Weierstraß-Institut
für Angewandte Analysis und Stochastik
Leibniz-Institut im Forschungsverbund Berlin e. V.

Preprint ISSN 0946 – 8633

Modelling compressible electrolytes with phase transition

Wolfgang Dreyer[1], Jan Giesselmann[2], Christiane Kraus[1]

submitted: May 26, 2014

[1] Weierstrass Institute
Mohrenstr. 39
10117 Berlin
Germany
E-Mail: Wolfgang.Dreyer@wias-berlin.de
Christiane.Kraus@wias-berlin.de

[2] University of Stuttgart
Department of Mathematics
Pfaffenwaldring 57
70569 Stuttgart
Germany
E-Mail: giesselmann@ians.uni-stuttgart.de

No. 1955
Berlin 2014

2010 *Mathematics Subject Classification.* 78A57, 80A17, 92E20, 35C20, 35R35, 76T10, 76T30, 35Q30, 35Q35, 76D45, 76N10, 76T99, 76A02, 80A22, 82B26, 34B15.

Key words and phrases. Multi-component flow, phase transition, electrochemical reactions, partial balances, entropy principle, asymptotic analysis, sharp interface limit, free boundary problems, Poisson-Boltzmann, Allen-Cahn equation, Navier-Stokes system, Euler system.

C.K. would like to thank the DFG Research Center “Mathematics for Key Technologies” MATHEON in Berlin (Germany) for supporting this project.

Edited by
Weierstraß-Institut für Angewandte Analysis und Stochastik (WIAS)
Leibniz-Institut im Forschungsverbund Berlin e. V.
Mohrenstraße 39
10117 Berlin
Germany

Fax: +49 30 2044975
E-Mail: preprint@wias-berlin.de
World Wide Web: http://www.wias-berlin.de/

Abstract

A novel thermodynamically consistent diffuse interface model is derived for compressible electrolytes with phase transitions. The fluid mixtures may consist of N constituents with the phases liquid and vapor, where both phases may coexist. In addition, all constituents may consist of polarizable and magnetizable matter. Our introduced thermodynamically consistent diffuse interface model may be regarded as a generalized model of Allen–Cahn/Navier–Stokes/Poisson type for multi-component flows with phase transitions and electrochemical reactions. For the introduced diffuse interface model, we investigate physically admissible sharp interface limits by matched asymptotic techniques. We consider two scaling regimes, i.e. a non-coupled and a coupled regime, where the coupling takes place between the smallness parameter in the Poisson equation and the width of the interface. We recover in the sharp interface limit a generalized Allen-Cahn/Euler/Poisson system for mixtures with electrochemical reactions in the bulk phases equipped with admissible interfacial conditions. The interfacial conditions satisfy, for instance, a generalized Gibbs-Thomson law and a dynamic Young–Laplace law.

1 Introduction

In this study, we propose a model for chemically reacting viscous fluid mixtures that may develop a transition between a liquid and a vapor phase. The mixture consists of N constituents which may consist of polarizable and magnetizable matter. The system is described by N partial mass balance equations, a single equation of balance for the barycentric momentum and an equation of Poisson type. To describe phase transitions, we introduce an artificial phase field indicating the present phase by assigning the values 1 and -1 to the liquid and the vapor phase, respectively. Within the transition layer between two adjacent phases, the phase field smoothly changes between 1 and -1. However, usually the transition layers are very thin leading to steep gradients of the phase field.

This model belongs to the class of diffuse interface models. An alternative model class, that likewise represents phase transitions in fluid mixtures, contains sharp interface models. From the modeling point of view, sharp interface models have a simpler physical basis than diffuse interface models. For this reason, there arises always the non-trivial question if the sharp interface limits of a given diffuse model lead to admissible sharp interface models.

While diffuse interface models solve partial differential equations in the transition region, sharp interface models deal with jump conditions across the interface between the phases. Sometimes the jump conditions are mixed with geometric partial differential equations.

For the isothermal and quasi-static setting of electrodynamics, our newly introduced diffuse interface model is given by the following system of PDEs for the partial mass densities ρ_α, the barycentric velocity $\boldsymbol{v}$, the phase field parameter χ and the electrical potential φ, where the equation for ρ_N is replaced by the evolution equation for $\rho = \sum_{\alpha=1}^N \rho_\alpha$:

$$
\begin{aligned}
0 =& \partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \boldsymbol{v}) - \operatorname{div}\Bigg(\sum_{\beta=1}^{N-1} M_{\alpha\beta} \Big(\nabla \frac{\mu_\beta - \mu_N}{T} + \frac{1}{T}\Big(\frac{z_\beta e_0}{m_\beta} - \frac{z_N e_0}{m_N} \Big) \nabla \varphi \Big) \Bigg) \\
& - \sum_{i=1}^{N_R} m_\alpha \gamma_\alpha^i M_{\mathrm{r}}^i \Bigg(1 - \exp\Bigg(\frac{1}{kT} \sum_{\beta=1}^{N} m_\beta \gamma_\beta^i \mu_\beta \Bigg) \Bigg), \qquad \alpha = 1, ..., N-1, \\
0 =& \partial_t \rho + \operatorname{div}(\rho \boldsymbol{v}), \\
0 =& \partial_t (\rho \boldsymbol{v}) + \operatorname{div}(\rho \boldsymbol{v} \otimes \boldsymbol{v}) + \nabla \Bigg(\sum_{\alpha=1}^N \rho_\alpha \mu_\alpha - \rho f - W - \frac{\gamma}{2} |\nabla \chi|^2 \Bigg) + \gamma \operatorname{div}(\nabla \chi \otimes \nabla \chi) \\
& - \operatorname{div}(\boldsymbol{\sigma}^{\mathrm{NS}}) + \varepsilon_0 \operatorname{div}\left((1 + s(\chi)) \left(\frac{1}{2} |\nabla \varphi|^2 \mathbf{1} - \nabla \varphi \otimes \nabla \varphi \right) \right), \\
0 =& \partial_t \chi + \boldsymbol{v} \cdot \nabla \chi + \frac{\tau}{\rho} \left(W' - \gamma \Delta \chi + \frac{\partial(\rho f)}{\partial \chi} - \frac{\varepsilon_0}{2} s'(\chi) |\nabla \varphi|^2 \right), \\
0 =& \varepsilon_0 \operatorname{div}((1 + s(\chi)) \nabla \varphi) + n^{\mathrm{F}},
\end{aligned}
$$

where $M_{\alpha\beta}$, M_{r}^i are the mobilities, μ_α the chemical potentials, T is the temperature, m_α the atomic mass, e_0 the elementary charge, ε_0 is the vacuum permittivity, the numbers z_α are integers and k is the Boltzmann constant. The system is based on the following free energy

$$
\rho \psi := W(\chi) + \frac{\gamma}{2} |\nabla \chi|^2 + h(\chi) \rho \psi_{\mathrm{L}}(\rho_1, \ldots, \rho_N) + (1 - h(\chi)) \rho \psi_{\mathrm{V}}(\rho_1, \ldots, \rho_N) - \frac{\varepsilon_0}{2} s(\chi) |\boldsymbol{E}|^2,
$$

where $W(\chi) := (\chi - 1)^2 (\chi + 1)^2$, $\rho\psi_{\mathrm{L}}, \rho\psi_{\mathrm{V}}$ are the free energy functions of the pure phases, $\boldsymbol{E}$ is the electric field and $h : \mathbb{R} \to [0, 1]$ is a smooth interpolation function satisfying

$$
h(z) = \begin{cases} 1 & \text{for} \quad z \geq 1, \\ 0 & \text{for} \quad z \leq -1, \end{cases}
$$

such that $h'(z) = 0$ for all $|z| \geq 1$. Similarly, we assume

$$
s(\chi) = h(\chi) s_{\mathrm{L}} + (1 - h(\chi)) s_{\mathrm{V}},
$$

where $s_{\mathrm{L/V}}$ are the susceptibilities of the pure phases. For brevity, we define

$$
\begin{aligned}
(\rho f)((\rho_\alpha)_\alpha, \chi) &:= (\rho f)(\rho_1, \ldots, \rho_N, \chi) \\
&:= h(\chi) \rho \psi_{\mathrm{L}}(\rho_1, \ldots, \rho_N) + (1 - h(\chi)) \rho \psi_{\mathrm{V}}(\rho_1, \ldots, \rho_N).
\end{aligned}
$$

By definition, the chemical potentials are given by

$$
\mu_\alpha := \frac{\partial(\rho \psi)}{\partial \rho_\alpha} = \frac{\partial(\rho f)}{\partial \rho_\alpha}.
$$

In addition, $n^{\mathrm{F}} := e_0 \sum_{\alpha=1}^N \frac{z_\alpha}{m_\alpha} \rho_\alpha$ is the free charge density, $\boldsymbol{\sigma}^{\mathrm{NS}}$ denotes the Navier-Stokes stress and τ, γ are (positive) constants.

If electrical effects are neglected, our compressible model for multi-phase flows reduces to an Allen–Cahn/Navier–Stokes type model which has been studied in [11]. Moreover, in case there is only one constituent (undergoing liquid-vapor phase transitions) this model is quite similar to the model derived by Blesgen [8]. Blesgen's model has been investigated analytically in

[16, 13], where existence of strong local-in-time solutions and weak solutions has been shown. A modified version of Blesgen's model can be found in [25].

Related to our work *without chemical reactions* are diffuse interface models for incompressible and quasi-incompressible fluids. A diffuse interface model of Navier-Stokes-Cahn-Hilliard type for two incompressible, viscous Newtonian fluids, having the same densities, has been introduced by Hohenberg and Halperin in [15]. That model has been modified in several thermodynamically consistent ways such that different densities are allowed, see e.g. [14, 18, 4]. For existence results of strong local-in-time solutions and weak solutions, we refer to [1, 2, 3]. A diffuse interface model for two incompressible constituents which permits the transfer of mass between the phases due to diffusion and phase transitions has been proposed in [6, 5]. The densities of the fluids may be different, which leads to quasi–incompressibility of the mixture.

The work is organized as follows. In the upcoming section we derive the thermodynamically consistent model for multi-component flows with phase transitions and electrochemical reactions, which is the main contribution of this work. The third section is devoted to the non-dimensionalization, the introduction of two interesting scaling regimes of the system and the setting of asymptotic analysis. Finally, in Sections 5 and 6, we determine the sharp interface limits for the two different scaling regimes introduced previously.

2 The electrolyte model

Constituents and phases. We consider a fluid mixture consisting of N constituents A_1, $A_2, ..., A_N$ indexed by $\alpha \in \{1, 2, ..., N\}$. The constituents have (atomic) masses $(m_\alpha)_{\alpha=1,2,...,N}$ and may be carrier of charges $(z_\alpha e_0)_{\alpha=1,2,...,N}$. The constant e_0 is the elementary charge and the numbers z_α are positive or negative integers including the value zero. All constituents may consist of polarizable and magnetizable matter.

The fluid mixture may exist in the two phases liquid(L) and vapor(V). The two phases may coexist. In this paper, we describe the phases in the diffuse interface setting, where the interface between adjacent liquid and vapor phases is modeled by a thin layer. Within the layer, certain thermodynamic quantities smoothly change from values in one phase to different values in the adjacent phase. However, usually steep gradients occur.

Among the N constituents we have neutral molecules and positive and negative ions which are the products of dissociation reactions. There are N_R reactions, indexed by $i \in \{1, 2, ..., N_R\}$, of the general type

$$a_1^i A_1 + a_2^i A_2 + ... + a_N^i A_N \rightleftarrows b_1^i A_1 + b_2^i A_2 + ... + b_N^i A_N. \tag{2.1}$$

The constants $(a_\alpha^i)_{\alpha=1,2,...,N}$ and $(b_\alpha^i)_{\alpha=1,2,...,N}$ are positive integers and $\gamma_\alpha^i = b_\alpha^i - a_\alpha^i$ denote the stoichiometric coefficients of the reaction i.

Basic quantities and basic variables. Two phase mixtures can be modeled within three different model classes, denoted by Class I - Class III. Class I considers as basic variables the number densities $(n_\alpha)_{\alpha=1,2,...,N}$ of the constituents, the barycentric velocity $\boldsymbol{v}$, the temperature T of the mixture, the electromagnetic field $(\boldsymbol{E}, \boldsymbol{B})$ and the phase field χ. The basic variables of Class II are the number densities $(n_\alpha)_{\alpha=1,2,...,N}$, the velocities $(\boldsymbol{v}_\alpha)_{\alpha=1,2,...,N}$ of the constituents, the temperature T, the electromagnetic field $(\boldsymbol{E}, \boldsymbol{B})$ and the phase field χ. Finally, in Class III we have the number densities $(n_\alpha)_{\alpha=1,2,...,N}$, the velocities $(\boldsymbol{v}_\alpha)_{\alpha=1,2,...,N}$, the temperatures $(T_\alpha)_{\alpha=1,2,...,N}$ of the constituents, the electromagnetic field $(\boldsymbol{E}, \boldsymbol{B})$ and the phase field χ. In this study, we choose a description within Class I.

The mixture occupies a region $\Omega \subset \mathbb{R}^3$. At any time $t \geq 0$, the thermodynamic state of the mixture is described by N partial mass densities $(\rho_\alpha)_{\alpha=1,2,\dots,N}$, the barycentric velocity $\boldsymbol{v}$, the temperature T of the mixture and the electromagnetic field $(\boldsymbol{E}, \boldsymbol{B})$. These quantities may be functions of time $t \geq 0$ and space $\boldsymbol{x} = (x_i)_{i=1,\dots,3} = (x_1, x_2, x_3)$. However, the magnetic field and the temperature as variables appear only in the modeling part (Section 2). Finally, we restrict ourselves to isothermal processes and, moreover, we ignore magnetic fields so that $\boldsymbol{B}$ is omitted and T appears only as a constant parameter in the equations.

In order to indicate the present phase at $(t, \boldsymbol{x})$, we introduce the so called phase field χ as a further basic variable. The phase field assumes values in the interval $[-1, 1]$ with $\chi = 1$ in the liquid and $\chi = -1$ in the vapor.

Multiplication of the number densities by m_α and $e_0 z_\alpha$, respectively, gives the partial mass densities and the partial free charge densities:

$$\rho_\alpha = m_\alpha n_\alpha, \qquad n_\alpha^{\mathrm{F}} = e_0 z_\alpha n_\alpha. \tag{2.2}$$

Multiplication of the velocities by $n_\alpha m_\alpha$ and $n_\alpha z_\alpha e_0$, respectively, gives the mass fluxes and the free currents:

$$\boldsymbol{j}_\alpha = \rho_\alpha \boldsymbol{v}_\alpha, \qquad \boldsymbol{j}_\alpha^F = e_0 z_\alpha \boldsymbol{v}_\alpha n_\alpha. \tag{2.3}$$

The mass density of the mixture and the barycentric velocity are defined by

$$\rho = \sum_{\alpha=1}^{N} \rho_\alpha, \qquad \boldsymbol{v} = \frac{1}{\rho} \sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{v}_\alpha. \tag{2.4}$$

Non-convective mass fluxes and non-convective currents are defined by

$$\boldsymbol{J}_\alpha = \rho_\alpha \boldsymbol{u}_\alpha, \qquad \boldsymbol{J}_\alpha^{\mathrm{F}} = \frac{z_\alpha e_0}{m_\alpha} \boldsymbol{J}_\alpha, \quad \text{where} \quad \boldsymbol{u}_\alpha = \boldsymbol{v}_\alpha - \boldsymbol{v} \tag{2.5}$$

denotes the diffusion velocity. The definitions $(2.5)_{1,3}$ imply the identity

$$\sum_{\alpha=1}^{N} \boldsymbol{J}_\alpha = 0 \ . \tag{2.6}$$

Total free charge density and total free current are calculated by

$$n^{\mathrm{F}} = \sum_{\alpha=1}^{N} n_\alpha^{\mathrm{F}}, \qquad \boldsymbol{j}^{\mathrm{F}} = n^{\mathrm{F}} \boldsymbol{v} + \sum_{\alpha=1}^{N} \boldsymbol{J}_\alpha^{\mathrm{F}} \ . \tag{2.7}$$

The application of Maxwell's theory to continuous matter shows that the total electric charge density n^{e} and the total electric current $\boldsymbol{j}^{\mathrm{e}}$ consist of two additive contributions. We write

$$n^{\mathrm{e}} = n^{\mathrm{F}} + n^{\mathrm{P}}, \qquad \boldsymbol{j}^{\mathrm{e}} = \boldsymbol{j}^{\mathrm{F}} + \boldsymbol{j}^{\mathrm{P}}. \tag{2.8}$$

Besides free charge densities and free currents there are charge densities and currents due to polarization and magnetization [20].

$$n^{\mathrm{P}} = -\mathrm{div}(\boldsymbol{P}), \qquad \boldsymbol{j}^{\mathrm{P}} = \frac{\partial \boldsymbol{P}}{\partial t} + \mathrm{curl}(\boldsymbol{P} \times \boldsymbol{v} + \boldsymbol{M}) \ , \tag{2.9}$$

where $\boldsymbol{P}$ and $\boldsymbol{M}$ denote the vectors of polarization and magnetization, respectively. Polarization embodies phenomena that are caused by microscopic charges, for example, atomic dipoles within atoms and molecules. Microscopic currents are macroscopically represented by the magnetization vector.

Finally, we introduce the total number density of the mixture and the atomic fractions of the constituents.

$$n = \sum_{\alpha=1}^{N} n_\alpha, \qquad y_\alpha = \frac{n_\alpha}{n} \quad \text{with} \quad \sum_{\alpha=1}^{N} y_\alpha = 1 \ . \tag{2.10}$$

Equations of balance for matter. The basic variables are determined by a coupled system of partial differential equations relying on the quasi-static Maxwell equations and balance equations for matter. At first we introduce the balance equations for matter within the Class I model where we need the partial equations of balance for the mass of the constituents and the balance equations for the momentum and energy of the mixture. They read

$$\partial_t \rho_\alpha + \mathrm{div}(\rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) = r_\alpha, \qquad \alpha = 1, 2, ..., N, \tag{2.11}$$

$$\partial_t(\rho \boldsymbol{v}) + \mathrm{div}(\rho \boldsymbol{v} \otimes \boldsymbol{v} - \boldsymbol{\sigma}) = \rho \boldsymbol{b} + \boldsymbol{k}, \tag{2.12}$$

$$\partial_t\Big(\rho e + \frac{\rho}{2}|\boldsymbol{v}|^2\Big) + \mathrm{div}\Big((\rho e + \frac{\rho}{2}|\boldsymbol{v}|^2)\boldsymbol{v} + \boldsymbol{q} - \boldsymbol{v}\cdot\boldsymbol{\sigma}\Big) = \rho \boldsymbol{b}\cdot\boldsymbol{v} + \pi. \tag{2.13}$$

Moreover, we propose a balance equation for the phase field,

$$\partial_t(\rho\chi) + \mathrm{div}(\rho\chi\boldsymbol{v} + \boldsymbol{J}_\chi) = \xi_\chi. \tag{2.14}$$

Besides the basic variables and the diffusion fluxes from the last paragraph there occur new quantities (here): r_α - mass production of constituent A_α, $\boldsymbol{\sigma}$ - stress, ρe - internal energy density, $\boldsymbol{q}$ - heat flux, $\boldsymbol{J}_\chi$ - non-convective flux of the phase field, ξ_χ - phase field production. The force density is decomposed into two different types: $\rho\boldsymbol{b}$ - force density due to gravitation and inertia, $\boldsymbol{k}$ - Lorentz force density due to electromagnetic fields. Likewise the power of force is decomposed into: $\rho\boldsymbol{b}\cdot\boldsymbol{v}$ - power due to gravitation and inertia, π - power due to Joule heat. In the following, we neglect the force density $\boldsymbol{b}$ and set $\boldsymbol{b} = 0$.

Forward and backward reactions contribute to the mass production rate of constituent A_α. The corresponding reactions rates R^i_f and R^i_b give the number of forward and backward reactions per volume and per time. We write

$$r_\alpha = \sum_{i=1}^{N_\mathrm{R}} m_\alpha \gamma^i_\alpha (R^i_\mathrm{f} - R^i_\mathrm{b}). \tag{2.15}$$

The conservation of charge and mass for every single reaction $i \in \{1, 2, ..., N_\mathrm{R}\}$ reads

$$\sum_{\alpha=1}^{N} z_\alpha \gamma^i_\alpha = 0 \quad \text{and} \quad \sum_{\alpha=1}^{N} m_\alpha \gamma^i_\alpha = 0, \quad \text{implying} \quad \sum_{\alpha=1}^{N} r_\alpha = 0. \tag{2.16}$$

The condition $(2.16)_3$ represents the conservation law of total mass.

Summing up the partial mass balances (2.11) yields the total mass balance of the mixture, i.e.

$$\partial_t \rho + \mathrm{div}(\rho\boldsymbol{v}) = 0. \tag{2.17}$$

Herein, the definitions (2.4) and the conditions $(2.16)_3$ and (2.6) have been used.

A short reminder on Maxwell's equations. The determination of the electromagnetic field $(\boldsymbol{E}, \boldsymbol{B})$ relies on Maxwell's equations. They can be written as, [20],

$$\partial_t \boldsymbol{B} + \mathrm{curl}(\boldsymbol{E}) = 0, \qquad \mathrm{div}(\boldsymbol{B}) = 0, \tag{2.18}$$

$$-\frac{1}{c^2}\partial_t \boldsymbol{E} + \mathrm{curl}(\boldsymbol{B}) = \mu_0 \boldsymbol{j}^\mathrm{e}, \qquad \mathrm{div}(\boldsymbol{E}) = \frac{1}{\varepsilon_0} n^\mathrm{e}. \tag{2.19}$$

The electric and magnetic constants are related to the speed of light by $c^2 = 1/(\varepsilon_0\mu_0)$. The total electric charge density n^{e} and the total electric current density $\boldsymbol{j}^{\mathrm{e}}$ are given by the representations (2.7)–(2.10).

Suitable multiplications of Maxwell's equations by $\boldsymbol{E}$ and $\boldsymbol{B}$, respectively, lead to two new equations of balance, viz.

$$\partial_t \boldsymbol{m}^{\mathrm{e}} + \mathrm{div}(-\boldsymbol{\sigma}^{\mathrm{e}}) = -n^{\mathrm{e}}\boldsymbol{E} - \boldsymbol{j}^{\mathrm{e}} \times \boldsymbol{B}, \qquad \partial_t e^{\mathrm{e}} + \mathrm{div}(\boldsymbol{q}^{\mathrm{e}}) = -\boldsymbol{j}^{\mathrm{e}} \cdot \boldsymbol{E}\ . \tag{2.20}$$

These equations are interpreted as the equations of balance for electromagnetic momentum and electromagnetic energy. The corresponding densities and fluxes have the unique representations

$$\boldsymbol{m}^{\mathrm{e}} = \varepsilon_0 \boldsymbol{E} \times \boldsymbol{B}, \qquad \boldsymbol{\sigma}^{\mathrm{e}} = \varepsilon_0 \boldsymbol{E} \otimes \boldsymbol{E} + \frac{1}{\mu_0}\boldsymbol{B} \otimes \boldsymbol{B} - \frac{1}{2}(\varepsilon_0|\boldsymbol{E}|^2 + \frac{1}{\mu_0}|\boldsymbol{B}|^2)\mathbf{1}, \tag{2.21}$$

$$e^{\mathrm{e}} = \frac{\varepsilon_0}{2}|\boldsymbol{E}|^2 + \frac{1}{2\mu_0}|\boldsymbol{B}|^2, \qquad \boldsymbol{q}^{\mathrm{e}} = \frac{1}{\mu_0}\boldsymbol{E} \times \boldsymbol{B}. \tag{2.22}$$

The balance equations of the electromagnetic momentum and energy are now added to the corresponding balance equations of matter. We obtain the equations of balance for total momentum and total energy. The postulate that total momentum and total energy both are conserved quantities implies the identification of the Lorentz force and its power, viz.

$$\boldsymbol{k} = n^{\mathrm{e}}\boldsymbol{E} + \boldsymbol{j}^{\mathrm{e}} \times \boldsymbol{B}, \qquad \pi = \boldsymbol{j}^{\mathrm{e}} \cdot \boldsymbol{E}\ . \tag{2.23}$$

On the quasi-static setting of electrodynamics. There is large confusion in the electrochemical literature about the quasi-static approximation of Maxwell's equations. For this reason, a short discussion of the subject is necessary.

At first we rescale time, space, the magnetic and the electric field and the conductivity σ according to

$$t = t_0\tilde{t}, \quad \boldsymbol{x} = x_0\tilde{\boldsymbol{x}}, \quad \boldsymbol{E} = E_0\tilde{\boldsymbol{E}}, \quad \boldsymbol{B} = \frac{E_0}{c}\tilde{\boldsymbol{B}}, \quad \sigma = \sigma_0\tilde{\sigma}, \quad n^{\mathrm{F}} = n_0^{\mathrm{F}}\tilde{n}^{\mathrm{F}}. \tag{2.24}$$

From Ohm's law we know that $\boldsymbol{j}^{\mathrm{e}} = \sigma_0\tilde{\sigma}E_0\tilde{\boldsymbol{E}} =: \sigma_0 E_0\tilde{\boldsymbol{j}}^{\mathrm{e}}$. The rescaled magnetic field has the same dimension as the electric field so that both fields can be compared. Furthermore, we set $x_0/t_0 = v_0$ with v_0 as a typical diffusion velocity of matter, i.e. we set $n_0^{\mathrm{F}}v_0 = \sigma_0 E_0$. Suppressing the tildes in our notation we obtain

$$\frac{v_0}{c}\partial_t\boldsymbol{B} + \mathrm{curl}(\boldsymbol{E}) = 0, \qquad \mathrm{div}(\boldsymbol{B}) = 0, \tag{2.25}$$

$$-\frac{v_0}{c}\partial_t\boldsymbol{E} + \mathrm{curl}(\boldsymbol{B}) = c\mu_0 x_0\sigma_0\boldsymbol{j}^{\mathrm{e}}, \qquad \mathrm{div}(\boldsymbol{E}) = \frac{\sigma_0 t_0}{\varepsilon_0}n^{\mathrm{e}}. \tag{2.26}$$

The dimensionless quantity $c\mu_0\sigma_0 x_0$ is of order 1. The time derivatives in the two equations $(2.18)_1$, $(2.19)_1$ are thus multiplied by the small factor v_0/c. Returning to dimensional quantities, the leading order Maxwell's equations reduce to

$$\mathrm{curl}(\boldsymbol{E}) = 0, \qquad \mathrm{div}(\boldsymbol{B}) = 0, \tag{2.27}$$

$$\mathrm{curl}(\boldsymbol{B}) = \mu_0\boldsymbol{j}^{\mathrm{e}}, \qquad \mathrm{div}(\boldsymbol{E}) = \frac{1}{\varepsilon_0}n^{\mathrm{e}}, \tag{2.28}$$

which we call the quasi-static version of the Maxwell equations. A similar argument shows that the Lorentz force is given by

$$\boldsymbol{k} = n^{\mathrm{e}}\boldsymbol{E}, \tag{2.29}$$

and its power is as before. In the quasi-static setting the electric field can be derived from an electric potential φ. Thus, we have by (2.19)

$$\boldsymbol{E} = -\nabla\varphi, \qquad \varepsilon_0 \Delta\varphi = -n^{\mathrm{e}}, \tag{2.30}$$

and the magnetic field follows from $(2.28)_1$.

Note that the modeling part of this paper relies on the full system of Maxwell's equations, but in the application we will use the quasi-static setting only.

The balance equation for the internal energy. We form the scalar product of the momentum balance (2.12) with the velocity $\boldsymbol{v}$ to obtain the balance of the kinetic energy. Then this balance is subtracted from the energy balance (2.13). The result is the balance of the internal energy, which can be written as

$$\partial_t(\rho e)+\mathrm{div}(\rho e\boldsymbol{v}+\boldsymbol{q}) = \boldsymbol{\sigma} : D(\boldsymbol{v})+\Bigg(\sum_{\alpha=1}^{N}\frac{z_\alpha e_0}{m_\alpha}\boldsymbol{J}_\alpha+\dot{\boldsymbol{P}}+\boldsymbol{P}\mathrm{div}(\boldsymbol{v})-\boldsymbol{P}\cdot\nabla\boldsymbol{v}+\mathrm{curl}(\boldsymbol{M})\Bigg)\cdot\boldsymbol{\mathcal{E}}. \tag{2.31}$$

Here, $\dot{\boldsymbol{P}} = \partial_t \boldsymbol{P} + \boldsymbol{v}\cdot\nabla\boldsymbol{P}$ indicates the material time derivative of the polarization, and $\boldsymbol{\mathcal{E}} = \boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B}$ defines the electromotive intensity. The right hand side of (2.31) represents the production of internal energy due to mechanical stresses, diffusion of free charges and polarization and magnetization.

Constitutive model, Part 1: General strategy. We choose as variables of our model the quantities $(\rho_\alpha)_{\alpha=1,2,\ldots,N}$, $\boldsymbol{v}$, T, χ, $\boldsymbol{E}$ and $\boldsymbol{B}$. Their determination relies on (i) the balance equations for the partial masses (2.11), for the (barycentric) momentum (2.12), and for the phase field (2.14), (ii) the internal energy balance (2.31), (iii) Maxwell's equations (2.18) and (2.19).

These equations contain further quantities that are not in the list of our variables: In the mass balances we have the reaction rates $R^i_{\mathrm{f,b}}$ and the diffusion fluxes $\boldsymbol{J}_\alpha$. The constitutive quantities of the momentum balance are the stress $\boldsymbol{\sigma}$, the charge density n^{e} and the electric current $\boldsymbol{j}^{\mathrm{e}}$. The latter quantities also occur in Maxwell's equations. The phase field balance contains the phase field flux $\boldsymbol{J}_\chi$ and the production rate ξ_χ. Finally, the constitutive quantities of the internal energy balance are the internal energy ρe, the heat flux $\boldsymbol{q}$, the stress $\boldsymbol{\sigma}$, the magnetization $\boldsymbol{M}$ and the polarization $\boldsymbol{P}$. The constitutive quantities must be related to the variables in material dependent manner, i.e. they must be given by constitutive equations. Thermodynamically consistent constitutive equations have to satisfy (i) the *principle of material frame indifference* and (ii) the *entropy principle.*

The principle of material frame indifference makes a statement on constitutive functions of objective tensors, viz. constitutive functions of objective tensors must remain invariant with respect to *Euclidean transformations.*

To introduce these concepts we first consider Euclidean transformations, which are the most general transformation between two Cartesian coordinate systems with coordinates written as $(t, x_1, \ldots, x_3) = (t, x_i)_{i=1,\ldots,3}$ and $(t^*, x^*_1, \ldots, x^*_3) = (t^*, x^*_i)_{i=1,\ldots,3}$, respectively:

$$t^* = t + a, \quad x^*_i = O_{ij}(t)x_j + b_i(t), \quad \mathbf{O}(t)\mathbf{O}(t)^{\mathsf{T}} = \mathbf{1}. \tag{2.32}$$

Next we define the notion of *objective scalars, vectors and tensors (of rank two)* if their components transform according to

$$s^* = \det(\mathbf{O})^p s \qquad \text{for scalars,} \tag{2.33}$$

$$v^*_i = \det(\mathbf{O})^p O_{ij} v_j \qquad \text{for vectors,} \tag{2.34}$$

$$T^*_{ij} = \det(\mathbf{O})^p O_{ik} O_{jl} T_{kl} \qquad \text{for rank two tensors.} \tag{2.35}$$

Scalars and vectors are also called tensor of rank 0 and 1, respectively. For $p = 0$ the objective tensor is called absolute objective tensor and for $p = 1$ we have an axial objective tensor.

As an example, we consider an objective absolute tensor $\boldsymbol{T}$, i.e. we have $T^*_{ij} = O_{ik}O_{jl}T_{kl}$. Let us further assume that $\mathbf{T}$ is a function of $\nabla\mathbf{v}$, so that in general we have

$$T_{ij} = f_{ij}\Big(\frac{\partial v_k}{\partial x_l}\Big), \quad \text{respectively } T^*_{ij} = f^*_{ij}\Big(\frac{\partial v^*_k}{\partial x^*_l}\Big). \tag{2.36}$$

Then, with $v^*_i = O_{ij}(v_j + \dot{O}_{jl}O_{kl}(x^*_k - b_k) - \dot{b}_j)$, objectivity amounts to

$$f^*(\mathbf{O}(t)\nabla\mathbf{v}\,\mathbf{O}(t)^\mathsf{T} + \dot{\mathbf{O}}(t)\mathbf{O}(t)^\mathsf{T}) = \mathbf{O}(t)f(\nabla\mathbf{v})\mathbf{O}(t)^\mathsf{T}. \tag{2.37}$$

In this case, the principle of material frame indifference states that $f^* = f$. In other words it implies that f is an *isotropic function*. Moreover, f can only depend on the symmetric part $\mathbf{D}$ of $\nabla\mathbf{v}$ which follows from (2.37) by choosing $\mathbf{O} = \mathbf{1}$ and $\dot{\mathbf{O}} = -\mathbf{R}$, where $\mathbf{R}$ is the anti-symmetric part of $\nabla\mathbf{v}$.

Classification 1: Transformation properties of important quantities. In this paragraph, we indicate the transformation properties of some important quantities. There are kinematic and non-kinematic quantities. While the transformation properties of kinematic quantities can be derived, the transformation properties of non-kinematic quantities must be postulated. More details and motivations can be found in [20] and [24]. Kinematic quantities are for example the barycentric velocity and the diffusion velocities. The diffusion velocities and the symmetric part of the velocity gradient are absolute objective tensors. The barycentric velocity and the antisymmetric velocity gradients are non-objective quantities. Here is a list with properties of important quantities:

Absolute objective scalars: mass densities, internal energy density, phase field, reaction rates, phase field production.

Absolute objective vectors: diffusion fluxes, phase field flux, charge potential, Lorentz force, polarization and electromotive force.

Axial objective vectors: magnetization, magnetic flux density.

Absolute objective tensor: (Cauchy) stress tensor.

Note that the internal energy density is only an objective scalar if the stress is symmetric, because then the antisymmetric part of the velocity gradient in (2.31) drops out and the mechanical power $\boldsymbol{\sigma} : D(\boldsymbol{v})$ is formed with the symmetric part $D(\boldsymbol{v})$ of the velocity gradient. The electric field $\boldsymbol{E}$ and the magnetic current potential $\boldsymbol{H}$ are not objective quantities. However, the sum of the electromagnetic terms in (2.31) is an objective scalar.

Classification 2: Parity of important quantities. The formulation of the 2^{nd} law of thermodynamics needs a further classification of the involved quantities, which is related to their physical dimensions. If the units of time and electric current, i.e. ”second” and "ampere", respectively, of a given quantity q appear such that the sum of their powers is uneven, we assign the factor -1 according to $\mathcal{P}q = -1$. If the sum of the powers of "second" and "ampere" is even we assign $\mathcal{P}q = +1$. Then the quantity q has negative and positive parity, respectively. It is to be understood that we choose the units of the SI system.

For example, the parity of the density of mass, momentum, internal energy and magnetic indiction are then given by

$$[\rho] = \frac{\text{kg}}{\text{m}^3} \to +1, \qquad [\rho\mathbf{v}] = \frac{\text{kg}}{\text{m}^2\text{s}} \to -1, \qquad [\rho e] = \frac{\text{kg}}{\text{m}\,\text{s}^2} \to +1 \qquad [\mathbf{B}] = \frac{\text{Vs}}{\text{m}^2} \to -1. \tag{2.38}$$

Evidently, the time derivative of a quantity has the opposite parity, while spatial derivatives keep the parity unchanged.

Formulation of the entropy principle. Any solution of the above systems of partial differential equations, composed of (2.11), (2.12), (2.14), (2.31), (2.18) and (2.19), is called a *thermodynamic process*. Here, by solutions we just mean functions which satisfy the balance equations in a local sense. In particular, the value of a quantity and of its spatial derivatives can be chosen independently. With this concept, the 2^{nd} law of thermodynamics consists of four universal and two material dependent axioms. For detailed motivation and further discussion see [9].

(I) There is an entropy/entropy-flux pair $(\rho s, \boldsymbol{\Phi})$ as a material dependent quantity, where ρs is an absolute objective scalar and $\boldsymbol{\Phi}$ is an absolute objective vector. The entropy has the physical dimension $\mathrm{J\,kg^{-1}\,K^{-1}} = \mathrm{m^2 s^{-2} K^{-1}}$, hence is of positive parity. The entropy flux and the entropy production ζ thus have negative parity.

(II) The pair $(\rho s, \boldsymbol{\Phi})$ satisfies the balance equation

$$\partial_t(\rho s) + \operatorname{div}(\rho s \mathbf{v} + \boldsymbol{\Phi}) = \zeta. \tag{2.39}$$

(III) Any admissible entropy/entropy-flux is such that
(i) ζ consists of a sum of binary products according to

$$\zeta = \sum_m \mathcal{N}_m \mathcal{P}_m, \tag{2.40}$$

where the $\mathcal{N}_m$ denote quantities of negative parity, while $\mathcal{P}_m$ refers to positive parity.
(ii) $\mathcal{N}_m \mathcal{P}_m \geq 0$ for all m and for every thermodynamic process.

(IV) A thermodynamic process where $\zeta = 0$ is said to be in thermodynamic equilibrium. This statement is to be understood in a pointwise sense; in particular, this must not hold everywhere, i.e. thermodynamic equilibrium can be attained locally.
A thermodynamic process is called reversible if $\zeta = 0$ everywhere.

In addition, to these universal axioms, we impose two further ones which refer to the most general constitutive models we are interested in. These are:

(V) There are the following *dissipative mechanisms* for fluid mixtures under consideration: *diffusion of mass and charge*, *chemical reaction*, *viscous flow*, *heat conduction*, *phase transition due to diffusion* and *phase transition due to phase production*. Correspondingly, in equilibrium we have

$$\boldsymbol{u}_\alpha = 0, \quad R_{\mathrm{f}}^i = R_{\mathrm{b}}^i, \quad D(\boldsymbol{v}) = 0, \quad \boldsymbol{q} = 0, \quad \boldsymbol{J}_\chi = 0, \quad \xi_\chi = 0. \tag{2.41}$$

(VI) For the class of fluid mixtures under consideration, we restrict the dependence of the entropy according to

$$\rho s = \rho \tilde{s}(\rho e - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P}, \rho_1, \ldots, \rho_N, \boldsymbol{\mathcal{E}}, \boldsymbol{B}, \chi, \nabla\chi), \tag{2.42}$$

where $\rho\tilde{s}$ is a *concave function* which satisfies the principle of material frame indifference. By means of this function, we define the *(absolute) temperature* T, the *chemical potentials* $(\mu_i)_{i=1,2,\dots,N}$ of the constituents and the chemical potential of the phases μ_χ as

$$\frac{1}{T} := \frac{\partial \rho\tilde{s}}{\partial(\rho e - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P})}, \qquad \frac{\mu_i}{T} := -\frac{\partial \rho\tilde{s}}{\partial \rho_i}, \qquad \frac{\mu_\chi}{T} := -\Big(\frac{\partial \rho\tilde{s}}{\partial \chi} - \nabla \cdot \frac{\partial \rho\tilde{s}}{\partial \nabla\chi}\Big). \tag{2.43}$$

Identification of the entropy production. To calculate the entropy production, we introduce the material time derivative in (2.39) and insert the entropy function (2.42). The intermediate result is

$$\zeta = \frac{1}{T}((\rho e)^{\cdot} - \dot{\boldsymbol{P}} \cdot \boldsymbol{\mathcal{E}} - \boldsymbol{P} \cdot \dot{\boldsymbol{\mathcal{E}}}) - \sum_{\alpha=1}^{N} \frac{\mu_\alpha}{T}\dot{\rho}_\alpha + \frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} \cdot \dot{\boldsymbol{\mathcal{E}}} + \frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}} \cdot \dot{\boldsymbol{B}} + \frac{\partial \rho\tilde{s}}{\partial \chi}\dot{\chi} + \frac{\partial \rho\tilde{s}}{\partial \nabla\chi} \cdot (\nabla\chi)^{\cdot} \\ + \rho s \operatorname{div}(\boldsymbol{v}) + \operatorname{div}(\boldsymbol{\Phi}) \ . \tag{2.44}$$

Next, we eliminate the time derivatives of internal energy, partial mass densities and phase field by means of the corresponding balance equations. Moreover, the term $(\nabla\chi)^{\cdot}$ is substituted by the identity

$$(\nabla\chi)^{\cdot} = \nabla\dot{\chi} - \nabla\boldsymbol{v} \cdot \nabla\chi. \tag{2.45}$$

Finally, we use the identity

$$\boldsymbol{\mathcal{E}} \cdot \operatorname{curl}(\boldsymbol{M}) = -\operatorname{div}(\boldsymbol{\mathcal{E}} \times \boldsymbol{M}) + \boldsymbol{M} \cdot \operatorname{curl}(\boldsymbol{\mathcal{E}}) \tag{2.46}$$

and substitute $\operatorname{curl}(\boldsymbol{\mathcal{E}})$ by a variant of $(2.18)_1$, viz.

$$\operatorname{curl}(\boldsymbol{\mathcal{E}}) = -\dot{\boldsymbol{B}} - \boldsymbol{B}\operatorname{div}(\boldsymbol{v}) + \boldsymbol{B} \cdot \nabla\boldsymbol{v}. \tag{2.47}$$

After rearranging terms we obtain

$$\zeta = \operatorname{div}\Bigg(\boldsymbol{\Phi} - \frac{1}{T}(\boldsymbol{q} + \boldsymbol{\mathcal{E}} \times \boldsymbol{M}) + \frac{1}{T}\sum_{\alpha=1}^{N}\mu_\alpha \boldsymbol{J}_\alpha + \frac{\partial \rho\tilde{s}}{\partial \nabla\chi}\dot{\chi} - \frac{1}{\rho}\Big(\frac{\partial \rho\tilde{s}}{\partial \chi} - \nabla \cdot \frac{\partial \rho\tilde{s}}{\partial \nabla\chi}\Big)\boldsymbol{J}_\chi\Bigg) \\ + \Big(\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} - \frac{\boldsymbol{P}}{T}\Big) \cdot (\dot{\boldsymbol{\mathcal{E}}} + \nabla\boldsymbol{v} \cdot \boldsymbol{\mathcal{E}}) + \Big(\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}} - \frac{\boldsymbol{M}}{T}\Big) \cdot (\dot{\boldsymbol{B}} - \boldsymbol{B} \cdot \nabla\boldsymbol{v}) \\ + \frac{1}{T}\Bigg(\boldsymbol{\sigma} - T\frac{\partial \rho\tilde{s}}{\partial \nabla\chi} \otimes \nabla\chi - T\boldsymbol{\mathcal{E}} \otimes \frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} + T\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}} \otimes \boldsymbol{B} \\ - \Big(\rho e - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P} - T\rho\tilde{s} - \sum_{\alpha=1}^{N}\rho_\alpha \mu_\alpha + \boldsymbol{M} \cdot \boldsymbol{B}\Big)\boldsymbol{1}\Bigg) : \nabla\boldsymbol{v} \\ + (\boldsymbol{q} + \boldsymbol{\mathcal{E}} \times \boldsymbol{M}) \cdot \nabla\frac{1}{T} - \sum_{\alpha=1}^{N}\boldsymbol{J}_\alpha \cdot \Big(\nabla\frac{\mu_\alpha}{T} - \frac{z_\alpha}{m_\alpha T}\boldsymbol{\mathcal{E}}\Big) - \frac{1}{T}\sum_{i=1}^{N_{\mathrm{R}}}(R_{\mathrm{f}}^i - R_{\mathrm{b}}^i)\Big(\sum_{\alpha=1}^{N} m_\alpha \gamma_\alpha \mu_\alpha\Big) \\ - \boldsymbol{J}_\chi \cdot \nabla\frac{\mu_\chi}{T} - \frac{1}{T}\xi_\chi \mu_\chi \ . \tag{2.48}$$

Remarks on the composition and classification of terms in (2.48):
1. The combinations $\dot{\boldsymbol{\mathcal{E}}} + \nabla(\boldsymbol{v}) \cdot \boldsymbol{\mathcal{E}}$ and $\dot{\boldsymbol{B}} - \boldsymbol{B} \cdot \nabla\boldsymbol{v}$, respectively, form objective vectors because we have

$$\dot{\mathcal{E}}_i^* + \nabla_i^*(v_k^*)\mathcal{E}_k^* = O_{ij}(\dot{\mathcal{E}}_j + \nabla_j(v_k)\mathcal{E}_k), \qquad \dot{B}_i^* + \nabla_k^*(v_i^*)B_k^* = \det(O)O_{ij}(\dot{B}_j + \nabla_k(v_j)B_k). \tag{2.49}$$

2. The principle of material frame indifference restricts the entropy function to the form

$$\rho\tilde{s}(\rho e - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P}, \rho_1, \ldots, \rho_N, \boldsymbol{\mathcal{E}}, \boldsymbol{B}, \chi, \nabla\chi) = \rho\bar{s}(\rho e - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P}, \rho_1, \ldots, \rho_N, |\boldsymbol{\mathcal{E}}|^2, |\boldsymbol{B}|^2, (\boldsymbol{\mathcal{E}}\cdot\boldsymbol{B})^2, \chi, |\nabla\chi|^2), \tag{2.50}$$

implying that the terms

$$\frac{\partial\rho\tilde{s}}{\partial\nabla\chi}\otimes\nabla\chi, \qquad -\boldsymbol{\mathcal{E}}\otimes\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{\mathcal{E}}} + \frac{\partial\rho\tilde{s}}{\partial\boldsymbol{B}}\otimes\boldsymbol{B} \tag{2.51}$$

are symmetric objective tensors.

3. For this reason, the factor of $\nabla\boldsymbol{v}$ is symmetric and only the symmetric part $D(\boldsymbol{v})$ of the velocity gradient appears in the third line of (2.44).

4. Thus the representation (2.44) consists of a divergence and a sum of binary products with objective factors of negative, respectively positive parity.

To satisfy Axiom (III-i), we choose the entropy flux as

$$\boldsymbol{\Phi} = \frac{1}{T}(\boldsymbol{q} + \boldsymbol{\mathcal{E}}\times\boldsymbol{M}) - \frac{1}{T}(\sum_{\alpha=1}^{N}\mu_\alpha\boldsymbol{J}_\alpha + \frac{1}{\rho}\mu_\chi\boldsymbol{J}_\chi) - \frac{\partial\rho\tilde{s}}{\partial\nabla\chi}\dot{\chi}. \tag{2.52}$$

Then, the remaining part of (2.48) is identified as the entropy production according to Axiom (IV):

$$\begin{aligned}
\zeta = \ & \left(\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{\mathcal{E}}} - \frac{\boldsymbol{P}}{T}\right)\cdot(\dot{\boldsymbol{\mathcal{E}}} + \nabla(\boldsymbol{v})\cdot\boldsymbol{\mathcal{E}}) + \left(\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{B}} - \frac{\boldsymbol{M}}{T}\right)\cdot(\dot{\boldsymbol{B}} - \boldsymbol{B}\cdot\nabla\boldsymbol{v}) \\
& + \frac{1}{T}\Bigg(\boldsymbol{\sigma} - T\frac{\partial\rho\tilde{s}}{\partial\nabla\chi}\otimes\nabla\chi - T\boldsymbol{\mathcal{E}}\otimes\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{\mathcal{E}}} + T\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{B}}\otimes\boldsymbol{B} \\
& \qquad - \Big(\rho e - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P} - T\rho\tilde{s} - \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha + \boldsymbol{M}\cdot\boldsymbol{B}\Big)\boldsymbol{1}\Bigg) : D(\boldsymbol{v}) \\
& + \boldsymbol{q}\cdot\nabla\frac{1}{T} - \sum_{\alpha=1}^{N}\boldsymbol{J}_\alpha\cdot\Big(\nabla\frac{\mu_\alpha}{T} - \frac{z_\alpha e_0}{m_\alpha T}\boldsymbol{\mathcal{E}}\Big) - \frac{1}{T}\sum_{i=1}^{N_{\mathrm{R}}}(R_{\mathrm{f}}^i - R_{\mathrm{b}}^i)\Big(\sum_{\alpha=1}^{N} m_\alpha\gamma_\alpha\mu_\alpha\Big) \\
& - \boldsymbol{J}_\chi\cdot\nabla\frac{\mu_\chi}{T} - \frac{1}{T}\xi_\chi\mu_\chi\ .
\end{aligned} \tag{2.53}$$

Each product describes a dissipative mechanism and couples a quantity of negative parity with a quantity of positive parity. This representation of the entropy production allows to formulate constitutive functions for polarization, magnetization, stress, heat flux, diffusion fluxes, reaction rates, phase flux and the phase production rate. Cross effects between the various dissipative mechanisms may be included. If these are introduced by mixing within the same parity class so that the entropy production is conserved, then we obtain the so called Onsager symmetry as a consequence. This remarkable fact is established and carefully described in [9]. For illustration, we simply couple heat conduction and diffusion later on.

Polarization and magnetization. At first we discuss constitutive equations for $\boldsymbol{M}$ and $\boldsymbol{P}$. To satisfy Axiom III-ii we choose

$$\boldsymbol{P} = T\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{\mathcal{E}}} - \tau_{\mathcal{E}}(\dot{\boldsymbol{\mathcal{E}}} + \nabla(\boldsymbol{v})\cdot\boldsymbol{\mathcal{E}}) \quad \text{and} \quad \boldsymbol{M} = T\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{B}} - \tau_B(\dot{\boldsymbol{B}} - \boldsymbol{B}\cdot\nabla(\boldsymbol{v})), \tag{2.54}$$

where $\tau_{\mathcal{E}} \geq 0$ and $\tau_{\ B} \geq 0$ are phenomenological coefficients. We observe that the constitutive quantities $\boldsymbol{P}$ and $\boldsymbol{M}$ depend on the variables of the entropy function and, additionally, on

$\nabla \boldsymbol{v}$ and the time derivatives of $\boldsymbol{\mathcal{E}}$ and $\boldsymbol{B}$. These constitutive equations embody a variety of complex phenomena, for example hysteresis and inertia of free charges leading to frequency dependent refraction indices. A special case arises if we set $\tau_{\mathcal{E}} = 0$ and $\tau_B = 0$. Then we have the simple constitutive equations

$$\boldsymbol{P} = T\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} \quad \text{and} \quad \boldsymbol{M} = T\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}} \tag{2.55}$$

that still include, piezo-electricity, paramagnetism and related phenomena.

Stress. The constitutive equation for the stress that identically satisfies Axiom III-ii can be read off from the second line of (2.48). We substitute $D(\boldsymbol{v})$ by the sum of its trace and the traceless part $D^\circ(\boldsymbol{v})$. Abbreviating the factor of $D(\boldsymbol{v})$ by $\boldsymbol{A}$, the second line of (2.48) reads $1/3\ \mathrm{Tr}(\boldsymbol{A})\mathrm{div}(\boldsymbol{v}) + \boldsymbol{A}^\circ : D^\circ(\boldsymbol{v})$. Then Axiom III-ii is satisfied for the constitutive equations

$$\frac{1}{3}\mathrm{Tr}(\boldsymbol{A}) = (\lambda + \frac{2}{3}\eta)\mathrm{div}(\boldsymbol{v}) \quad \text{and} \quad \boldsymbol{A}^\circ = 2\eta D^\circ(\boldsymbol{v}). \tag{2.56}$$

The phenomenological coefficients $\lambda + \frac{2}{3}\eta \geq 0$ and $\eta \geq 0$ are called bulk and shear modulus, respectively. Thus the constitutive equation for the traceless part of the stress reads

$$\begin{aligned}\boldsymbol{\sigma}^\circ = T\Big(&\Big(\frac{\partial \rho\tilde{s}}{\partial \nabla\chi} \otimes \nabla\chi - \frac{1}{3}\frac{\partial \rho\tilde{s}}{\partial \nabla\chi} \cdot \nabla\chi\boldsymbol{1}\Big) \\ &+ \Big(\boldsymbol{\mathcal{E}} \otimes \frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} - \frac{1}{3}\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} \cdot \boldsymbol{\mathcal{E}}\boldsymbol{1}\Big) - \Big(\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}} \otimes \boldsymbol{B} - \frac{1}{3}\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}} \cdot \boldsymbol{B}\boldsymbol{1}\Big)\Big) + 2\eta D^\circ(\boldsymbol{v}),\end{aligned} \tag{2.57}$$

and for the trace of the stress we obtain

$$\begin{aligned}\mathrm{Tr}(\boldsymbol{\sigma}) =& \frac{T}{3}\Big(\frac{\partial \rho\tilde{s}}{\partial \nabla\chi} \cdot \nabla\chi + \frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} \cdot \boldsymbol{\mathcal{E}} - \frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}} \cdot \boldsymbol{B}\Big) - \Big(\rho e - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P} - T\rho\tilde{s} - \sum_{\alpha=1}^{N} \rho_\alpha\mu_\alpha + \boldsymbol{M} \cdot \boldsymbol{B}\Big) \\ &+ (3\lambda + 2\eta)\mathrm{div}(\boldsymbol{v}).\end{aligned} \tag{2.58}$$

Hence, the trace of the stress and the deviatoric stress as well contain parts that vanish in equilibrium, viz. the terms proportional to velocity gradients. For this reason, we prefer a further decomposition of the stress into a so-called viscous and a non-viscous part. We denote the viscous part by $\boldsymbol{\sigma}^{\mathrm{NS}}$ to refer to the Navier-Stokes system, while the non-viscous part is simply denoted by $\boldsymbol{\sigma}^{\mathrm{nv}}$. The Navier-Stokes part can then be written as

$$\boldsymbol{\sigma}^{\mathrm{NS}} = \lambda\mathrm{div}(\boldsymbol{v}) + 2\eta D(\boldsymbol{v}), \tag{2.59}$$

and for the non-viscous part we have

$$\boldsymbol{\sigma}^{\mathrm{nv}} = T\Big(\frac{\partial \rho\tilde{s}}{\partial \nabla\chi}\otimes\nabla\chi + \boldsymbol{\mathcal{E}}\otimes\frac{\partial \rho\tilde{s}}{\partial \boldsymbol{\mathcal{E}}} - \frac{\partial \rho\tilde{s}}{\partial \boldsymbol{B}}\otimes\boldsymbol{B}\Big) - \Big(\rho e - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P} - T\rho\tilde{s} - \sum_{\alpha=1}^{N} \rho_\alpha\mu_\alpha + \boldsymbol{M}\cdot\boldsymbol{B}\Big)\boldsymbol{1}. \tag{2.60}$$

Thermo-diffusion. Bothe and Dreyer [9] have established a new method to introduce cross effects. For illustration, we consider the coupling of heat flux and diffusion fluxes. At first, we only consider dissipation due to diffusion. The corresponding entropy production is

$$\zeta^{\mathrm{D}} = -\sum_{\alpha=1}^{N} \boldsymbol{J}_\alpha \cdot \Big(\nabla\frac{\mu_\alpha}{T} - \frac{z_\alpha e_0}{m_\alpha T}\boldsymbol{\mathcal{E}}\Big) = -\sum_{\alpha=1}^{N-1} \boldsymbol{J}_\alpha \cdot \Big(\nabla\frac{\mu_\alpha - \mu_N}{T} - \frac{1}{T}\Big(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_N e_0}{m_N}\Big)\boldsymbol{\mathcal{E}}\Big). \tag{2.61}$$

Due to the side condition (2.6), constitutive equations are only needed for $(N-1)$ fluxes. The simplest choice of constitutive functions without coupling is

$$\boldsymbol{J}_\alpha = -M_\alpha \left(\nabla \frac{\mu_\alpha - \mu_N}{T} - \frac{1}{T}\Big(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_N e_0}{m_N}\Big)\boldsymbol{\mathcal{E}} \right), \tag{2.62}$$

where the mobilities $M_\alpha \geq 0$ are non-negative phenomenological coefficients. To introduce coupling between the constituents of the mixture we proceed as follows. We start from (2.61) and abbreviate for a moment the factors of the diffusion fluxes by $\mathcal{P}_\alpha$, i.e. we write

$$\zeta^{\mathrm{D}} = -\sum_\alpha \boldsymbol{J}_\alpha \cdot \mathcal{P}_\alpha.$$

Then we introduce two matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ of dimension $(N-1)^2$. We choose $\boldsymbol{A}^{\mathrm{T}} = \boldsymbol{B}^{-1}$ and obtain

$$\zeta^{\mathrm{D}} = -\sum_{\alpha=1}^{N-1} \boldsymbol{J}_\alpha \cdot \mathcal{P}_\alpha = -\sum_{\alpha=1}^{N-1} \left(\sum_{\gamma=1}^{N-1} A_{\alpha\gamma} \boldsymbol{J}_\gamma \right) \cdot \left(\sum_{\delta=1}^{N-1} B_{\alpha\delta} \mathcal{P}_\delta \right). \tag{2.63}$$

Now we formulate constitutive equations as before, viz.

$$\sum_{\gamma=1}^{N-1} A_{\alpha\gamma} \boldsymbol{J}_\gamma = -\tilde{M}_\alpha \sum_{\delta=1}^{N-1} B_{\alpha\delta} \mathcal{P}_\delta \quad \text{with} \quad \tilde{M}_\alpha \geq 0. \tag{2.64}$$

Solution for the diffusion fluxes yields the constitutive equation

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta} \mathcal{P}_\beta \quad \text{with} \quad M_{\alpha\beta} = \sum_{\gamma=1}^{N-1} B_{\gamma\alpha} \tilde{M}_\gamma B_{\gamma\beta}. \tag{2.65}$$

The new mobility matrix $\boldsymbol{M}$ is positive definite and (!)symmetric. Thus, if cross effects do not lead to additional entropy production, the Onsager symmetry is a consequence.

As a further example we now consider the entropy production ζ^{HD} of the combined dissipative mechanisms of heat conduction and diffusion. We have

$$\zeta^{\mathrm{HD}} = \boldsymbol{q} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^{N-1} \boldsymbol{J}_\alpha \cdot \mathcal{P}_\alpha. \tag{2.66}$$

The conventional choice of constitutive functions for $(N-1)$ diffusion fluxes $(\boldsymbol{J}_\alpha)_{\alpha=1,2,\ldots,N-1}$ and the heat flux $\boldsymbol{q}$ are

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta} \left(\nabla \frac{\mu_\beta - \mu_N}{T} - \frac{1}{T}\Big(\frac{z_\beta e_0}{m_\beta} - \frac{z_N e_0}{m_N}\Big)\boldsymbol{\mathcal{E}} \right) + L^{\mathrm{J}}_\alpha \nabla \frac{1}{T}, \tag{2.67}$$

$$\boldsymbol{q} = -\sum_{\alpha=1}^{N-1} L^{\mathrm{q}}_\alpha \left(\nabla \frac{\mu_\alpha - \mu_N}{T} - \frac{1}{T}\Big(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_N e_0}{m_N}\Big)\boldsymbol{\mathcal{E}} \right) + a\, \nabla \frac{1}{T}, \tag{2.68}$$

where the kinetic coefficients must satisfy the condition that the matrix

$$\begin{pmatrix} M_{\alpha\beta} & L^{\mathrm{J}}_\alpha \\ L^{\mathrm{q}}_\alpha & a \end{pmatrix} \quad \text{is positive definite.} \tag{2.69}$$

Classically, the cross effects in (2.67) and (2.68) are related to each other by postulating the Onsager symmetry relations

$$M_{\alpha\beta} = M_{\beta\alpha} \quad \text{and} \quad L^{\mathrm{J}}_\alpha = L^{\mathrm{q}}_\alpha. \tag{2.70}$$

According to Bothe and Dreyer [9], the Onsager symmetry is achieved as follows:
The symmetry of the diffusion matrix is taken to be granted from the last example. To derive the symmetry $L^{\mathrm{J}}_\alpha = L^{\mathrm{q}}_\alpha$, we go back to the entropy production (2.63) and introduce the thermo-diffusion coefficients D_α by adding two terms to ζ^{HD} that conserve ζ^{HD}:

$$\zeta^{\mathrm{HD}} = \left(\boldsymbol{q} + \sum_{\alpha=1}^{N-1}(D_\alpha - D_N)\boldsymbol{J}_\alpha)\right) \cdot \nabla\frac{1}{T} - \sum_{\alpha=1}^{N-1}\boldsymbol{J}_\alpha \cdot \left(\mathcal{P}_\alpha - (D_\alpha - D_N)\nabla\frac{1}{T}\right). \tag{2.71}$$

Then we propose two constitutive equations for $(N-1)$ diffusion fluxes $(\boldsymbol{J}_\alpha)_{\alpha=1,2,\ldots,N-1}$ and the heat flux $\boldsymbol{q}$ by the simple relations

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla\Big(\frac{\mu_\beta}{T} - \frac{\mu_N}{T}\Big) - \frac{1}{T}\Big(\frac{z_\beta e_0}{m_\beta} - \frac{z_N e_0}{m_N}\Big)\boldsymbol{\mathcal{E}}\right) + \sum_{\beta=1}^{N-1} M_{\alpha\beta}(D_\beta - D_N)\nabla\frac{1}{T}, \tag{2.72}$$

$$\boldsymbol{q} = -\sum_{\alpha=1}^{N-1}(D_\alpha - D_N)\boldsymbol{J}_\alpha + a\nabla\left(\frac{1}{T}\right). \tag{2.73}$$

A comparison with (2.67) and (2.68) yields

$$L^{\mathrm{J}}_\alpha = \sum_{\beta=1}^{N-1} M_{\alpha\beta}(D_\beta - D_N) \quad \text{and} \quad L^{\mathrm{q}}_\alpha = \sum_{\beta=1}^{N-1} M_{\beta\alpha}(D_\beta - D_N).$$

Thus the symmetry $M_{\alpha\beta} = M_{\beta\alpha}$ implies the symmetry $L^{\mathrm{J}}_\alpha = L^{\mathrm{q}}_\alpha$. This is a further example that the Onsager symmetry is a consequence of cross effects that conserve the entropy production.

A detailed discussion of the creation of cross effects by mixing within the parity classes is found in [9]. For very special cases there are various proofs of the Onsager symmetries within the phenomenological setting. For example, Truesdell [23] and Müller [20] prove the symmetries under some assumptions within a Class II model.

Constitutive equations for special cases. In this study, we are not interested in the most general constitutive model possible. In fact, we only consider the special case, where we have

1 $\tau_{\mathcal{E}} = 0$, $\tau_{\boldsymbol{B}} = 0$

2 no magnetization, i.e. $\boldsymbol{M} = 0$,

3 isothermal processes,

4 no coupling between dissipative mechanisms,

5 the Allen-Cahn equation for the phase field, i.e. $\boldsymbol{J}_\chi = 0$.

Then the inequality (2.44) may be identically satisfied by the simple constitutive laws

$$\begin{aligned}
\boldsymbol{P} &= T\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{\mathcal{E}}}, \qquad \frac{\partial\rho\tilde{s}}{\partial\boldsymbol{B}} = 0, & (2.74)\\
\boldsymbol{\sigma}^{\mathrm{NS}} &= \lambda\mathrm{div}(\boldsymbol{v}) + 2\eta D(\boldsymbol{v}), & (2.75)\\
\boldsymbol{\sigma}^{\mathrm{nv}} &= T\frac{\partial\rho\tilde{s}}{\partial\nabla\chi}\otimes\nabla\chi + T\boldsymbol{\mathcal{E}}\otimes\frac{\partial\rho\tilde{s}}{\partial\boldsymbol{\mathcal{E}}} - \Big(\rho e - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P} - T\rho\tilde{s} - \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha\Big)\mathbf{1}, & (2.76)\\
\boldsymbol{J}_\alpha &= -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\nabla\left(\frac{\mu_\beta-\mu_N}{T} - \frac{1}{T}\Big(\frac{z_\beta e_0}{m_\beta} - \frac{z_N e_0}{m_N}\Big)\boldsymbol{\mathcal{E}}\right), & (2.77)\\
\ln\left(\frac{R_{\mathrm{b}}^i}{R_{\mathrm{f}}^i}\right) &= \frac{1}{kT}\sum_{\alpha=1}^{N} m_\alpha\gamma_\alpha^i\mu_\alpha \quad \text{for} \quad i = 1,2,...,N_{\mathrm{R}}, & (2.78)\\
\xi_\chi &= -\tau\mu_\chi. & (2.79)
\end{aligned}$$

The equation (2.78) is an ansatz for chemical reactions far from equilibrium. The corresponding part of the entropy production is non-negative due to $-\ln\big(R_{\mathrm{b}}^i/R_{\mathrm{f}}^i\big)(R_{\mathrm{f}}^i - R_{\mathrm{b}}^i) \geq 0$.

Introduction of the (Helmholtz) free energy density. Usually, one prefers to have the temperature as an independent variable instead of the internal energy density. To this end, we introduce the (Helmholtz) free energy density

$$\rho\psi = \rho e - \boldsymbol{P}\cdot\boldsymbol{\mathcal{E}} - T\rho s.$$

In the entropy function we change the variable $\rho e - \boldsymbol{P}\cdot\boldsymbol{\mathcal{E}}$ to T with $\rho e = \rho\hat{e}(T,\rho_1,...,\rho_N,\boldsymbol{\mathcal{E}},\chi,\nabla\chi)$. Then, for $\psi = \hat{\psi}(T,\rho_1,...,\rho_N,\boldsymbol{\mathcal{E}},\chi,\nabla\chi)$ we obtain from (2.43) and (2.74)

$$\rho s = -\frac{\partial\rho\hat{\psi}}{\partial T}, \quad \mu_\alpha = \frac{\partial\rho\hat{\psi}}{\partial\rho_\alpha}, \quad \rho e = -T^2\frac{\partial}{\partial T}\left(\frac{\rho\hat{\psi}}{T}\right), \quad \boldsymbol{P} = -\frac{\partial\rho\hat{\psi}}{\partial\boldsymbol{\mathcal{E}}}, \quad \mu_\chi = \frac{\partial\rho\hat{\psi}}{\partial\chi} - T\nabla\cdot\frac{1}{T}\frac{\partial\rho\hat{\psi}}{\partial\nabla\chi}. \tag{2.80}$$

In terms of the free energy densities, the representation (2.76) of the non-viscous part of the stress reads

$$\boldsymbol{\sigma}^{\mathrm{nv}} = -\frac{\partial\rho\hat{\psi}}{\partial\nabla\chi}\otimes\nabla\chi + \frac{1}{2}(\boldsymbol{\mathcal{E}}\otimes\boldsymbol{P} + \boldsymbol{P}\otimes\boldsymbol{\mathcal{E}}) + \Big(\rho\psi - \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha\Big)\mathbf{1}. \tag{2.81}$$

It is convenient to introduce the pressure p by

$$p = -\rho\psi + \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha. \tag{2.82}$$

Then, this relation is called *Gibbs-Duhem equation.*

The free energy density is the central constitutive quantity of a mixture of charged and neutral constituents. Its explicit choice is given in the next section.

3 Choice of energy density and non-linear stability

We consider the quasi-static setting of electrodynamics such that $\boldsymbol{B}$ drops out and $\boldsymbol{\mathcal{E}} = \boldsymbol{E} = -\nabla\varphi$. Moreover, we choose the following free energy density

$$\rho\psi := W(\chi) + \frac{\gamma}{2}|\nabla\chi|^2 + h(\chi)\rho\psi_{\mathrm{L}}(\rho_1,\dots,\rho_N) + (1-h(\chi))\rho\psi_{\mathrm{V}}(\rho_1,\dots,\rho_N) - \frac{\varepsilon_0}{2}s(\chi)|\boldsymbol{E}|^2, \tag{3.1}$$

where $W(\chi) := (\chi-1)^2(\chi+1)^2$, $h : \mathbb{R} \to [0,1]$ is a smooth interpolation function satisfying

$$h(z) = \begin{cases} 1 & \text{for} \quad z \geq 1, \\ 0 & \text{for} \quad z \leq -1, \end{cases} \tag{3.2}$$

such that $h'(z) = 0$ for all $|z| \geq 1$. In (3.1), $\rho\psi_{\mathrm{L}}, \rho\psi_{\mathrm{V}} : (0,\infty)^N \longrightarrow [0,\infty)$ are the free energy functions of the pure phases which we assume to be given by a combination of isotropic elastic response and entropy of mixing, i.e.,

$$\rho\psi_{\mathrm{L/V}} = \sum_\alpha \rho_\alpha \psi_\alpha^{\mathrm{R}} + (K_{L/V} - p^{\mathrm{R}})\Big(1 - \frac{n}{n^{\mathrm{R}}}\Big) + K_{L/V}\frac{n}{n^{\mathrm{R}}}\ln\Big(\frac{n}{n^{\mathrm{R}}}\Big) + kT\sum_\alpha n_\alpha \ln\Big(\frac{n_\alpha}{n}\Big),$$

where $K_{L/V}$ are the bulk moduli, and n^{R}, p^{R}, ψ_α^{R} are reference number density, reference pressure and reference energies, respectively. Note that (3.1) and (3.2) imply that $\chi = +1(-1)$ corresponds to liquid (vapor). Similarly, we assume

$$s(\chi) = h(\chi)s_{\mathrm{L}} + (1 - h(\chi))s_{\mathrm{V}}, \tag{3.3}$$

where $s_{\mathrm{L/V}}$ are the susceptibilities of the pure phases. For brevity, we define

$$\begin{aligned}(\rho f)((\rho_\alpha)_\alpha, \chi) &:= (\rho f)(\rho_1, \ldots, \rho_N, \chi) \\ &:= h(\chi)\rho\psi_{\mathrm{L}}(\rho_1, \ldots, \rho_N) + (1 - h(\chi))\rho\psi_{\mathrm{V}}(\rho_1, \ldots, \rho_N).\end{aligned} \tag{3.4}$$

By definition, the chemical potentials are given by

$$\mu_\alpha := \frac{\partial(\rho\psi)}{\partial\rho_\alpha} = \frac{\partial(\rho f)}{\partial\rho_\alpha}. \tag{3.5}$$

This leads to the following system of equations for the partial mass densities ρ_α, the barycentric velocity $\boldsymbol{v}$, the phase field parameter χ and the electrical potential φ, where the equation for ρ_N is replaced by the evolution equation for $\rho = \sum_{\alpha=1}^N \rho_\alpha$:

$$\begin{aligned}
0 =& \partial_t\rho_\alpha + \mathrm{div}(\rho_\alpha\boldsymbol{v}) - \mathrm{div}\Bigg(\sum_{\beta=1}^{N-1} M_{\alpha\beta}\Big(\nabla\frac{\mu_\beta - \mu_N}{T} + \frac{1}{T}\Big(\frac{z_\beta e_0}{m_\beta} - \frac{z_N e_0}{m_N}\Big)\nabla\varphi\Big)\Bigg) \\
&- \sum_{i=1}^{N_R} m_\alpha\gamma_\alpha^i M_{\mathrm{r}}^i\Bigg(1 - \exp\Big(\frac{1}{kT}\sum_{\beta=1}^{N} m_\beta\gamma_\beta^i\mu_\beta\Big)\Bigg), \qquad \alpha = 1, ..., N-1, \\
0 =& \partial_t\rho + \mathrm{div}(\rho\boldsymbol{v}), \\
0 =& \partial_t(\rho\boldsymbol{v}) + \mathrm{div}(\rho\boldsymbol{v}\otimes\boldsymbol{v}) + \nabla\Big(\sum_{\alpha=1}^N \rho_\alpha\mu_\alpha - \rho f - W - \frac{\gamma}{2}|\nabla\chi|^2\Big) + \gamma\,\mathrm{div}(\nabla\chi\otimes\nabla\chi) \\
&- \mathrm{div}(\boldsymbol{\sigma}^{\mathrm{NS}}) + \varepsilon_0\mathrm{div}\left((1 + s(\chi))\left(\frac{1}{2}|\nabla\varphi|^2\mathbf{1} - \nabla\varphi\otimes\nabla\varphi\right)\right), \\
0 =& \partial_t\chi + \boldsymbol{v}\cdot\nabla\chi + \frac{\tau}{\rho}\left(W' - \gamma\Delta\chi + \frac{\partial(\rho f)}{\partial\chi} - \frac{\varepsilon_0}{2}s'(\chi)|\nabla\varphi|^2\right), \\
0 =& \varepsilon_0\,\mathrm{div}((1 + s(\chi))\nabla\varphi) + n^{\mathrm{F}},
\end{aligned} \tag{3.6}$$

where $n^{\mathrm{F}} := e_0\sum_{\alpha=1}^N \frac{z_\alpha}{m_\alpha}\rho_\alpha$ is the free charge density and $M_{\mathrm{r}}^i := R_{\mathrm{f}}^i$.

3.1 Energy inequality

With respect to the stability of the system (3.6), we can prove an energy inequality. Let $\Omega(t) \subset \mathbb{R}^3$ be a moving open and bounded material domain with C^1-boundary, and $T_f > 0$ some time up to which we assume classical solutions of (3.6) to exist.

Lemma 3.1 (Energy inequality)**.** *Let $((\rho_\alpha)_\alpha, \boldsymbol{v}, \chi, \varphi)$ be a classical solution of* (3.6) *in $\Omega_{T_f} := \bigcup_{t\in(0,T_f)} \Omega(t) \times \{t\}$ and let φ satisfy the Laplace equation in $\mathbb{R}^3 \setminus \Omega(t)$ for all $t \in (0, T_f)$. In addition, let the following boundary conditions be satisfied on $\partial\Omega(t)$ for all $t \in (0, T_f)$: $\boldsymbol{J}_\alpha = 0, \nabla\chi \cdot \boldsymbol{n} = 0$, where $\boldsymbol{n}$ denotes the normal vector to $\partial\Omega(t)$. Then the following inequality holds:*

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\Big(\int_\Omega W(\chi) + \frac{\gamma}{2}|\nabla\chi|^2 + (\rho f)((\rho_\alpha)_\alpha, \chi) + \frac{\varepsilon_0}{2}(1 + s(\chi))|\nabla\varphi|^2 + \frac{\rho}{2}|\boldsymbol{v}|^2 \,\mathrm{d}\,\boldsymbol{x} + \int_{\mathbb{R}^3\setminus\Omega} \frac{\varepsilon_0}{2}|\nabla\varphi|^2 \,\mathrm{d}\,\boldsymbol{x}\Big)$$
$$= \int_{\partial\Omega} \varepsilon_0 \boldsymbol{v} \cdot \Big(\nabla\varphi_+ \otimes \nabla\varphi_+ - \nabla\varphi_- \otimes \nabla\varphi_- + (|\nabla\varphi_-|^2 - |\nabla\varphi_+|^2)\mathbf{1}\Big) \cdot \boldsymbol{n} \,\mathrm{d}\,\boldsymbol{a} - T\int_\Omega \zeta \,\mathrm{d}\,\boldsymbol{x}. \tag{3.7}$$

Proof. By definition of $\rho\psi$, we may write the left hand side of (3.7) as

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\Big(\int_\Omega \rho e - T\rho s + e^{\mathrm{e}} + \frac{\rho}{2}|\boldsymbol{v}|^2 \,\mathrm{d}\,\boldsymbol{x} + \int_{\mathbb{R}^3\setminus\Omega} e^{\mathrm{e}} \,\mathrm{d}\,\boldsymbol{x}\Big) =: \frac{\mathrm{d}}{\mathrm{d}\,t}A. \tag{3.8}$$

Using transport theorems, we can express $\frac{\mathrm{d}}{\mathrm{d}\,t}A$ as

$$\frac{\mathrm{d}}{\mathrm{d}\,t}A = \int_\Omega \Big(\Big(\rho e + \frac{\rho}{2}|\boldsymbol{v}|^2 + e^{\mathrm{e}}\Big)_t + \operatorname{div}\Big((\rho e + \frac{\rho}{2}|\boldsymbol{v}|^2 + e^{\mathrm{e}})\boldsymbol{v}\Big)\Big) \,\mathrm{d}\,\boldsymbol{x}$$
$$+ \int_{\partial\Omega} (e^{\mathrm{e}}_- - e^{\mathrm{e}}_+)\, \boldsymbol{v} \cdot \boldsymbol{n} \,\mathrm{d}\,\boldsymbol{a} - T\int_\Omega \Big((\rho s)_t + \operatorname{div}(\rho s \boldsymbol{v})\Big) \,\mathrm{d}\,\boldsymbol{x}, \tag{3.9}$$

where e^{e}_-, e^{e}_+ denotes the trace of e^{e} on $\partial\Omega$ from the inside and outside of Ω, respectively. In view of the local balances (2.13) and $(2.20)_2$, we infer

$$\frac{\mathrm{d}}{\mathrm{d}\,t}A = \int_{\partial\Omega} \Big(-\boldsymbol{q} \cdot \boldsymbol{n} + \boldsymbol{v} \cdot \boldsymbol{\sigma}\boldsymbol{n} + (e^{\mathrm{e}}_- - e^{\mathrm{e}}_+)\boldsymbol{v} \cdot \boldsymbol{n} + T\boldsymbol{\Phi} \cdot \boldsymbol{n}\Big) \,\mathrm{d}\,\boldsymbol{a} - T\int_\Omega \zeta \,\mathrm{d}\,\boldsymbol{x}.$$

Inserting the definition of $\boldsymbol{\Phi}$ in (2.52) and noting that $\boldsymbol{J}_\alpha = 0$ on the boundary and $\boldsymbol{J}_\chi = 0$ due to our choice of a model of Allen-Cahn type, we find

$$\frac{\mathrm{d}}{\mathrm{d}\,t}A = \int_{\partial\Omega} \boldsymbol{v} \cdot \Big(\boldsymbol{\sigma} + (e^{\mathrm{e}}_- - e^{\mathrm{e}}_+)\mathbf{1}\Big) \cdot \boldsymbol{n} \,\mathrm{d}\,\boldsymbol{a} - T\int_\Omega \zeta \,\mathrm{d}\,\boldsymbol{x}.$$

From the momentum balance we infer

$$\boldsymbol{\sigma}^{\mathrm{e}}_+ = \boldsymbol{\sigma} + \boldsymbol{\sigma}^{\mathrm{e}}_-, \tag{3.10}$$

where $\boldsymbol{\sigma}^{\mathrm{e}}_-, \boldsymbol{\sigma}^{\mathrm{e}}_+$ are the corresponding traces. Note, that in the quasi-static case

$$\boldsymbol{\sigma}^{\mathrm{e}} = \varepsilon_0 \nabla\varphi \otimes \nabla\varphi - e^{\mathrm{e}}\mathbf{1}. \tag{3.11}$$

Therefore, $\frac{\mathrm{d}}{\mathrm{d}\,t}A$ becomes

$$\frac{\mathrm{d}}{\mathrm{d}\,t}A = \int_{\partial\Omega} \varepsilon_0 \boldsymbol{v} \cdot \Big(\nabla\varphi_+ \otimes \nabla\varphi_+ - \nabla\varphi_- \otimes \nabla\varphi_- + (|\nabla\varphi_-|^2 - |\nabla\varphi_+|^2)\mathbf{1}\Big) \cdot \boldsymbol{n} \,\mathrm{d}\,\boldsymbol{a} - T\int_\Omega \zeta \,\mathrm{d}\,\boldsymbol{x}.$$

□

Remark 3.2. Only in case $\boldsymbol{v} = 0$ on $\partial\Omega$ the available free energy A is a Lyapunov function. In the current context, the admissible boundary conditions for Maxwell's equations are

$$\boldsymbol{n} \times \nabla\varphi_+ = \boldsymbol{n} \times \nabla\varphi_-, \quad \text{and} \quad \varepsilon_0(1 + s(\chi_-))\nabla\varphi_- \cdot \boldsymbol{n} = \varepsilon_0\nabla\varphi_+ \cdot \boldsymbol{n} + n^F_{\partial\Omega},$$

where $n^F_{\partial\Omega}$ are free charges on $\partial\Omega$. Thus, even if $n^F_{\partial\Omega} = 0$ the normal component of the electric field is not continuous, in general.

4 Non-dimensionalization

To avoid physically meaningless scalings, we nondimensionalize problem (3.6). To this end, we introduce reference quantities denoted by superscript ^{c} and non-dimensional quantities denoted by *, i.e.,

$$\begin{aligned}
&\boldsymbol{x} = x^c\boldsymbol{x}^*,\ t = t^c t^*,\ \rho_\alpha = \rho^c\rho^*_\alpha,\ \boldsymbol{v} = v^c\boldsymbol{v}^*,\ \lambda_{1,2} = \lambda^c\lambda^*_{1,2},\ \tau = \tau^c\tau^*,\ M_{\alpha\beta} = M^c M^*_{\alpha\beta},\\
&M^i_{\mathrm{r}} = M^c_{\mathrm{r}}(M^i_{\mathrm{r}})^*,\ \gamma_\beta = \gamma^c_{\mathrm{r}}(\gamma^i_\beta)^*,\ m_\beta = m^c m^*_\beta,\ W = W^c W^*,\ \rho f = (\rho f)^c(\rho f)^*,\ \gamma = \gamma^c\gamma^*,\\
&\frac{\mu_\beta}{T} = \mu^c\mu^*_\beta,\ \varphi = \varphi^c\varphi^*,\ s = s^c s^*,\ \varepsilon_0 = \varepsilon^c_0\varepsilon^*_0,\ e_0 z_\alpha = z^c z^*_\alpha.
\end{aligned}$$

Note that χ and $h(\chi)$ do not need to be nondimensionalized and $\rho = \rho^c\rho^*$ with $\rho^* = \sum_\alpha \rho^*_\alpha$. As we are interested in hyperbolic scalings we set $x^c = v^c t^c$ and $(\rho f)^c = \rho^c\mu^c$ and define the following Mach and Reynolds numbers

$$\mathrm{M}_W := v^c\sqrt{\frac{\rho^c}{W^c}}, \quad \mathrm{M}_{\rho f} := v^c\sqrt{\frac{\rho^c}{(\rho f)^c}}, \quad \mathrm{Re} := \frac{\rho^c v^c x^c}{\lambda^c}, \tag{4.1}$$

as well as additional non-dimensional quantities related to the reaction and diffusion rates

$$\bar{M}_{\mathrm{d}} := \frac{M^c\mu^c}{v^c x^c\rho^c}, \quad \bar{M}_{\mathrm{r}} := \frac{M^c_{\mathrm{r}}\gamma^c_{\mathrm{r}} m^c t^c}{\rho^c}, \quad \bar{A} := \frac{m^c\gamma^c_{\mathrm{r}}\mu^c}{kT}, \quad \bar{\tau} := \frac{\tau^c t^c W^c}{\rho^c}, \tag{4.2}$$

and the electrical effects

$$\bar{M}_{\mathrm{e}} := \frac{M^c z^c\varphi^c}{\rho^c m^c v^c x^c}, \quad \bar{\varepsilon} := \frac{\varepsilon^c_0(\varphi^c)^2}{\rho^c(v^c)^2(x^c)^2}, \quad \underline{\varepsilon} := \frac{\varepsilon^c_0 m^c\varphi^c}{(x^c)^2 z^c\rho^c}. \tag{4.3}$$

We assume that the small parameter

$$\delta := \sqrt{\frac{\gamma^c}{(x^c)^2 W^c}} \tag{4.4}$$

is proportional to the width of the interfacial layer. This can be justified by Γ-limit techniques, cf. [22, 21, 12, 19]. Then, suppressing * in the notation, the nondimensionalized version of (3.6) reads

$$
\begin{aligned}
0 =&\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \boldsymbol{v}) - \operatorname{div}\left(\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\bar{M}_{\mathrm{d}} \nabla(\mu_\beta - \mu_N) + \bar{M}_{\mathrm{e}}\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right)\nabla\varphi\right)\right)\\
&- \bar{M}_{\mathrm{r}} \sum_{i=1}^{N_R} m_\alpha \gamma_\alpha^i \Big(1 - \exp\Big(\bar{A}\sum_{\beta=1}^{N} m_\beta \gamma_\beta^i \mu_\beta\Big)\Big),\\
0 =&\partial_t \rho + \operatorname{div}(\rho \boldsymbol{v}),\\
0 =&\partial_t(\rho\boldsymbol{v}) + \operatorname{div}(\rho\boldsymbol{v}\otimes\boldsymbol{v}) + \frac{1}{\mathrm{M}_{\rho f}^2}\nabla\Big(\sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha - \rho f\Big) - \frac{1}{\mathrm{M}_W^2}\nabla\big(W + \frac{\gamma}{2}\delta^2|\nabla\chi|^2\big)\\
&+\frac{\gamma\delta^2}{\mathrm{M}_W^2}\operatorname{div}\big(\nabla\chi\otimes\nabla\chi\big) - \frac{1}{\mathrm{Re}}\operatorname{div}(\boldsymbol{\sigma}^{\mathrm{NS}}) + \bar{\varepsilon}\varepsilon_0 \operatorname{div}\left((1+s^c s(\chi))\left(\frac{|\nabla\varphi|^2}{2}\mathbf{1} - \nabla\varphi\otimes\nabla\varphi\right)\right),\\
0 =&\partial_t\chi + \boldsymbol{v}\cdot\nabla\chi + \bar{\tau}\frac{\tau}{\rho}\left(W' - \gamma\delta^2\Delta\chi + \frac{\mathrm{M}_W^2}{\mathrm{M}_{\rho f}^2}\frac{\partial\rho f}{\partial\chi} - \bar{\varepsilon}\,\mathrm{M}_W^2\, s^c\frac{\varepsilon_0}{2}s'(\chi)|\nabla\varphi|^2\right),\\
0 =&\underline{\varepsilon}\varepsilon_0 \operatorname{div}((1+s^c s(\chi))\nabla\varphi) + n^F.
\end{aligned}
\tag{4.5}
$$

In the sequel, we will consider two scaling regimes. In both of them we choose

$$
\bar{A} = 1,\; s^c = 1,\; \bar{M}_{\mathrm{d}} = 1,\; \bar{M}_{\mathrm{r}} = 1,\; \bar{M}_{\mathrm{e}} = 1,\; \mathrm{M}_W = \sqrt{\delta},\; \mathrm{Re} = \frac{1}{\delta^2},\; \mathrm{M}_{\rho f} = 1,\; \bar{\tau} = \frac{1}{\delta^2}.
$$

In the *uncoupled regime* we consider

$$
\bar{\varepsilon} = \underline{\varepsilon} = 1, \tag{4.6}
$$

while we consider

$$
\bar{\varepsilon} = \underline{\varepsilon} = \delta \tag{4.7}
$$

in the *coupled regime*.

5 Sharp interface limit of the uncoupled regime

In this section we are going to establish the sharp interface limit of the uncoupled regime, i.e., here the "small" parameter in the electro-static equations is not coupled to the thickness of the interfacial layer. We use the methodology of matched asymptotic expansions. For a detailed exposition of this method we refer to e.g. [17, 10]. The treatment of a simplified version of the model at hand (without electrical effects) can be found in [11]. For any quantity f indexed by α we will write $(f_\alpha)_\alpha$ instead of $(f_\alpha)_{\alpha=1,\dots,N}$ for brevity.

We begin by defining outer, inner and matching solutions. The outer equations are obtained by inserting expansions of the quantities in δ into the scaled system of equations.

Definition 5.1. A tuple $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0)$ with

$$
\begin{aligned}
\rho_{\alpha,0} &\in C^0([0,T_f), C^2(\Omega^\pm, \mathbb{R}_+)) \cap C^1([0,T_f), C^0(\Omega^\pm, \mathbb{R}_+)),\\
\boldsymbol{v}_0 &\in C^0([0,T_f), C^1(\Omega^\pm, \mathbb{R}^3)) \cap C^1([0,T_f), C^0(\Omega^\pm, \mathbb{R}^3)),\\
\chi_0 &\in C^0([0,T_f), C^2(\Omega^\pm, \mathbb{R})),\\
\chi_1 &\in C^0([0,T_f), C^1(\Omega^\pm, \mathbb{R})),\\
\varphi_0 &\in C^0([0,T_f), C^2(\Omega^\pm, \mathbb{R}))
\end{aligned}
\tag{5.1}
$$

is called an *outer solution of the uncoupled regime* provided

$$
\begin{aligned}
0 =& \partial_t \rho_{\alpha,0} + \mathrm{div}(\rho_{\alpha,0}\boldsymbol{v}_0) - \mathrm{div}\Big(\sum_{\beta=1}^{N-1} M_{\alpha\beta} \nabla(\mu_{\beta,0} - \mu_{N,0} + \Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\Big)\varphi_0)\Big) \qquad (5.2)\\
& - \sum_{i=1}^{N_R} m_\alpha \gamma_\alpha^i M_\mathrm{r}^i \Big(1 - \exp\Big(\sum_{\beta=1}^{N} m_\beta \gamma_\beta^i \mu_{\beta,0}\Big)\Big),\\
0 =& \partial_t \rho_0 + \mathrm{div}(\rho_0 \boldsymbol{v}_0), \qquad (5.3)\\
0 =& W'(\chi_0), \text{ in particular, } \nabla(W(\chi_0)) = 0, \qquad (5.4)\\
0 =& \partial_t(\rho_0 \boldsymbol{v}_0) + \mathrm{div}(\rho_0 \boldsymbol{v}_0 \otimes \boldsymbol{v}_0) + \nabla\Big(\sum_{\alpha=1}^{N} \rho_{\alpha,0}\mu_{\alpha,0} - \rho f_0 \Big) - \nabla\big(W'(\chi_0)\chi_1\big) \qquad (5.5)\\
& + \varepsilon_0 \,\mathrm{div}\left((1+s(\chi_0)) \left(\frac{1}{2}|\nabla\varphi_0|^2 \mathbf{1} - \nabla\varphi_0 \otimes \nabla\varphi_0 \right)\right),\\
0 =& W''(\chi_0)\chi_1 + \frac{\partial \rho f}{\partial \chi}(\rho_{1,0}, \dots, \rho_{N,0}, \chi_0) - \frac{\varepsilon_0}{2} s'(\chi_0)|\nabla\varphi_0|^2, \qquad (5.6)\\
0 =& \varepsilon_0 \mathrm{div}((1+s(\chi_0))\nabla\varphi_0) + \sum_{\alpha=1}^{N} \frac{z_\alpha}{m_\alpha}\rho_{\alpha,0} \qquad (5.7)
\end{aligned}
$$

are satisfied, where we used the following abbreviations

$$
\mu_{\alpha,0} = \mu_\alpha(\rho_{1,0}, \dots, \rho_{N,0}, \chi_0), \quad \rho f_0 = \rho f(\rho_{1,0}, \dots, \rho_{N,0}, \chi_0). \qquad (5.8)
$$

Note that (5.2) holds for $\alpha = 1, \dots, N-1$.

The equations defining inner solutions are obtained from the scaled equations by a change of variables and inserting expansions in δ.

Definition 5.2. A tuple $((R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ with $X_0 \not\equiv 0$ and

$$
\begin{aligned}
R_{\alpha,0} &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R}_+))),\\
R_{\alpha,1} &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R}))),\\
\boldsymbol{V}_0 &\in C^0([0,T_f), C^0(U, C^1(\mathbb{R}^3))),\\
X_0 &\in C^0([0,T_f), C^1(U, C^0(\mathbb{R}))) \cap C^0([0,T_f), C^0(U, C^2(\mathbb{R}))), \qquad (5.9)\\
X_1 &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R}))),\\
\Phi_0 &\in C^0([0,T_f), C^1(U, C^0(\mathbb{R}))) \cap C^0([0,T_f), C^0(U, C^2(\mathbb{R}))),\\
\Phi_1 &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R})))
\end{aligned}
$$

is called an *inner solution of the uncoupled regime* with normal velocity $w_{\boldsymbol{\nu}}$ provided

$$0 = \left(\frac{1}{2}(1+s(X_0))|\Phi_{0,z}|^2 - (1+s(X_0))|\Phi_{0,z}|^2\right)_z, \tag{5.10}$$

$$0 = \left(\sum_{\beta=1}^{N-1} M_{\alpha\beta}(\mathcal{M}_{\beta,0} - \mathcal{M}_{N,0})_z\right)_z \text{ for } \alpha = 1,\dots,N-1, \tag{5.11}$$

$$0 = W'(X_0) - \gamma X_{0,zz}, \text{ in particular, } 0 = \boldsymbol{\nu}(-W(X_0) + \frac{\gamma}{2}X_{0,z}^2)_z, \tag{5.12}$$

$$0 = (R_0(\boldsymbol{V}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}}))_z = (j_0)_z, \tag{5.13}$$

$$\begin{aligned}0 &= j_0 \boldsymbol{V}_{0,z} + \boldsymbol{\nu}\left(\sum_{\alpha=1}^{N} R_{\alpha,0}\mathcal{M}_{\alpha,0} - RF_0 - W'(X_0)X_1\right)_z \\ &\quad + \gamma\boldsymbol{\nu}(X_{0,z}X_{1,zz} + X_{0,zz}X_{1,z} - \kappa X_{0,z}^2) - \nabla_\Gamma W(X_0) + \gamma X_{0,zz}\nabla_\Gamma(X_0) \\ &\quad + \frac{\varepsilon_0}{2}\left((\Phi_{1,z})^2 + |\nabla_\Gamma \Phi_0|^2\right)(1+s(X_0))_z\boldsymbol{\nu} - \varepsilon_0((1+s(X_0))\Phi_{1,z})_z\left(\Phi_{1,z}\boldsymbol{\nu} + \nabla_\Gamma\Phi_0\right),\end{aligned} \tag{5.14}$$

$$\begin{aligned}0 &= \frac{j_0}{\tau}X_{0,z} + W''(X_0)X_1 - \gamma X_{1,zz} + \gamma\kappa X_{0,z} + \frac{\partial RF_0}{\partial\chi} \\ &\quad - \frac{\varepsilon_0}{2}s'(X_0)\left((\Phi_{1,z})^2 + |\nabla_\Gamma\Phi_0|^2\right),\end{aligned} \tag{5.15}$$

$$0 = ((1+s(X_0))\Phi_{1,z})_z, \tag{5.16}$$

$$\begin{aligned}0 &= (R_{\alpha,0}(\boldsymbol{V}_0\cdot\boldsymbol{\nu} - w_{\boldsymbol{\nu}}))_z - \sum_{\beta=1}^{N-1} M_{\alpha\beta}\Big((\mathcal{M}_{\beta,1} - \mathcal{M}_{N,1})_{zz} - \kappa(\mathcal{M}_{\beta,0} - \mathcal{M}_{N,0})_z \\ &\quad + (\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N})\Phi_{1,zz}\Big),\end{aligned} \tag{5.17}$$

where $\boldsymbol{\nu}$ denotes the unit normal vector to the zeroth-order interface pointing into the liquid, ∇_Γ is the surface gradient and κ is the mean curvature of the interface. In addition, we used

$$\begin{aligned}&\mathcal{M}_{\beta,0} := \mu_\beta(R_{1,0},\dots,R_{N,0},X_0), \ RF_0 = \rho f(R_{1,0},\dots,R_{N,0},X_0), \\ &\frac{\partial RF_0}{\partial\chi} := \frac{\partial\rho f}{\partial\chi}(R_{1,0},\dots,R_{N,0},X_0), \quad j_0 := R_0(\boldsymbol{V}_0\cdot\boldsymbol{\nu} - w_{\boldsymbol{\nu}}), \\ &\mathcal{M}_{\beta,1} := \sum_{\alpha=1}^{N}\frac{\partial\mu_\beta}{\partial\rho_\alpha}(R_{1,0},\dots,R_{N,0},X_0)R_{\alpha,1} + \frac{\partial\mu_\beta}{\partial\chi}(R_{1,0},\dots,R_{N,0},X_0)X_1.\end{aligned} \tag{5.18}$$

Note that we have already simplified (5.11)–(5.17) using $\Phi_{0,z} = 0$ which is an easy consequence of (5.10), provided the matching condition $\Phi_{0,z}(z) \to 0$ for $z \to \pm\infty$ is satisfied. This seems reasonable to keep the notation short(er) and is justified as we will only consider matching solutions in the sequel.

Finally, we define matching solutions which consist of compatible outer and inner solutions.

Definition 5.3. A tuple $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0, (R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ is called a *matching solution of the uncoupled regime* provided $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0)$ is an outer- and $((R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ is an inner solution and both are linked by the standard matching conditions, see [17, 10].

Theorem 5.1. *Let* $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0, (R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ *be a* **matching solution of the uncoupled regime***, then the following equations are satisfied in the* *bulk regions* $\Omega^\pm$*:*

$$\pm 1 = \chi_0, \chi_1 = 0, \tag{5.19}$$

$$0 = \partial_t \rho_{\alpha,0} + \operatorname{div}(\rho_{\alpha,0}\boldsymbol{v}_0) - \operatorname{div}\Big(\sum_{\beta=1}^{N-1} M_{\alpha\beta}\nabla\Big(\mu_{\beta,0} - \mu_{N,0} + \Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\Big)\varphi_0\Big)\Big) \tag{5.20}$$

$$- \sum_{i=1}^{N_R} m_\alpha \gamma_\alpha^i M_{\mathrm{r}}^i \Big(1 - \exp\Big(\sum_{\beta=1}^{N} m_\beta \gamma_\beta^i \mu_{\beta,0}\Big)\Big),$$

$$0 = \partial_t \rho_0 + \operatorname{div}(\rho_0 \boldsymbol{v}_0), \tag{5.21}$$

$$0 = \partial_t(\rho_0\boldsymbol{v}_0) + \operatorname{div}(\rho_0\boldsymbol{v}_0 \otimes \boldsymbol{v}_0) + \nabla\left(\sum_{\alpha=1}^{N} \rho_{\alpha,0}\mu_{\alpha,0} - \rho f_0 + \frac{\varepsilon_0}{2}(1 + s(\chi_0))|\nabla\varphi_0|^2\right) \tag{5.22}$$

$$- \left(\varepsilon_0(1 + s(\chi_0))\nabla\varphi_0 \otimes \nabla\varphi_0\right),$$

$$0 = \varepsilon_0 \operatorname{div}((1 + s(\chi_0))\nabla\varphi_0) + \sum_{\alpha=1}^{N} \frac{z_\alpha}{m_\alpha}\rho_{\alpha,0}, \tag{5.23}$$

where (5.20) *is valid for* $\alpha = 1, \ldots, N-1$*. Moreover, the following conditions are fulfilled at the interface:*

$$0 = [\![\mu_{\alpha,0} - \mu_{N,0}]\!], \tag{5.24}$$

$$0 = [\![\rho_0(\boldsymbol{v}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}})]\!], \tag{5.25}$$

$$0 = [\![\rho_{\alpha,0}(\boldsymbol{v}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}})]\!] - \left[\!\!\left[\sum_{\beta=1}^{N-1} M_{\alpha\beta}\nabla\Big(\mu_{\beta,0} - \mu_{N,0} + \Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\Big)\varphi_0\Big)\boldsymbol{\nu}\right]\!\!\right], \tag{5.26}$$

$$0 = \left[\!\!\left[j_0\boldsymbol{v}_0 + \Big(\sum_{\alpha=1}^{N} \rho_{\alpha,0}\mu_{\alpha,0} - \rho f_0\Big)\boldsymbol{\nu} + \varepsilon_0(1 + s(\chi_0))\left(\frac{1}{2}|\nabla\varphi_0|^2 - \nabla\varphi_0 \otimes \nabla\varphi_0\right)\boldsymbol{\nu}\right]\!\!\right] \tag{5.27}$$

$$- \gamma\kappa\boldsymbol{\nu}\int_{-\infty}^{\infty} (X_{0,z})^2 \,\mathrm{d}\,z,$$

$$0 = \left[\!\!\left[\frac{j_0^2}{2\rho_0^2} + \mu_{N,0}\right]\!\!\right] + \frac{j_0}{\tau}\int_{-\infty}^{\infty} \frac{1}{R_0}(X_{0,z})^2 \,\mathrm{d}\,z, \tag{5.28}$$

$$0 = [\![(1 + s(\chi_0))\nabla\varphi_0 \cdot \boldsymbol{\nu}]\!], \tag{5.29}$$

$$0 = [\![\varphi_0]\!], \tag{5.30}$$

where $j_0 := \rho_0^\pm(\boldsymbol{v}_0^\pm \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}})$ *and* (5.24), (5.26) *hold for* $\alpha = 1, \ldots, N-1$*. Moreover,* (5.30) *implies*

$$[\![\nabla\varphi_0 - (\nabla\varphi_0 \cdot \boldsymbol{\nu})\boldsymbol{\nu}]\!] = 0. \tag{5.31}$$

Remark 5.4. Note that all jump conditions in Theorem 5.1 are physically meaningful. Equations (5.24), (5.28) and (5.27) are generalised Gibbs-Thompson laws, (5.25) ensures conservation of mass, while (5.27) is a dynamic Young-Laplace law which shows that we have surface tension of order δ^0. Equation (5.29) shows that in this scaling the electrical displacement is continuous across the interface, while (5.30) shows the continuity of the electrical potential which causes the continuity of the tangential part of the electric field, i.e. (5.31).

We will decompose the proof of Theorem 5.1 into several lemmas. Our first lemma ascertains that the electrical potential is continuous across the interface.

Lemma 5.5. *Any Φ_0 satisfying* (5.10) *and the matching conditions, fulfils* $\Phi_{0,z} = 0$. *Thus,* (5.30) *and* (5.31) *are satisfied.*

Proof. We have $(1 + s(X_0))|\Phi_{0,z}|^2 = k \in \mathbb{R}$. Because of the matching condition $k = 0$ and therefore $s \geq 0$ implies $[\![\varphi_0]\!] = 0$. Forming the surface gradient of $[\![\varphi_0]\!] = 0$ gives (5.31). □

Next we use the continuity of the mass flux across the interface to remove the normal velocity from the equations.

Remark 5.6. Equation (5.13) is satisfied if and only if $\boldsymbol{V}_0 \cdot \boldsymbol{\nu} = \frac{j_0}{R_0} + w_{\boldsymbol{\nu}}$ for some j_0 independent of z.

The following lemma shows that we have pure phases in the bulk.

Lemma 5.7. *Let χ_0, χ_1 be given as in Definition 5.3, then*

$$\chi_0 \in \{-1, 1\} \quad \text{and} \quad \chi_1 = 0.$$

Furthermore, all solutions $\Psi \in C^2(\mathbb{R})$ of the ordinary differential equation

$$W'(\Psi) - \gamma \partial_{zz} \Psi = 0 \tag{5.32}$$

with $\partial_z \Psi \to 0, \Psi \to \pm 1$ as $z \to \pm\infty$ are given by the one parameter family

$$\Psi(z) = \bar{\Psi}(z - \bar{z}), \quad \bar{z} \in \mathbb{R}, \tag{5.33}$$

where $\bar{\Psi}$ is the unique monotonically increasing solution of (5.32) *satisfying $\bar{\Psi}(0) = 0$. In particular, all X_0 as in Definition 5.3 are given by the one parameter family*

$$X_0(t, \boldsymbol{s}, \cdot) = \bar{\Psi}(\cdot - \bar{z}(t, \boldsymbol{s})), \quad \bar{z} \in \mathbb{R}.$$

Proof. From (5.5) we know $\chi_0 \in \{\pm 1, 0\}$. Thus, by continuity, χ_0 is constant in $\Omega^\pm$. A phase portrait analysis which can be found in [7] shows that (5.32) implies (5.33) and $\chi_0^\pm = \pm 1$. Hence, $\chi_0 = \pm 1$ in $\Omega^\pm$ and $\frac{\partial \rho f}{\partial \chi}(\rho_{1,0}, \ldots, \rho_{N,0}, \chi_0) = 0 = s'(\chi_0)$ because of (3.2). Thus, $\chi_1 = 0$ because of $W''(\pm 1) \neq 0$ and equation (5.6). □

Now we reformulate some of the equations (5.11)-(5.17) so that we obtain a system from which we can compute the $R_{\alpha,0}$ independently of Φ_1, X_1.

Lemma 5.8. *For X_0 given as in Lemma 5.7 equations* (5.11), (5.14), (5.15), (5.16) *are equivalent to* (5.11), (5.14), (5.16) *and*

$$\frac{j_0}{R_0} \left(\frac{j_0}{R_0} \right)_z + (\mathcal{M}_{\alpha,0})_z = -\frac{j_0}{R_0 \tau} (X_{0,z})^2 \tag{5.34}$$

for any $\alpha = 1, \ldots, N$, where $R_0 := \sum_{\alpha=1}^N R_{\alpha,0}$.

Proof. Combining (5.15) and the normal part of (5.14) we get

$$\begin{aligned}
&j_0 (\boldsymbol{V}_0 \cdot \boldsymbol{\nu})_z + \Big(\sum_{\alpha=1}^N R_{\alpha,0} \mathcal{M}_{\alpha,0} - RF_0 - W'(X_0) X_1\Big)_z + \gamma X_{0,zz} X_{1,z} \\
&\quad + \frac{\varepsilon_0}{2} \left((\Phi_{1,z})^2 + |\nabla_\Gamma \Phi_0|^2 \right) (1 + s(X_0))_z - \varepsilon_0 ((1 + s(X_0)) \Phi_{1,z})_z \Phi_{1,z} \\
&= -\gamma (X_{0,z} X_{1,zz} - \kappa X_{0,z}^2) \\
&= -\frac{j_0}{\tau} (X_{0,z})^2 - W''(X_0) X_{0,z} X_1 - \frac{\partial RF_0}{\partial \chi} X_{0,z} + \frac{\varepsilon_0}{2} s'(X_0) X_{0,z} \left((\Phi_{1,z})^2 + |\nabla_\Gamma \Phi_0|^2 \right).
\end{aligned} \tag{5.35}$$

Because of (5.16) equation (5.35) implies

$$j_0(\boldsymbol{V}_0\cdot\boldsymbol{\nu})_z+\left(\sum_{\alpha=1}^{N}R_{\alpha,0}\mathcal{M}_{\alpha,0}-RF_0-W'(X_0)X_1\right)_z+\gamma X_{0,zz}X_{1,z}$$
$$=-\frac{j_0}{\tau}(X_{0,z})^2-W''(X_0)X_{0,z}X_1-\frac{\partial RF_0}{\partial\chi}X_{0,z}. \quad (5.36)$$

This can be equivalently phrased as

$$j_0(\boldsymbol{V}_0\cdot\boldsymbol{\nu})_z+\left(\sum_{\alpha=1}^{N}R_{\alpha,0}\mathcal{M}_{\alpha,0}-RF_0\right)_z=-\frac{j_0}{\tau}(X_{0,z})^2-\frac{\partial RF_0}{\partial\chi}X_{0,z} \quad (5.37)$$

making use of (5.12). Applying the definition of μ_α, this is equivalent to

$$j_0(\boldsymbol{V}_0\cdot\boldsymbol{\nu})_z+\sum_{\alpha=1}^{N}R_{\alpha,0}(\mathcal{M}_{\alpha,0})_z=-\frac{j_0}{\tau}(X_{0,z})^2. \quad (5.38)$$

Due to (5.11) and the positivity of R_0 this implies (5.34). □

Note that (5.11) and (5.34) form a system of N equations in which only the $R_{\alpha,0}$ are unknown, as we already know X_0 up to a translational constant. Thus, we may determine $(R_{\alpha,0})_\alpha$ up to the translational constant. As the equations do not contain Φ_0,Φ_1 we can use a result from [11].

Lemma 5.9. *Let $\rho_1^-,\dots,\rho_N^->0$ be given. Let $j_0\in\mathbb{R}$ with $|j_0|$ small enough, $\rho^-:=\sum_\alpha\rho_\alpha^-$ and $\mu_\alpha^-:=\mu_\alpha(\rho_1^-,\dots,\rho_N^-,-1)$. Then, there exist $R_{1,0},\dots,R_{N,0}\in C^0(\mathbb{R},\mathbb{R}_+)$ and $\rho_1^+,\dots,\rho_N^+>0$ so that* (5.24), (5.28) *and*

$$0=\mu_\alpha(R_{1,0}(z),\dots,R_{N,0}(z),X_0(z))-\mu_N(R_{1,0}(z),\dots,R_{N,0}(z),X_0(z))-\mu_\alpha^-+\mu_N^-, \quad (5.39)$$
$$0=\mu_N(R_{1,0}(z),\dots,R_{N,0}(z),X_0(z))+\frac{j_0^2}{2\sum_\alpha R_{\alpha,0}^2(z)}+\frac{j_0}{\tau}\int_{-\infty}^{z}\frac{(X_{0,z}(\tilde z))^2}{\sum_\alpha R_{\alpha,0}(\tilde z)}\,\mathrm{d}\,\tilde z, \quad (5.40)$$
$$0=\lim_{z\to\pm\infty}R_{\alpha,0}(z)-\rho_\alpha^\pm \quad (5.41)$$

are satisfied, where (5.39), (5.41) *are valid for $\alpha=1,\dots,N$. In particular, the $R_{1,0},\dots,R_{N,0}$ solve* (5.11) *and* (5.34).

Thus, only the solvability criteria for Φ_1, X_1, $(R_{\alpha,1})_\alpha$ and the tangential part of $\boldsymbol{V}_0$ are left to be determined.

Lemma 5.10. *For X_0 as in Lemma 5.7, the function Φ_1 from Definition 5.3 satisfies*

$$\Phi_{1,z}=\frac{k}{1+s(X_0)} \quad (5.42)$$

for some $k\in\mathbb{R}$. Such an k can be found if and only if (5.29) *holds.*

Proof. As $s\geq 0$ the equivalence of (5.16) to (5.42) is clear. The equivalence to the interface condition (5.29) follows from the matching conditions. □

Lemma 5.11. *The normal part of* (5.14) *can be written as*

$$\mathcal{L}X_1 = \left(\frac{j_0^2}{\sum_{\alpha=1}^N R_{\alpha,0}}\right)_z + (\sum_{\alpha=1}^N R_{\alpha,0}\mathcal{M}_{\alpha,0} - RF_0)_z - \gamma\kappa X_{0,z}^2 \\ - \frac{\varepsilon_0}{2}((1+s(X_0))(\Phi_{1,z})^2)_z + \frac{\varepsilon_0}{2}|\nabla_\Gamma \Phi_0|^2(1+s(X_0))_z \quad (5.43)$$

with

$$\mathcal{L} : W^{2,1}(\mathbb{R}) \to L^1(\mathbb{R}), \quad \Psi \mapsto (W'(X_0)\Psi - \gamma X_{0,z}\Psi_z)_z.$$

Equation (5.43) *has a solution if and only if the normal part of* (5.27) *is true.*

Proof. The equivalence of the normal part of (5.14) and (5.43) is straightforward. Thus, we focus on the solvability condition. The only solutions of the homogeneous adjoint problem to (5.43), i.e.,

$$W'(X_0)\Xi_z + \gamma(X_{0,z}\Xi_z)_z = 0 \quad (5.44)$$

in $L^\infty(\mathbb{R})$ are given by $\Xi(z) = k$ for all $z \in \mathbb{R}$ for some parameter $k \in \mathbb{R}$, see [11, Lemma 4.11]. Hence, by Fredholm's Theorem, (5.43) has a solution if and only if

$$0 = \int_{-\infty}^{\infty} \left(\frac{j_0^2}{\sum_{\alpha=1}^N R_{\alpha,0}}\right)_z + (\sum_{\alpha=1}^N R_{\alpha,0}\mathcal{M}_{\alpha,0} - RF_0)_z - \gamma\kappa X_{0,z}^2 \\ - \frac{\varepsilon_0}{2}((1+s(X_0))(\Phi_{1,z})^2)_z + \frac{\varepsilon_0}{2}|\nabla_\Gamma \Phi_0|^2(1+s(X_0))_z \,\mathrm{d}\,z. \quad (5.45)$$

This is

$$\left[\!\left[\frac{j_0^2}{\rho_0} + \sum_{\alpha=1}^N \rho_{\alpha,0}\mu_{\alpha,0} - \rho f_0 - \frac{\varepsilon_0}{2}(1+s(\chi_0))\left((\nabla\varphi_0\cdot\boldsymbol{\nu})^2 - (|\nabla\varphi_0|^2 - (\nabla\varphi_0\cdot\boldsymbol{\nu})^2)\right)\right]\!\right] \\ = \int_{-\infty}^{\infty} \gamma\kappa X_{0,z}^2 \,\mathrm{d}\,z, \quad (5.46)$$

which is the normal part of (5.27). □

Next, we show that the tangential part of (5.27) is a condition for the existence of the tangent part of $\boldsymbol{V}_0$. Let us note that due to (5.29), (5.31) the tangential part of (5.27) equals

$$j_0[\![\boldsymbol{v}_0 - (\boldsymbol{v}_0\cdot\boldsymbol{\nu})\boldsymbol{\nu}]\!] = 0. \quad (5.47)$$

Lemma 5.12. *The tangential part of* (5.14) *has a solution if and only if* (5.47) *holds.*

Proof. For any vector $\mathbf{t}$ tangent to the zeroth order interface Γ multiplication of (5.14) by $\mathbf{t}$ gives

$$0 = j_0(\boldsymbol{V}_0\cdot\mathbf{t})_z - \nabla_\Gamma W(X_0)\cdot\mathbf{t} + \gamma X_{0,zz}\nabla_\Gamma(X_0)\cdot\mathbf{t} - \varepsilon_0\left((1+s(X_0))\Phi_{1,z}\right)_z\nabla_\Gamma\Phi_0\cdot\mathbf{t}. \quad (5.48)$$

Due to (5.12) and (5.16) this is

$$0 = j_0(\boldsymbol{V}_0\cdot\mathbf{t})_z, \quad (5.49)$$

which can be solved if and only if (5.47) holds. □

Finally, we study solvability of (5.17).

Lemma 5.13. *Let* $((R_{\alpha,0})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_1)$ *be given. Then, there exist* $(R_{\alpha,1})_\alpha$ *satisfying* (5.17) *if and only if* (5.26) *is fulfilled.*

Proof. According to [11, Lemma 4.8] the map

$$(0,\infty)^N \to \mathbb{R}^N, \qquad (\rho_\alpha)_{\alpha=1,\dots,N} \mapsto (\mu_1((\rho_\alpha)_{\alpha=1,\dots,N},\chi), \dots, \mu_N((\rho_\alpha)_{\alpha=1,\dots,N},\chi))^T$$

is a diffeomorphism for any fixed $\chi \in [-1,1]$ such that for fixed $\chi \in [-1,1]$, the matrix

$$\Big(\frac{\partial \mu_\beta}{\partial \rho_\gamma}((\rho_\alpha)_{\alpha=1,\dots,N},\chi)\Big)_{\beta,\gamma=1,\dots,N}$$

is invertible for any $\rho_1, \dots, \rho_N > 0$.

Thus, instead of studying criteria determining whether there exist functions $(R_{\alpha,1})_\alpha$ solving (5.17) we may search for criteria for the existence of functions $\mathcal{M}_{\alpha,1} : \mathbb{R} \to \mathbb{R}$, $\alpha = 1, \dots, N$ satisfying (5.17). Once we have ensured the existence of the $(\mathcal{M}_{\alpha,1})_\alpha$ the corresponding $(R_{\alpha,1})_\alpha$ can be computed from (5.18). Conversely, if no $(\mathcal{M}_{\alpha,1})_\alpha$ solving (5.17) exist, there are no solutions in terms of $(R_{\alpha,1})_\alpha$. From (5.11) and the matching conditions we know

$$(\mathcal{M}_{\beta,0} - \mathcal{M}_{N,0})_z = 0 \quad \text{for all } \beta = 1, \dots, N.$$

Thus, (5.17) reads

$$0 = (R_{\alpha,0}(\boldsymbol{V}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}}))_z - \sum_{\beta=1}^{N-1} M_{\alpha\beta}\Big((\mathcal{M}_{\beta,1} - \mathcal{M}_{N,1})_{zz} + \Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\Big)\Phi_{1,zz}\Big) \tag{5.50}$$

for $\alpha = 1, \dots, N-1$. In fact, only the differences $\psi_\beta := \mathcal{M}_{\beta,1} - \mathcal{M}_{N,1}$ for $\beta = 1, \dots, N-1$ are relevant in (5.50). We will use the Fredholm alternative theorem to determine the solvability conditions for the $(\psi_\beta)_\beta$. To this end, we choose (arbitrary) auxiliary functions $\Xi_\beta \in C^\infty(\mathbb{R})$ for $\beta = 1, \dots, N-1$ such that

$$\Xi_\beta(z) = \begin{cases} (\nabla(\mu_{\beta,0} - \mu_{N,0}))^+ \cdot \boldsymbol{\nu} z + (\mu^+_{\beta,1} - \mu^+_{N,1}) & \text{for} \quad z > 1 \\ (\nabla(\mu_{\beta,0} - \mu_{N,0}))^- \cdot \boldsymbol{\nu} z + (\mu^-_{\beta,1} - \mu^-_{N,1}) & \text{for} \quad z < -1. \end{cases}$$

We will see that the solvability conditions are independent of the chosen auxiliary functions. Defining $\Psi_\beta = \psi_\beta - \Xi_\beta$, we are interested in the following auxiliary problem: Find $(\Psi_\beta)_{\beta=1,\dots,N-1} \in L^1(\mathbb{R})$ such that

$$\sum_{\beta=1}^{N-1} (M_{\alpha\beta}(\Psi_\beta)_z)_z = (R_{\alpha,0}(\boldsymbol{V}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}}))_z - \sum_{\beta=1}^{N-1} M_{\alpha\beta}\Big((\Xi_\beta)_z + (\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N})\Phi_{1,z}\Big)_z. \tag{5.51}$$

The solvability conditions for (5.51) are determined by the solutions of the homogenous adjoint system of equations in $L^\infty(\mathbb{R})$. The homogenous adjoint system of equations reads

$$\sum_{\beta=1}^{N-1} (M_{\alpha\beta}(Z_\beta)_z)_z = 0 \quad \text{for } \alpha = 1, \dots, N-1, \quad (Z_\beta)_{\beta=1,\dots,N-1}. \tag{5.52}$$

As the matrix $M_{\alpha\beta}$ is constant in z and positive definite there are $N-1$ linearly independent solutions of (5.52) in $L^\infty(\mathbb{R})$, i.e. $\alpha = 1, \dots, N-1$, which can be chosen as

$$Z_\beta(z) = \delta_{\alpha\beta}, \qquad z \in \mathbb{R}.$$

The Fredholm alternative theorem asserts that (5.51) is solvable if and only if

$$\int_{\mathbb{R}} (R_{\alpha,0}(\boldsymbol{V}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}}))_z - \sum_{\beta=1}^{N-1} \Big(M_{\alpha\beta}(\Xi_\beta)_z + (\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N})\Phi_{1,z} \Big)_z \,\mathrm{d}\, z = 0 \tag{5.53}$$

for $\alpha = 1, ..., N-1$. Integrating (5.53) gives (5.26). □

Proof of Theorem 5.1. We obtain the interface conditions and the properties of χ_0, χ_1 by combining the preceeding lemmas. Concerning the bulk equations, (5.20) is (5.2), (5.21) is (5.3), (5.23) is (5.7) and (5.22) follows from (5.5) as $\chi_1 = 0$.

□

6 Sharp interface limit of the coupled regime

This section is devoted to establishing the sharp interface limit of the coupled regime, i.e., the "small" parameter in the electro-static equations is proportional to the thickness of the interfacial layer. As usual we begin by defining outer, inner and matching solutions.

The outer equations are obtained by inserting expansions of the quantities in δ into the scaled system of equations.

Definition 6.1. A tuple $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0)$ with

$$\begin{aligned}
\rho_{\alpha,0} &\in C^0([0,T_f), C^2(\Omega^\pm, \mathbb{R}_+)) \cap C^1([0,T_f), C^0(\Omega^\pm, \mathbb{R}_+)),\\
\boldsymbol{v}_0 &\in C^0([0,T_f), C^1(\Omega^\pm, \mathbb{R}^3)) \cap C^1([0,T_f), C^0(\Omega^\pm, \mathbb{R}^3)),\\
\chi_0 &\in C^0([0,T_f), C^2(\Omega^\pm, \mathbb{R})),\\
\chi_1 &\in C^0([0,T_f), C^1(\Omega^\pm, \mathbb{R})),\\
\varphi_0 &\in C^0([0,T_f), C^2(\Omega^\pm, \mathbb{R}))
\end{aligned} \tag{6.1}$$

is called an *outer solution of the coupled regime* provided (5.2), (5.3), (5.4), and

$$0 = \partial_t(\rho_0 \boldsymbol{v}_0) + \operatorname{div}(\rho_0 \boldsymbol{v}_0 \otimes \boldsymbol{v}_0) + \nabla\Big(\sum_{\alpha=1}^N \rho_{\alpha,0}\mu_{\alpha,0} - \rho f_0\Big) - \nabla(W'(\chi_0)\chi_1), \tag{6.2}$$

$$0 = W''(\chi_0)\chi_1 + \frac{\partial \rho f}{\partial \chi}(\rho_{1,0}, \dots, \rho_{N,0}, \chi_0), \tag{6.3}$$

$$0 = \sum_{\alpha=1}^N \frac{z_\alpha}{m_\alpha}\rho_{\alpha,0} \tag{6.4}$$

are satisfied. Note that we used the following abbreviations

$$\mu_{\alpha,0} = \mu_\alpha(\rho_{1,0}, \dots, \rho_{N,0}, \chi_0), \quad \rho f_0 = \rho f(\rho_{1,0}, \dots, \rho_{N,0}, \chi_0). \tag{6.5}$$

The equations defining inner solutions are obtained from the scaled equations by a change of variables and inserting expansions in δ.

Definition 6.2. A tuple $((R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ with $X_0 \not\equiv 0$ and

$$\begin{aligned}
R_{\alpha,0} &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R}_+))), \\
R_{\alpha,1} &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R}))), \\
\boldsymbol{V}_0 &\in C^0([0,T_f), C^0(U, C^1(\mathbb{R}^3))), \\
X_0 &\in C^0([0,T_f), C^1(U, C^0(\mathbb{R}))) \cap C^0([0,T_f), C^0(U, C^2(\mathbb{R}))), \\
X_1 &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R}))), \\
\Phi_0 &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R}))), \\
\Phi_1 &\in C^0([0,T_f), C^0(U, C^2(\mathbb{R})))
\end{aligned} \tag{6.6}$$

is called an *inner solution of the coupled regime* with normal velocity $w_{\boldsymbol{\nu}}$ provided (5.13) and

$$0 = ((1+s(X_0))\Phi_{0,z})_z, \tag{6.7}$$

$$0 = \left(\sum_{\beta=1}^{N-1} M_{\alpha\beta}(\mathcal{M}_{\beta,0} - \mathcal{M}_{N,0})_z + \left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N} \right) \Phi_{0,z} \right)_z, \tag{6.8}$$

$$0 = \boldsymbol{\nu}(-W(X_0) + \gamma\boldsymbol{\nu} X_{0,z}^2 - \frac{\varepsilon_0}{2}(1+s(X_0))(\Phi_{0,z})^2)_z, \tag{6.9}$$

$$0 = W'(X_0) - \gamma X_{0,zz} - \frac{\varepsilon_0}{2} s'(X_0)(\Phi_{0,z})^2, \tag{6.10}$$

$$\begin{aligned}
0 = j_0 \boldsymbol{V}_{0,z} &+ \boldsymbol{\nu}\Big(\sum_{\alpha=1}^{N} R_{\alpha,0}\mathcal{M}_{\alpha,0} - RF_0 - W'(X_0)X_1 \Big)_z \\
&+ \gamma\boldsymbol{\nu}(X_{0,z}X_{1,zz} + X_{0,zz}X_{1,z} - \kappa X_{0,z}^2) - \nabla_\Gamma W(X_0) + \gamma X_{0,zz}\nabla_\Gamma(X_0),
\end{aligned} \tag{6.11}$$

$$0 = \frac{j_0}{\tau} X_{0,z} + W''(X_0)X_1 - \gamma X_{1,zz} + \gamma\kappa X_{0,z} + \frac{\partial RF_0}{\partial \chi}, \tag{6.12}$$

$$\begin{aligned}
0 = (R_{\alpha,0}(\boldsymbol{V}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}}))_z - \sum_{\beta=1}^{N-1} M_{\alpha\beta}\Big(&(\mathcal{M}_{\beta,1} - \mathcal{M}_{N,1})_{zz} - \kappa(\mathcal{M}_{\beta,0} - \mathcal{M}_{N,0}) \\
&+ \Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N} \Big)\Phi_{1,zz} - \kappa\Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N} \Big)\Phi_{0,z} \Big),
\end{aligned} \tag{6.13}$$

$$0 = ((1+s(X_0))\Phi_{1,z})_z + \sum_{\alpha=1}^{N} \frac{z_\alpha}{m_\alpha} R_{\alpha,0} \tag{6.14}$$

are fulfilled, where we used the abbreviations from (5.18). Note that we already simplified (6.11), (6.12) and (6.14) using $\Phi_{0,z} = 0$ which is an easy consequence of (6.7), provided the matching condition $\Phi_{0,z}(z) \to 0$ for $z \to \pm\infty$ is satisfied. This seems reasonable to keep the notation short(er) and is justified as we will only consider matching solutions in the sequel.

We need one more definition to state our theorem. We introduce matching solutions which consist of compatible outer and inner solutions.

Definition 6.3. A tuple $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0, (R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ is called a *matching solution of the coupled regime* provided $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0)$ is an outer- and $((R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ is an inner solution and both are linked by the matching conditions.

Theorem 6.1. *Let* $((\rho_{\alpha,0})_\alpha, \boldsymbol{v}_0, \chi_0, \chi_1, \varphi_0, (R_{\alpha,0})_\alpha, (R_{\alpha,1})_\alpha, \boldsymbol{V}_0, X_0, X_1, \Phi_0, \Phi_1)$ *be a* **matching solution of the coupled regime**, *then the following equations are satisfied in the bulk* *regions $\Omega^\pm$:*

$$\pm 1 = \chi_0, \chi_1 = 0, \tag{6.15}$$

$$0 = \partial_t \rho_{\alpha,0} + \mathrm{div}(\rho_{\alpha,0}\boldsymbol{v}_0) - \mathrm{div}\Big(\sum_{\beta=1}^{N-1} M_{\alpha\beta}\nabla\Big(\mu_{\beta,0} - \mu_{N,0} + \Big(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\Big)\varphi_0\Big)\Big) \tag{6.16}$$

$$- \sum_{i=1}^{N_R} m_\alpha \gamma_\alpha^i M_{\mathrm{r}}^i \Big(1 - \exp\Big(\sum_{\beta=1}^{N} m_\beta \gamma_\beta^i \mu_{\beta,0}\Big)\Big),$$

$$0 = \partial_t \rho_0 + \mathrm{div}(\rho_0 \boldsymbol{v}_0), \tag{6.17}$$

$$0 = \partial_t(\rho_0 \boldsymbol{v}_0) + \mathrm{div}(\rho_0 \boldsymbol{v}_0 \otimes \boldsymbol{v}_0) + \nabla\left(\sum_{\alpha=1}^{N} \rho_{\alpha,0}\mu_{\alpha,0} - \rho f_0\right), \tag{6.18}$$

$$0 = \sum_{\alpha=1}^{N} \frac{z_\alpha}{m_\alpha}\rho_{\alpha,0}. \tag{6.19}$$

Moreover, the following conditions are fulfilled at the interface:

$$0 = [\![\mu_{\alpha,0} - \mu_{N,0}]\!], \tag{6.20}$$

$$0 = [\![\rho_0(\boldsymbol{v}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}})]\!], \tag{6.21}$$

$$0 = [\![\rho_{\alpha,0}(\boldsymbol{v}_0 \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}})]\!] - \Big[\!\!\Big[\sum_{\beta=1}^{N-1} M_{\alpha\beta}\nabla\Big(\mu_{\beta,0} - \mu_{N,0} + (\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N})\varphi_0\Big)\cdot \boldsymbol{\nu}\Big]\!\!\Big], \tag{6.22}$$

$$0 = \left[\!\!\left[j_0 \boldsymbol{v}_0 + \left(\sum_{\alpha=1}^{N} \rho_{\alpha,0}\mu_{\alpha,0} - \rho f_0\right)\boldsymbol{\nu}\right]\!\!\right] - \gamma\kappa\boldsymbol{\nu}\int_{-\infty}^{\infty} (X_{0,z})^2 \,\mathrm{d}\,z, \tag{6.23}$$

$$0 = \Big[\!\!\Big[\frac{j_0^2}{2\rho_0^2} + \mu_{N,0}\Big]\!\!\Big] + \frac{j_0}{\tau}\int_{-\infty}^{\infty} \frac{1}{R_0}(X_{0,z})^2 \,\mathrm{d}\,z, \tag{6.24}$$

$$0 = [\![(1 + s(\chi_0))\nabla\varphi_0 \cdot \boldsymbol{\nu}]\!] - \int_{-\infty}^{\infty}\left(\sum_{\alpha=1}^{N} \frac{z_\alpha}{m_\alpha} R_{\alpha,0}(z)\right)\mathrm{d}\,z, \tag{6.25}$$

$$0 = [\![\varphi_0]\!], \tag{6.26}$$

where $j_0 := \rho_0^\pm(\boldsymbol{v}_0^\pm \cdot \boldsymbol{\nu} - w_{\boldsymbol{\nu}})$ *and* $\alpha = 1, \dots, N-1$ *in* (6.20) *and* (6.22)*. Moreover,* (5.30) *implies*

$$[\![\nabla\varphi_0 - (\nabla\varphi_0 \cdot \boldsymbol{\nu})\boldsymbol{\nu}]\!] = 0. \tag{6.27}$$

Remark 6.4. We can use the evolution equations for $(\rho_{\alpha,0})_\alpha$ together with the closure relation (6.19) and the charge conservation

$$\sum_\alpha \tfrac{z_\alpha}{m_\alpha} r_\alpha = 0$$

to obtain the following elliptic problem for φ_0 :

$$0 = \mathrm{div}\left(\sum_{\alpha,\beta=1}^{N-1} M_{\alpha\beta}\left(\left(\frac{z_\alpha}{m_\alpha} - \frac{z_N}{m_N}\right)\nabla(\mu_\beta - \mu_N) + \left(\frac{z_\alpha}{m_\alpha} - \frac{z_N}{m_N}\right)\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right)\nabla\varphi_0\right)\right). \tag{6.28}$$

Note that

$$\sum_{\alpha,\beta=1}^{N-1} M_{\alpha\beta}\left(\frac{z_\alpha}{m_\alpha} - \frac{z_N}{m_N}\right)\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right) > 0,$$

provided $\frac{z_\alpha}{m_\alpha} - \frac{z_N}{m_N} \neq 0$ for at least one α, due to the positive definiteness of $M_{\alpha\beta}$.

The proof of Theorem 6.1 works along the same lines as the proof of Theorem 5.1. Thus, we will only highlight the differences.

Lemma 6.5. *Let Φ_0 be given as in Definition 6.3 then $\Phi_{0,z} = 0$ and therefore $[\![\varphi_0]\!] = 0$.*

Proof. By integrating (6.7) and using the matching conditions we obtain

$$(1 + s(X_0))\Phi_{0,z} = 0.$$

Because of $s \geq 0$ this implies the claim of the lemma. □

Due to Lemma 6.5 equation (6.10) simplifies to

$$0 = W'(X_0) - \gamma X_{0,zz} \tag{6.29}$$

and Lemma 5.7 applies. Concerning the normal velocity Remark 5.6 is true in this regime, as well. Moreover, (6.8) becomes

$$0 = \left(\sum_{\beta=1}^{N-1} M_{\alpha\beta}(\mathcal{M}_{\beta,0} - \mathcal{M}_{N,0})_z \right)_z . \tag{6.30}$$

Similarly to Lemma 5.8, we construct a subsystem of equations from which we can compute the $(R_{\alpha,0})_\alpha$.

Lemma 6.6. *For X_0 given as in Lemma 5.7 equations* (6.11), (6.12), (6.29), (6.30) *are equivalent to* (6.11), (6.29), (6.30) *and*

$$\frac{j_0}{R_0}\left(\frac{j_0}{R_0}\right)_z + (\mathcal{M}_{\alpha,0})_z = -\frac{j_0}{R_0\tau}(X_{0,z})^2, \tag{6.31}$$

for any $\alpha \in \{1, \ldots, N\}$, where $R_0 := \sum_{\alpha=1}^{N} R_{\alpha,0}$.

Proof. The proof is analogous to the proof of Lemma 5.8. □

Equations (6.30) and (6.31) coincide with (5.11) and (5.34). Thus, Lemma 5.9 also applies in the scaling at hand.

Lemma 6.7. *The normal part of* (6.11) *can be written as*

$$\mathcal{L}X_1 = \left(\frac{j_0^2}{\sum_{\alpha=1}^{N} R_{\alpha,0}} \right)_z + \left(\sum_{\alpha=1}^{N} R_{\alpha,0}\mathcal{M}_{\alpha,0} - RF_0 \right)_z - \gamma\kappa X_{0,z}^2 \tag{6.32}$$

with

$$\mathcal{L} : W^{2,1}(\mathbb{R}) \to L^1(\mathbb{R}), \quad \Psi \mapsto (W'(X_0)\Psi - \gamma X_{0,z}\Psi_z)_z.$$

Equation (6.32) *has a solution if and only if the normal part of* (6.23) *is satisfied.*

Proof. The only solutions of the homogeneous adjoint problem to (6.32), i.e.,

$$W'(X_0)\Xi_z + \gamma(X_{0,z}\Xi_z)_z = 0 \tag{6.33}$$

in L^∞ are given by $\Xi = k$ for $k \in \mathbb{R}$, see [11, Lemma 4.11]. Thus, the solvability condition for (6.32) is

$$0 = \int_{-\infty}^{\infty} \left(\left(\frac{j_0^2}{\sum_{\alpha=1}^N R_{\alpha,0}} \right)_z + \left(\sum_{\alpha=1}^N R_{\alpha,0} \mathcal{M}_{\alpha,0} - RF_0 \right)_z - \gamma\kappa X_{0,z}^2 \right) \mathrm{d}\, z,$$

which is equivalent to (6.23). □

Then, we consider the tangential part of $\boldsymbol{V}_0$. All the arguments are the same as in Lemma 5.12, only the φ and Φ terms are not present. Thus, we obtain:

Lemma 6.8. *The tangential part of* (6.11) *has a solution if and only if the tangential part of* (6.23) *holds.*

Integrating (6.14) leads to the statement:

Lemma 6.9. *Let* $(R_{\alpha,0})_\alpha$ *and* X_0 *be given. Then, it exists a solution* Φ_1 *of* (6.14) *if and only if* (6.25) *holds.*

Finally, analogous to Lemma 5.13, we obtain the following result:

Lemma 6.10. *Equation* (6.13) *has a solution if and only if* (6.22) *holds.*

Proof of Theorem 5.1. We obtain the interface conditions and the properties of χ_0, χ_1 by combining the preceeding lemmas. Concerning the bulk equations, (6.16) is (5.2), (6.17) is (5.3), (6.19) is (6.4) and (6.18) follows from (6.2) as $\chi_1 = 0$. □

Acknowledgment

The authors would like to thank Clemens Guhlke for fruitful discussions and advices on some topics related to the paper.

References

[1] H. Abels. Existence of weak solutions for a diffuse interface model for viscous, incompressible fluids with general densities. *Comm. Math. Phys.*, 289:45–73, 2009.

[2] H. Abels. Strong well-posedness of a diffuse interface model for a viscous, quasi-incompressible two-phase flow. *SIAM J. Math. Anal.*, 44:316–340, 2012.

[3] H. Abels, D. Depner, and H. Garcke. Existence of Weak Solutions for a Diffuse Interface Model for Two-Phase Flows of Incompressible Fluids with Different Densities. *J. Math. Fluid Mech., DOI 10.1007/s00021-012-0118-x*, 2012.

[4] H. Abels, H. Garcke, and G. Grün. Thermodynamically consistent frame indifferent diffuse interface models for incompressible two-phase flows with different densities. *Math. Mod. Meth. Appl. S.*, 22:1150013 (40 pages), 2012.

[5] G. L. Aki, J. Daube, W. Dreyer, J. Giesselmann, M. Kränkel, and C. Kraus. A diffuse interface model for quasi-incompressible flows : Sharp interface limits and numerics. In *ESAIM Proc. Vol. 38*, pages 54–77, 2012.

[6] G. L. Aki, W. Dreyer, J. Giesselmann, and C. Kraus. A quasi-incompressible diffuse interface model with phase transition. *Math. Mod. Meth. Appl. S.*, 24(5):827–861, 2014.

[7] S. Benzoni-Gavage, R. Danchin, S. Descombes, and D. Jamet. Stability issues in the Euler-Korteweg model. *Contemporary Mathematics, A.M.S.*, 426:103–127, 2007.

[8] T. Blesgen. A generalization of the navier–stokes equations to two-phase flows. *J. Phys. D: Appl. Phys. 32*, 32:1119–1123, 1999.

[9] D. Bothe and W. Dreyer. Rational thermodynamics of chemically reacting multicomponent fluid mixtures. WIAS Preprint 1909.

[10] G. Caginalp and P. C. Fife. Dynamics of layered interfaces arising from phase boundaries. *SIAM J. Appl. Math.*, 48:506–518, 1988.

[11] W. Dreyer, J. Giesselmann, and C. Kraus. A compressible mixture model with phase transition. *Phys. D*, 273-274:1–13, 2014.

[12] W. Dreyer and C. Kraus. On the van der Waals–Cahn–Hilliard phase-field model and its equilibria conditions in the sharp interface limit. *Proc. R. Soc. Edinb., Sect. A, Math.*, 140(6):1161–1186, 2010.

[13] E. Feireisl, H. Petzeltová, E. Rocca, and G. Schimperna. Analysis of a phase-field model for two-phase compressible fluids. *Math. Mod. Meth. Appl. S.*, 20(7):1129–1160, 2010.

[14] M. E. Gurtin, D. Polignone, and J. Vinals. Two-phase binary fluids and immiscible fluids described by an order parameter. *Math. Mod. Meth. Appl. S.*, 6:815–831, 1996.

[15] P. C. Hohenberg and B. I. Halperin. Theory of dynamic critical phenomena. *Rev. Mod. Phys.*, 49:435–479, 1977.

[16] M. Kotschote. Strong solutions of the Navier-Stokes equations for a compressible fluid of Allen-Cahn type. *Arch. Ration. Mech. Anal.*, 206(2):489–514, 2012.

[17] P. A. Lagerstrom. *Matched Asymptotic Expansions: Ideas and Techniques.* Springer-Verlag, New York, 1988.

[18] J. S. Lowengrub and L. Truskinovsky. Quasi-incompressible Cahn-Hilliard fluids and topological transitions. *R. Soc. Lond. Proc. Ser. A Math. Phys. Eng. Sci.*, 454:2617–2654, 1998.

[19] S. Luckhaus and L. Modica. The Gibbs-Thompson relation within the gradient theory of phase transitions. *Arch. Ration. Mech. Anal.*, 107(1):71–83, 1989.

[20] I. Müller. *Thermodynamics.* Pitman Advanced Publishing Program. XVII, Boston - London - Melbourne, 1985.

[21] N. C. Owen, J. Rubinstein, and P. Sternberg. Minimizers and gradient flows for singularly perturbed bi-stable potentials with a Dirichlet condition. *Proc. Roy. Soc. London Ser. A*, 429(1877):505–532, 1990.

[22] P. Sternberg. The effect of a singular perturbation on nonconvex variational problems. *Arch. Ration. Mech. Anal.*, 101(3):209–260, 1988.

[23] C. Truesdell. *Rational thermodynamics.* McGraw-Hill Book Co., New York, 1969.

[24] C. Truesdell and R. Toupin. The classical field theories. In *Handbuch der Physik, Bd. III/1*, pages 226–793; appendix, pp. 794–858. Springer, Berlin, 1960.

[25] G. Witterstein. Phase change flows with mass exchange. *Adv. Math. Sci. Appl.*, 21(2):559–611, 2011.