nabla\tilde{u}^\varepsilon + D\Phi^{-T}\partial_t\nabla\tilde{u}^\varepsilon]] && \text{in } \Omega_S^\varepsilon(0), \\
\tilde{\sigma}_S(\nabla\eta)\nu &= (-(\partial_t\tilde{\sigma}_S)(\tilde{U}^\varepsilon) + 3k_S h^{*\prime}(\tilde{u}^\varepsilon)\partial_t\tilde{u}^\varepsilon)\nu && \text{on } \partial\Omega(0), \\
(\tilde{\sigma}_S(\nabla\eta) - \frac{3k_L}{\varepsilon^3 r_i}\fint_{I_i^\varepsilon(0)}(\eta\cdot\nu))\nu &= (-(\partial_t\tilde{\sigma}_S)(\nabla\tilde{U}^\varepsilon) + [-\frac{3k_L}{\varepsilon^3 r_i^2}\fint_{I_i^\varepsilon(0)}(\tilde{U}^\varepsilon\cdot\nu) - \frac{2\sigma}{r_i^2} \\
&\quad - 3k_L {h_L^*}'(r_i) + 3k_S h^{*\prime}(u_{int}(r_i))u'_{int}(r_i)]\dot{r}_i)\nu && \text{on } I_i^\varepsilon(0)\ \forall i \in N,
\end{aligned}$$

where

$$\begin{aligned}
(\partial_t\tilde{\sigma}_S)^{ij}(\nabla\tilde{U}^\varepsilon) := \lambda_S[&\partial_t g^{ij} e_{k\|l}(\nabla\tilde{U}^\varepsilon)\, g^{kl} + g^{ij}(\partial_t e)_{k\|l}(\tilde{U}^\varepsilon)\, g^{kl} + g^{ij} e_{k\|l}(\nabla\tilde{U}^\varepsilon)\, \partial_t g^{kl}] \\
+ \mu_S[&\partial_t g^{ik} e_{k\|l}(\nabla\tilde{U}^\varepsilon)\, g^{jl} + g^{ik}(\partial_t e)_{k\|l}(\tilde{U}^\varepsilon)\, g^{jl} + g^{ik} e_{k\|l}(\nabla\tilde{U}^\varepsilon)\, \partial_t g^{jl} \\
+ &\partial_t g^{il} e_{l\|k}(\nabla\tilde{U}^\varepsilon)\, g^{jk} + g^{il}(\partial_t e)_{l\|k}(\tilde{U}^\varepsilon)\, g^{jk} + g^{il} e_{l\|k}(\nabla\tilde{U}^\varepsilon)\, \partial_t g^{jk}]
\end{aligned}$$

and

$$(\partial_t e)_{i\|j}(\tilde{U}^\varepsilon) := -\partial_t\Gamma^q_{ji}\tilde{U}^\varepsilon_q.$$

We see that the r.h.s. of the problem for the velocity depends on data, which is in $\mathcal{O}(\tilde{h})$ if $\partial_t\tilde{u}^\varepsilon$ and $\dot{r}_i$ are bounded pointwise in space. Hence we have $\tilde{v} = \partial_t\tilde{U}^\varepsilon = \eta$ in the approximation of small displacement gradients and hence we can work with $v = \partial_t U^\varepsilon$ in our approximation.

Appendix C.

Single droplet problem

Here we consider a problem of type (SDP) as defined in Section 2.1. We recall that this means $\Omega(t) = B_{R_{bd}(t)}(0)$, $\mathcal{N}^0 = 1$ and $X_1 = 0$. Regarding the notation we write $r_I = r_1$ and $I = I_1$. We define $r = |x - X_1| = |x|$.

C.1. Single droplet problem for regime (DC) – Problem A

We consider the regime (DC) i.e. Problem B, where we replace (2.178) by

$$u = \overline{u}(t) \quad \forall x, |x| = R_{bd}(t) \quad \forall t \in (0, \mathcal{T}) \tag{C.1}$$

with $\overline{u}(t)$ a given function, which is smooth in t and with given time derivative $\dot{\overline{u}}$.

Furthermore we set here $R_{bd}(t) = R_{ext}$ fixed in time. For this two modifications we have in mind to get a formal homogenisation of the many droplet Problem D by coupling single droplet problems together, which communicate only by a mean field $\overline{u}$. This is in done in Section 3.3, in this appendix we derive as far as possible explicit solutions of the single droplet problems. Our single droplet problems play the role of the “cell problems”, which are used in standard homogenisation theory, see e.g. [CD99]. We refer to (3.23) – (3.33) in this case as Problem A.

Since the data is spherically symmetric w.r.t. the origin, all quantities are here in spherical symmetry, too. In the whole of this Appendix C we exploit the spherical symmetry. In particular the mechanical BVP (3.23) – (3.25) can be solved explicitly then. We follow the solution of the mechanical single droplet problem in [DD08] closely, but we do not assume from the beginning, that $r_I/R_{ext} \to 0$.

We work with $\frac{r_I}{R_{ext}} \sim \varepsilon^4$ as in Section 3.1, i.e. we consider the dilute scaling regime, and assume w.l.o.g.

$$r_I \ll \varepsilon^{-4} R_{ext}. \tag{C.2}$$

Furthermore we use the scaling of h^* with ε^9.

C.1.1. Explicit solution of the mechanical BVP

Theorem C.1 (Mechanical BVP for a single droplet in spherical symmetry)**.** *In the case of spherical symmetry we can give an explicit solution formula for U^r_ε in our approximation of small displacement gradients.*

$$U^r_\varepsilon(r) = a^\varepsilon r + \frac{b^\varepsilon}{r^2} + c^\varepsilon_I(r) r, \tag{C.3}$$

where

$$a^\varepsilon = -\frac{(4G_S+3k_L)((4G_S+3k_S)\frac{\overline{p}-p_0}{3k_S} + 4G_S\varepsilon^9 h^*(\overline{u}) + \frac{6(-2G_S+k_S)}{R_{ext}^3}\int_{\varepsilon^4 r_I}^{R_{ext}} z^3\varepsilon^9 h^{*\prime}(u(z))\partial_z u(z)dz)}{(4G_S+3k_S)(-(4G_S+3k_L) + \frac{\varepsilon^9 r_I^3}{R_{ext}^3}4G_S(1-\frac{k_L}{k_S}))}$$

$$+ \frac{\frac{\varepsilon^9 r_I^3}{R_{ext}^3}(4G_S+3k_S)\frac{4G_S}{3k_S}(\frac{2\sigma}{r_I} - 3k_L(\delta^R + h_L^*(r_I)) + (4G_S+3k_L)\varepsilon^9 h^*(u_{int}(r_I)))}{(4G_S+3k_S)(-(4G_S+3k_L) + \frac{\varepsilon^9 r_I^3}{R_{ext}^3}4G_S(1-\frac{k_L}{k_S}))}, \tag{C.4}$$

$$b^\varepsilon := b_I^\varepsilon \varepsilon^9 r_I^3, \tag{C.5}$$

$$b^\varepsilon = \frac{(4G_S+3k_S)(\frac{2\sigma}{r_I} - 3k_L(\delta^R + h_L^*(r_I)) + (4G_S+3k_L)\varepsilon^9 h^*(u_{int}(r_I)))}{(4G_S+3k_S)(-(4G_S+3k_L) + \frac{\varepsilon^{12} r_I^3}{R_{ext}^3}4G_S(1-\frac{k_L}{k_S}))} \tag{C.6}$$

$$- \frac{3(k_S-k_L)((4G_S+3k_S)\frac{\overline{p}-p_0}{3k_S} + 4G_S\varepsilon^9 h^*(\overline{u}) + \frac{6(-2G_S+k_S)}{R_{ext}^3}\int_{\varepsilon^4 r_I}^{R_{ext}} z^3\varepsilon^9 h^{*\prime}(u(z))\partial_z u(z)dz)}{(4G_S+3k_S)(-(4G_S+3k_L) + \frac{\varepsilon^{12} r_I^3}{R_{ext}^3}4G_S(1-\frac{k_L}{k_S}))},$$

$$c_I^\varepsilon(r) := \frac{3k_S}{4G_S+3k_S}\varepsilon^9(h^*(u(r)) - \frac{1}{r^3}\int_{\varepsilon^4 r_I}^{r} z^3 h^{*\prime}(u(z))u'(z)dz). \tag{C.7}$$

The pressure in the liquid is then

$$p_L = \overline{p} - 3k_L(a^\varepsilon + b_I^\varepsilon + c_I^\varepsilon(r_I) - \delta^R). \tag{C.8}$$

Proof. In spherical coordinates σ_S is diagonal. By assuming radial symmetry of U_ε i.e. $U_\varepsilon = (U_\varepsilon^r(r), 0, 0)^T$ we rewrite (2.119)

$$\begin{aligned}
\hat{\sigma}_S^{r,r}(U_\varepsilon) &= (k_S - \frac{2}{3}G_S)(\partial_r U_\varepsilon^r + 2\frac{U_\varepsilon^r}{r}) + 2G_S\partial_r U_\varepsilon^r, \\
\hat{\sigma}_S^{\phi,\phi}(U_\varepsilon) = \hat{\sigma}_S^{\theta,\theta}(U_\varepsilon) &= (k_S - \frac{2}{3}G_S)(\partial_r U_\varepsilon^r + 2\frac{U_\varepsilon^r}{r}) + 2G_S\frac{U_\varepsilon^r}{r}, \\
\hat{\sigma}_S^{r,\phi}(U_\varepsilon) = \hat{\sigma}_S^{r,\theta}(U_\varepsilon) = \hat{\sigma}_S^{\phi,\theta}(U_\varepsilon) &= 0.
\end{aligned}$$

We plug this into (2.173) – (2.175) and get

$$\partial_r\hat{\sigma}_S^{r,r}(U_\varepsilon) + \frac{2}{r}(\hat{\sigma}_S^{r,r}(U_\varepsilon) - \hat{\sigma}_S^{\phi,\phi}(U_\varepsilon)) = 3k_S\varepsilon^9 h^{*\prime}(u)\partial_r u \qquad \forall r \in (\varepsilon^4 r_I, R_{ext}), \tag{C.9}$$

$$\hat{\sigma}_S^{\phi,\phi}(U_\varepsilon) = \hat{\sigma}_S^{\theta,\theta}(U_\varepsilon) \qquad \forall r \in [\varepsilon^4 r_I, R_{ext}], \tag{C.10}$$

$$\hat{\sigma}_S^{r,\phi}(U_\varepsilon) = \hat{\sigma}_S^{r,\theta}(U_\varepsilon) = \hat{\sigma}_S^{\phi,\theta}(U_\varepsilon) = 0 \qquad \forall r \in [\varepsilon^4 r_I, R_{ext}], \tag{C.11}$$

$$\hat{\sigma}_S^{r,r}(U_\varepsilon) = \overline{p} - p_0 + 3k_S\varepsilon^9 h^*(\overline{u}) \qquad r = R_{ext}, \tag{C.12}$$

$$\begin{aligned}
\hat{\sigma}_S^{r,r}(U_\varepsilon) - 3k_L\frac{U_\varepsilon^r}{r_I} &= \frac{2\sigma}{r_I} - 3k_L(\delta^R + h_L^*(r_I)) \\
&\quad + 3k_S\varepsilon^9 h^*(u_{int}(r_I)) \qquad r = \varepsilon^4 r_I.
\end{aligned} \tag{C.13}$$

We abbreviate $g_0 = \overline{p} - p_0$ and $g_1 = \frac{2\sigma}{r_I} - 3k_L(\delta^R + h_L^*(r_I))$. Our problem simplifies to

$$\partial_{r,r}^2 U_\varepsilon^r + 2\frac{\partial_r U_\varepsilon^r}{r} - 2\frac{U_\varepsilon^r}{r^2} = 3k_S\varepsilon^9 h^{*\prime}(u)\partial_r u \qquad \forall r \in (\varepsilon^4 r_I, R_{ext}), \tag{C.14}$$

$$(k_S + \frac{4}{3}G_S)\partial_r U_\varepsilon^r + 2(k_S - \frac{2}{3}G_S)\frac{U_\varepsilon^r}{r} = g_0 + 3k_S\varepsilon^9 h^*(\overline{u}) \qquad r = R_{ext}, \tag{C.15}$$

and

$$(k_S + \frac{4}{3}G_S)\partial_r U^r_\varepsilon + 2(k_S - \frac{2}{3}G_S)\frac{U^r_\varepsilon}{r} - 3k_L \frac{U^r_\varepsilon}{r_I} = g_1 \qquad +3k_S\varepsilon^9 h^*(u_{int}(r_I)))r = \varepsilon^4 r_I. \tag{C.16}$$

Note that with taking (C.3) as ansatz

$$\partial_r U^r_\varepsilon = a^\varepsilon - 2b^\varepsilon_I \frac{\varepsilon^{12} r_I^3}{r^3} + c^\varepsilon_I(r) + c^{\varepsilon\prime}(r)r, \quad \frac{U^r_\varepsilon}{r} = a^\varepsilon + b^\varepsilon_I \frac{\varepsilon^{12} r_I^3}{r^3} + c^\varepsilon_I(r)$$

where $c^\varepsilon_I(r)' = \frac{3k_S}{4G_S+3k_S}\frac{3}{r^4}\int_{\varepsilon^4 r_I}^{r} z^3\varepsilon^9 h^{*\prime}(u(z))\partial_z u(z)dz$. It follows that c^ε_I fulfils the following ODE

$$(k_S + \frac{4}{3}G_S)(c^\varepsilon_I(r)''r + 4c^\varepsilon_I(r)') = 3k_S\varepsilon^9 h^{*\prime}(u)\partial_r u \quad \forall r \in (r_I, \varepsilon^{-4}R_{ext})$$

and see that (C.14) is hence fulfilled in our approximation. From the boundary conditions we get the following linear system of equations for the coefficients a^ε and b^ε

$$\begin{aligned} 3k_S a^\varepsilon - 4G_S\frac{\varepsilon^{12} r_I^3}{R_{ext}^3} b^\varepsilon_I &= g_0 + 3k_S\varepsilon^9 h^*(\overline{u}) - 3k_S c^\varepsilon_I(R_{ext}) - (3k_S + 4G_S)c^\varepsilon_I(R_{ext})'R_{ext}, \\ 3(k_S - k_L)a^\varepsilon - (4G_S + 3k_L)b^\varepsilon_I &= g_1 + 3k_S\varepsilon^9 h^*(u_{int}(r_I) - 3(k_S - k_L)c^\varepsilon_I(\varepsilon^4 r_I)). \end{aligned}$$

With

$$\begin{aligned} c^\varepsilon_I(\varepsilon^4 r_I) &= \frac{3k_S}{4G_S + 3k_S}\varepsilon^9 h^*(u_{int}(r_I)), \\ c^\varepsilon_I(R_{ext}) &= \frac{3k_S}{4G_S + 3k_S}\varepsilon^9 (h^*(\overline{u}) - \frac{1}{R_{ext}^3}\int_{\varepsilon^4 r_I}^{R_{ext}} z^3 h^{*\prime}(u(z))\partial_z u(z)dz). \end{aligned}$$

and $c^{\varepsilon\prime}_I(\varepsilon^4 r_I)$ this yields the linear system of equations for the coefficients a^ε and b^ε_I

$$\begin{aligned} 3k_S a^\varepsilon - 4G_S\frac{\varepsilon^{12} r_I^3}{R_{ext}^3} b^\varepsilon_I &= g_0 + 3k_S\frac{4G_S}{4G_S + 3k_S}\varepsilon^9 h^*(\overline{u}) \\ &\qquad + 18k_S\frac{-2G_S + k_S}{4G_S + 3k_S}\frac{1}{R_{ext}^3}\int_{\varepsilon^4 r_I}^{R_{ext}} z^3\varepsilon^9 h^{*\prime}(u(z))\partial_z u(z)dz, \\ 3(k_S - k_L)a^\varepsilon - (4G_S + 3k_L)b^\varepsilon_I &= g_1 + 3k_S\frac{4G_S + 3k_L}{4G_S + 3k_S}\varepsilon^9 h^*(u_{int}(r_I)) \end{aligned}$$

which has as unique solution

$$\begin{aligned} a^\varepsilon = &-\frac{(4G_S + 3k_L)(g_0 + 3k_S\frac{4G_S}{4G_S+3k_S}\varepsilon^9 h^*(\overline{u}) + 18k_S\frac{-2G_S+k_S}{4G_S+3k_S}\frac{1}{R_{ext}^3}\int_{\varepsilon^4 r_I}^{R_{ext}} z^3\varepsilon^9 h^{*\prime}(u(z))\partial_z u(z)dz)}{-3k_S(4G_S + 3k_L) + \frac{\varepsilon^{12} r_I^3}{R_{ext}^3}12G_S(k_S - k_L)} \\ &+ \frac{\frac{\varepsilon^{12} r_I^3}{R_{ext}^3}4G_S(g_1 + 3k_S\frac{4G_S+3k_L}{4G_S+3k_S}\varepsilon^9 h^*(u_{int}(r_I)))}{-3k_S(4G_S + 3k_L) + \frac{\varepsilon^{12} r_I^3}{R_{ext}^3}12G_S(k_S - k_L)} \\ b^\varepsilon_I = &\frac{3k_S(g_1 + 3k_S\frac{4G_S+3k_L}{4G_S+3k_S}\varepsilon^9 h^*(u_{int}(r_I)))}{-3k_S(4G_S + 3k_L) + \frac{\varepsilon^{12} r_I^3}{R_{ext}^3}12G_S(k_S - k_L)} \\ &- \frac{3(k_S - k_L)(g_0 + 3k_S\frac{4G_S}{4G_S+3k_S}\varepsilon^9 h^*(\overline{u}) + 18k_S\frac{-2G_S+k_S}{4G_S+3k_S}\frac{1}{R_{ext}^3}\int_{\varepsilon^4 r_I}^{R_{ext}} z^3\varepsilon^9 h^{*\prime}(u(z))\partial_z u(z)dz}{-3k_S(4G_S + 3k_L) + \frac{\varepsilon^{12} r_I^3}{R_{ext}^3}12G_S(k_S - k_L)} \end{aligned}$$

which simplifies to (C.4) and (C.6). By (C.8) we have a unique formula to determine p_L. $\square$

We calculate with the help of our result the densities in the solid

$$\rho_S = \overline{\rho}_S(1 - \operatorname{tr}(\nabla U)) = (M_{Ga}Y_{Ga_\alpha}(1) + M_{As}Y_{As}(1))n_G^R(1 - 3a^\varepsilon) \tag{C.17}$$

and in the liquid, respectively,

$$\rho_L = \overline{\rho}_L(1 - 3a_L^\varepsilon) = M(\overline{X}_L)n_L^R(1 - 3a_L^\varepsilon) = (M_{Ga}(1 - \overline{X}_L) + M_{As}\overline{X}_L)(3 - \overline{Y}_V)n_G^R(1 - 3(a^\varepsilon + b_I^\varepsilon)).$$

We see that under the Assumption 2.1 the displacement gradient ∇U_ε is of order $\mathcal{O}(\tilde{h})$ and hence consistent in our approximation.

With assuming as in the mean field model that $u \approx \overline{u}$ far away from droplets, see Subsect. 3.3.3, we have

$$\begin{aligned}
|\frac{1}{r^3}\int_{\varepsilon^4 r_I}^r z^3 h^{*\prime}(u(z))\partial_z u(z)dz| &\leq \frac{1}{r^3}\int_{\varepsilon^4 r_I}^r z^3|h^{*\prime}(u(z))\partial_z u(z)|dz \\
&\leq \frac{\varepsilon^4 r_I}{r^3}\int_{\varepsilon^4 r_I}^r z^3|h^{*\prime}(u(z))|\frac{|\overline{u} - u_{int}(z)|}{z^2}dz \\
&\leq \frac{\varepsilon^4 r_I}{r}\frac{1}{2}(1 - \frac{\varepsilon^8 r_I^2}{r^2}) \sup_{z\in(\varepsilon^4 r_I, R_{ext})} |h^{*\prime}(u(z))|(|\overline{u} - u_{int}(z)|) \\
&\leq \varepsilon^4 Const \qquad\qquad \text{for } r \gg \varepsilon^4 r_I.
\end{aligned}$$

Together with the assumption (C.2) our formulas (C.3) – (C.6) simplify in leading order in ε, where we keep for the moment the h^* terms, to

$$U^r(r) = ar + b_I\frac{\varepsilon^{12}r_I^3}{r^2} + c_I(r)r$$

where

$$a = \frac{\overline{p} - p_0}{3k_S} + \frac{4G_S}{4G_S + 3k_S}\varepsilon^9 h^*(\overline{u}) \tag{C.18}$$

$$\begin{aligned}
b_I = \frac{b}{\varepsilon^{12}r_I^3} = &\frac{3(k_S - k_L)\frac{\overline{p}-p_0}{3k_S} - \frac{2\sigma}{r_I} + 3k_L(\delta^R + h_L^*(r_I)) + 3(k_S - k_L)\frac{4G_S}{4G_S+3k_S}\varepsilon^9 h^*(\overline{u}))}{4G_S + 3k_L} \\
&- \frac{3k_S}{4G_S + 3k_S}\varepsilon^9 h^*(u_{int}(r_I)),
\end{aligned} \tag{C.19}$$

$$c_I(r) := \frac{3k_S}{4G_S + 3k_S}\varepsilon^9(h^*(u(r)) - \frac{1}{r^3}\int_{\varepsilon^{12}r_I}^r z^3 h^{*\prime}(u(z))u'(z)dz). \tag{C.20}$$

In leading order in ε we find

$$\hat{\sigma}_S^{<r,r>} = -4G_S b_I\frac{r_I^3}{r^3} \overset{r=r_I}{=} -4G_S b_I, \tag{C.21}$$

$$\rho_S = (M_{Ga}Y_{Ga_\alpha}(1) + M_{As}Y_{As}(1))n_G^R(1 - 3a) \tag{C.22}$$

$$\rho_L = M(\overline{X}_L)(3 - \overline{Y}_V)n_G^R(1 - 3(a + b_I)) \tag{C.23}$$

which will be needed for the formally homogenised problem. We find according to (2.111)

$$a_L = a + b_I + c_I(r_I) - \delta^R = \frac{(4G_S + 3k_S)\frac{\overline{p}-p_0}{3k_S} - \frac{2\sigma}{r_I} - 4G_S\delta^R + 3k_L h_L^*(r_I))}{4G_S + 3k_L}. \tag{C.24}$$

Hence the leading order terms in ε are identical to the formulas in [DD08].

C.1.2. Boundary conditions on interfaces for single droplet problem

We consider (2.133) and (2.134) in case of a spherically symmetric single droplet problem,

$$u_{int}^{\varepsilon}(r_I) = (\tilde{u}^{chem})^{-1}[\tilde{u}_L^{chem}(X_L(r_I)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I}], \tag{C.25}$$

$$\begin{aligned} 0 = \tilde{u}_L^{chem}(X_L(r_I)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} - \tilde{u}^{chem}(u_L^{chem}(X_L(r_I)) \\ + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}(h_L^*(X_L(r_I)) - a_L^{\varepsilon}(X_L(r_I), r_I, \overline{u}, u_{int}^{\varepsilon}(r_I)))). \end{aligned} \tag{C.26}$$

We explicitly solve (C.26) for $X_L(r_I)$ in our approximation. In particular we have $(X_L - \overline{X}_L) = \mathcal{O}(\tilde{h}^{1/2})$ and approximate $X_L \approx \overline{X_L}$ in the term $h_L^* - a_L$. We approximate

$$a_L^{\varepsilon}(X_L(r_I), r_I, \overline{u}, u_{int}^{\varepsilon}(r_I)))) \approx a_L(\overline{X}_L, r_I),$$

with a_L as defined in (C.24). Furthermore we use twice $h_L^* = 0$ for $X_L = \overline{X}_L$ and thus the h_L^* term drops out in a_L. Hence we approximate by

$$0 = \tilde{u}_L^{chem}(X_L(r_I)) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} - \tilde{u}^{chem}(u_L^{chem}(X_L(r_I)) - \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}a_L(r_I)). \tag{C.27}$$

We follow our arguments given in Appendix A.5 and use the spherical symmetry. This allows us to give an approximation in leading order in ε of X_L and u_{int}. We prove

Lemma C.1 (Well-posedness of boundary conditions on interfaces for a single droplet)**.**
Let

$$-\frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}a_L(r_I)) > 0. \tag{C.28}$$

1) If $r_I > r_{min} \geq \frac{2\sigma}{4G_S+3k_L}$, $\overline{X}_L \geq \frac{1}{2}$, $1 > \tilde{\mu} > \frac{1}{3}$ and $\tilde{m} > 1$, then exists a unique solution to $(u_{int}, X_L) \in \mathcal{J}_u \times \mathcal{J}_{X_L}$, as defined in (2.125) *and* (2.124)*, of the interface conditions (2.128) and (2.129) for all parameters $r_I \in \mathcal{J}_r := (r_{min}, \infty)$.*

2) u_{int} and X_L depend smoothly on r_I and are strictly monotone decreasing in r_I in our approximation from Assumption 2.1.

We see that the assumptions of the lemma are fulfilled for typical values of the material data, see Appendix D.

The statement of the lemma corresponds to the numerics in the study of Dreyer and Duderstadt [DD08], who consider different temperatures.

Proof. We define the function

$$\Phi(X_L; r_I) := \tilde{u}_L^{chem}(X_L) - \frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} - \tilde{u}^{chem}(u_L^{chem}(X_L) - \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}a_L(r_I)) \tag{C.29}$$

and show by means of the intermediate value theorem, that Φ has a zero.

We calculate now that Φ is strictly monotone in X_L. By deriving Φ w.r.t. X_L we get

$$\partial_{X_L}\Phi(X_L; r_I) = \tilde{u}_L^{chem\prime}(X_L) - \tilde{u}^{chem\prime}(u_L^{chem}(X_L) - \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}a_L(r_I))u_L^{chem\prime}(X_L). \tag{C.30}$$

According to (A.10) and (A.11) we have $\mu_{As}^{chem\prime}(y) > 0$ and $\mu_{Ga}^{chem\prime}(y) < 0$. For ease of presentation we introduce

$$c(u) := -\frac{\mu'_{Ga}(y(u))}{\mu'_{As}(y(u))} > 1,$$

where the inequality is due to (A.9) with $\tilde{\mu} < 1$. We calculate

$$\tilde{u}^{chem\prime}(u) = \tilde{u}^{chem\prime}(y(u))y'(u) = \frac{\tilde{u}^{chem\prime}(y(u))}{u'(y(u))} = \frac{1 + \frac{1}{\tilde{m}}c(u)}{1 + \frac{1}{\tilde{\mu}}c(u)},$$

that can be bounded if $\tilde{m} > \tilde{\mu} > 0$ i.e.

$$\tilde{\mu} < \frac{1 + \frac{1}{\tilde{m}}c(u)}{1 + \frac{1}{\tilde{\mu}}c(u)} < \tilde{u}^{chem\prime}(u) < \frac{\tilde{m}+1}{\tilde{\mu}+1}\frac{\tilde{\mu}}{\tilde{m}} < 1 \tag{C.31}$$

since $\partial_c \frac{1+\frac{1}{\tilde{m}}c}{1+\frac{1}{\tilde{\mu}}c} < 0$.

We use the estimate (C.31) in (C.30)

$$\partial_{X_L}\Phi(X_L; r_I) > \tilde{u}_L^{chem\prime}(X_L) - \frac{\tilde{m}+1}{\tilde{\mu}+1}\frac{\tilde{\mu}}{\tilde{m}} u_L^{chem\prime}(X_L) > 0, \tag{C.32}$$

which follows from the definitions of $\tilde{u}_L^{chem}$ and u_L^{chem} and $\tilde{m} > 1$.

We consider the range of Φ and start with plugging in $\overline{X}_L$

$$\Phi(\overline{X}_L; r_I) := -\frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} - \tilde{u}^{chem}(-\frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}a_L(r_I)), \tag{C.33}$$

where we use $u_L^{chem}(\overline{X}_L) = 0$ and $\tilde{u}_L^{chem}(\overline{X}_L) = 0$. We point out, that the argument of $\tilde{u}^{chem}$ is of order $\mathcal{O}(\tilde{h})$. We insert the expansion of $\tilde{u}^{chem}$ around $u = 0$, $\tilde{u}^{chem}(u) = u\mathcal{A}(y)$ (see (A.9))

$$\Phi(\overline{X}_L; r_I) := -\frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I} + \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}a_L(r_I)) < 0, \tag{C.34}$$

due to our assumption (C.28).

Since $-\ln(1 - X_L) \to \infty$ as $X_L \to 1-$ we can estimate for some fixed r_I and δ sufficiently small

$$\Phi(1-\delta; r_I) > -\frac{RT}{\tilde{m}}\ln(\delta) + \frac{RT}{\tilde{\mu}}\ln(\delta) + const$$

where the constant is independent of δ. Since $\tilde{\mu} < \tilde{m}$ this is strictly positive for small enough δ.

Furthermore Φ is strictly monotone in r_I. We use (C.24)

$$\partial_{r_I}\Phi(X_L; r_I) = (\frac{1}{\overline{n}_{As}} - \tilde{u}^{chem\prime}(u_L^{chem}(X_L) - \frac{3k_L}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}a_L(r_I))\frac{1}{\overline{n}_L}\frac{1-\tilde{\mu}}{\tilde{\mu}}\frac{3k_L}{4G_S + 3k_L})\frac{2\sigma}{r_I^2} > 0, \tag{C.35}$$

where the estimate follows by (C.31) and (C.28).

By the implicit function theorem applied to $\Phi(X_L; r_I) = 0$ we find smooth dependence of the explicit function X_L on r_I and since $\partial_{r_I}\Phi(X_L; r_I) < 0$ this yields the monotone decreasing behaviour of X_L w.r.t. r_I by the chain rule: We have on one hand

$$\frac{d}{dr_I}\Phi^{-1}(\Phi(X_L; r_I); r_I) = \partial_{r_I}1 = 0,$$

on the other hand

$$\partial_{r_I}\Phi^{-1}(\Phi(X_L;r_I);r_I)+\partial_{X_L}\Phi^{-1}(\Phi(X_L;r_I);r_I)\partial_{r_I}\Phi(X_L;r_I)$$

and this implies with (C.35)

$$\partial_{r_I}\Phi^{-1}(\Phi(X_L;r_I);r_I)=-\partial_{X_L}\Phi^{-1}(\Phi(X_L;r_I))\partial_{r_I}\Phi(X_L;r_I)<0.$$

We have furthermore $\lim_{r_I\to\infty}X_L(r_I)\geq\overline{X}_L-\tilde{h}$ and $\lim_{r_I\to\infty}u_{int}(r_I)\geq u(y=1-\tilde{h})$. ☐

Our lemma focused on arsenic-rich droplets i.e. we consider $\mathcal{J}_{X_L}=(\overline{X}_L(1-\tilde{h}),1)$. We remark, that also gallium-rich droplets with $X_L<\frac{1}{2}$ exist for a suitable choice of material constants.

Finally we give approximate solution formulas for X_L and u_{int} by Taylor expansions around the reference configuration and compare it with the classical Gibbs-Thomson law. We assume $\tilde{u}^{chem\prime}(u)=\frac{1+\frac{1}{\tilde{m}}}{1+\frac{1}{\tilde{\mu}}}$, which holds for sufficiently small $\overline{Y}$, and we linearise (C.27)

$$\begin{aligned}0&=\tilde{u}_L^{chem}(\overline{X}_L)+(X_L-\overline{X}_L)\tilde{u}_L^{chem\prime}(\overline{X}_L)-\frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I}-\tilde{u}^{chem}(u_L^{chem}(\overline{X}_L))\\&\quad-(X_L-\overline{X}_L)\frac{1+\frac{1}{\tilde{m}}}{1+\frac{1}{\tilde{\mu}}}u_L^{chem\prime}(\overline{X}_L),\end{aligned}$$

what yields with $u_L^{chem}(\overline{X}_L)=0$

$$X_L=\overline{X}_L+\frac{1}{\tilde{u}_L^{chem\prime}(\overline{X}_L)-\frac{1+\frac{1}{\tilde{m}}}{1+\frac{1}{\tilde{\mu}}}u_L^{chem\prime}(\overline{X}_L))}\frac{1}{\overline{n}_{As}}\frac{2\sigma}{r_I}.$$

This is of the form

$$X_L(r_I)=\overline{X}_L+c_1\frac{2\sigma}{r_I},\tag{C.36}$$

with the constant $c_1=\frac{1}{\tilde{u}_L^{chem\prime}(\overline{X}_L)-\frac{1+\frac{1}{\tilde{m}}}{1+\frac{1}{\tilde{\mu}}}u_L^{chem\prime}(\overline{X}_L)}\frac{1}{\overline{n}_{As}}$. Note, that the constant c_1 is strictly positive.

From (C.25) we find

$$u_{int}(r_I)=u(y=1+c_1\frac{2\sigma}{r_I})\tag{C.37}$$

or

$$y_{int}(r_I)=1+c_1\frac{2\sigma}{r_I}.\tag{C.38}$$

Note that the classical Gibbs-Thomson law $u_{int}=\frac{2\sigma}{r_I}$ ($u_{int}\approx\frac{1+\tilde{\mu}}{\tilde{\mu}}\ln(y_{int})$), see (A.17)), which is considered up to a factor in the Mullins-Sekerka model is just an approximation of a first order Taylor expansion of the general case. Note that we do not make use of this expansion at all.

C.1.3. Stefan condition for single droplet problem

We emphasise that we consider the single droplet problem for fixed external radius R_{ext}. From (C.3) we get an explicit formula for v,

$$v=\partial_t U_\varepsilon^r(r)e_r=[\partial_t a^\varepsilon+(\partial_t b_I^\varepsilon r_I+3b_I^\varepsilon\dot{r}_I)\frac{\varepsilon^{12}r_I^2}{r^3}+\partial_t c_I^\varepsilon(r)]re_r\tag{C.39}$$

With the abbreviations

$$\begin{aligned}\mathcal{Y}(r, r_I, \overline{u}) &= \partial_{r_I} b_I^\varepsilon + 3b_I^\varepsilon \frac{\varepsilon^{12} r_I^3}{r^3} + \partial_{r_I} c_I^\varepsilon(r),\\ \mathcal{Z}(r, r_I, \overline{u}) &= \partial_{\overline{u}} a^\varepsilon + \partial_{\overline{u}} b_I^\varepsilon \frac{\varepsilon^{12} r_I^3}{r^3} + \partial_{\overline{u}} c_I^\varepsilon(r),\end{aligned}$$

we can rewrite (C.39) as

$$v = (\mathcal{Y}(r, r_I, \overline{u})\dot{r}_I + \mathcal{Z}(r, r_I, \overline{u})\dot{\overline{u}}) r e_r. \tag{C.40}$$

On the interface this simplifies to

$$\begin{aligned}v|_{I_i} \cdot e_r &= [(\partial_{r_I} b_I^\varepsilon + \frac{3}{r_I} b_I^\varepsilon + \partial_{r_I} c_I^\varepsilon(r))\dot{r}_I + (\partial_{\overline{u}} a^\varepsilon + \partial_{\overline{u}} b_I^\varepsilon + \partial_{\overline{u}} c_I^\varepsilon(r))\dot{\overline{u}}] r_I\\ &= [\mathcal{Y}(r = r_I, r_I, \overline{u})\dot{r}_I + \mathcal{Z}(r = r_I, r_I, \overline{u})\dot{\overline{u}}] r_I.\end{aligned} \tag{C.41}$$

C.1.4. Diffusion problem for single droplet problem

Under our assumptions for a single droplet problem we can simplify (3.26) – (3.33) and get as the diffusion problem of **Problem A**

$$\begin{aligned}&\varepsilon\mathcal{X}(u(r,t), r_I, \overline{u}) \times (\partial_t u(r,t)\\ &+(\mathcal{Y}(r, r_I, \overline{u})\dot{r}_I + \mathcal{Z}(r, r_I, \overline{u})\dot{\overline{u}}) r \partial_r u(r,t))\\ &-(\frac{2}{r}\partial_r + \partial^2_{r,r})u(r,t) = 0 \qquad \forall r \in (\varepsilon^4 r_I(t), R_{ext}) \quad \forall t \in (0, \mathcal{T}) &\text{(C.42)}\\ &u(r_I(t), t) = u_{int}(r_I(t)) \qquad \forall t \in (0, \mathcal{T}), &\text{(C.43)}\\ &u(R_{ext}, t) = \overline{u}(t) \qquad \forall t \in (0, \mathcal{T}), &\text{(C.44)}\\ &u(r, t = 0) = u^0(r) \qquad \forall r \in (\varepsilon^4 r_I^0, R_{ext}) &\text{(C.45)}\end{aligned}$$

with free boundary $r_I(t)$. The motion of the free boundary is determined by the ODE

$$\begin{aligned}\dot{r}_I &= \varepsilon^4 \frac{\partial_r u(r_I(t), t)}{\mathbb{X}(r_I)} \qquad \forall t \in (0, \mathcal{T}), &\text{(C.46)}\\ r_I(t = 0) &= r_I^0. &\text{(C.47)}\end{aligned}$$

Since in case of the geometry (SDP) we can solve the mechanical BVP explicitly for given r_I and u, we have plugged in U and v in leading order term in ε into the diffusion problem, the boundary condition on the interface and the Stefan condition. We now solve formally the diffusion problem (C.42) – (C.45) coupled to the ODE (C.46) for the radii by transformation on fixed domain and an ansatz of an asymptotic expansion.

We remark again that we seek solutions of the diffusion problem $\Omega_\mathcal{T}$ where the time $\mathcal{T}$ has to be chosen such that $r_{min} < r_I < R_{ext}$ i.e. neither the droplet nor the solid vanishes.

In order to get rid of the difficulties with the time-dependent domain we transform our problem on fixed domain. We proceed similar as described in Appendix B.1.

We rescale $\Omega_S(t) = B_{R_{ext}}(0)\backslash\overline{B_{r_I(t)}(0)}$ onto the fixed domain $\Omega_S(0) := B_{R_{ext}}(0)\backslash\overline{B_{r_I(0)}}$ by applying the dilation

$$\psi_t : \rho \mapsto r := \psi_t(\rho) = \varepsilon^4 r_I(t) + \frac{R_{ext} - \varepsilon^4 r_I(t)}{R_{ext} - \varepsilon^4 r_I^0}(\rho - \varepsilon^4 r_I^0)$$

with

$$\partial_\rho \psi_t(\rho) = \frac{R_{ext} - \varepsilon^4 r_I(t)}{R_{ext} - \varepsilon^4 r_I^0} =: \Lambda(t).$$

We get as transformed problem

$$\begin{aligned}
&\varepsilon \mathcal{X}(\tilde{u}^\varepsilon(\rho,t), r_I, \overline{u})(\Lambda(t)\partial_t \tilde{u}^\varepsilon(\rho,t)\\
&\quad -\partial_\rho \tilde{u}^\varepsilon(\rho,t)((-\varepsilon^4 \frac{\rho - \varepsilon^4 r_I^0}{R_{ext} - \varepsilon^4 r_I^0}\\
&\quad -(\tilde{\mathcal{Y}}(\rho, r_I, \overline{u})\dot{r}_I + \tilde{\mathcal{Z}}(\rho, \overline{u}, r_I)\dot{\overline{u}})\rho)))\\
&\qquad -(\frac{2}{\rho}\partial_\rho + \partial^2_{\rho,\rho})\tilde{u}^\varepsilon(\rho,t) = 0 \qquad \forall \rho \in (\varepsilon^4 r_I^0, R_{ext}) \quad \forall t \in (0,\mathcal{T}),\\
&\tilde{u}^\varepsilon(r_I^0, t) = u_{int}(r_I(t)) \qquad \forall t \in (0,\mathcal{T}), \qquad (C.48)\\
&\tilde{u}^\varepsilon(R_{ext}, t) = \overline{u}(t) \qquad \forall t \in (0,\mathcal{T}), \qquad (C.49)\\
&\tilde{u}^\varepsilon(\rho, t=0) = u^0(\rho) \qquad \forall r \in (\varepsilon^4 r_I^0, R_{ext}). \qquad (C.50)
\end{aligned}$$

The function $r_I(t)$, which enters as parameter in the PDE, is determined by the ODE

$$\begin{aligned}
\dot{r}_I &= \varepsilon^4 \frac{\Lambda^{-1}\partial_\rho \tilde{u}^\varepsilon(r_I(t),t)}{\mathbb{X}(r_I)} && \forall t \in (0,\mathcal{T}), && (C.51)\\
r_I(t=0) &= r_I^0. && && (C.52)
\end{aligned}$$

The existence and uniqueness of a solution $\tilde{u}^\varepsilon \in C^1C^2, r_I \in C^1$ of (C.48) – (C.52) for all $t < \mathcal{T}$ follows from Th. 4.8 for initial data $u^0 \in H^1$.

For a formal solution we try an ansatz of an asymptotic expansion in ε

$$\tilde{u}^\varepsilon(\rho,t) = \tilde{u}_A(\rho,t) + \varepsilon \tilde{u}_B(\rho,t) + \mathcal{O}(\varepsilon^2).$$

According to our asymptotics for $\mathcal{X}$ in Appendix A.4 $\mathcal{X}$ is smooth, bounded and has bounded derivatives w.r.t. u. Hence we develop $\mathcal{X}$ around $\tilde{u}_A$ as $\mathcal{X}(\tilde{u}_A + \varepsilon\tilde{u}_B) = \mathcal{X}(\tilde{u}_A) + \varepsilon \tilde{u}_B \mathcal{X}'(\tilde{u}_A) + \mathcal{O}(\varepsilon^2)$.

We plug u^ε into (C.48) – (C.52) and get by neglecting higher order terms in ε

$$\begin{aligned}
(\frac{2}{\rho}\partial_\rho + \partial^2_{\rho,\rho})\tilde{u}_A(\rho,t) &= 0 && \forall \rho \in (\varepsilon^4 r_I^0, R_{ext}) \quad \forall t \in (0,\mathcal{T}),\\
\tilde{u}_A(r_I^0, t) &= u_{int}(r_I(t)) && \forall t \in (0,\mathcal{T}),\\
\tilde{u}_A(R_{ext}, t) &= \overline{u}(t) && \forall t \in (0,\mathcal{T}),
\end{aligned}$$

where $t \in (0,\mathcal{T})$. The solution $\tilde{u}_A$ of this standard problem is

$$\begin{aligned}
\tilde{u}_A(\rho,t) &= \frac{R_{ext}\overline{u}(t) - \varepsilon^4 r_I^0 u_{int}(r_I(t))}{R_{ext} - \varepsilon^4 r_I^0} - \frac{\overline{u}(t) - u_{int}(r_I(t))}{\rho}\frac{R_{ext}\varepsilon^4 r_I^0}{R_{ext} - \varepsilon^4 r_I^0}\\
&= \overline{u}(t) - \frac{\overline{u}(t) - u_{int}(r_I(t))}{\rho}\varepsilon^4 r_I^0 + \mathcal{O}(\varepsilon^4).
\end{aligned} \qquad (C.53)$$

Since the time derivative drops out on our time scale, the initial conditions does not enter in the problem for $\tilde{u}_A$. The initial condition can be fulfilled by asymptoting matching, but we are here only interested in times t of order ε^0. Let us assume that

$$u^0(\rho,t) = \tilde{u}_A(\rho,0) = \frac{R_{ext}\overline{u}(0) - \varepsilon^4 r_I^0 u_{int}(r_I^0)}{R_{ext} - \varepsilon^4 r_I^0} - \frac{\overline{u}(0) - u_{int}(r_I^0)}{\rho}\frac{R_{ext}\varepsilon^4 r_I^0}{R_{ext} - \varepsilon^4 r_I^0}. \qquad (C.54)$$

Since in the problem for $\tilde{u}_A$ time enters only as a parameter we can transform the problem back on time-dependent domain and calculate an explicit solution there, too.

We put (C.53) into (C.51) and get in leading order in ε

$$\dot{r}_I = \frac{\overline{u}(t) - u_{int}(r_I(t))}{r_I^0 \mathbb{X}(r_I)} \frac{R_{ext}}{R_{ext} - \varepsilon^4 r_I(t)} = \frac{\overline{u}(t) - u_{int}(r_I(t))}{r_I^0 \mathbb{X}(r_I)} + \mathcal{O}(\varepsilon^4) \qquad \forall t \in (0, \mathcal{T}). \tag{C.55}$$

In next order in ε we have to solve the following problem for $\tilde{u}_B$

$$(\frac{2}{\rho}\partial_\rho + \partial^2_{\rho,\rho})\tilde{u}_B(\rho,t) = f_B(\rho,t) \qquad \forall \rho \in (\varepsilon^4 r_I^0, R_{ext}) \quad \forall t \in (0,\mathcal{T}) \tag{C.56}$$

$$\tilde{u}_B(r_I^0, t) = u_{B,int}(r_I(t), \overline{u}(t)) \qquad \forall t \in (0,\mathcal{T}), \tag{C.57}$$

$$\tilde{u}(R_{ext}, t) = 0 \qquad \forall t \in (0,\mathcal{T}), \tag{C.58}$$

where we use (C.54) and where

$$\begin{aligned} f_B(\rho,t) &= \Lambda(t)\mathcal{X}(\tilde{u}_A(\rho,t), r_I, \overline{u})(\partial_t \tilde{u}_A(\rho,t) + \Lambda^{-1}(t)\partial_\rho \tilde{u}_A(\rho,t)(\tilde{\mathcal{Y}}(\rho, r_I, \overline{u}))\dot{r}_I) \\ &= \mathcal{X}(\tilde{u}_A(\rho,t), r_I, \overline{u})(u'_{int}(r_I(t))\frac{\varepsilon^4 r_I^0}{\rho}\dot{r}_I - \frac{\overline{u} - u'_{int}(r_I)}{\rho}\varepsilon^4 r_I^0(\tilde{\mathcal{Y}}(\rho, r_I, \overline{u}))\dot{r}_I) + \mathcal{O}(\varepsilon) \end{aligned}$$

is given since $\tilde{u}_A$ has been determined by (C.53). Furthermore we remind that $\dot{\overline{u}} \sim \varepsilon^0$.

$\tilde{u}_B$ solves a standard elliptic problem with smooth data, which is further independent of ε, $\tilde{u}_B$ is smooth and bounded uniformly in ε. Since in the problem for $\tilde{u}_B$ time enters only as a parameter we could transform the problem back on time-dependent domain and calculate an explicit solution there.

Since we found a simple Laplace equation with homogeneous Dirichlet boundary conditions we see that there exists a unique v_1 for each time $t \in (0, \mathcal{T})$.

If a droplet shrinks or growths depends in first order on the sign of $u_\Delta(t) := \overline{u}(t) - u_{int}(r_I(t))$. We see smooth dependence of solution $\tilde{u}_A$ on r_I and $\overline{u}$.

C.2. Single droplet problem in regime (IC) – Problem AI

The diffusion problem in regime (DC) is easily solved since we find $u = \overline{u}(t)$, which is constant in space. The mechanical boundary value problem is solved as for regime (DC), unless that the coefficient c_I^ε or c_I can be simplified to

$$c_I = c_I^\varepsilon = \varepsilon^9 \frac{3k_S}{4G_S + 3k_S} h^*(\overline{u}(t)). \tag{C.59}$$

and hence does not depend on r, which is contrary to regime (DC).

Appendix D.

Nomenclature

Here we give a compilation about the most important symbols, abbreviations, physical constants and material data, which we use. Unless otherwise mentioned all material parameters and parameters in experiments are given for $T = 1100$ K.

Symbol	Declaration
Geometry	
x	Eulerian coordinates of $\Omega_S(t) \subset \mathbb{R}^3$
$\mathbf{X}$	Lagrangian coordinates of $\Omega_S(0) \subset \mathbb{R}^3$
z	Coordinates of $\Omega_S(0) \subset \mathbb{R}^3$, which are linked to x by the transformation Φ
t	$\in \mathbb{R}_0^+$, time
$\mathcal{T}$	maximal time t, until which the model is considered
τ_i	point in time, when droplet i vanishes
$N(t)$	Index set of all liquid droplets, which exist at time t
$\mathcal{N}(t)$	$= \lvert N(t) \rvert$, number of liquid droplets existing at time t
$\Omega(t)$	Open bounded time-dependent domain in $\mathbb{R}^3$ representing the GaAs wafer
$\Omega_S(t)$	Simply connected open subset of Ω, solid part
$\Omega_L(t)$	Open subset of Ω, liquid part
$\Omega_L^i(t)$	Connected open subset of Ω, the liquid droplet with index $i \in N(t)$
$I_i(t)$	$:= \partial\Omega_L^i$, interface between droplet i and the solid
$I(t)$	Union of all interfaces $I_i(t)$, $i \in N(t)$
X_i	Fixed centre of droplet $i \in N(0)$
$R_{bd}(t)$	External radius if Ω is spherical
$r_i(t)$	Radius of interface I_i, $i \in N(t)$ if Ω_L is spherical
R_{ext}^i	Fixed external radius around a droplet centre, modelling its “influence”
$\mathbb{I}_S(x)$	The characteristic function of a set S, which is 1 if $x \in S$ and 0 if $x \notin S$
$\mathbb{I}_3$	$:= \delta^{ij}$, $1 \leq i, j \leq 3$, identity matrix in 3 dimensions
ν	Outer normal of a surface
τ_l	Tangential vectors of a surface
k_M	$:= -\text{div}\,\nu$, mean curvature of a surface

Symbol	**Declaration**
Operators	
∂_t	Partial derivative w.r.t. t
$\frac{d}{dt}$	Total derivative w.r.t. t
∇	$:= (\partial_{x_1}, \partial_{x_2}, \partial_{x_3})$, the Nabla operator
Δ	$:= \sum_{i=1}^{3} \partial_{x_i}^2$, the Laplace operator
D_t	$:= \partial_t + v \cdot \nabla$, the convective derivative, where v is a velocity of transport
tr	$:= \sum_{i=1}^{3} A^{ii}$, trace of a matrix A^{ij}, $1 \leq i, j \leq 3$
Variables and some dependent quantities	
$\tilde{U}$	Mechanical displacement in Lagrangian coordinates (for the definition see (2.10))
U	Mechanical displacement in Eulerian coordinates (for the def. see (2.10))
$\tilde{v}$	Barycentric velocity in Lagrangian coordinates
v	Barycentric velocity in Eulerian coordinates
u	"total" chemical potential, i.e. a linear combination of chemical potentials in the solid defined in (2.91), which appears in the diffusion fluxes j_{As} and j_{Ga}
$\mathcal{A}$	Available free energy (or availability) of the system
σ_S	Cauchy stress tensor
p	Pressure
a_L	scalar factor of the elastic deformation gradient matrix in the liquid, which is a multiple of $\mathbb{I}$
h^*	scalar factor of the inelastic deformation gradient matrix in the liquid/solid, which is a multiple of $\mathbb{I}$
n_{As}	Mole density of As atoms in the solid
X_S	Arsenic mole fraction in the solid
X_L	Arsenic mole fraction in the liquid
SL	Subset of sublattices in a solid GaAs crystal
$\mathbf{a_S}$	Subset of species in the solid GaAs crystal
$\mathbf{a_L}$	Subset of species in a liquid GaAs droplet
n_a	Mole density of atoms of species "a", $a \in \mathbf{a_S} \cup \mathbf{a_L}$
$\mathcal{X}$	$:= n'_{As}(u)$, appears in the diffusion equation, when we consider n_{As} as function of u
Ξ	$:= n_{As}(u)$, appears in the diffusion equation, when we consider n_{As} as function of u
$\mathbb{X}$	Abbreviation of the denominator of the Stefan condition for regime (DC)
$\mathbb{Z}$	Abbreviation of the denominator of the Stefan condition for regime (IC)
Natural constants	
R	$= 8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}$ universal gas constant
N_A	$= 6.0221 \cdot 10^{23}\,\mathrm{mol^{-1}}$ Avogadro's constant

Symbol	Declaration
Material data (cf. [DD08])	
M_{As}	$\approx 74.922\,\mathrm{g\,mol}^{-1}$, mole mass of arsenic
M_{Ga}	$\approx 69.723\,\mathrm{g\,mol}^{-1}$, mole mass of gallium
$\sigma(T)$	Surface tension of liquid GaAs, we use $\sigma \approx 7.5 \cdot 10^{-2}\mathrm{N\ m}^{-1}$ as guess as in [DD08]
$G_S(T)$	Shear modulus of crystalline GaAs within the isotropic approximation, $G_S \approx 3.5364 \cdot 10^{10}\ \mathrm{Nm}^{-2}$ for $T \approx 900\,\mathrm{K} - 1200\,\mathrm{K}$
$k_S(T)$	Bulk modulus of crystalline GaAs, $k_S \approx 7.5 \cdot 10^{10}\ \mathrm{N\,m}^{-2}$ for $T \approx 900\,\mathrm{K} - 1200\,\mathrm{K}$
$k_L(T)$	Bulk modulus of liquid GaAs, $k_L(T = 1100\,\mathrm{K}) \approx 6.25 \cdot 10^{9}\ \mathrm{N\,m}^{-2}$
$L_0(T)$ L_1	$\left.\begin{array}{l} = (-25485 - 4.4\,T\,\mathrm{K}^{-1})\ \mathrm{J\,mol}^{-1} \\ = 5174.7\ \mathrm{J\,mol}^{-1} \end{array}\right\}$ Redlich-Kister coefficients
The arsenic-rich reference standard system (cf. [DD08])	
X_0	$\approx 0.5 + 8.2 \cdot 10^{-5}$, mean mole fraction of arsenic for semi-insulating behaviour
$\overline{X}_L(T)$	≈ 0.9386, mole fraction of As in the liquid for the reference standard system
$\overline{X}_S(T)$	mole fraction of As in the solid for the reference standard system, can be calculated with $\overline{Y}_a$, $a \in \mathbf{a_S}$ from $X_S(y = 1)$
$\overline{Y}_{(As_\gamma)}(T)$	$\approx 1.0710 \cdot 10^{-4}$, lattice occupancy for interstitial As
$\overline{Y}_{V_\beta}(T)$	$\approx 2.1225 \cdot 10^{-17}$
$\overline{Y}_{V_\alpha}(T)$	$\approx 1.0300 \cdot 10^{-24}$
$\overline{Y}_{As_\alpha}(T)$	$\approx 8.2193 \cdot 10^{-7}$
$\overline{Y}_V(T)$	$= \sum_{a \in SL} \overline{Y}_{V_a} \approx 1 - 1.0710 \cdot 10^{-4}$, concentration of vacancies w.r.t. to sublattice places for the reference standard system
$\overline{\rho}_L(T)$	density of liquid GaAs, $\overline{\rho}_L(T = 1100\,\mathrm{K}) = \overline{n}_L M(\overline{X}_L) \approx 5.220 \cdot 10^{3}\ \mathrm{kg\,m}^{-3}$
$\overline{\rho}_S(T)$	density of pure crystal GaAs, $\overline{\rho}_S(T = 1100\,\mathrm{K}) \approx 5.351 \cdot 10^{3}\ \mathrm{kg\,m}^{-3}$
$\overline{n}_G(T)$	$\approx 37000\,\mathrm{mol\,m}^{-3}$, number density of sublattice places for the reference standard system
$\overline{n}_L(T)$	$\approx 70000\,\mathrm{mol\,m}^{-3}$, number density of atoms in the liquid for the reference standard system
$\delta^R(T)$	misfit parameter, calculated according to (2.110)
$\overline{p}(T)$	$\approx 1.7471 \cdot 10^{6}\ \mathrm{N\,m}^{-2}$, pressure in the reference standard system
Typical experimental data	
p_0	$\approx 10^{7}\ \mathrm{N\,m}^{-2}$, typical outer pressure used in experiments
D	$\approx 10^{-12}\ \mathrm{m}^2\,\mathrm{s}^{-1}$, diffusion constant, as given by Steinegger [Ste01]
$B^{(D)}$	$\approx 3.7 \cdot 10^{-8}\ \mathrm{mol\,m}^{-1}\,\mathrm{s}^{-1}$, mobility of interstitial GaAs in the bulk
B^I	$\approx 9.8 \cdot 10^{6}\ \mathrm{mol\,m}^{-2}\mathrm{s}^{-1}$, "common" interface mobility corresponding to (2.62) $\approx 10^{-23}\ \mathrm{mol\,m}^{-2}\mathrm{s}^{-1}$, as used for simulations in Section 6.6
N_0^R	typical number of atoms in a box with side length $\mathcal{D}_0$, $N_0^R = \frac{4\pi}{3}((\mathcal{D}_0/2)^3 - \mathcal{R}_0^3)\,2\overline{n}_G + \frac{4\pi}{3}\mathcal{R}_0^3\overline{n}_L \approx 3.9 \cdot 10^{-14}\ \mathrm{mol}$

Symbol	Declaration
Auxiliary quantities	
C_1	$= \overline{Y}_{V_\alpha}\overline{Y}_{V_\beta}\overline{Y}_{V_\gamma} \approx 2.1857 \cdot 10^{-41}$
C_2	$= \overline{Y}_{(As_\gamma)}\overline{Y}_{V_\beta}/(\overline{Y}_{V_\gamma}\overline{Y}_{As_\beta}) \approx 5.2775 \cdot 10^{-21}$
C_3	$= \overline{Y}_{As_\alpha}\overline{Y}_{V_\beta}/(\overline{Y}_{V_\alpha}\overline{Y}_{As_\beta}) \approx 1.6937 \cdot 10^{1}$
$\tilde{\mu}$	$= \frac{M_{Ga}}{M_{As}} \approx 0.9309$, relation of mole mass of gallium to arsenic
$\tilde{m}$	$= \frac{1-M_{Ga}\frac{\overline{n}_L}{\overline{\rho}_S}}{1-M_{As}\frac{\overline{n}_L}{\overline{\rho}_S}} \approx 4.3683$, a parameter that appears often e.g. in Subsection 2.6.3
ϱ	$= 1 - \frac{\overline{\rho}_L}{\overline{\rho}_S} \approx 2.43572 \cdot 10^{-2}$, useful for comparing $[[\rho]]$ against $\mathcal{O}(\tilde{h})$
Typical scales	
ε	scaling parameter
ε_0	$= 10^{-3/2}$ (critical regime), $= 10^{-1}$ (dilute regime), scaling parameter which corresponds to original system
$\mathcal{L}$	$= \varepsilon^0$, scaling of the initial outer boundary R^0_{bd}
$\mathcal{D}$	$= \varepsilon$, scaling of the mean value of initial distances between droplet centres d_{ij}, $i, j \in N(0)$
$\mathcal{R}$	$= \varepsilon^3$, scaling of the mean value of initial radii r^0_i, $i \in N(0)$
$\mathcal{L}_0$	between $3.16 \cdot 10^{-4}$ m and 10^{-5} m, typical length of the initial outer boundary R^0_{bd} in the original system
$\mathcal{D}_0$	$= 10^{-6}$ m, typical length of all initial distances between droplet centres d_{ij}, $i, j \in N(0)$ in the original system
$\mathcal{R}_0$	$= 10^{-9}$ m, typical length of all initial radii r^0_i, $i \in N(0)$ in the orig. system
$\mathcal{D}_\mathcal{M}$	mean value over d_{ij}, $i, j \in N(0)$ of a distribution ν^t_ε, with dimensions
$\mathcal{R}_\mathcal{M}$	mean value over r^0_i, $i \in N(0)$ of a distribution ν^t_ε, with dimensions
Quantities in the homogenisation	
$\textstyle\sum_{i\in N^\varepsilon}$	$:= \varepsilon^3/\mathcal{N}^0_0 \textstyle\sum_{i\in N^\varepsilon}$, a sum over droplets normalised to the initial number of droplets
ν^t_ε	Distribution of droplets for fixed ε
ν^t	Limit distribution of droplets as $\varepsilon \to 0$
$\overline{u}$	Mean field of u of the formal homogenisation
u^∞	Mean field of u of the rigorous homogenisation

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Selbständigkeitserklärung

Hiermit erkläre ich, dass ich die vorliegende Dissertation

Macroscopic diffusion models for precipitation in crystalline gallium arsenide

selbständig und ohne unerlaubte Hilfe angefertigt habe.

Berlin, den 20. April 2009

Sven-Joachim Kimmerle